KINETICS OF SALT FORMATION USING TEREPHTHALIC ACID AND N-METHYL-2-PYRROLIDINONE

by

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April 14, 2004

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I especially acknowledge my parents, C. C. Chou and R. T. Wang, for their endless love and support from the other side of the earth.

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ABSTRACT

Terephthalic acid (TA) is used as a raw material for producing polyesters. As the global demand for polyesters increases at a rate of 7% per year on average for the last few years and next 10-year forecast, the demand of TA also increases. The global production exceeded 27 million tons for the year 2003, and will be in excess of 30 million tons for the year 2004. Therefore improving the production or purification process for terephthalic acid becomes more and more important. A new purification method using N-methyl-2-pyrrolidinone (NMP) as solvent was recently developed. In this process, the salt complex consisting of TA and NMP was formed to exclude the impurities. The research topic of this thesis was to characterize the salt formation rate and develop possible explanations for salt formation kinetics.

Gas Chromatography was used to determine the percentage of salt in the salt formation samples as prepared by varying mixing times, temperatures and loadings. The TA-salt transition (salt formation) was found to behave as first-order solid-solid phase transition with a temperature range where both phases coexist. The salt formation rate was explained using the combination of reaction rate and salt formation possibility.

INTRODUCTION AND THEORY

Terephthalic Acid

Terephthalic acid, also simply called TA, is a white, odorless, stable solid crystal at room temperature. It is used as a raw material for producing polyesters. The global demand for polyesters increased at a rate of 7% per year on average for the last few years. This same trend is predicted to continue for the next 10 years. And therefore the demand for terephthalic acid has also increased. The global production exceeded 27 million tons for year 2003, and will be over 30 million tons for year 2004. Therefore improving the production or purification process for terephthalic acid becomes more and more important.

The physical properties of terephthalic acid are listed in Table 1. The structure of a single terephthalic acid molecule is shown in Figure 1.

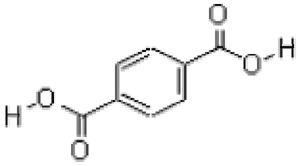

Figure 1. Structure of Terephthalic Acid Molecule

Table 1. The Physical Properties of Terephthalic Acid

Name	**Terephthalic Acid**
Synonyms	1,4-benzenedicarboxylic acid, TPA, TA
Molecular Formula	$C_8H_6O_4$
Formula Weight	166.13
Melting Point	427°C
Sublimation Point	402°C
Solubility in Water	< 0.1%
Specific Gravity	1.58

The crystal structure of terephthalic acid was determined using powder X-ray diffraction (M. Bailey and C. J. Brown, 1967). Two forms, Form I and Form II, of triclinic structure were found. In both forms, terephthalic acid molecules are bonded by double hydrogen bonds of length 2.608 Å to form infinite chains shown in Figure 2. The chains are parallel to each other to form a layer, and the layers pack parallel to one other. In Form I, shown in Figure 3, the benzene rings of a chain are adjacent to the carboxyl groups of the next chain. And the benzene rings of a layer are adjacent to the benzene rings of the next layer. In Form II, shown in Figure 4, the benzene rings of a chain are adjacent to the benzene rings of the next chain, and the benzene rings of a layer are adjacent to the carboxyl groups of the next layer. The original unit cell dimensions of Form I and Form II are listed in Table 2.

Table 2. Unit Cell Dimensions of Terephthalic Acid (M. Bailey and C. J. Brown, 1967)

	Form I	Form II
a	9.54 Å	9.54 Å
b	7.73 Å	5.34 Å
c	3.74 Å	5.02 Å
α	109°9’	86°57’
β	73°36’	134°39’
γ	137°46’	94°48’

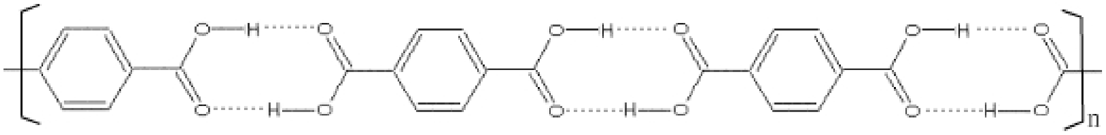

Figure 2. Infinite Chain of Terephthalic Acid Bonded by Double Hydrogen Bonds

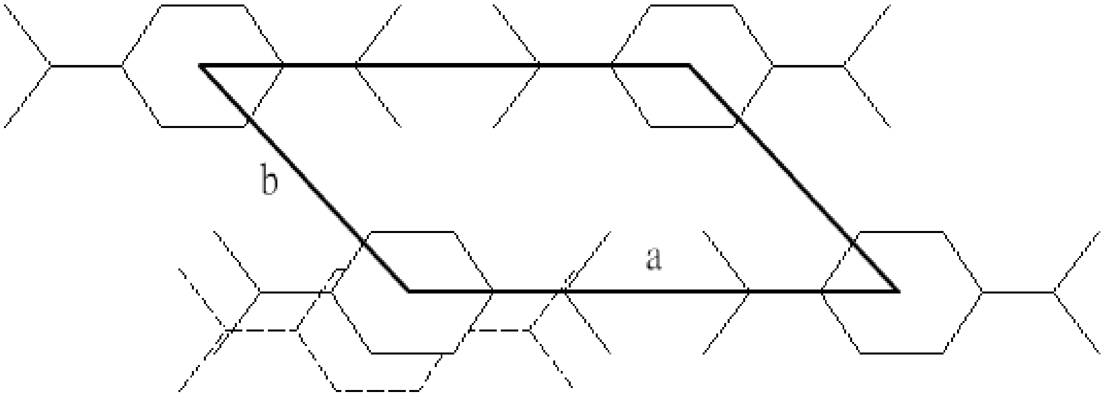

Figure 3. The Molecular Packing of Form I of Terephthalic Acid. The Molecule with Dotted Lines is within the Layer below the Molecules with Solid Lines.

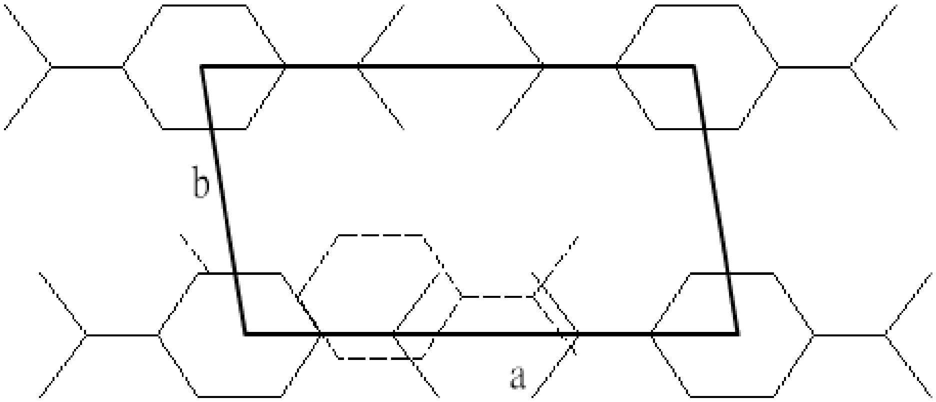

Figure 4. The Molecular Packing of Form II of Terephthalic Acid. The Molecule with Dotted Lines is within the Layer below the Molecules with Solid Lines.

Terephthalic acid is used as a raw material for polyesters. It is reacted with various glycols to form many types of polyesters with different physical properties for a variety of applications. Three major polyester products synthesized from terephthalic acid are polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT) and polybutylene terephthalate (PBT). The polymerization methods were all developed during the 1940's. Table 3 shows the reactants and polymerization products of the three polyesters.

Table 3. Polymerization Reactions of Polyesters

Polyester	Reactants	Product
PET	$HOCH_2CH_2OH + HOOCC_6H_4COOH$ Ethylene Glycol Terephthalic Acid	$(-OCH_2CH_2$ $OOCC_6H_4CO-)_n$
PTT	$HOCH_2CH_2CH_2OH + HOOCC_6H_4COOH$ 1,3-Propane Diol Terephthalic Acid	$(-OCH_2CH_2$ $CH_2OOCC_6H_4CO-)_n$
PBT	$HOCH_2CH_2CH_2CH_2OH + HOOCC_6H_4COOH$ 1,4-Butane Diol Terephthalic Acid	$(-OCH_2CH_2$ $CH_2CH_2OOCC_6H_4CO-)_n$

Considering all the polyesters, polyethylene terephthalate (PET) has the most applications and the largest requirement for terephthalic acid. The advantages of PET, such as flexibility, resistance to chemicals and weathering, adhesion and clarity, allow it to be used in a variety of home and industrial products. The applications of PET make up about 50% of solid-state resins such as food and drink containers and packaging, 43% of polyester fibers used for clothing, furnishings and industries, 3% of polyester films and tapes, 4% of others such as coating and adhesives.

Because of the numerous applications of polyesters, demand for the raw material, terephthalic acid, has increased each year. The forecast for terephthalic acid demand is about 7% - 8% growth rate per year (MIB, Japan, 2003). Table 4 lists the global purified terephthalic acid (PTA) demand for the year 2001 and predicted demand for the year 2007 and the growth rate from 2001 to 2007.

Table 4. Global PTA Demand (Ministry of Economy, Trade and Industry, Japan, 2003)

(Unit: million tons, %)

	Total of the World	Total of Asia							Western Europe	North America	Middle East
			South Korea	Taiwan	China	AS-EAN	India	Japan			
Demand											
2001	23.1	15.3	2.9	2.6	5.1	2.1	1.3	1.0	2.3	3.8	0.1
2007	37.0	24.6	3.9	3.2	11.1	3.1	2.0	0.9	3.0	5.4	0.7
Increase 01-07	13.9	9.3	1.0	0.6	6.0	1.0	0.7	-0.1	0.7	1.4	0.6
Growth 01-07	8.1	8.3	5.0	3.6	13.8	7.1	7.0	-1.1	4.7	6.0	30.3

Such versatility and growth has established terephthalic acid and its production and purification processes extremely important.

Commercial Methods of Terephthalic Acid Production and Purification

Currently, the most popular method for making terephthalic acid is the Amoco process. This process was originally called the Mid-Century process (R. S. Barker et al., 1955) and was developed by Mid-Century Corporation. This technology was purchased by Amoco Chemical. The most popular method for purifying terephthalic acid was also developed by Amoco Chemical (D. H. Meyer, 1967), and is known as the Amoco purification process. Amoco merged with BP and the technology is now owned and licensed by BP. Today, more than 70% of terephthalate feedstocks are produced using Amoco oxidation process. Almost 100% of new terephthalic acid facilities use this process. Also more than 60% of terephthalate feedstock is purified using the Amoco purification process.

The Amoco oxidation process uses acetic acid as the solvent, with a combination of cobalt, manganese and bromine as catalysts to oxidize the p-xylene through several steps producing terephthalic acid. Cobalt and manganese are present as salts, and the bromine source can be HBr or NaBr. Because of the highly corrosive bromine-acetic acid environment, some equipment requires titanium lining. Compressed air is added to the reactor to reach the oxygen stoichiometric ratio requirement. Due to the limited solubility of p-xylene and oxygen in acetic acid, high temperatures and pressures are required. The operating temperature is 176 – 225°C, and the pressure is 1500 – 3000 kPa. Residence time is about 2 hours. The actual oxidation reaction is a sequence and has several intermediates. The reaction sequence is shown in Figure 5.

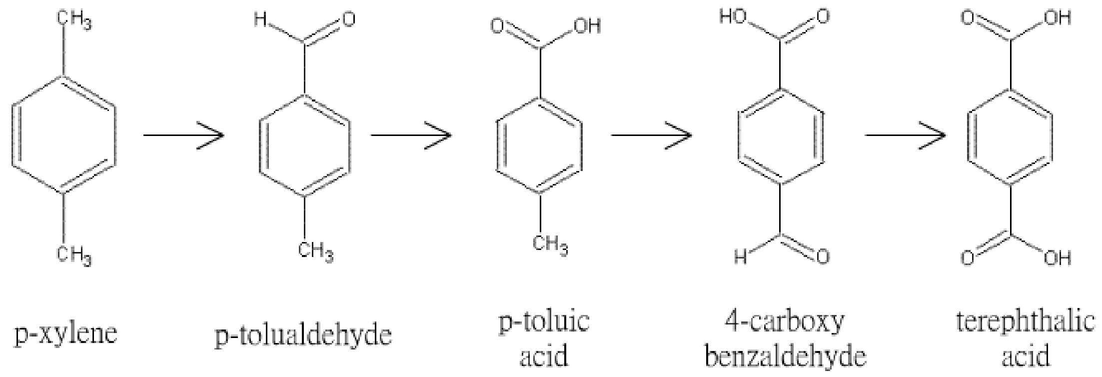

Figure 5. Amoco Oxidation Sequence from p-Xylene to Terephthalic Acid

Water is a byproduct of the reaction. The overall reaction is shown below:

C_8H_{10} (p-xylene) + 3 $O_2 \rightarrow C_8H_6O_4$ (terephthalic acid) + 2 H_2O

The reaction is highly exothermic, and releases $2*10^8$ J per kilogram of p-xylene reacted. Because the solubility of terephthalic acid is much lower than p-xylene in acetic acid, most of terephthalic acid precipitates while it forms. Therefore it is actually a three-phase system within the reactor. The liquid phase contains acetic acid and water with dissolved catalyst and chemicals including terephthalic acid. The solid phase contains terephthalic acid crystals and some impurities. The gas phase contains acetic acid and water vapor, nitrogen and some undissolved oxygen. After the pressure is released at the final stage, solid terephthalic acid crystals are recovered and dried. By the end of the process, over 98% of the p-xylene has reacted, and the yield rate of terephthalic acid is greater than 95%. Small amounts of p-xylene and acetic acid are lost due to burn losses. The final product is crude terephthalic acid which is usually > 99% purity. The major impurity which is also an intermediate of the reaction is 4-carboxybenzaldehyde (4CBA). The final product may contain up to 5000 ppm 4CBA. The concentration allowance for 4CBA in terephthalic acid in the polyester feedstock is usually less than 50 ppm. So further purification processes are needed to reach the purity requirement for purified terephthalic acid (PTA).

Because of the similar chemical structure of 4-carboxybenzaldehyde and terephthalic acid, they also have similar physical properties which make it almost impossible to separate 4-carboxybenzaldehyde from terephthalic acid by normal separation processes, e.g. extraction, adsorption, and membranes. It is also hard to find a proper solvent which has good selectivity to separate 4-carboxybenzaldehyde and terephthalic acid using crystallization.

The Amoco purification process (D. H. Meyer, 1967) includes two major steps, hydrogenation and crystallization. First, crude terephthalic acid is dissolved in water at high temperature. It requires 259°C to dissolve 20 grams of terephthalic acid per 100 grams of water, and requires 272°C to dissolve 30 grams of terephthalic acid per 100 grams of water. Pressure in excess of the vapor pressure is needed to maintain the liquid phase. The solution is fed to the hydrogenation reactor containing a carbonsupported palladium catalyst, and hydrogen is introduced. 4-Carboxybenzaldehyde is hydrogenized to p-toluic acid. The reaction is shown below:

$$C_8H_6O_3 \text{ (4-carboxybenzaldehyde)} + 2\ H_2 \rightarrow C_8H_8O_2 \text{ (p-toluic acid)} + H_2O$$

This reaction is highly selective. The loss of terephthalic acid by carboxylic acid reduction or ring hydrogenation is less than 1%. The solution then passes a series of flash crystallizers where the pressure and temperature are sequentially decreased. P-toluic acid and other impurities have a higher solubility than terephthalic acid in water, and therefore remain in the mother liquor while terephthalic acid is crystallized out. The terephthalic acid crystals are recovered, filtered and dried. The final PTA product has a concentration of 4-carboxybenzaldehyde less than 25 ppm. Over 95% of the incoming terephthalic acid can be recovered as purified product. A block process diagram of the Amoco oxidation and purification process for producing purified terephthalic acid is shown in Figure 6.

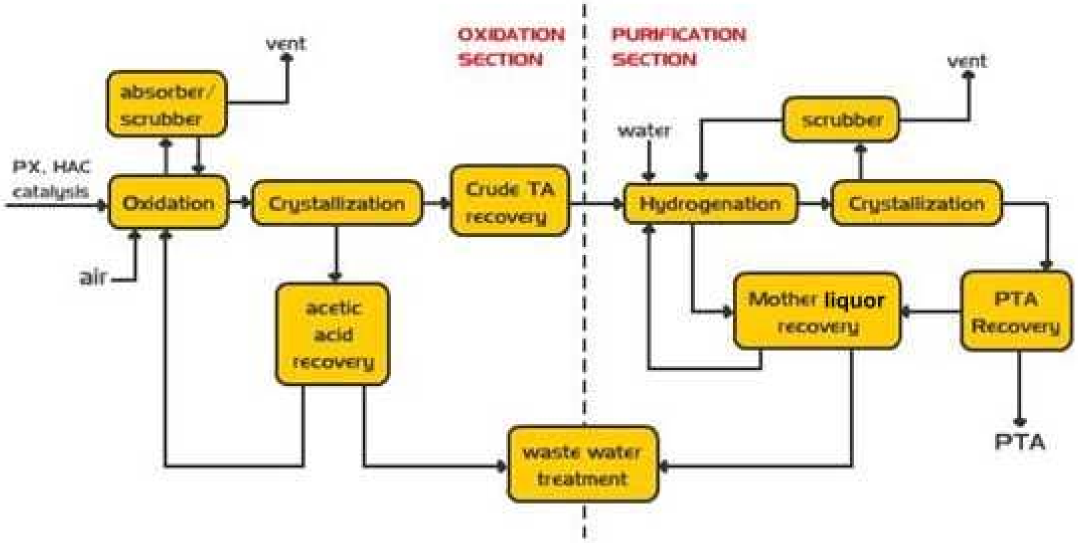

Figure 6. Amoco Oxidation and Purification Process for Producing Purified Terephthalic Acid (http://www.gtchouston.com/technologie/otech-pta.htm)

The other commercial method for purifying terephthalic acid is the dimethyl terephthalate (DMT) process. Like the Amoco oxidation process, p-xylene is first oxidized to terephthalic acid. Terephthalic acid is then esterfied with methanol to become dimethyl terephthalate. The reaction is shown below:

$C_8H_6O_4$ (terephthalic acid) + 2 CH_3OH (methanol) → $C_{10}H_{10}O_4$ (dimethyl terephthalate) + 2 H_2O

Because the boiling point of dimethyl terephthalate is 288°C and relatively lower than the other impurities including 4-carboxybenzaldehyde, purification by distillation can be easily achieved. Dimethyl terephthalate collected at the top of the distillation column is hydrolyzed back to terephthalic acid.

Because of economic and efficiency considerations, the DMT method is being replaced by the Amoco process.

N-Methyl-2-pyrrolidinone

N-Methyl-2-pyrrolidinone, or simply NMP, is a clear, stable liquid at room temperature. The physical properties of N-methyl-2-pyrrolidinone are listed in Table 5. The molecular structure of N-methyl-2-pyrrolidinone is shown in Figure 7.

Table 5. The Physical Properties of N-Methyl-2-pyrrolidinone

Name	N-Methyl-2-pyrrolidinone
Synonyms	N-Methylpyrrolidinone, NMP
Molecular Formula	C_5H_9NO
Formula Weight	99.13
Melting Point	-24.4°C
Boiling Point	202°C
Solubility in Water	100%
Specific Gravity	1.028
Vapor Pressure	< 0.3 mmHg (20°C)

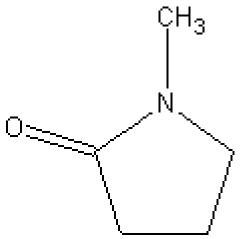

Figure 7. Molecular Structure of N-Methyl-2-pyrrolidinone

The major advantages of N-methyl-2-pyrrolidinone are high solvency, low volatility, low toxicity, and miscibility with water and various organic solvents, e.g. alcohols, glycol ethers and ketones. These advantages allow N-methyl-2-pyrrolidinone to be used in many applications, such as photoresist stripper in the electronics industry, graffiti remover, herbicide solvent in agriculture, high temperature coating solvent, and as a solvent for synthetic procedures in the pharmaceuticals industries. In the chemical and petrochemical industries, N-methyl-2-pyrrolidinone is widely used as an extraction solvent for unsaturated hydrocarbons, aromatics and sulfur-bearing gases.

Salt Complex

Purification of terephthalic acid using N-methyl-2-pyrrolidinone was first mentioned in United States patent US2,949,483 assigned to The Chemstrand

Corporation (George E. Ham et al., 1960). In the description of the patent, terephthalic acid was completely dissolved in N-methyl-2-pyrrolidinone within the temperature range of 50°C to 130°C. The solution was then cooled to the temperature range of 10°C to 45°C and the solid was precipitated. The solid in this case is not terephthalic acid crystal, but a “salt complex” which contains terephthalic acid and N-methyl-2-pyrrolidinone. Ham et al. (1960) mentioned the salt contained two moles of N-methyl-2-pyrrolidinone for each mole of terephthalic acid. The solid salts formed at low temperature were filtered and washed by N-methyl-2-pyrrolidinone to remove the adhering impurities. The salt was then washed with water between 10°C to 100°C. Because N-methyl-2-pyrrolidinone is totally miscible with water at all temperatures, the salt was destroyed as the water washed the N-methyl-2-pyrrolidinone from the salt. The remaining terephthalic acid was filtered and dried. The patent claimed a recovery rate of about 60% to 95% of the weight of the crude terephthalic acid.

Current research has shown that this purification is due primarily to the high selectivity of salt to terephthalic acid. However, this selectivity was not mentioned in Ham’s patent.

The salt complex structure and the salt formation mechanism were also not mentioned in Ham’s patent. Actually, the purified terephthalic acid recovered using this process cannot be directly used for polyester production, even if it reaches the purity requirement. Although Ham’s patent states that the precipitated, rinsed terephthalic acid was filtered and dried, these steps are exceedingly difficult. The terephthalic acid crystals formed from salts are extremely fine. The ratio of surface area/volume is too high for efficient drying. These fine crystals form a hard cake or block during filtration. Once a hard cake or block is formed, it is very difficult to process further. Even re-dissolving the block in a different solvent presents problems. To prevent formation of a hard block, terephthalic acid fines should remain in a large amount of water with agitation, where the slurry can then go to a water crystallizer. In order to have a flowable slurry, there should be a low solid concentration because of high surface area/volume ratio of the crystals. Due to these disadvantages, this process was not considered commercially viable.

After almost 40 years, this process was investigated by Glitsch International Inc. (Fu-Ming Lee et al., Jun/1998, US5,767,311). In an attempt to find an organic solvent with higher solubility for terephthalic acid than water, N-methyl-2-pyrrolidinone was considered as a reasonable candidate. The solubility of terephthalic acid, 4-carboxybenzaldehyde and other impurities in N-methyl-2-pyrrolidinone were studied. The differences between the solubility of terephthalic acid and the impurities were sufficient to potentially use crystallization as the purification process. The solubility curves of terephthalic acid (TPA), 4-carboxybenzaldehyde and other impurities in N-methyl-2-pyrrolidinone are shown in Figure 8. The process of Ham (1960) was improved in several aspects. The process was split into two cooling crystallization stages. In the first crystallizer, crude terephthalic acid was dissolved in N-methyl-2-pyrrolidinone at the temperature range of 140°C to 190°C, then cooled down to the temperature range of 10°C to 20°C to form salts. The salts were filtered and washed with pure N-methyl-2-pyrrolidinone. The salts were then redissolved in

N-methyl-2-pyrrolidinone in the second stage crystallizer at the temperature range of 140°C to 190°C. The solution was cooled down to a temperature range of 30°C to 60°C to form salts again. The salts were initially washed with pure N-methyl-2-pyrrolidinone at 45°C to displace the remaining mother liquor on the surface, and then washed with low-boiling solvent, such as methanol, to break the salts and displace N-methyl-2-pyrrolidinone. The purified terephthalic acid crystals resulting from salts breaking are still fine. But by using a low-boiling solvent instead of water as the wash, the fines are easier to dry, and it is simpler to recover the purified terephthalic acid.

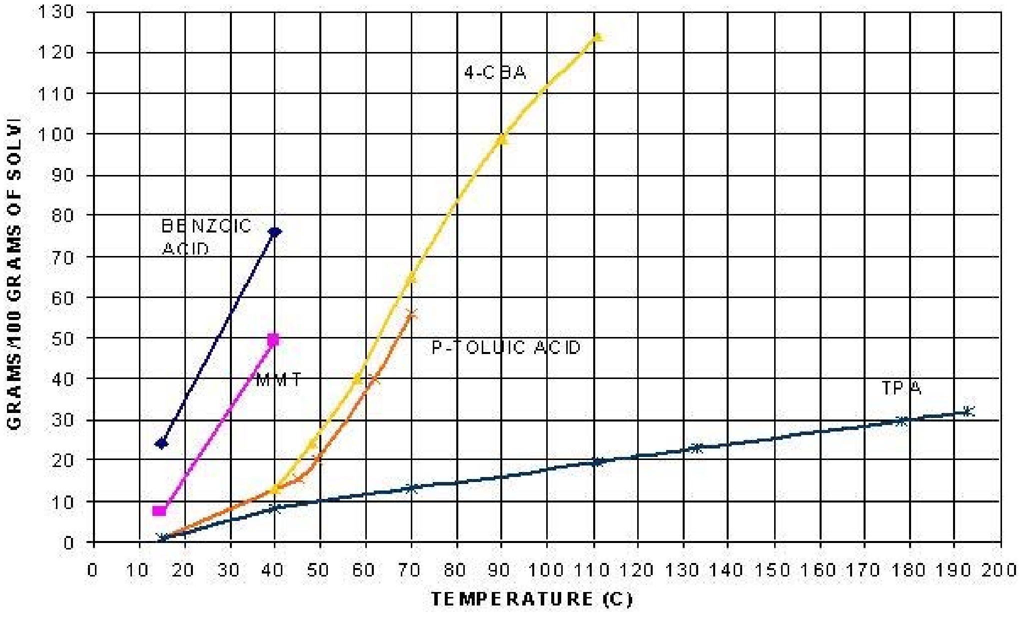

Figure 8. Solubility Curves of Terephthalic Acid and Selected Impurities in N-Methyl-2-pyrrolidinone (Fu-Ming Lee et al., Jun/1998)

Further study and improvements were made by HFM International Incorporation (Fu-Ming Lee et al., Nov/1998, US5,840,968), which owned Glitsch International Inc. Additional physical properties of the terephthalic acid-N-methyl-2-pyrrolidinone salt were disclosed in this patent. It showed that salts are bright, transparent and slightly pale crystals, which can be easily differentiated from the opaque, white terephthalic acid crystals. Because the solvent can be trapped inside during the formation of the salt crystals, Lee's empirical molar ratio of N-methyl-2-pyrrolidinone/terephthalic acid in the salt varied from 2.04 to 3.11 instead of 2 as proposed by Ham. Based on the pH measurement of terephthalic acid and salts, Lee also postulated the following as a means to describe the salt formation:

Terephthalic Acid $_{(s)}$ + 2 N-Methyl-2-pyrrolidinone $_{(l)}$ → (Terephthalic Acid : 2 N-Methyl-2-pyrrolidinone) $_{(s)}$

The study also showed that with increasing temperature, the salt crystals begin to decompose at about 50°C. This indicates that salts are stable below about 50°C, unstable between 50°C and 60°C, and terephthalic acid crystals are stable above 60°C. So the reaction can be written reversibly as below:

Terephthalic Acid $_{(s)}$ + 2 N-Methyl-2-pyrrolidinone $_{(l)}$ $\begin{array}{l} \rightarrow (T < 50^{\circ}C) \\ (T > 60^{\circ}C)\leftarrow \end{array}$ (Terephthalic Acid : 2 N-Methyl-2-pyrrolidinone) $_{(s)}$

Based on this observation, the purification process was further improved. First, crude terephthalic acid was dissolved in N-methyl-2-pyrrolidinone in a cooling crystallizer between 140°C to 200°C. In order to achieve good impurities rejection using selective salt formation, the crystallizer was cooled to a temperature range of 30°C to 50°C. The resulting salts were filtered and washed using pure N-methyl-2-pyrrolidinone. The salt slurry was then redissolved at the temperature range of 140°C to 200°C and fed to the second stage which was a series of flash crystallizers. In the series of flash crystallizers, the temperature and the pressure were both reduced by steps, with the final temperature in the range of 50°C to 60°C where no salt should be formed. Flash crystallizers were used to produce good crystal shape and size. The purified terephthalic acid crystals were then filtered and washed by pure N-methyl-2-pyrrolidinone and water, and then dried.

Because of the excellent solvency of N-methyl-2-pyrrolidinone and the high selectivity of terephthalic acid-N-methyl-2-pyrrolidinone salt formation, this new method of purification using organic solvent has a great potential. But the salt crystal structure and the mechanism of salt formation still need to be studied, which provides the topic for this thesis.

Solid-Liquid Reaction Crystallization

Solid-liquid reaction crystallization is the heterogeneous reaction which uses solid and liquid reactants and produces a solid. The reaction conditions are chosen so that upon formation, the product will precipitate. Since the reaction usually results in product crystals, it is performed within a crystallizer. Solid-liquid reactions occur at the interface between the solid and liquid, and are highly dependent on mass transfer within the interface region. Although solid-liquid reaction crystallization is important for some chemical manufacturing, it is not widely studied because of its complexity. The factors that affect the mass transfer at the solid-liquid interface include temperature, solute distribution, mixing or Reynolds number, particle size, diffusion, dissolution, gassing rate and the reaction itself. Some of the factors have been discussed separately with examples (B. Zare Nezhad et al., 1996; Brend Bechtloff et al., 2001; T. Elperin et al., 2001; K. Fukui et al., 2002; R. P. Fishwick et al., 2003; Heidi Markus et al., 2004). Generally, higher temperatures and solute distribution, better mixing, faster diffusion and dissolution rate, and reducing gassing rate will result in a faster solid-liquid reaction rate.

Because at least one of the reactants and products are solids, and at least one of the reactants is liquid, there are four different major models of macro kinetics which can be used to describe the solid-liquid reaction crystallization (Brend Bechtloff et al., 2001). These models are shown in Figure 9 where solid reactant A reacts with liquid reactant B and forms the solid product P. If A has very limited solubility in B, based upon the different porosities of A and diffusivities of B and the reaction rates, models (a), (b) and (c) can be observed. If the system has low porosity of A and/or low diffusivity of B, the “shrinking core” model is appropriate. In this situation, if the reaction rate is high, the interface of A and P would be sharp reaction surfaces (Figure 1a), otherwise they would be unsharp reaction zones (Figure 1b). If the system has high porosity of A and/or high diffusivity of B, the continuous conversion model (Figure 1c) can be observed. However, if solid A is more soluble in liquid B, A can be dissolved first and then react with B to form solid P independently at different locations (Figure 1d). In some cases of the shrinking core model, with extremely low diffusivity of liquid B in product P, the reactant A can be blocked by P and the reaction stops.

Although the mechanism of terephthalic acid-N-methyl-2-pyrrolidinone salt formation is not quite the same as solid-liquid reaction crystallization, some of the theories and models can be applied. These models are useful in explaining the mass transfer and kinetics at the terephthalic acid solid and the N-methyl-2-pyrrolidinone liquid interface and with the formation of salt, as will be seen in the Results and Discussion section of this thesis.

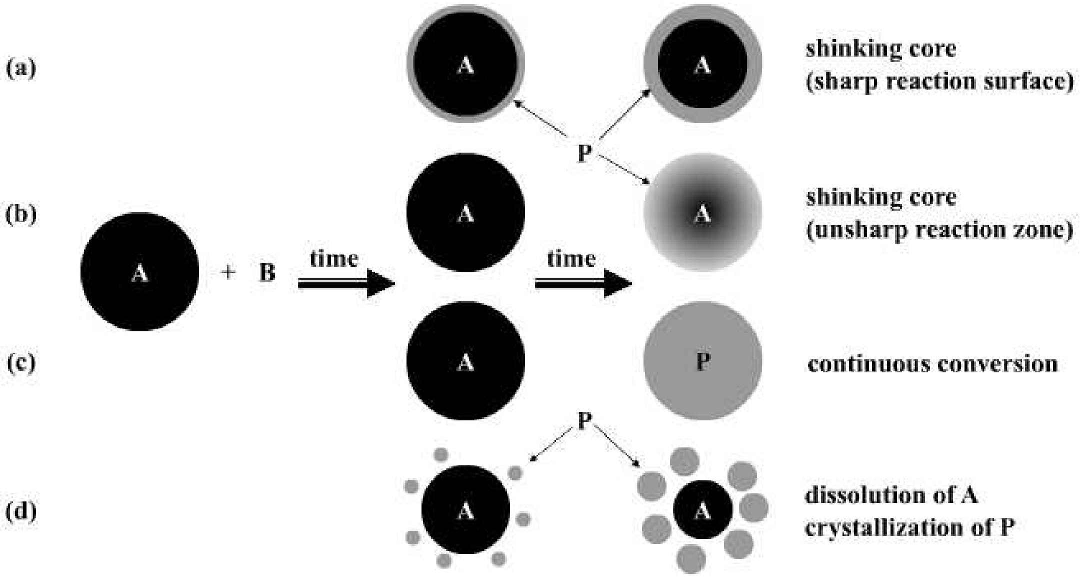

Figure 9. Macro Kinetics Models of Heterogeneous Solid-liquid Reaction Crystallization (Brend Bechtloff et al., 2001)

Phase Transition of Crystals

Since terephthalic acid-N-methyl-2-pyrrolidinone salt formation is not actually a chemical reaction, crystal phase transition can be used to help understand the phenomena. Most solids have more than one solid phase depending on conditions such as temperature, pressure and composition. When the conditions change, one phase of the solid could change to the other. The phase transitions can be sorted by the lowest derivative of the free energy that is discontinuous at the transition into two basic types: first-order phase transition and second-order phase transition. The first-order phase transitions are those that involve latent heat. This means that when a transition occurs, it either absorbs or releases energy. And because the energy cannot be transferred instantly between the system and environment, at that transition temperature or pressure point or range, it has the “mixed phase” with different portions of each phase depending on the amount of energy absorbed or released. The first-order phase transitions for solid/liquid/gas phases usually have temperature or pressure points where the transitions occur. The common example is water. However, the first-order phase transitions for solid/solid phase usually have transition ranges where the compositions of different phases vary with different temperatures or pressures in those ranges. The second-order phase transition is without latent heat. Because of this, the phase changes instantly at a certain point of temperature or pressure. An example is ferromagnetic transition in some materials.

The transition from pure terephthalic acid crystal to salt crystal has characteristics more similar to first-order phase transition between solids.

At a certain condition of temperature, pressure and composition, a solid should only have one phase, called the stable phase, that exhibits minimum free energy. All other solid phases at this condition are called metastable phases. But metastable solid phases can actually be fairly stable and have long lives in the stable phase environments. An example of this metastable phase is diamond, whose stable phase at room temperature and pressure should be graphite. However, the metastable solid phase is still likely to transition to the stable solid phase, if possible, to have the lower free energy. One way for solid phase to undergo transition is for the molecules or atoms in the solid to rearrange and form the other phase accompanied with energy absorbed or released. The other way is to put the solid in a solvent in which the solid can be dissolved, and the solid phase transition would occur in association with the solvent. A theory of the mechanism of crystal phase transition in a solvent medium was presented by P. T. Cardew et al. (1985). As shown in Figure 10, at temperature T_x, the solution composition goes from x_A to x_2. At composition x_A, the solution is supersaturated relative to both metastable phase 1 and stable phase 2. So both phases could be crystallized out until the composition reaches x_1. At composition x_1, the solution is not supersaturated relative to phase 1, but still supersaturated relative to phase 2. This results in stable solid phase 2 crystallization while there are still many crystals with metastable solid phase 1 in the slurry. In the region between composition x_1 and x_2, such as x_B, the solution becomes unsaturated relative to phase 1. So the crystals consisting of metastable phase 1 start to dissolve in the solvent and re-crystallize out as crystals consisting of stable phase 2. This process continues until all the crystals consisting of metastable phase 1 are dissolved and the remaining crystals consist of stable phase 2. This theory is very useful for explaining the salt formation rate of terephthalic acid using N-methyl-2-pyrrolidinone as the solvent.

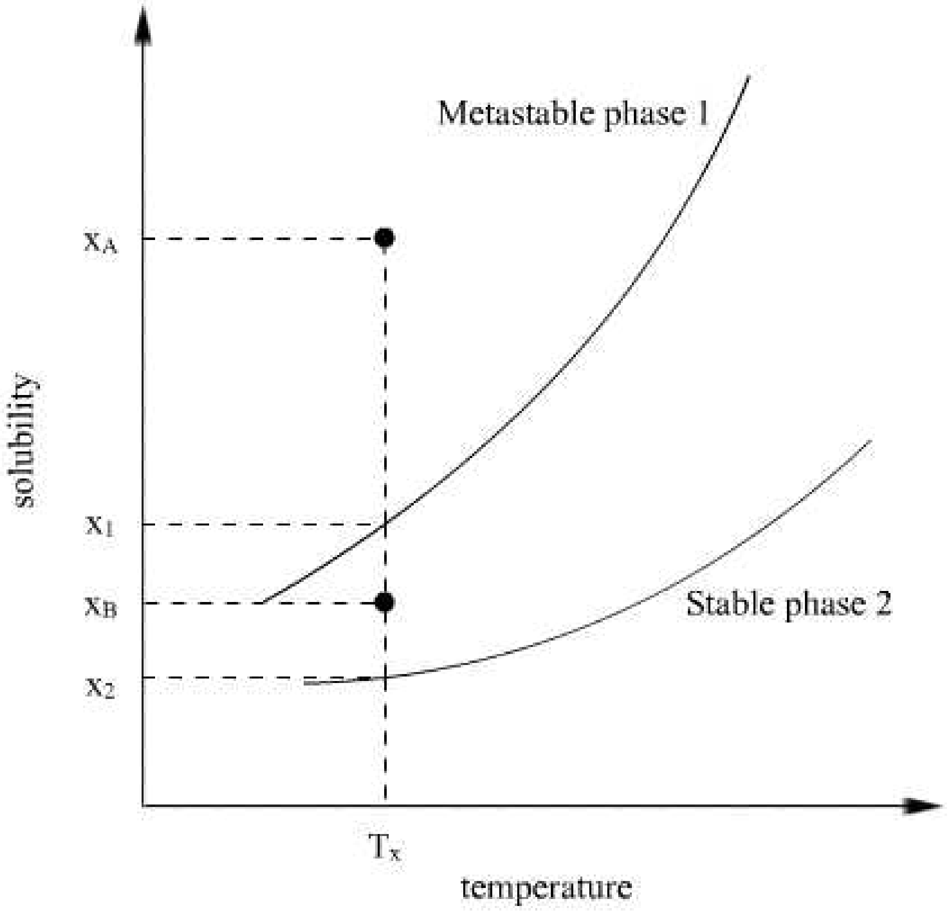

Figure 10. Solubility Curves for Two-phase Solid (P. T. Cardew et al., 1984)

Thesis Goal

The goal of this thesis was to investigate the salt formation rate in various environments in order to gain a better understanding of the salt formation kinetics.

Research Objectives

1. Find the crystal structure of terephthalic acid-N-methyl-2-pyrrolidinone salt.
2. Find the salt formation rates at various temperatures (0°C - 60°C) in the time range of 10 minutes to 24 hours.
3. Find the salt formation rates at various solid/liquid compositions (20g – 40g terephthalic acid/100g N-methyl-2-prrolidinone) in the time range of 10 minutes to 24 hours.

MATERIALS AND METHODS

Chemicals

Three chemicals were used for the experiments. The suppliers, purities, and usages of chemicals are listed in Table 6. The terephthalic acid-N-methyl-2-pyrrolidinone salt crystals were produced by totally dissolving the terephthalic acid in N-methyl-2-pyrrolidinone at elevated temperatures, cooling the solution to room temperature (~25°C), and maintaining the temperature for more than one week with or without agitation.

Table 6. Chemicals Information

Chemical	Supplier	Purity	Usage
Terephthalic Acid $C_8H_6O_4$	Acros	99+ %	Salt formation experiments, standards
N-Methyl-2-pyrrolidinone C_5H_9NO	EMD	99.77 %	Salt formation experiments, standards
N,N-Dimethylformamide C_3H_7NO	Burdick & Jackson	99.9+ %	Solvent for GC analysis, standards

Analytical Methods

3-D X-ray Diffraction

3-D x-ray diffraction was used to determine the crystal structure of the terephthalic acid-N-methyl-2-pyrrolidinone salt. 3-D x-ray diffraction data were collected using Siemens P4 upgraded Nicolet R3m automated four-circle diffractometer with a graphite monochrometer. Twelve reflections selected from a rotation photograph were centered and used to identify the unit cell and determine approximate lattice parameters.

Powder X-ray Diffraction

Powder x-ray diffraction was initially chosen to be the analytical method for determining the composition of the salt. Due to the different crystal structures of salt crystal and pure terephthalic acid crystal, the x-ray graphs with different peak positions for each crystal were expected. Although powder x-ray diffraction is generally used for qualitative analysis, quantitative analysis was attempted for this research since terephthalic acid/salt peaks should be proportional to the ratio of terephthalic acid/salt concentration of the samples.

The model of powder x-ray diffraction used for the analysis was Scintag X1 XGEN-4000. Every sample was scanned from $2\theta = 8°$ to $2\theta = 30°$ with step size 0.02° and scan rate 4.0 deg/min.

Calibration for the Compositional Analysis Using Powder X-ray Diffraction

To perform the compositional calibration using powder x-ray diffraction, the pure terephthalic acid crystal powder and the pure pre-ground salt crystal powder were analyzed. The peaks that did not overlap and were of adequate size were chosen as representative peaks for terephthalic acid or salt crystals. The chosen peaks should appear on the x-ray diffraction graphs of terephthalic acid/salt mixture. Three standards of different ratios of terephthalic acid/salt: 3 (25% salt), 1 (50% salt), 0.33 (25% salt) were prepared and scanned. The areas of the representative peaks for terephthalic acid or salt were integrated and quantified. Considering the quantified peak areas, the peaks that resulted in the most linear area ratio were chosen for the calibration.

Gas Chromatography

Gas Chromatography (GC) was chosen as the primary analytical method. The gas chromatograph used for the analysis was a Hewlett Packard (HP) 5890 series II. One microliter of each sample was injected by a Hewlett Packard (HP) 7673 automatic injector. The detector was flame ionization detector (FID). The column was an HP-5, made by J&W Scientific, with the dimension of 30 meters length, 0.32 mm internal diameter and 0.1 um film thickness. The carrier gas was helium. A simple schematic of a gas chromatograph is shown in Figure 11. The temperature of the injector was 320°C and the temperature of detector was 320°C. Temperature and pressure programs were designed to achieve the best peak resolution. The temperature program is shown in Table 7, and the pressure program is shown in Table 8. The total residence time was 10 minutes for each injection.

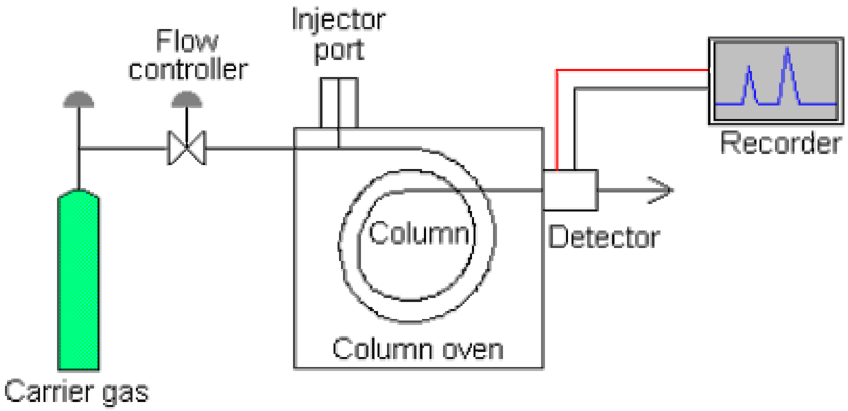

Figure 11. Simple Schematic of a Gas Chromatograph

Table 7. Temperature Program for GC Analysis

	Rate (°C/minute)	Final Temperature (°C)	Final Time (minute)
Initial	—	130	—
Level 1	10	160	0
Level 2	40	230	1.76
Level 3	26.1	321	0

Table 8. Pressure Program for GC Analysis

	Rate (psi/minute)	Final Pressure (psi)	Final Time (minute)
Initial	—	6.0	—
Level 1	1.0	6.0	2.5
Level 2	18.0	2.0	2.5
Level 3	84.0	25.0	4.5

All the samples for GC analysis were dissolved in N,N-dimethylformamide and put in GC vials ready for analysis. One microliter of each dissolved sample was injected in to the GC and carried by helium through the column. Three chemicals, N,N-dimethylformamide, N-methyl-2-pyrrolidinone and terephthalic acid, were separated and detected by the FID detector. N,N-dimethylformamide was the first compound to come out, N-methyl-2-pyrrolidinone was the second, and terephthalic acid was the last. From the areas of the peaks and the calibration equations, the concentrations of terephthalic acid and N-methyl-2-pyrrolidinone can easily be calculated. By knowing the ratio of terephthalic acid/N-methyl-2-pyrrolidinone (TA/NMP) in the salt by analyzing the pure salt first, a further calculation can be made to determine the salt percentage of each sample.

Calibration for the Compositional Analyses Using Gas Chromatography

Six vials containing different weight ratios of N-methyl-2-pyrrolidinone to terephthalic acid were prepared and analyzed. The concentrations of terephthalic acid in all vials were about the same, but the concentrations of N-methyl-2-pyrrolidinone in the vials varied from 4% to 67% relative to the total mass of terephthalic acid and N-methyl-2-pyrrolidinone. The areas of the terephthalic acid and N-methyl-2-pyrrolidinone peaks as determined from the standards were automatically integrated and the area ratios calculated relative to the total area. By plotting the area ratio as the x axis and weight ratio as the y axis, a linear calibration curve was obtained and calibration equations were determined for terephthalic acid and N-methyl-2-pyrrolidinone.

Experiment 1: Pure Salt Analysis – Salt Composition Determination

A large salt crystal grown using the method described in the Chemicals section (page 25) with the approximate dimension of 0.3cm×0.3cm×1.2cm was dissolved in N,N-dimethylformamide for analysis by GC. Because NMP solvent can be trapped in the crystals during formation, the purpose of this experiment was to determine the actual ratio of terephthalic acid to N-methyl-2-pyrrolidinone that could be expected in a salt crystal.

Experiment 2: Entrained Solvent and Salt Breaking Rate Analysis

After each salt formation test, the samples were filtered prior to analysis. Solvent entrained on the crystal surface must be removed so as to not interfere with the salt analysis. However, we cannot use a normal rinsing process to get rid of the solvent entrained on the surface of the crystals. The reason is that the other low-boiling solvents, including water, that are miscible with N-methyl-2-pyrrolidinone and have good rinsing efficiency could also dissolve the N-methyl-2-pyrrolidinone in the salt crystal structure and break the salts. The salts would decompose to the fine terephthalic acid crystals previously described and the N-methyl-2-pyrrolidinone would be removed with the rinsing solvent. Drying the slurry by baking would also break the salt structure by vaporizing the N-methyl-2-pyrrolidinone. Therefore a dry filtration process using air and a Buchner funnel with vacuum was chosen. The appropriate amount of time to pull air through the crystals in order to remove entrained solvent was determined.

A simple vacuum filtration setup was used and is shown in Figure 12. To determine the approximate amount of entrained solvent that would remain on the crystals after different filtration durations, a small amount of hot solvent (> 80°C) was poured on a layer of pure terephthalic acid and the vacuum was instantly applied. Hot solvent was used to ensure that no salt would form while the solvent was in contact with the crystals. Samples were then taken at different periods of time and analyzed by GC to determine the amount of entrained solvent remaining on the crystals.

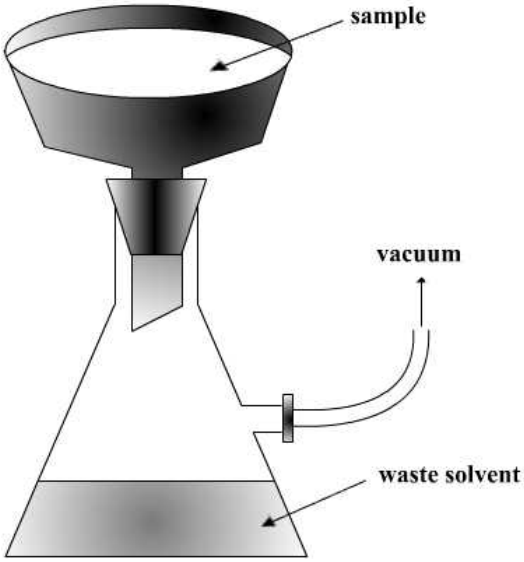

Figure 12. Filtration Setup

Because the humidity in the air could potentially dissolve the N-methyl-2-pyrrolidinone and break the salts, a test for finding salt breaking rate versus the vacuum filtration time has also been performed. The pure salt crystals were made by the method described in the Chemicals section (page 25) with agitation. The salt crystals were filtered using the same setup shown in Figure 12 and the samples were taken at the same period of time as the entrained solvent test. The salt sample before filtration and the samples taken during the filtration were analyzed by GC to determine the salt breaking rate during the filtration process.

Comparing the results of entrained solvent test and salt breaking rate test, a filtration time corresponding to negligible entrained solvent and minimal salt breaking can be chosen.

Experiment 3: Solubility Test

Salt formation experiments used saturated solvent. Therefore accurate knowledge as to the solubility of terephthalic acid in N-methyl-2-pyrrolidinone was crucial. The solubility of terephthalic acid in N-methyl-2-pyrrolidinone was verified for the salt formation temperature range: 0°C - 60°C.

The solution was agitated using a stir bar in a 250-ml flask. The temperature control used an ice bath for the temperature below ambient conditions and digital hotplate for the temperatures above ambient conditions. At each temperature, no more than 0.15 grams of terephthalic acid were added to the solution at a time until it was visually determined that the solute was not dissolving for at least 30 minutes. The total amounts of terephthalic acid added at each temperature to reach the solubility limit were summed and plotted to get the solubility curve.

Experiment 4: Isothermal Salt Formation

The salt formation was tested isothermally using a 250-ml beaker and an overhead digital mixer. The beaker containing the TA/NMP solution was placed in an ice bath if tested at a temperature below ambient conditions, and on the hotplate if tested at a temperature above ambient conditions. The experimental setup is shown in Figure 13.

Figure 13. Salt Formation Test Setup: Ice Bath (Left); Hotplate (Right)

The variables tested were temperature, mixing time, and loading, which was the amount of pure terephthalic acid added relative to 100 grams of pure solvent. The temperature range for the experiments was 0°C - 60°C. The range of mixing time was 5 minutes – 1440 minutes (24 hours). And the range of loading was 20 grams – 40 grams per 100 grams of pure solvent.

Before terephthalic acid was added at the specified solids loading, the 100 grams of pure solvent was saturated by adding and dissolving terephthalic acid up to the solubility limit. The mixing time was measured beginning at the time the terephthalic acid was added into the saturated solvent. The amount of time required to add the terephthalic acid varied depending upon the amount added, but was no longer than two minutes. After salt formation, the mixer was stopped and the mixture was filtered using the filtration setup shown in Figure 12. The elapsed time between turning off the mixer and filtration was no longer than 15 seconds. The crystals were vacuum-filtered for a specific time, then samples were taken from three different positions on the filter, dissolved in N,N-dimethylformamide, and analyzed by GC.

RESULTS AND DISCUSSION

Crystal Structure of Terephthalic Acid-N-Methyl-2-pyrrolidinone Salt

The salt crystal structure was revealed by 3-D x-ray diffraction. The unit composition of 1 mole of terephthalic acid to 2 moles of N-methyl-2-pyrrolidinone was confirmed. As shown in Figure 14, this unit has one hydrogen bond on each side of the terephthalic acid connecting to the oxygen atom of N-methyl-2-pyrrolidinone. The 3-D packing structure is shown in Figure 15.

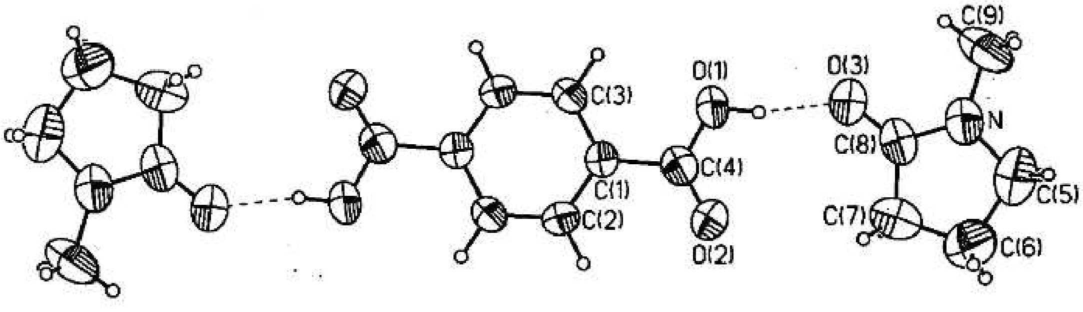

Figure 14. Molecular Structure and Labeling Scheme for $C_8H_6O_4 \cdot 2C_5H_9NO$

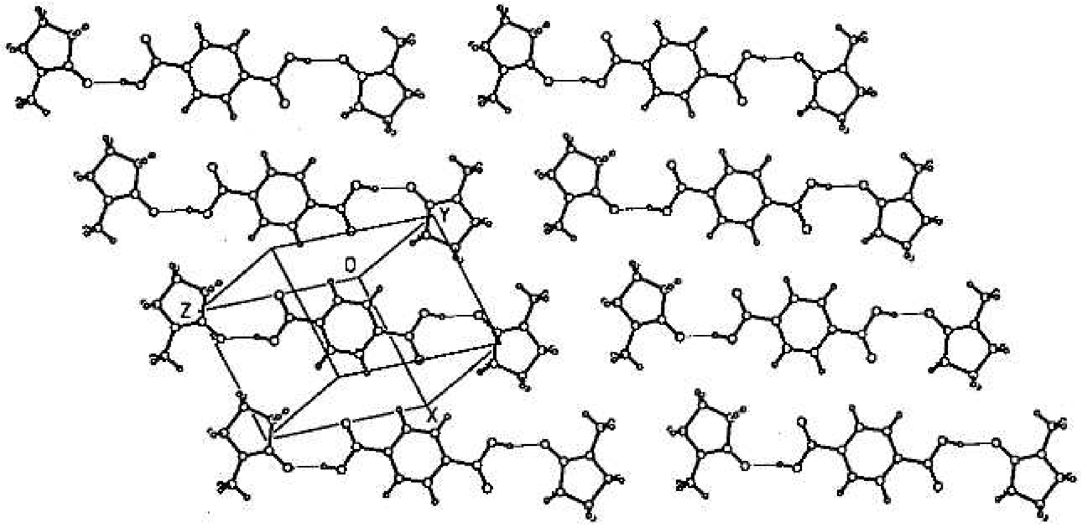

Figure 15. 3D Packing Structure for Salt Crystal

In the absence of mixing, the kinetics of salt formation could be represented by the shrinking core model (Figure 9a, 9b) based on the visual observations using a microscope with the rate primarily dependant on diffusion. However, with good mixing like the experiments in this thesis, the crystal is easy to break apart. This is because there are only two hydrogen bonds in a unit of salt crystal and no hydrogen bond between units (Figure 15), compared with two hydrogen bonds between molecules that form a chain in the terephthalic acid crystal (Figure 2). If the solid-liquid reaction resulted in a layer of salt around terephthalic acid crystal, with mixing this layer could easily be broken off by the mixer or the particles around it. Moreover, both terephthalic acid and salt could dissolve in the solvent to produce the supersaturated solvent. For these reasons, the salt formation kinetics for the experiments in this thesis were considered as model (d) of Figure 9 and no diffusion factor was included in the explanation.

Calibration for the Compositional Analyses Using Powder X-ray Diffraction

Powder x-ray diffraction was initially intended to be used for quantitative analysis by calibrating the area ratio of the specific peaks of terephthalic acid or salt relative to the weight ratio. Unfortunately, the method did not provide adequate quantification of the compounds and so was not used.

Calibration for the Compositional Analyses Using Gas Chromatography

Without being able to use powder x-ray diffraction for quantitative analysis, gas chromatography (GC) was considered as the analytical method of choice. First, the peak retention time for N,N-dimethylformamide, N-methyl-2-pyrrolidinone and terephthalic acid were determined using the GC method described in Methods and Theory (page 28-29). The identification of these peaks in a chromatogram is shown in Figure 19 (whole screen) and Figure 20 (maximized screen). From the peak area ratio determined by GC, the weight ratio of terephthalic acid and N-methyl-2-pyrrolidinone was determined by the calibration equation. By knowing the composition of the salt, it is easy to calculate the percentage of salt in the samples from the weight ratio of terephthalic acid and N-methyl-2-pyrrolidinone.

Six standards were prepared containing various concentrations of terephthalic acid and N-methyl-2-pyrrolidinone. These standards were then analyzed to determine the calibration equation. From previous experience, it was known that the GC analytical results were more consistent if the concentration of terephthalic acid was above 4% relative to the solution. Therefore, all standards were prepared with the terephthalic acid concentration of 4.6% (the solubility of terephthalic acid in N,N-dimethylformamide is ~5%). Table 11 shows the percentage of terephthalic acid and N-methyl-2-pyrrolidinone relative to the sum of both for each standard.

Table 9. Compositions of Standards for Gas Chromatography Analysis (on a N,N-dimethylformamide-free basis)

Standard	TA %	NMP %
1	95.80 %	4.20 %
2	82.13 %	17.87 %
3	67.73 %	32.27 %
4	56.17 %	43.83 %
5	45.02 %	55.98 %
6	33.88 %	66.12 %

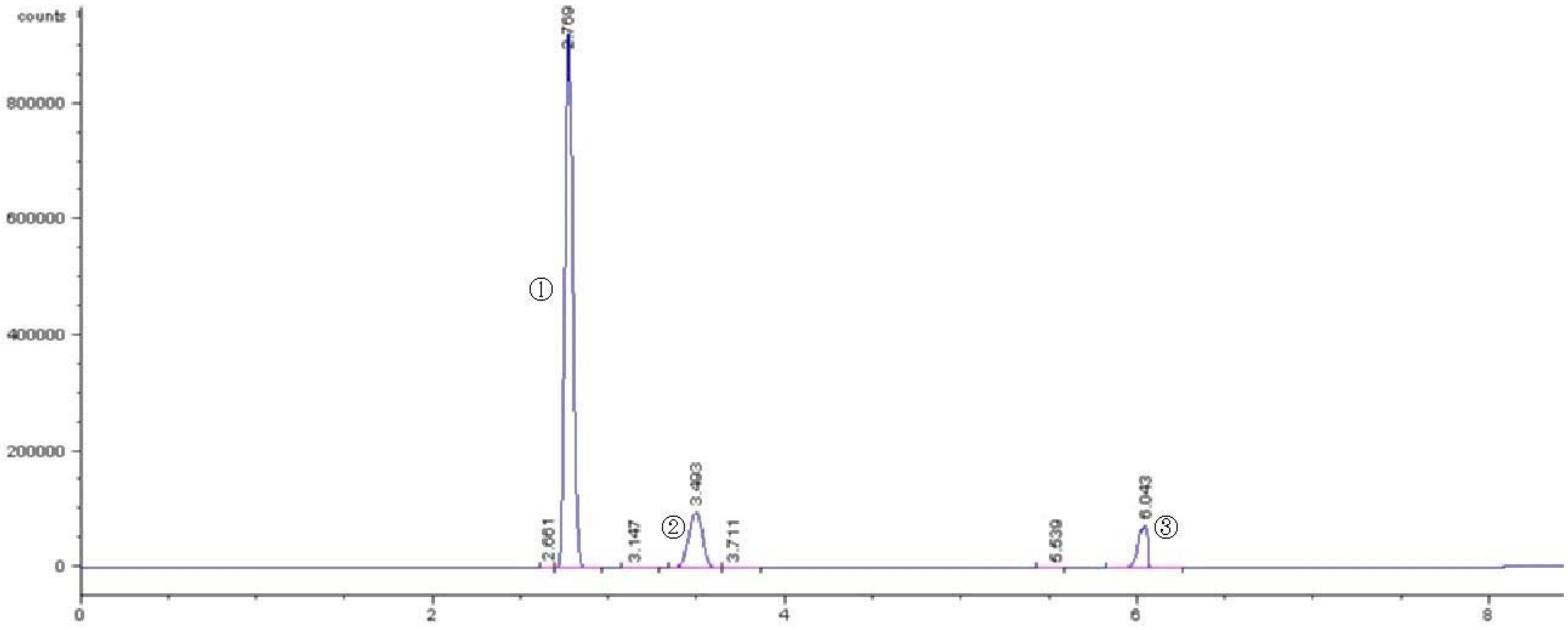

Figure 16. Gas Chromatography of Standard (whole screen): (1) N,N-dimethyl formamide; (2) N-methyl-2-pyrrolidinone; (3) terephthalic acid

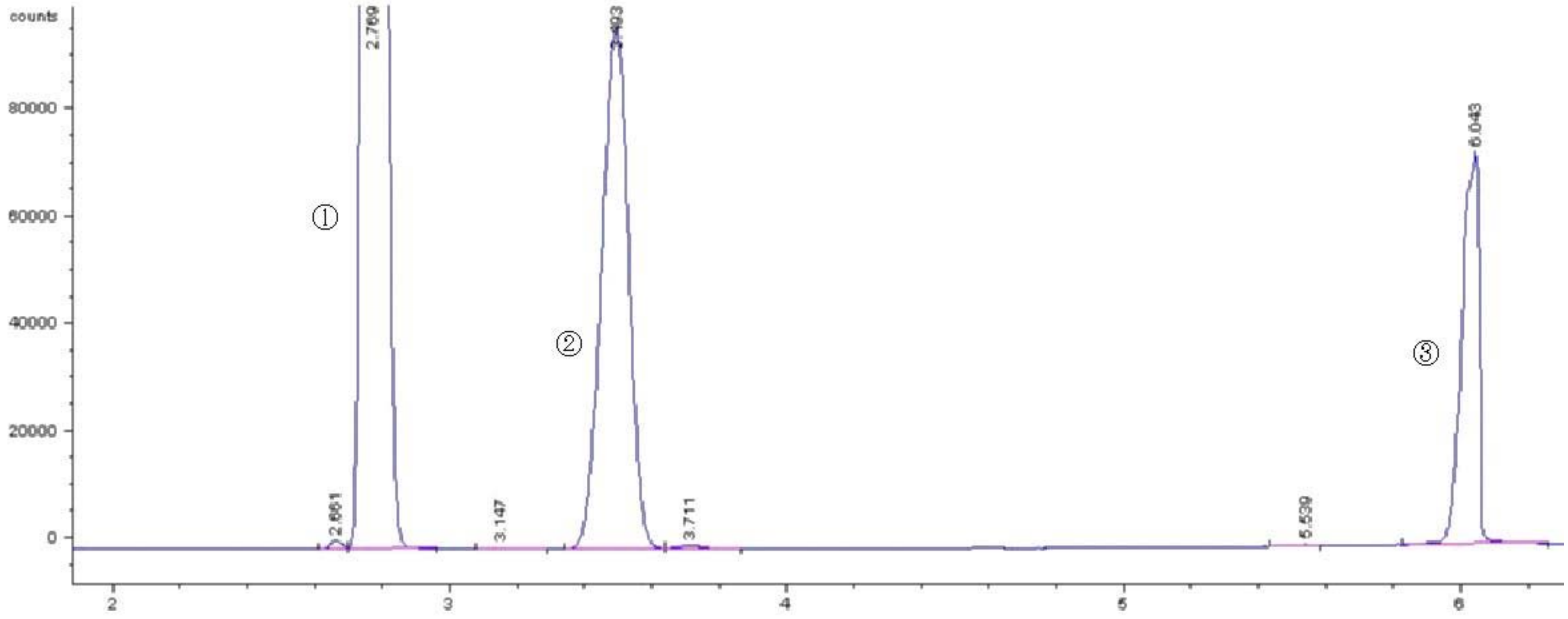

Figure 17. Gas Chromatography of Standard (maximized screen): (1) N,N-dimethyl formamide; (2) N-methyl-2-pyrrolidinone; (3) terephthalic acid

After the peak areas of the standards were integrated, the calibration curve and equation were calculated for N-methyl-2-pyrrolidinone, shown in Figure 21.

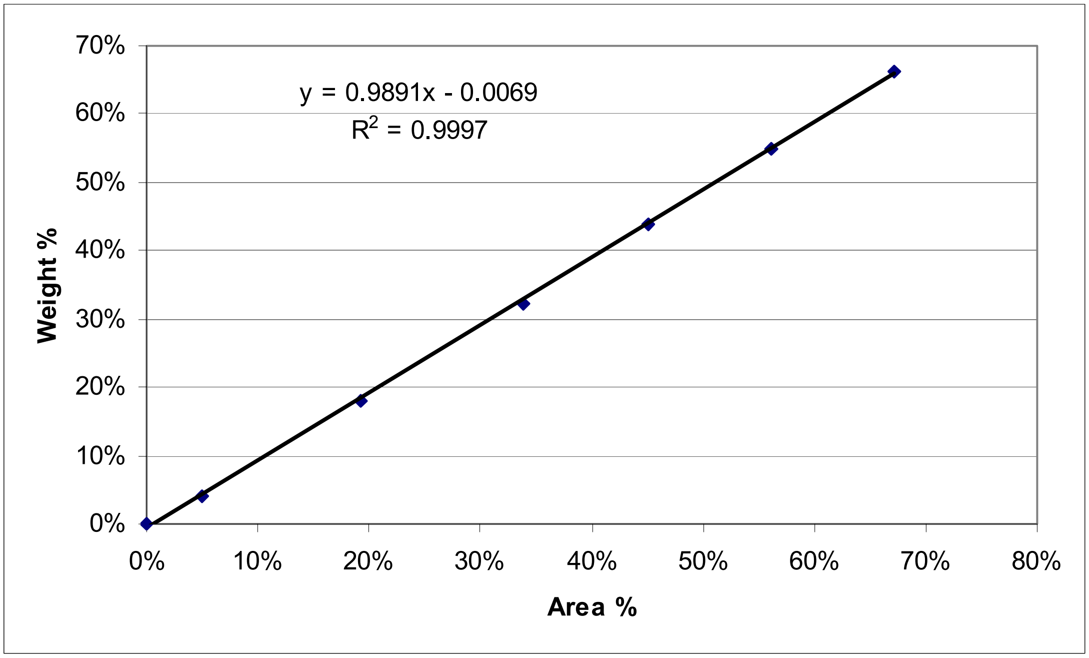

Figure 18. Calibration Curve and Equation for N-Methyl-2-pyrrolidinone

The accuracy of this calibration using gas chromatography was tested using six samples with known concentrations in the range of calibration. The errors were between 0.2 % - 1.2 % of sample concentration. The reproducibility was also tested by analyzing the same sample four times with at least one-hour interval between each analysis. The standard deviation was 0.23 %.

Experiment 1: Pure Salt Analysis – Salt Composition Determination

A large pure salt crystal was analyzed by GC and determined to be 57.7 % N-methyl-2-pyrrolidinone and 42.3 % terephthalic acid by weight. Using the molecular weights of N-methyl-2-pyrrolidinone and terephthalic acid, we determined that the molar ratio of N-methyl-2-pyrrolidinone/terephthalic acid in the salt was 2.29. That means for a large salt crystal, crystallized by natural cooling, 0.29 mole of additional N-methyl-2-pyrrolidinone had been trapped within one mole of salt molecule.

Experiment 2: Entrained Solvent and Salt Breaking Rate Analysis

Entrained Solvent Test

Two sets of tests were performed using pure terephthalic acid and hot N-methyl-2-pyrrolidinone, and the samples were taken after 1, 3, 5, 7 and 10 minutes of vacuum filtration. The analytical results are shown in Table 12. These results were compared with the results of salt breaking rate to determine the appropriate time for filtration.

Table 10. The Analytical Results of Entrained Solvent Tests

Time of vacuum applied	1st Set		2nd Set	
	TA %	NMP %	TA %	NMP %
1 min	94.5 %	5.5 %	97.4 %	2.6 %
3 min	95.8 %	4.2 %	98.9 %	1.1 %
5 min	98.2 %	1.8 %	99.5 %	0.5 %
7 min	99.6 %	0.4 %	99.6 %	0.4 %
10 min	99.1 %	0.9 %	99.7 %	0.3 %

Salt Breaking Rate Test

Three sets of tests were performed using pure salt crystals, and the samples were taken after 1, 3, 5, 7 and 10 minutes of vacuum filtration. The analytical results are shown in Table 13.

Table 11. The Analytical Results of Salt Breaking Rate Tests

Time of vacuum applied	1st Set			2nd Set			3rd Set		
	TA %	NMP %	Molar NMP/TA	TA %	NMP %	Molar NMP/TA	TA %	NMP %	Molar NMP/TA
1 min	42.5%	57.5%	2.27	42.8%	57.2%	2.24	42.3%	57.7%	2.28
3 min	57.3%	42.7%	2.25	42.4%	57.6%	2.27	42.5%	57.5%	2.27
5 min	56.8%	43.2%	2.21	43.5%	56.5%	2.18	43.1%	56.9%	2.21
7 min	56.9%	43.1%	2.21	43.2%	56.8%	2.20	42.8%	57.2%	2.24
10 min	55.2%	44.8%	2.06	44.3%	55.7%	2.11	44.2%	55.8%	2.12

Comparison and Determination of Filtration Time

As can be seen in Table 12, the amount of entrained solvent decreased as the time the vacuum was applied increased. This can be explained as follows; as the air passed through the particles, it removed solvent vapor and/or the humidity in the air grabbed the entrained solvent making it more volatile. As for the salt crystals, the same reason can be applied, only in this case, as the solvent is removed, the salt breaks. The compositions at one minute (molar ratio = 2.24 – 2.28) were still close to the composition of the big salt crystal (molar ratio = 2.29). As filtration increased, the salt crystals kept decomposing and losing solvent to reach the molar ratio of 2.06 – 2.12 after ten minutes of air passing through.

In order to minimize the amount of entrained solvent and percentage of salt breaking, 7 minutes of filtration time was chosen as the standard procedure for all salt formation experiments. About 0.5% of entrained solvent remained after 7 minutes filtration time and was considered as the error in the results. The average salt composition after 7 minutes filtration time was about 57% N-methyl-2-pyrrolidinone and 43% terephthalic acid. This composition was taken as the standard pure salt composition for the salt formation experiments. To calculate the weight percentage of salt in each sample, the weight percentage of N-methyl-2-pyrrolidinone from the analytical results of each sample is divided by 57%. For instance, if the analytical result of N-methyl-2-pyrrolidinone percentage was 40%, then the salt percentage in this sample would be 40% ÷ 57% = 70.2%.

Experiment 3: Solubility Test

Solubility of terephthalic acid in N-methyl-2-pyrrolidinone was tested in order to prepare the saturated solvent at a given temperature. Eleven points of solubility were tested between the temperatures of 3°C and 61°C. The solubility curve was well represented by a second-order equation. The solubility curve and equation are shown in Figure 22.

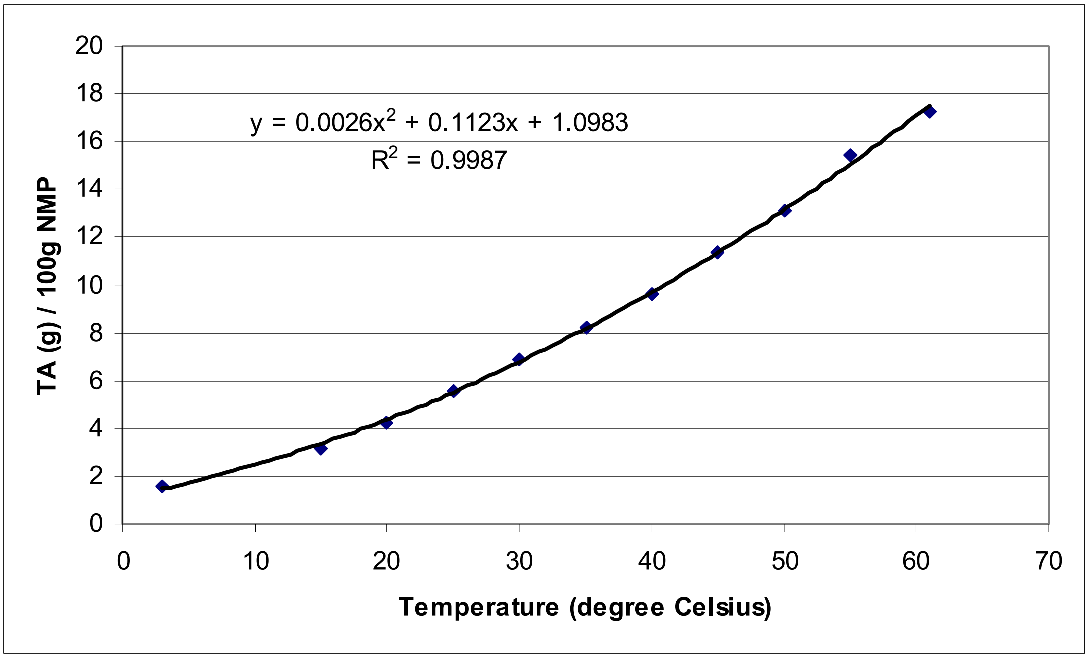

Figure 19. Solubility Curve of Terephthalic Acid in N-Methyl-2-pyrrolidinone

Experiment 4: Isothermal Salt Formation

Varying Temperatures and Mixing Times

The salt formation at six different temperatures (3°C, 25°C, 40°C, 50°C, 58°C and 60°C) and six different mixing times (10 min, 30 min, 60 min, 180 min, 720 min and 1440 min) at a constant loading of 30g terephthalic acid/100g pure solvent were tested. The test at 60°C was modified with a loading of only 10g terephthalic acid/100g pure solvent due to the number of fine crystals present and the problems of filtration. The results are shown in Table 14, Figure 23 (x = 0-1500 min, y = 0-110%

salt), Figure 24 (x = 0-200 min, y = 10-110% salt), and Figure 25 (x = 0-200 min, y = 70-110% salt). The condition of 40°C, 60 min, 30g/100g was tested five times and the condition of 50°C, 60 min, 30g/100g was tested four times to calculate the experimental and analytical deviations. The results are shown in Table 15, and the error bars of ±1 standard deviation values are shown in Figure 25.

Table 12. Salt Percentage in the Solids from Experiments with Constant Loading of 30g TA/100g NMP (except 10g TA/100g NMP for 60°C)

	3°C	25°C	40°C	50°C	58°C	60°C
0 min	0	0	0	0	0	0
10 min	88.8 %	76.2 %	80.1 %	82.7 %		
30 min	97.4 %	82.5 %	82.7 %	87.1 %	82.0 %	
60 min	100.3 %	85.5 %	85.0 %	89.1 %		
180 min	102.1 %	94.2 %	88.7 %	91.2 %	82.2 %	
720 min		103.0 %			82.7 %	
1440 min		103.2 %	95.7 %	96.0 %		7.6 %

Table 13. Reproducibility Test Results for Two Conditions

	1st	2nd	3rd	4th	5th	Average	Deviation
40°C, 60min, 30g/100g	84.1 %	84.6 %	86.4 %	85.3 %	84.5 %	85.0 %	0.89 %
50°C, 60min, 30g/100g	89.0 %	89.0 %	88.7 %	89.5 %		89.1 %	0.31 %

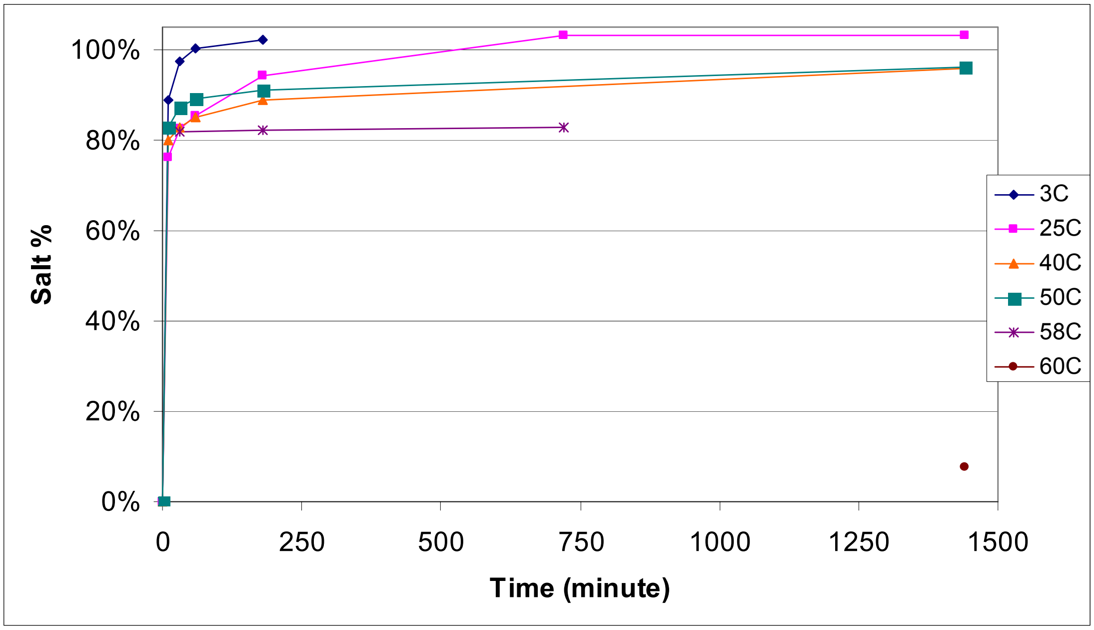

Figure 20. Salt Percentage in the Solids from Experiments with Constant Loading of 30g TA/100g NMP (except 10g TA/100g NMP for 60°C)

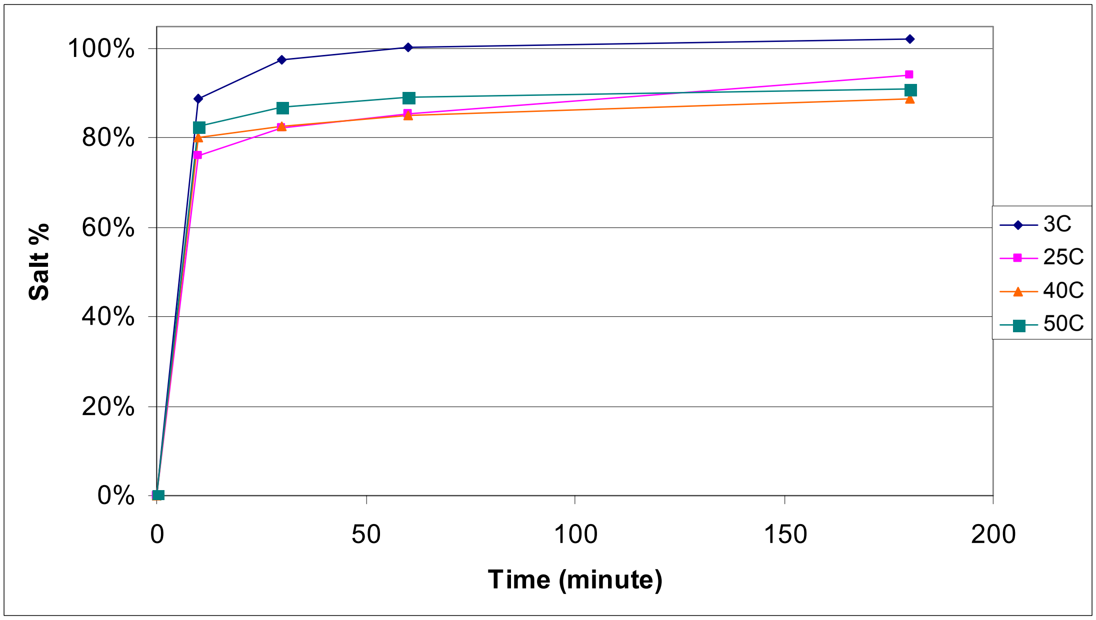

Figure 21. Magnified Graph of Figure 20

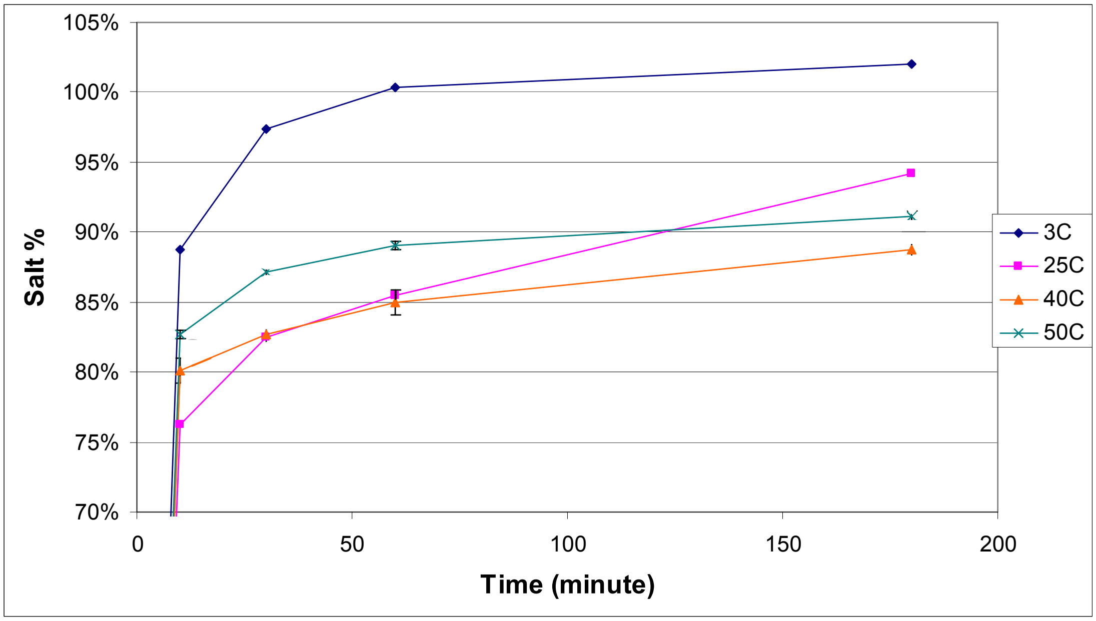

Figure 22. Magnified Graph of Figure 21

Some points exceed 100% salt due to the error associated in determining the excess NMP trapped within the salt. This error affects the weight percentage of TA and NMP and the calculation shown on page 47. But this error should not affect the trend.

Temperature Range for Salt Formation

As shown in Figure 23, a temperature range for the TA-Salt transition was established. With the loading of 30g TA/100g NMP, salt formation at 25°C reached steady state of about 103% salt after 720 minutes. The slope of the line of salt formation at 40°C was a little greater than 50°C and their lines crossed at 1440 minutes. So, once steady state was reached, higher percentage salt for 40°C than for 50°C would be expected. Salt formation at 58°C reached steady state at about 82% salt after 30 minutes. It was observed for the temperatures above 25°C that salt formation at higher temperature reached the percentage salt near steady state faster. Therefore the 7% salt formation at 1440 minutes for 60°C could be considered as steady state. From these results, a temperature range between 25°C to around 60°C for TA-salt transition can be expected. In this temperature range for TA/salt transition, the percentage of salt formed at steady state varied from 0% to 100% depending upon the temperature. At temperatures closer to 60°C a higher percentage of TA was present at steady state, and at temperature closer to 25°C a higher percentage of salt was present at steady state. The exact high and low limits for this transition temperature range cannot be determined by these experiments.

The TA-salt transition consists of the solvent molecules disassociating and associating in the solid phase. At steady state it was found that the result was very similar to first-order solid-solid phase transition with a temperature range where two phases coexist.

Salt Formation Rate before Steady State

As shown in Figures 23 to 25, the initial salt formation rate at 3°C reached steady state very quickly. Then the initial salt formation rate decreased as the temperature decreased from 50°C to 25°C. That is why the salt formation lines for

25°C, 40°C and 50°C crossed each other because the percentage salt at steady state for 25°C is higher than 40°C, and higher than 50°C. This trend can be explained by the combination of reaction rate and Cardew's (1984) theory.

As for the transition reaction itself, the rate should be higher with higher temperature. But the trend observed for salt formation goes down from 3°C to 25°C, then goes up from 25°C to 50°C. To explain this phenomenon, the Cardew's (1984) theory needs to be introduced and combined with the reaction rate.

Unlike the solubility curves shown in Figure 10, in a salt formation system, the curves would look more like what is shown in Figure 26. The solubility of the stable phase 2 (salt) is the solubility that can be measured from the solubility test as described in this thesis. Above the stable phase 2, hypothetically there exists a metastable phase 1 (terephthalic acid) that grows closer to stable phase 2 at higher temperatures. As explained using this model, before the 20g – 40g of terephthalic acid was added, the saturated solution was right on the curve of stable phase 2, such as a1 at 3°C, b1 at 25°C, and c1 at 50°C. After adding terephthalic acid and mixing, some of the terephthalic acid would be dissolved and make the solution supersaturated. That means the concentrations at 3°C, 25°C and 50°C rose to the points above a1, b1 and c1, assuming the largest magnitude of supersaturation they could rise was the same, which is a1 to a2, b1 to b2, and c1 to c2. At 3°C, the supersaturation does not reach the solubility of metastable phase 1. So, once the solution gets supersaturated, only salt will be crystallized out. At 25°C, it is possible for the solution to be supersaturated above the solubility of metastable phase 1. Once the concentration is supersaturated above the solubility of metastable phase 1, both terephthalic acid solid and salt could crystallize. At 50°C, it is also possible, and has higher chance for the solution to reach the supersaturation above the solubility of metastable phase 1, and result in both terephthalic acid solid and salt crystallizing. Based on this hypothesis, there are more chances to exceed the solubility of metastable phase 1 and crystallize both solid phases at higher temperature. That also means that the "salt conversion possibility" is lower at higher temperature, and could be 100% at low temperature such as 3°C. The "salt formation possibility" here was defined as the possibility to convert to salt from TA when the solution gets supersaturated.

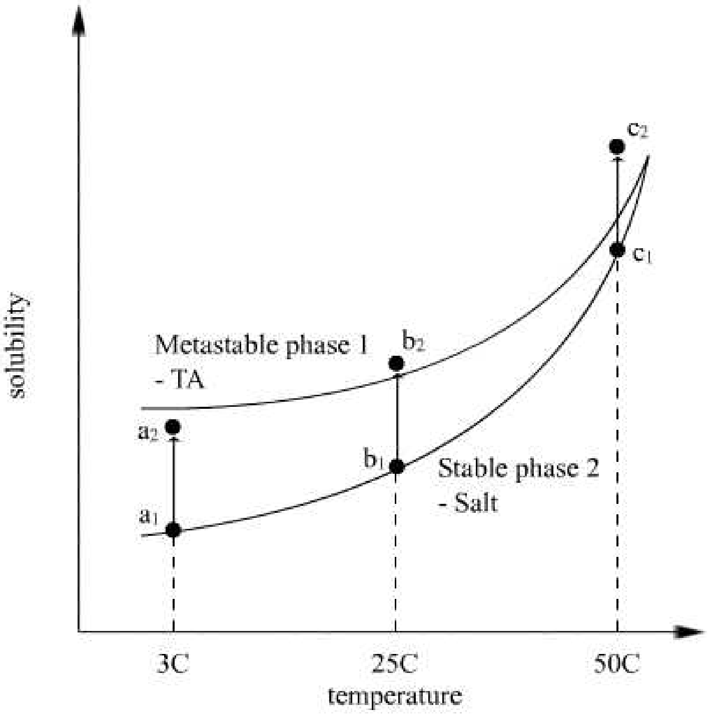

Figure 23. The Hypothetical Solubility Curves in Salt Formation System

An illustration and simple simulation based upon this hypothesis was performed using Excel and is explained in the Appendix. The results from these calculations were found to qualitatively match the experimental observations.

Varying Loadings and Mixing Times

The salt formation at five different solid loadings (20g, 25g, 30g, 35g and 40g TA per 100g NMP) and four different mixing times (10 min, 30 min, 60 min and 180 min) at constant temperature of 25°C were tested. The results are shown in Table 16, Figure 27 (x = 0-200 min, y = 0-110% salt) and Figure 28 (x = 0-200 min, y = 70-110% salt).

Table 14. Salt Percentage in the Solids from Experiments at Constant Temperature of 25°C

	20g TA /100g NMP	25g TA /100g NMP	30g TA /100g NMP	35g TA /100g NMP	40g TA /100g NMP
0 min	0	0	0	0	0
10 min	80.2 %	78.3 %	76.2 %	80.7 %	79.8 %
30 min	83.7 %	83.3 %	82.5 %	83.9 %	83.5 %
60 min	87.4 %	88.6 %	85.5 %	89.7 %	88.0 %
180 min	95.9 %	98.0 %	94.2 %	93.3 %	89.7 %

The percentage of salt formation at 10 min, 30 min and 60 min were very close and some were within the ranges of experimental and analytical deviation. When the mixing time was 180 minutes, the values had larger differences. This can be explained roughly by there being less free solvent molecules in the solutions with higher loading. This explanation can be used to describe the trend of increasing salt formation rate from 40g TA/100g NMP to 25g TA/100g NMP. But no proper explanation can be made for the anomalous value of 20g TA/100g NMP at 180 minutes.

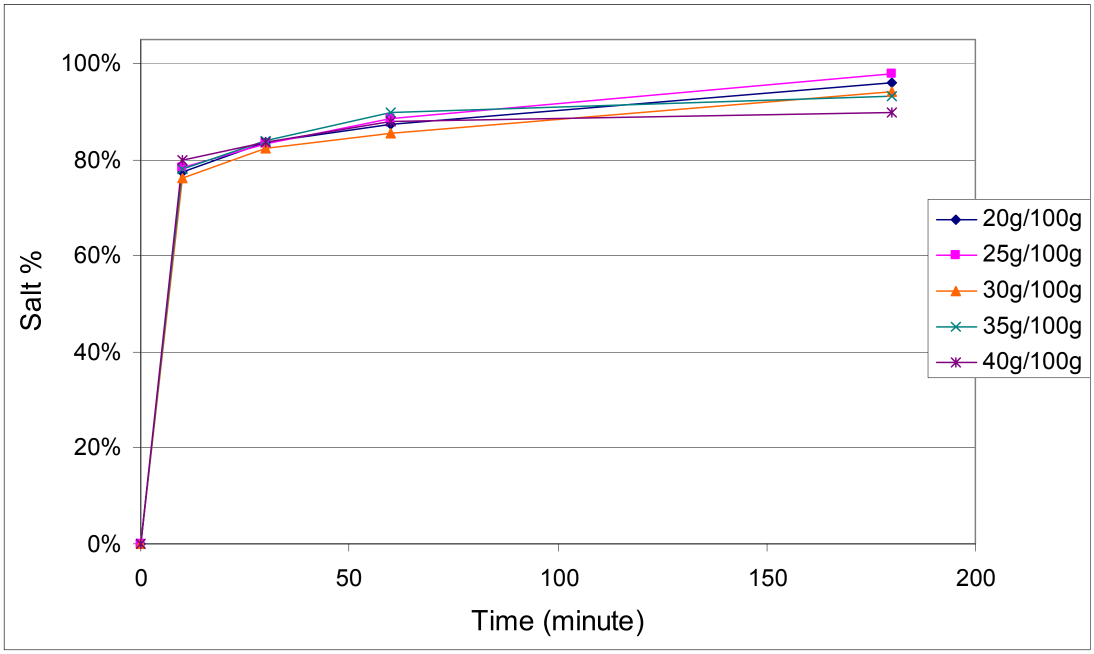

Figure 24. Salt Percentage in the Solids from Experiments at Constant Temperature of 25°C

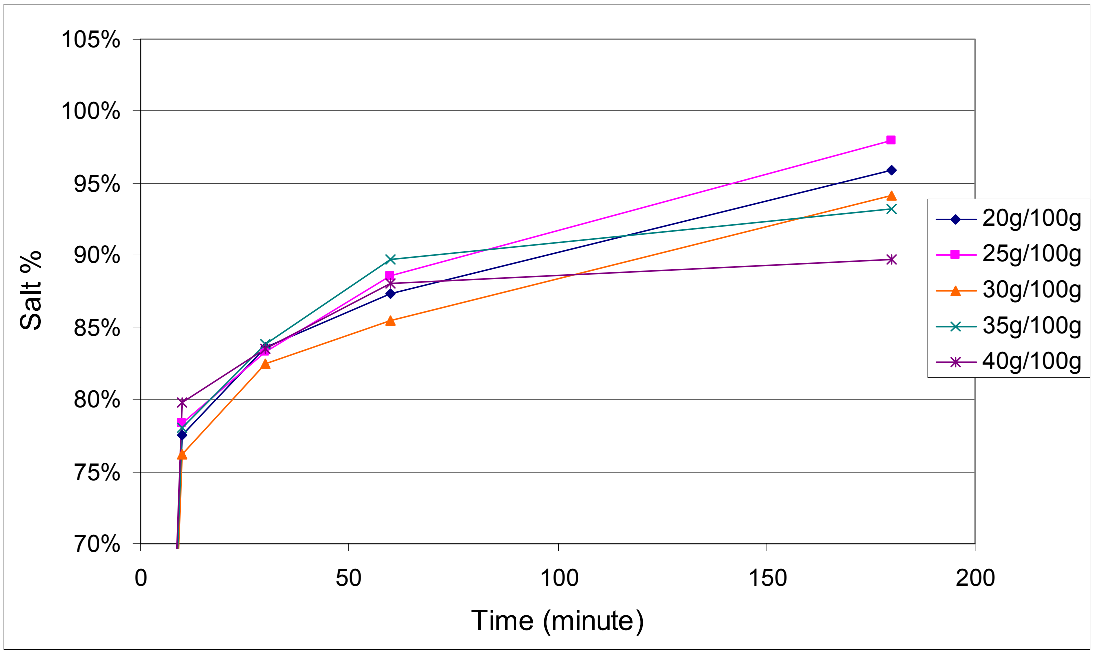

Figure 25. Magnified Graph of Figure 24

CONCLUSIONS

Based on a series of tests performed regarding terephthalic acid-N-methyl-2-pyrrolidinine salt and the salt formation, several conclusions may be stated:

1. The crystal structure of terephthalic acid-N-methyl-2-pyrrolidinine salt has been revealed. Comparing this structure to the crystal structure of pure terephthalic acid, the salt crystal can be easily broken. Because of this, the diffusion factor in salt formation should be negligible.
2. The analytical method of gas chromatography, combined with the calculation based on the pure salt composition, is effective for determining the composition of the mixture (terephthalic acid + salt) samples.
3. The dissolution-crystallization model is the kinetic model that best fits the observed results of salt formation.
4. Salt formation behaves as first-order solid-solid phase transition over a temperature range of 25°C (not the exact lower limit) and 60°C (not the exact upper limit). In this range both the solid phase of terephthalic acid and the salt coexist at steady state.
5. The salt formation rate for the temperature points tested in this thesis decreased from 3°C to 25°C, and increased from 25°C to 50°C. This trend can

be explained by a theory combining reaction rate and Cardew’s (1984) theory (solid-solid phase transition in the solvent).

RECOMMENDATIONS FOR FUTURE WORK

Since this is the first research regarding the kinetics and mechanism of terephthalic acid-N-methyl-2-pyrrolidinone salt formation, further research is recommended to add to the understanding of salt formation and to move closer to a production design:

1. Place pure salt in radio-labeled solvent at various temperatures and time in order to study the molecular mass transfer rate between N-methyl-2-pyrrolidinone in the solvent and N-methyl-2-pyrrolidinone in the salt.
2. If the mass transfer rate between N-methyl-2-pyrrolidinone in the solvent and N-methyl-2-pyrrolidinone in the salt is low, redo the same experiments in this thesis but using radio-labeled solvent for salt formation and non-radio-labeled solvent for rinsing. This method should be able to wash nearly all the labeled entrained solvent off the crystals. The results can be used to confirm the results in this thesis.
3. Additional temperature points between 25°C and 60°C should be tested at the long mixing times (>1440 minutes) to determine the high and low temperature limits of TA-salt phase transition.
4. It should be possible to prove the salt formation rate hypothesis by applying gentle mixing to avoid a large extent of supersaturation. Then the simple

reaction rate can be measured at various temperatures. By further calculations, if the hypothesis in this thesis is true, a trend line of salt formation possibility could be determined.

5. Study additional factors that might influence salt formation rate, e.g. crystal size, mixing rate, impurities, etc.
6. Additional, experiments should be performed to investigate salt formation while changing temperature instead of isothermal salt formation.

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APPENDIX

ILLUSTRATION FOR THE COMBINED THEORY FOR THE SALT FORMATION RATE AT VARIOUS TEMPERATURES

The theory used to explain the trend of salt formation rate at various temperatures is the combination of two factors, reaction rate and salt formation possibility. Due to the difficulty of measuring the single factor, the values of the factors were assumed which resulted in a match between the combined factors and the experimental results.

The salt formation reaction rate was defined as the percentage of the remaining solid terephthalic acid that was available go through the dissolution-crystallization process per time. The salt formation possibility (shown in Figure 26 and explained in discussion) was defined as the percentage salt of solid that had crystallized out from dissolution-crystallization process. The combination is simply the product of these two factors and describes the percentage of the remaining solid terephthalic acid that successfully converts to salt.

The values of reaction rate were assumed by exponentially increasing temperature. The values of salt formation possibility were assumed to be exponentially decreasing by temperature. The values of salt percentage at steady state were assumed based on the experimental results. The values are shown in Table 17 and Figure 29. The temperatures of 3°C, 25°C, 40°C and 50°C were chosen in this illustration for easy comparison to the experimental results. The calculation started from 0% salt at time zero for all the temperatures, and was made by the following equation to determine the salt percentage for the time points after zero:

[(steady state value - previous value) * combination value] + previous value

Table 15. Assumed Values for the Illustration of Combined Theory

	3°C	25°C	40°C	50°C
Reaction rate	30 %	40 %	68 %	95 %
Salt formation possibility	100 %	25 %	17 %	15 %
Combination	30 %	10 %	11.6 %	14.3 %
Steady state salt %	100 %	100 %	97.5 %	97 %

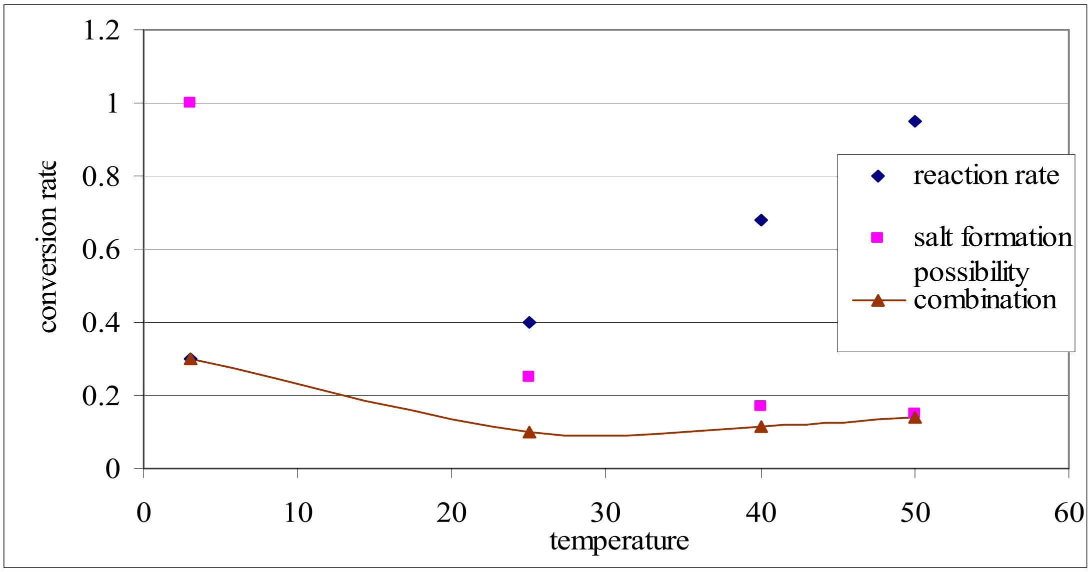

Figure 26. Assumed Values for the Illustration of Combined Theory

The calculated results based on the assumed values are shown in Figure 30 (y = 0-110% salt) and Figure 31 (y = 70-110% salt).

The trend of the calculated values of this illustration (Figure 30, 31) matches the trend of experimental results fairly well (Figure 23, 24, 25). The overall, or combination salt formation rate, from high to low is in the sequence of 3°C, 50°C, 40°C then 25°C. And because of the different steady state salt percentages for each temperature, the line of 25°C crosses the lines of 40°C and 50°C, and the lines of 40°C and 50°C subsequently cross each other.

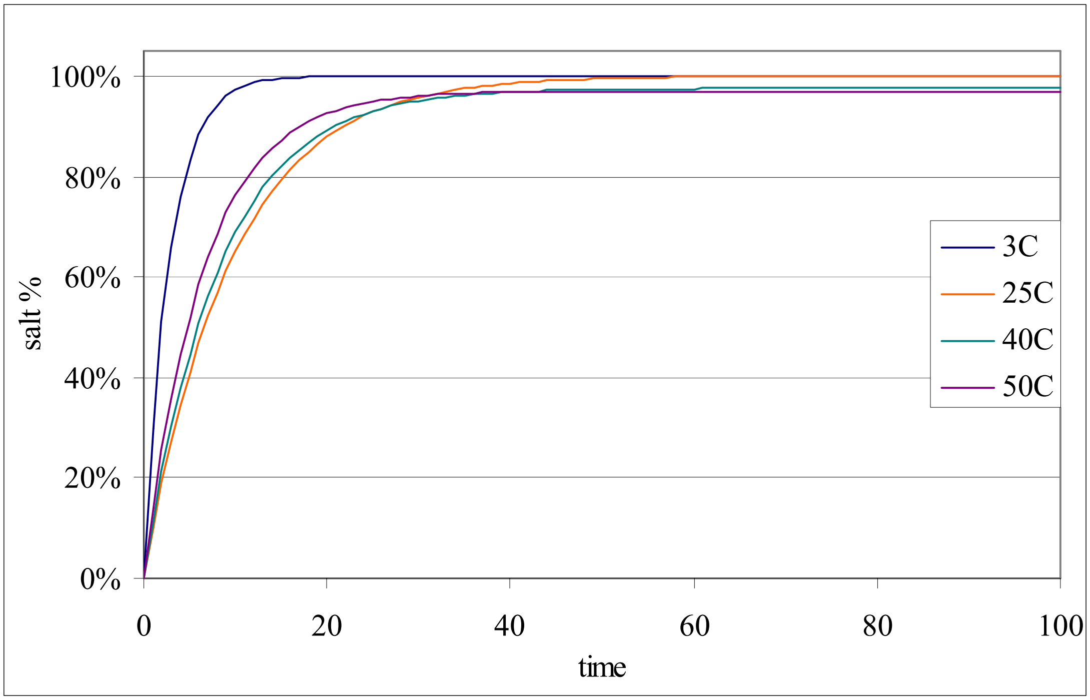

Figure 27. Calculation Result of the Illustration of Combined Theory

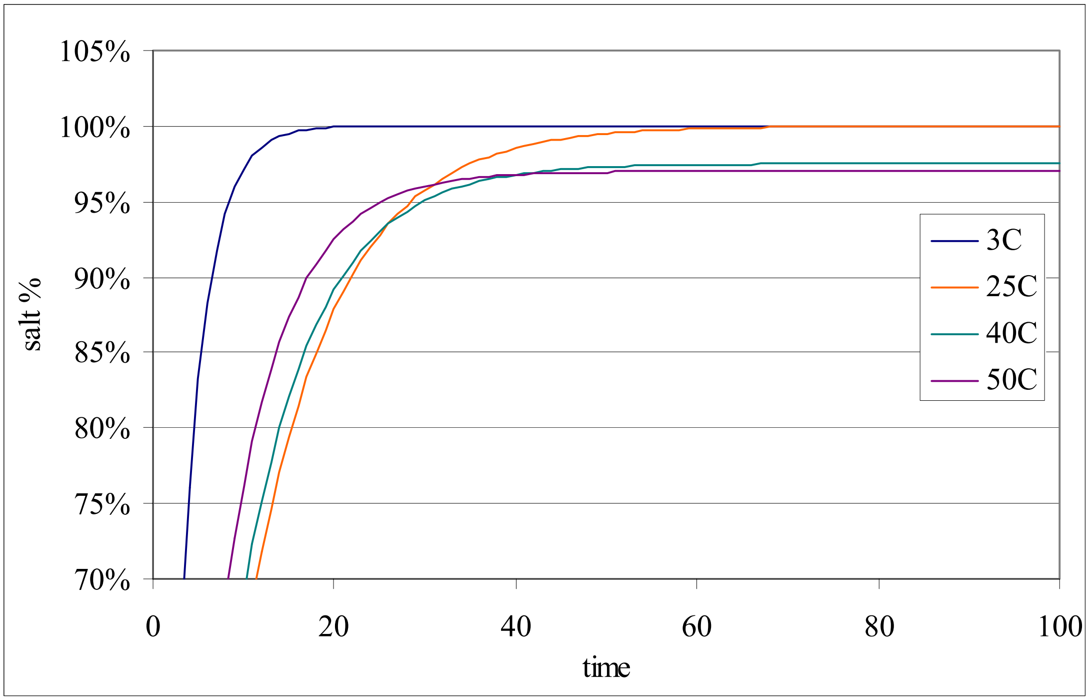

Figure 28. Magnified Graph of Figure 27