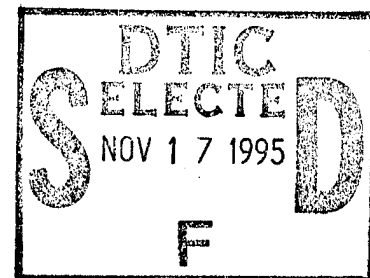


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**A STUDY OF FREEZING AND  
VACUUM FLASHING TO  
RECOVER ACETONE FROM  
ACETONE -WATER-ENERGETIC  
MIXTURES**

**REPORT NUMBER  
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**Prepared for:**

**US ARMY ENVIRONMENTAL CENTER  
Edgewood Area  
Aberdeen Proving Ground  
Maryland 21010-5401**

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by

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for

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## SECTION 1

### EXECUTIVE SUMMARY

In this work thermodynamic data is obtained on acetone-water-energetic mixtures. Also, two processes, freezing and flashing, are evaluated for recovery of acetone from the mixtures. The specific energetic compounds used in this work are dinitrotoulene and trinitrobenzene.

Current environmental legislation requires clean-up of contamination by energetic compounds at military industrial facilities. The energetic compounds (explosives, propellants and pyrotechnics) contaminate soils, buildings, and equipment. Probably the most significant contamination occurs in the lagoon sediment at some of these facilities.

A number of methods have been developed for clean-up of the contamination. No single method is best for all contamination problems. Extraction of contaminants from lagoon sediment using a solvent such as acetone is useful, for example, to reduce the concentrations to levels at which other techniques may be more cost effective.

The use of acetone as a solvent has been established in previous works in laboratory tests. The disadvantage to the use of acetone has been its recovery for re-use. The recovery of the acetone is necessary to protect the environment, to reduce consumption of this industrially important chemical, and to make the extraction process more cost effective.

Safety considerations make recovery of acetone impractical using the more traditional method of distillation. To make the separation safer, the approach taken here is to reduce the temperature to recover the acetone.

The lack of thermodynamic data for acetone-water-energetic mixtures, especially in low temperature, low pressure, conditions requires predicting properties from theoretical calculations and running experiments to verify the calculations or to obtain missing data. Experiments are conducted to determine the feasibility of recovering the acetone from the mixtures.

The results show that binary mixtures of acetone and energetics apparently form solid solutions which do not readily separate upon freezing. Differential scanning calorimetry (DSC) indicates that the binary mixture of up to 13% energetic freezes close to the freezing point of acetone,  $-95^{\circ}\text{C}$ . Freezing of the tertiary mixture of acetone-water-energetic shows that substantial separation can be obtained into two tertiary mixtures, one that is acetone-energetic rich and one that is water rich. This latter may provide a useful method for recovering water from the mixture.

Solvent flashing takes advantage of the high vapor pressure of the acetone compared to the vapor pressures of water and energetics. The results of the experiments show that nearly pure acetone can be recovered by vacuum flashing the acetone from acetone-water mixture at moderate temperatures of about  $40^{\circ}\text{C}$  while pulling a vacuum of 52 cm Hg (24 cm Hg abs pressure).



## SECTION 2

### INTRODUCTION

#### 2.1 PROBLEM STATEMENT

Acetone has the potential for being used as a solvent for extracting energetic compounds from contaminated soils and sediments. To be used as a solvent, environmentally and economically the acetone must be recovered from the wash mixture. For safety reasons, the acetone cannot be recovered by the traditional method of distillation. The purpose of this work is to evaluate methods of freezing and flashing at low temperatures and pressures that would provide a safe method to recover the acetone.

#### 2.2 OBJECTIVES:

The objectives of this work are to evaluate freezing and vacuum flashing as potential methods for recovery of acetone from mixtures of acetone, water, and energetics.

#### 2.3 TECHNOLOGICAL SIGNIFICANCE

Acetone can be used as a solvent to remove the energetic compounds (explosives, propellants, and pyrotechnics), which contaminated soils, buildings, and equipment at industrial facilities used to manufacture the materials (Wentsel et.al. (1981)). Environmental protection and cost effectiveness of the extraction process requires recovery of the acetone.

Beaudet *et. al.* (1983) estimated that the cost of sediment clean up would be on the order of \$90 per cubic yard on a wet basis. Dry soil weighs about one ton per cubic yard, hence wet soil will weigh about two tons per cubic yard and the cost is on the order of \$200 per ton of dry treated soil. The plant cost index (Chemical Engineering, 1994) for 1993 is \$ 359.2 (for 1957-59 = \$100) and for 1983 is \$316.9. Hence, multiplying \$200/ton by 359.2/316.9 gives an estimate of \$ 227/ton. Recent technological advances in soil washing by solvents and water, such as using counter current augers (Kuhlman and Karlsson, 1994), may significantly reduce this cost further.

The bulk rate of acetone currently is about \$0.20 per gallon. Beaudet *et.al.* (1983) use 1 pound of acetone per pound of soil for the extraction. This gives the cost of acetone to be about \$60 per ton. If the acetone is not recovered, then the cost of the treatment would be increased to about \$287 per ton which is about the same as the current cost required for incineration (Sisk, 1994). Hence, the recovery of the acetone makes this process significantly more cost effective than direct soil incineration.

#### 2.4 SCOPE OF WORK

Recovery of acetone is the primary objective of the experiments. Safe operation with energetic compounds constrains the process operating conditions. In particular the explosive nature of the compounds requires low to moderate temperatures.

The processes evaluated in this research are:

- (1) The direct freezing of the acetone and the energetic mixtures, and
- (2) Flash vaporization of acetone from acetone-water mixture by applying vacuum.

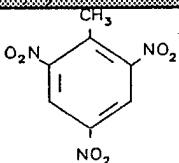
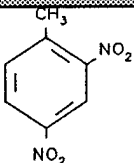
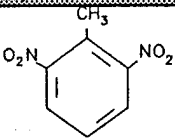
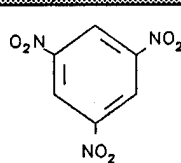
The temperature constraint eliminates a number of separation schemes such as distillation. The freezing experiments are carried out between -150°C and 20°C using liquid nitrogen as a coolant. The flashing

experiments are performed at 40°C using a constant temperature bath. The flashing process is performed at moderately low pressures using a vacuum pump of 51 cm Hg. capacity.

The experiments are performed with methyl catechol, dinitrotoulene (DNT) and trinitrobenzene (TNB). Methyl Catechol is used because its density, and its boiling and melting points are similar to TNT. Also, its non explosive nature as compared to TNT makes it useful to practice experiments before working with the energetic compounds. DNT and TNB are selected because they are more stable than TNT but are still considered energetic compounds and are also found in the soils contaminated with TNT. The physical properties of DNT and TNB are very similar to TNT as shown in Table 2.1 and are suitable for this initial work.

The experiments with the DSC are run with solutions of Methyl Catechol, DNT, and TNB in acetone. The freezing experiments are carried out with DNT and acetone. The flashing experiments are done with aqueous solutions of acetone.

Table 2-1. Properties of 2,4,6-TNT, 2,4-DNT, 2,6-DNT, and 1,3,5-TNB.

COMPOUND	2,4,6-TNT	2,4-DNT	2,6-DNT	1,3,5-TNB
STRUCTURE				
FORMULA	$\text{CH}_3\text{C}_6\text{H}_2(\text{NO}_2)_3$	$\text{CH}_3\text{C}_6\text{H}_3(\text{NO}_2)_2$	$\text{CH}_3\text{C}_6\text{H}_3(\text{NO}_2)_2$	$\text{C}_6\text{H}_3(\text{NO}_2)_3$
MOLEC WT	227.1	182.1	182.1	213.1
SPEC GRAV	1.65	1.32	1.28	1.69
MELT PT °C	81	71	66	121
BOIL PT °C	240 EXPLODES	300 EXPLODES OR DECOMPOSES		312
WATER SOLUBILITY IN 100 PARTS	0.013 INSOL	0.03 INSOL	0.001 INSOL	0.030 INSOL
ALCOHOL SOLUBILITY IN 100 PARTS	1.5 SL SOL	1.2 SL SOL	SOL	1.9 SOL
OTHER SOLVENTS IN 100 PARTS	5 IN ETHER V SOL IN ACETONE 109 IN BENZENE	9 IN ETHER SOL IN ACETONE SOL IN BENZENE	SOL IN ETHER SOL IN ACETONE SOL IN BENZENE	1.5 IN ETHER 59 IN ACETONE
VAP PRESS	$10^{-4}$ mm @ 20°C	$5.1 \times 10^{-3}$ mm @ 20°C	0.018 mm @ 20°C	$2.2 \times 10^{-4}$ mm @ 20°C
TOXICITY	TOXIC EFFECT (ANEMIA & LIVER DAMAGE)	SUSPECTED CARCINOGEN	CARCINOGEN	TOXIC

## 2.5 SUMMARY OF RESULTS

All experiments in our work have been carried out with low concentrations of energetics in the solvent acetone. Experiments are performed to determine the feasibility of freezing and flashing process for solvent recovery of acetone. Thermodynamic data, like bubble point pressures are calculated to determine the temperature of operation for the flashing process.

### (1) Differential Scanning Calorimetry:

Experiments are carried out in Differential Scanning Calorimeter (DSC) to observe phase transitions in the frozen acetone-energetic mixtures. The samples are taken to temperatures as low as  $-150^{\circ}\text{C}$  and then heated gradually to a temperature of  $25^{\circ}\text{C}$ . The results show that acetone and the energetics form a solid solution. A peak in the DSC curves at  $-94^{\circ}\text{C}$  (freezing point of acetone), indicates the phase transition of the acetone-energetic mixture from solid to the liquid phase. A small peak in the DSC curves at  $-20^{\circ}\text{C}$  coincides with the flash point of acetone and probably is due to acetone vaporization. Freezing experiments collaborate with this observation that the energetics do not phase separate out of the solution at this temperature.

### (2) Freezing of dinitrotoulene-acetone mixtures:

Mixtures of Acetone and Dinitrotoulene are frozen to determine if the energetics stay in solution with the acetone or not. The frozen mixtures are allowed to partially melt, and then the solid and liquid phases are separated. The analysis shows that the composition of both the solid and liquid phases is the same at low concentrations (1-9 % by weight energetic in acetone) of energetic in acetone. At higher concentrations of DNT in acetone (12% by weight DNT in acetone) the energetic compound is slightly more in the solid phase than in the liquid phase. But, this concentration difference is not significant enough to make an efficient separation via freezing.

These results tell us that DNT stays in solution with acetone.

### (3) Flash Vaporization of Aqueous Solutions of Acetone:

The flash vaporization process takes advantage of the high volatility of the acetone and the relatively low volatility of the water and energetics. The experimental results show that at  $40^{\circ}\text{C}$ , a solution of 55% (mass) acetone in water mixture can easily be flashed to remove more than 90% of the acetone at 51 cm Hg vacuum.

The Experimental results suggest that flashing is a very potential method to recover acetone from aqueous solutions of acetone.

## SECTION 3

### BACKGROUND

#### 3.1 ENERGETIC COMPOUND CONTAMINATION PROBLEMS

Energetic compounds contaminate equipment, soil, buildings, and munitions. The contamination is a result of manufacturing processes, handling demilitarization processes, and use of compounds. One of the more significant contamination problems is the sediment in wastewater lagoons where the top 3 to 5 inches of the sediment may be contaminated with up to 20% explosives on a dry mass basis.

Bove *et al.* (1983) reviewed a number of technologies for soil decontamination including thermal degradation and incineration, chemical reactions, stripping, extracting, and biological treatment. Probably the most significant conclusion that can be drawn from Bove's report is that there is not one "best" method applicable to all contamination problems and that each technology has its advantages and disadvantages. As a result, many decontamination techniques must be developed to provide the coverage needed to clean up soils and sediment.

This project focuses upon the use of solvent (acetone) for removal of energetics from soils and sediment. In particular this project is to develop a means of recovering acetone from the extract for reuse.

#### 3.2 ADVANTAGES AND DISADVANTAGES OF USING SOLVENTS

The use of solvents have a number of advantages and disadvantages. Some of the more important advantages are:

##### Advantages to use of solvents:

- Versatile, can be used for decontamination of buildings, equipment and materials as well as soils and sediment.
- Can be used where other techniques such as composting may not be effective (such as cold climates).
- Can be used to remove contaminants from pores and cracks of rocks and other materials without the necessity of grinding or breaking the rock into smaller sizes.
- Can be rapid as long as the solvent readily wets the material surfaces.
- Does not require a large processing plant.
- Can be applied at small or large scale of operation.
- High temperatures not required.
- Can reduce contaminant concentrations to levels at which other methods become more effective.
- Concentrated extract can be disposed of by incineration or can be mixed with fuel for burning to produce steam and thus recovering the chemical energy.

The method is robust and can operate in a wide range of weather conditions, soil properties, and with large variations in the contaminant type and concentration.

##### Disadvantages of use of solvents:

- Solvents are chemicals and must be properly handled.

- Handling of solvent and solvent wet materials may be more complicated than with operations such as soil incineration.
- Not all of the solvent will immediately drain from cleaned soil and may require post treatment. In this process the acetone was followed by water to extract the acetone out of the soil. An alternative process, which is not considered here, would be to remove the acetone from the soil under vacuum and/or mild heating.
- Solvent may attack materials such as Rubber and Plexiglas.
- To be cost effective it is expected that the solvent must be recovered and reused.
- Solvent recovery may be complicated if fine particles are entrained in the wash liquid.

The use of solvents to extract contaminants is not expected to solve all of the clean-up problems; however it can potentially provide an economical alternative to direct soil incineration or biotreatment.

### 3.3 SELECTION OF ACETONE AS THE SOLVENT

Some extraction studies have used acetone as a solvent for removing contaminants such as from soils. Wentzel *et.al.* (1981) show acetone to be effective as a solvent in removing energetic compounds from soils in laboratory studies. Acetone is a good solvent for all organic explosives except nitrocellulose. Acetone is miscible with water and can penetrate into wet soils and wet surfaces.

Economic operation of an acetone solvent extraction process requires recovery and reuse the acetone (Beaudet *et.al.*, 1983). The main disadvantage of using acetone is its flammability. The flash point of acetone is -20°C. The upper and lower explosion limits of acetone are 12.8 and 2.6 volume percent in air, respectively. However, acetone is safely used throughout industry as long as proper precautions are taken.

Dao *et.al.* (1983) found that methanol and acetone are used most frequently as solvents for soil pesticide extraction analyses. Non-polar solvents such as hexane are seldom used; Freeman and Cheung (1981) suggest that the reason for this is failure to properly match the solubility parameter of the extracting solvent with that of the soil organic matter which results in low recovery regardless of equilibration time. This apparent contradiction of the equilibrium thermodynamics is explained as failure of the non-polar solvents to "wet" the internal pore surfaces of the soil matrix (Jenkins and Leggett, 1985). This wetting problem prevents the non-polar from approaching equilibrium concentrations within practical time constraints.

### 3.4 METHODS OF SOLVENT RECOVERY

Beaudet *et. al.* (1983) studied the cleanup of lagoon sediment using acetone as a solvent. Their process diagrammed in Figure 3.1 uses a distillation column for separating the acetone-water-energetics mixture. This process could work except for the safety concern that heating concentrated explosives at the bottom of the distillation column may cause an explosion (Sisk, 1994).

*Flash Vaporization* is most useful when one chemical species is much more volatile than the others. In the acetone-water-energetic mixture the acetone is much more volatile than the other compounds. Flash Vaporization is applied in some of the experiments in this work.

*Crystallization* has the advantage of safe operation at low temperature. Our work shows that a solution of acetone and energetics (DNT) form a solid solution and will not separate efficiently by crystallization.

There are several other methods that may be useful for separating these compounds, such as crystallization, liquid-liquid-solid extraction, membranes, chromatography and salting. These methods are not applied in this work but are briefly discussed here.

*Liquid-Liquid-Solid extraction* potentially could be done at ambient temperature and pressure. However this would require introducing a second solvent that will form another phase. This would actually complicate the separation process and make the separation more expensive.

*Membrane Separation* technology has progressed significantly over the past 15 years. Separations typically occur at ambient temperature and high pressure and can be very effective with low concentration solutions. Membranes may be found that can separate out each of the components. However, the closer the chemical species are in size and nature, the more difficult the separation.

*Chromatography* can be very effective in separating the three compounds, depending on the chromatographic material. However, the process is slow and may not work well with high concentration solutions.

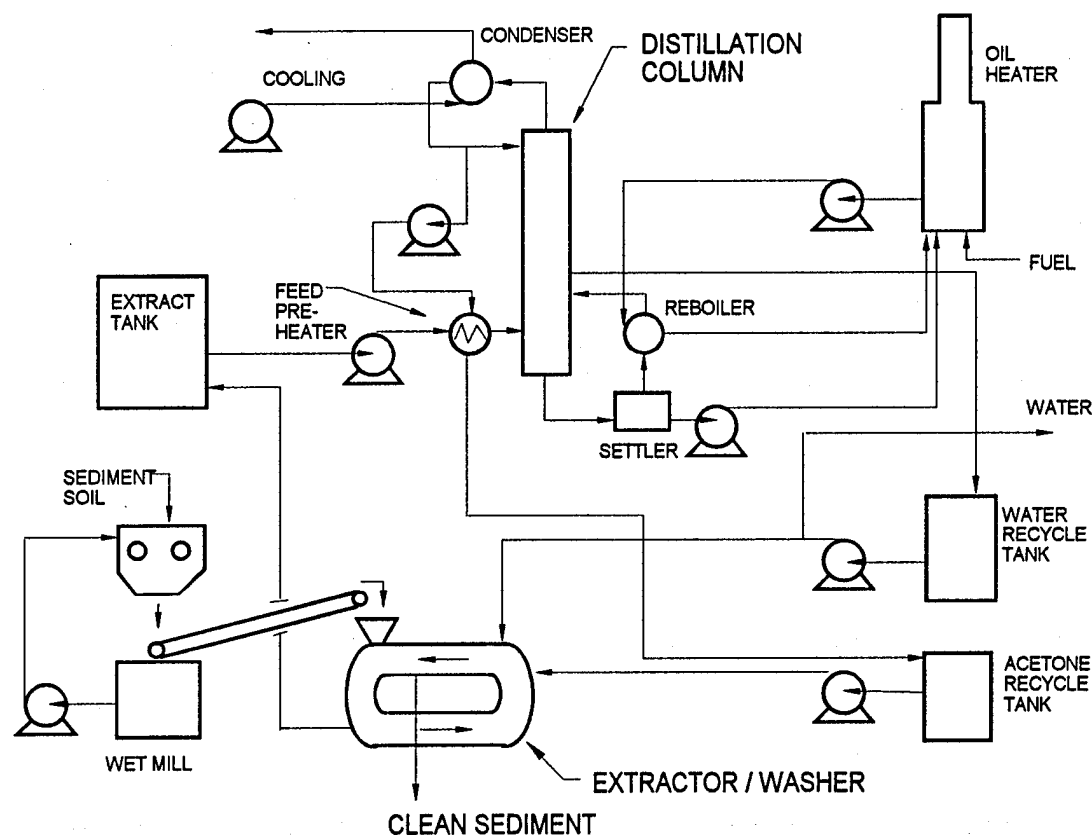


Figure 3.1. Solvent extraction system process flow diagram (Beaudet *et. al.*, 1983).

*Salting* is an approach that has not been fully investigated. By adding salt to the acetone-water solution it is possible to cause a phase separation. Presumably the energetics would stay in the acetone phase. The economics of recovering the salt or its effect on the energetic incineration must be investigated.

Tetrahydrofuran is also a potential solvent for removing energetics (Leggett, Personal Communication, 1994). Data show that salting can potentially recover more of the Tetrahydrofuran than acetone. The Salting out data (Tabata *et. al.*) for the phase-separation by sodium chloride is shown in Table 3.1.

Tetrahydrofuran as a solvent, instead of acetone also has many disadvantages:

Tetrahydrofuran is a dangerous fire hazard from heat, flame, and powerful oxidizing materials. Heat decomposition emits irritating fumes. It has a higher boiling point, 65.4°C, than acetone, (56.48°C) and a

lower freezing point of  $-108.5^{\circ}\text{C}$  than acetone,  $(-94.6^{\circ}\text{C})$ . This extends the operating temperature range of either flashing or freezing. It is a much more highly regulated compound than acetone in the sense that the OSHA allows concentration levels upto 200 ppm compared to acetone, 1000 ppm.

The most important fact is that tetrahydrofuran is a much more expensive solvent than acetone. For a given grade and concentration, tetrahydrofuran is almost twice as expensive as acetone. In addition to this, by adding salt to the system we are complicating the whole process by involving a total of four compounds just to separate acetone and energetic compounds. The costs of the process would also increase because of the usage of salt

Table 3-1. Salting-out data for the phase-separation by sodium chloride.

Solvent	Volume/ $\text{cm}^3$		Chloride in organic phase	Water Concentration in the organic phase	
	Organic Phase	Aqueous Phase	$10^{-2} \text{ mol dm}^{-3}$	%(w/w)	x(mole fraction)
Acetone	3.11	6.99	9.62	17.3	.390
Tetrahydrofuran	4.66	5.65	0.162	5.99	.203

## SECTION 4

### METHOD OF FREEZING

#### 4.1 LITERATURE REVIEW

Freezing has some advantages over competitive methods. Separations can often be accomplished at low temperatures, minimizing decomposition of heat-sensitive compounds. In addition to separation and purification, freezing is also useful for concentrating solutions and suspensions by solvent removal. Since high temperatures are not involved, volatile components are not lost (Karger *et al.*, 1973).

Crystallizing from a solvent is like evaporating under vacuum or with an inert gas. The reason for considering it is for reducing operating temperatures. Recovery of the solvent in most systems is limited by the presence of a eutectic. Further freezing at this point simply freezes both components in the same proportion as they are present in the solution (Wynn, 1992).

If an aqueous solution consists of water and small amounts of organic solvents such as glycerol or methanol, freezing may also concentrate the solvent. When the temperature is above the freezing point of the organic solvent, liquid domains of organic solvent may be performed between ice crystals. Studies revealed that both solute and organic solvent molecules are excluded from growing ice crystals during freezing to form the "puddles" of organic solvent in which the solute molecules are concentrated, when the aqueous solution containing small amounts of organic solvent is quickly frozen (Kano *et al.*, 1985).

The solid-liquid equilibrium diagram of water-acetone binary system is shown in Figure 4.1 (Rosso *et al.*, 1975). From the diagram it is seen that at  $-19^{\circ}\text{C}$ , the system forms a peritectic. Table 4.1 shows the invariant reactions for the water-acetone binary system.

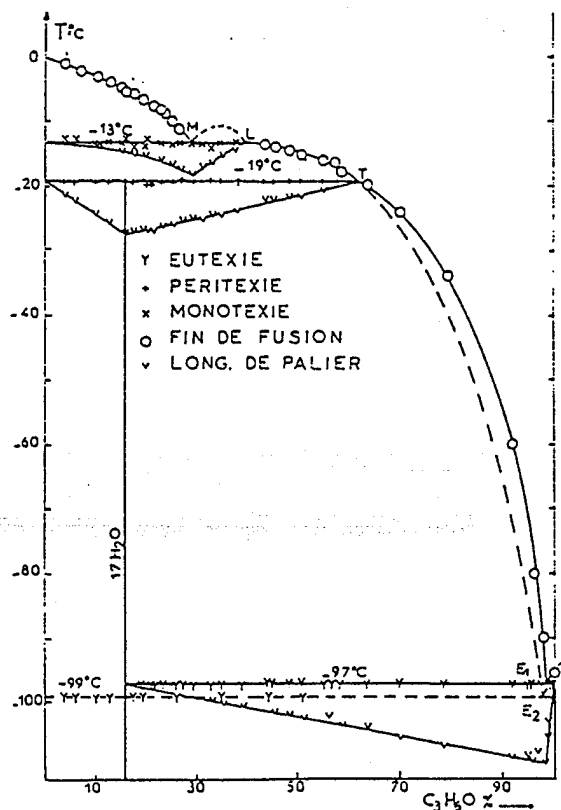


Figure 4.1. Phase diagram of the water-acetone binary system.



Table 4.1. The invariant reactions for water-acetone binary system:

Nature of the invariant reaction	Temperature (°C)	Mass Concentration Acetone (%)	Invariant Reaction
Eutectic stable E <sub>1</sub>	-97	98.5	Liq E <sub>1</sub> → Ac.17 aq + Ac(s)
Eutectic metastable E <sub>2</sub>	-99	97.5	Liq E <sub>2</sub> → Glace + Ac(s)
Peritectic stable T	-19	61.5	Glace + Liq T → Ac.17 aq
Monotectic stable L	-13	40.0	Liq M(29.5) → Glace + Liq L

To investigate the feasibility of freezing to separate the compounds two experiments are conducted. One experiment uses a differential scanning calorimeter to detect heat absorption during phase change and the other uses direct freezing to detect concentration changes in the phases.

## 4.2 DIFFERENTIAL SCANNING CALORIMETER

A Differential Scanning Calorimeter (DSC) can provide quantitative information about the heat changes during these phase transitions. A continuous, usually linear, temperature change in the calorimeter is used in the scanning mode of operation. Heat is absorbed or liberated during phase change. Phase change in the system can be determined from the heat flow data given out by the DSC.

### 4.2.1 DESCRIPTION OF EXPERIMENTS

The experimental results from the DSC are useful in predicting the phase transitional behavior of the Acetone-Energetic mixtures. If the energetics stay in solution with acetone, there will be only one phase change from solid to liquid for the entire heating cycle.

A Dupont Instruments model 910 DSC system is used for the melt scans. The acetone-energetic liquid sample is hermetically sealed in a high pressure sample pan to avoid volatilization losses, placed in a sealed glass tube, and the sample is frozen in a bath of liquid nitrogen for 10 minutes. The sample pan is placed in the DSC cell and cooled to -150°C. During the experiment the sample is heated to room temperature at a heating rate of 3°C/min.

A desired composition of energetic compound in acetone is made by weighing the solute in a glass vial and then adding the required acetone (density 0.7848 gm/cc) to this solute. Thus the composition of the solution in terms of weight percent of solute (energetic compound) and solvent (acetone) is known.

Ten to twenty microliters of this solution is loaded into an aluminium pan using a micro syringe. The pan is covered with a lid and hermetically sealed. Another pan (empty) is also covered with lid and sealed. This second pan is used as a reference pan in the DSC.

The pans are placed in the DSC and allowed to cool to a temperature of about -150 °C using liquid nitrogen as a freezant. Nitrogen gas is used as a draft around the pans to keep the environment from fluctuating. Once the instrument is equilibrated at this temperature, the temperature is linearly increased at a given heating rate (in this case, the ramp is 3°C/min) from -150°C to 25°C (room temperature). The heat flow data is automatically measured by the instrument. A plot of temperature versus heat flow (W/g) is drawn by the instrument, and the results analyzed.

The experiment is repeated for different compositions of the energetics in the solvent.

#### 4.2.2 EXPERIMENTAL RESULTS

The dynamic scan procedure is used to generate the melt curves. The complete set of experimental results from the DSC for the three binary mixtures (1) Acetone-Methyl Catechol, (2) Acetone-TNB and (3) Acetone-DNT are shown in Appendix A. The different curves in each figure correspond to the different compositions of energetic compounds in solution with acetone. All of the experiments are carried out with low concentrations of the energetics in the solution. A typical melt curve for pure acetone is shown in Figure 4.2.

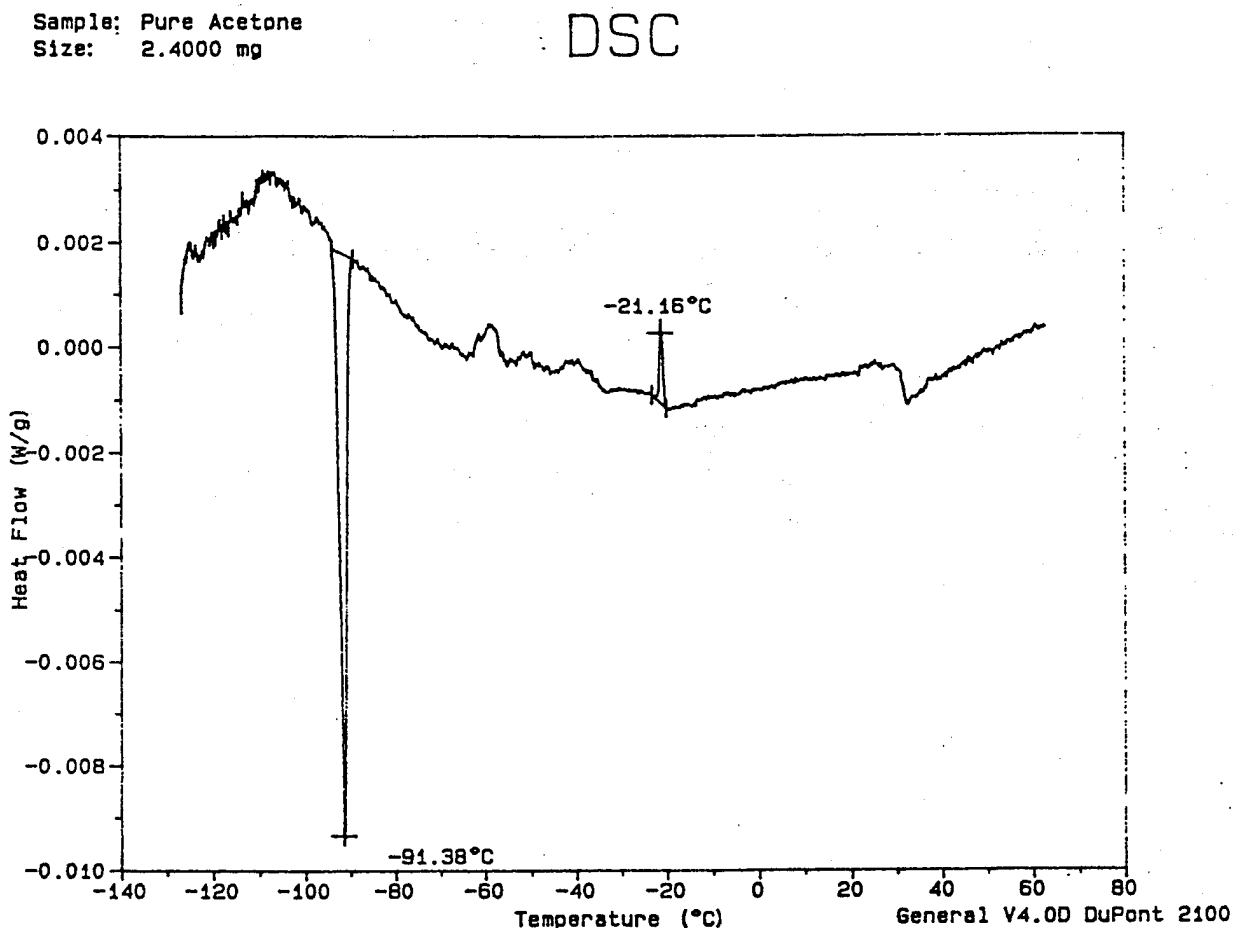


Figure 4.2. Typical DSC scan for pure acetone. Sample weight 2.40 mg; molecular weight 58.08; initial temperature -150°C; final temperature 25°C; heating rate 3°C Min<sup>-1</sup>.

#### 4.2.3 DISCUSSION OF RESULTS

Figure 4.2 shows a DSC scan for pure acetone. It has two significant peaks. The first peak occurs at about -92°C which corresponds very closely to the reported melting point of acetone of -94.7°C.

The second peak in Figure 4.2 occurs near -21°C. For acetone this temperature is very close to its flash point temperature which corresponds to the temperature at which the acetone has a significant vapor pressure. It is speculated, but not proven by these experiments, that this peak is due to vaporizing some of the acetone in the sample pan.

Figure A.1 through A.3 in appendix A show the DSC results for acetone solvent with either methyl catechol, TNB or DNT as solutes in low concentration. Nearly all of the curves show the same peaks at approximately  $-91^{\circ}\text{C}$  and  $-21^{\circ}\text{C}$  (plus or minus a few degrees).

Peaks that occur at temperatures less than  $-94^{\circ}\text{C}$  are not of interest and are not considered further. A few of the plots show the peaks near  $-21^{\circ}\text{C}$  switching from endothermic to exothermic. No explanation can be given for the switch at this time.

What the plots do show is a consistent lack of additional peaks other than those already described. This suggests that the mixture behaves just like the pure acetone and that the solid phase may form a solid solution of the same composition as the liquid phase.

### **4.3 DIRECT FREEZING**

The direct freezing experiments of DNT-acetone are carried out to determine whether freezing causes the energetics to concentrate in one phase or the other.

In this experiment, the solutions of desired composition of energetic compound in acetone are made by weighing the solute in a glass vial and then adding the required acetone (density  $0.7848\text{ gm/cc}$ ) to this solute. Thus the composition of the solution in terms of weight percent of solute (energetic compound) and solvent (acetone) is known. The experiments are performed using four different compositions of 0.5%, 4%, 8%, 12% by weight dinitrotoulene in acetone.

#### **4.3.1 DESCRIPTION OF EXPERIMENTS**

The prepared samples (solutions) are immersed in a bath of liquid nitrogen. Sufficient time is allowed for the samples to freeze completely. The frozen solution is removed from the bath and kept outside so that the solution melts. As it melts we have two phases present in the glass vial. The amount of liquid phase present in the vial depends on the time that has lapsed from when it was removed from the liquid nitrogen.

The liquid phase is separated from the solid phase by simple decantation. This is repeated at different times, so that the amount of liquid phase differs for each sample. The vials are capped and the weight of the solid phase and the liquid phase are noted down. The caps are removed and the solvent is allowed to evaporate. After complete evaporation, the amount of solute in the solid phase and in the liquid phase are measured.

#### **4.3.2 EXPERIMENTAL RESULTS**

A plot of the percent amount of total energetics in the two phase sample that is contained in the liquid phase versus the fractional mass of liquid to the total two-phase mass is shown in Figure 4.3. Each curve is for a different starting mixture concentration, as indicated.

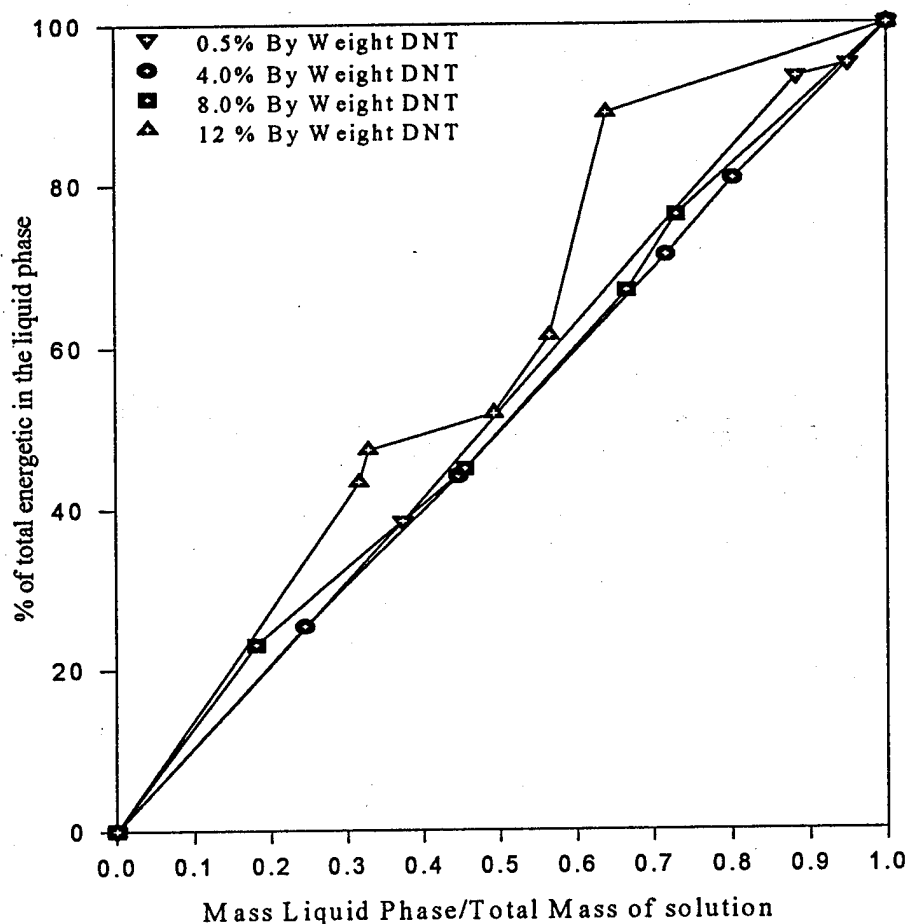


Figure 4.3. Solute Distribution between solid and liquid phases for different solutions of Dinitrotoulene in Acetone.

#### 4.3.3 DISCUSSION OF RESULTS

The slope of the curves show that the total mass of energetic going into the liquid phase is proportional to the mass of liquid decanted. This also shows that the solute and the solvent are forming complete solid solutions. This supports the similar conclusion drawn from the DSC freezing experiments previously described. This suggests that the freezing experiments will not yield good solvent recovery.

The 12% DNT curve indicates that the solid phase is slightly more concentrated than the liquid phase. However, the concentration difference may not be enough to effectively recover the acetone in a large scale operation.

## SECTION 5

### METHOD OF VACUUM FLASHING

#### 5.1 LITERATURE REVIEW

Vacuum evaporation both removes the solvent and cools the solution (Wynn, 1992). Lowering the pressure on a binary mixture increases relative volatility of the components and it decreases the operating temperature. This minimizes heat losses and permits the use of cheaper energy sources for heating. Often vacuum evaporation is the only practical recourse for thermally sensitive compounds (Bose and Palmer, 1984). When a liquid evaporates, the vapor-liquid interface is cooled and, for mixtures, is depleted of the more volatile component.

For flash vaporization of a volatile substance from a relatively nonvolatile one, operation can be carried out under reduced pressure, but not so low that ordinary cooling water will not condense the vapor product (Treybal, R.E, 1981).

Important to understanding the feasibility of using vacuum flashing, we must have the vapor pressure data for pure acetone and bubble pressure data of acetone-water mixtures. This information is given in the following subsections.

##### 5.1.1 VAPOR PRESSURE OF PURE ACETONE:

The vapor pressure data (Raikes and Bowen, 1927) of pure acetone is plotted in Figure 5.1, with temperature as abscissa and vapor pressure as ordinates. This is also the bubble pressure plot for pure acetone.

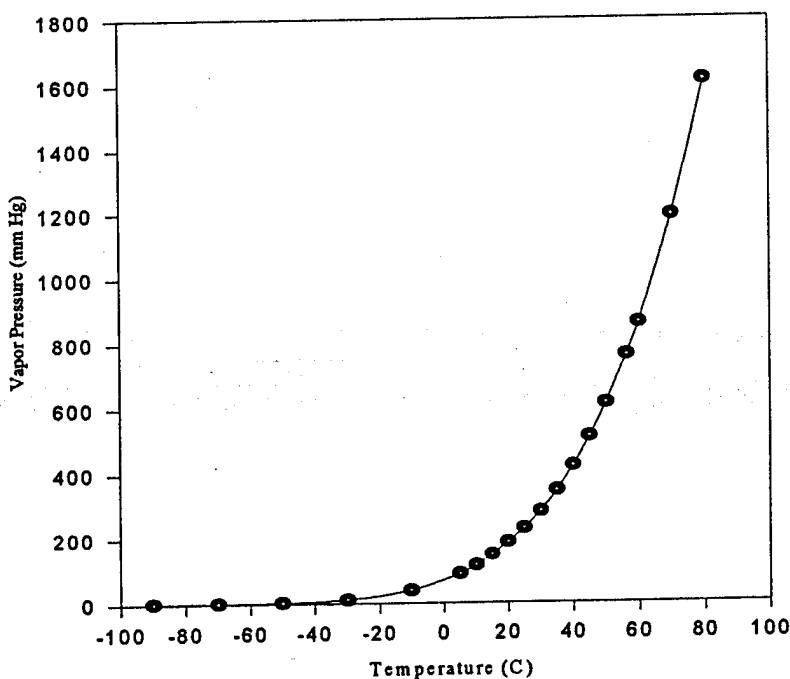


Figure 5.1. Vapor Pressure plot for pure acetone.

### 5.1.2 BUBBLE PRESSURE OF WATER-ACETONE BINARY MIXTURES:

The knowledge of bubble pressure as a function of temperature and composition for the binary system under study is essential to determine the operating conditions of the flash vaporization process. For a given vacuum pump and desired separation required, the operating temperature can be calculated from the bubble pressure plot.

The bubble pressure data (Gmehling *et al.*, 1988) are plotted in Figure 5.2. The figure gives the invariant temperature required to flash the acetone for an applied vacuum and desired final composition. The curve for 40°C is interpolated from the data of 35°C and 45°C plots. In our experiment, the pump could achieve only 510 mm Hg. vacuum i.e. an absolute pressure 250 mm Hg. From the bubble pressure plot in Figure 5.2, the temperature corresponding to a pressure of 250 mm Hg. and final equilibrium composition of 25% mass concentration acetone is 40°C. Hence we ran the experiment at a temperature of 40°C.

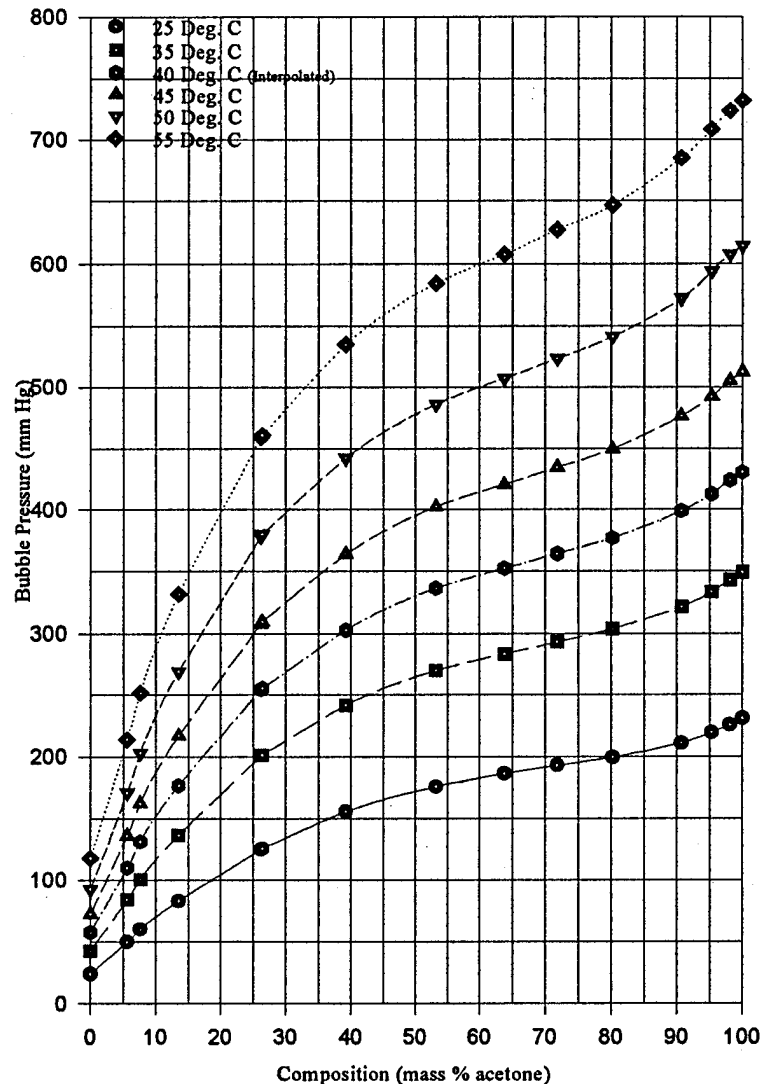


Figure 5.2. Bubble pressure plot for water-acetone mixtures. Different curves are the isotherms for different temperatures.

## 5.2 FLASH VAPORIZATION OF AQUEOUS SOLUTIONS OF ACETONE

Because an acetone-water mixture has a higher vapor pressure than pure water, vaporization will occur at a lower temperature and the rate of evaporation will be higher. Also, the higher vapor pressure of the solution means a given vacuum will evaporate more liquid. As boiling continues, the mass fraction of water in the solution increases causing the boiling rate to decrease.

Aqueous solutions of acetone are flash vaporized to determine the efficiency of the flashing process in separating acetone from water. The bubble pressure plot in Figure 5.2 is used here to determine the operating conditions for the successful flash vaporization process.

In order to flash the acetone at a lower temperature than its normal boiling point ( $56.1^{\circ}\text{C}$ ), the pressure on the acetone-water mixture is lowered. This is achieved by using a vacuum pump. The vacuum pump used in our experiment has a suction (vacuum) rating of 510 mm Hg. This means that the applied absolute pressure on the solution placed in the conical flask is 250 mm Hg. From the bubble pressure plot, the temperature corresponding to this pressure and final composition of 25% mass concentration acetone, is  $40^{\circ}\text{C}$  (313 K).

### 5.2.1 DESCRIPTION OF EXPERIMENTS

The schematic of the experimental setup for the flashing experiments is shown in Figure 5.3. A solution of 55% mass concentration acetone in water is placed in a conical flask. The flask is placed in a constant temperature bath and the temperature is maintained at  $40^{\circ}\text{C}$ . The pressure in the flask is measured by a manometer. Vacuum is applied to the contents of the flask by connecting the inlet port of the vacuum pump to the flask. A condenser is placed between the pump and the flask to condense the vapors from the flask. Cold water is circulated in the condenser as a cooling medium. The condensate is collected in a separate flask. The uncondensed gases are sent to the hood.

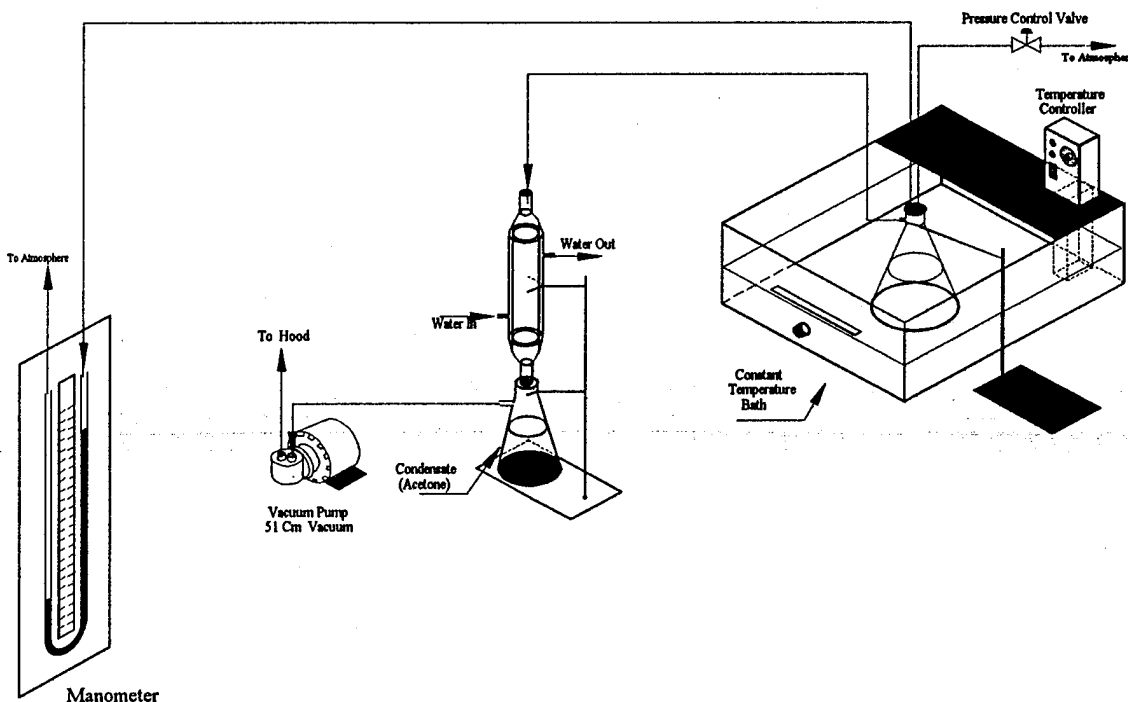


Figure 5.3. Schematic of the experimental setup for flashing acetone from its aqueous solution.

### 5.2.2 EXPERIMENTAL RESULTS

The solutions are analyzed, in a gas chromatograph, to determine the concentration of acetone in the condensate and in the unflashed liquid. The gas chromatograph results show that a solution of initial composition of 55% mass concentration of acetone in water is flashed to recover 74% of the acetone in the solution, with the final composition of 24.23% mass concentration acetone in the unflashed liquid, which very closely complies with the concentration (25.5% acetone) from the bubble pressure plot in Figure 5.2.

The experiment only ran 2 hour 20 minutes. When run under higher vacuum greater recoveries approaching 90% are possible. Hiatt (1994) shows that recovery approaching 100% may be possible. Figure 5.4 shows a time plot of the concentration change of acetone in the flash chamber. A mass balance could yield how much acetone was lost to the hood, but was not done in this work. For scale-up, a more efficient design would be to increase the surface area of contact per volume of mixture.

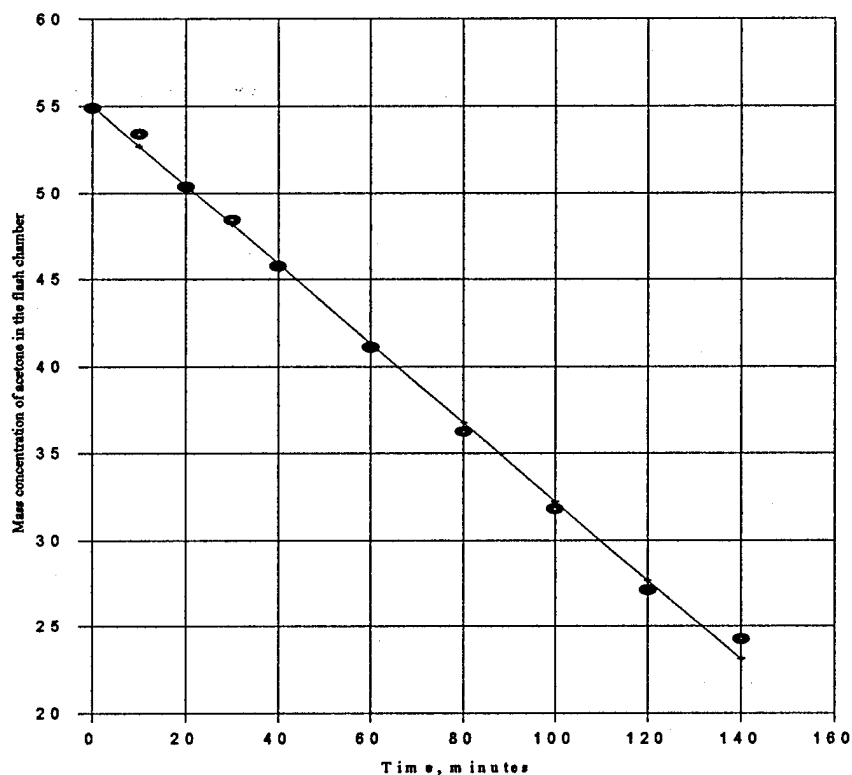


Figure 5.4. Time plot of concentration of acetone in the flash chamber.

### 5.2.3 DISCUSSION OF THE RESULTS

The results of flash vaporization suggest that flashing is a good process to efficiently recover the acetone. The efficiency of the process can be further improved by using a stronger vacuum pump, by using a colder medium other than water in the condenser, and by increasing the vacuum surface area.



## SECTION 6

### CHEMICAL ANALYSIS OF AQUEOUS SOLUTIONS OF ACETONE

This section deals in finding a convenient method for measuring the acetone concentration in aqueous solutions.

The methods considered to measure the acetone concentration in a mixture of acetone and water are: (1) Gravimetric analysis (2) Viscosity measurements and (3) Gas Chromatography Analysis.

#### 6.1 GRAVIMETRIC ANALYSIS

This method uses density measurements to determine the amount of acetone in a given aqueous solution of acetone. The data is obtained using empirical equations (Liley *et. al.*, 1984), that correlate 'Density of the solution' to 'Weight % of acetone' at different temperatures.

The data is plotted with weight % of acetone as abscissa and density of the solution as ordinates. The data is calculated for five different temperatures at 0, 4, 15, 20, 25°C. The graph is shown in Figure 6.1.

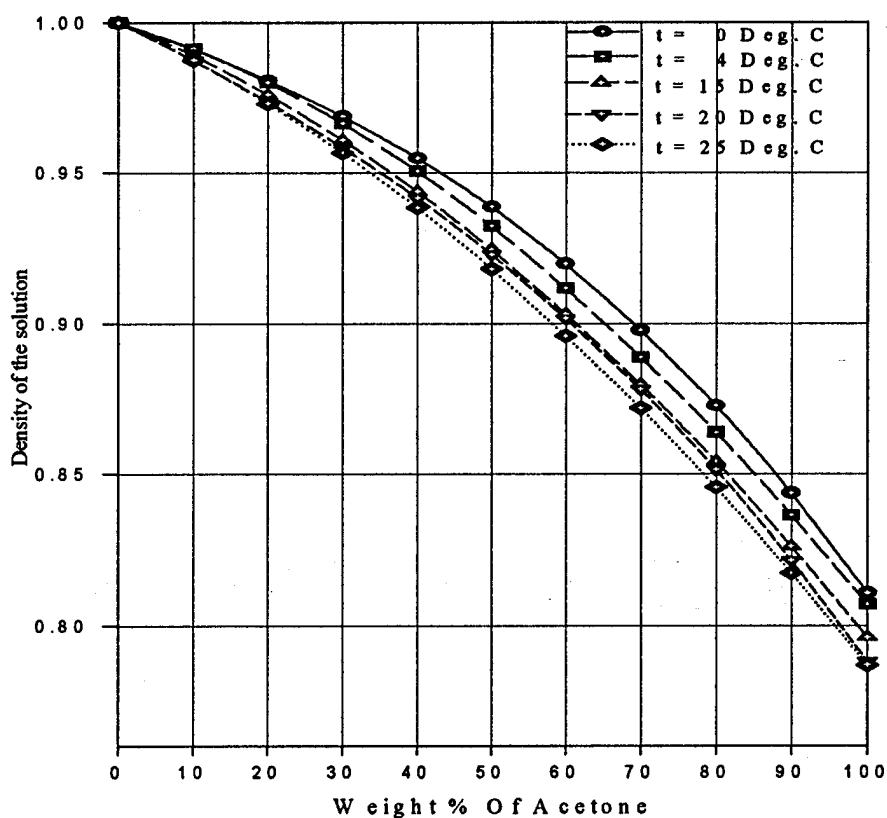


Figure 6.1. Densities of Aqueous Solutions of Acetone as a function of Temperature and Composition.

## 6.2 VISCOSITY MEASUREMENTS

This method uses absolute viscosity data (Barr, 1929) for the determination of the amount of acetone present in a given mixture of acetone and water. Plots of Viscosity as a function of temperature and composition are shown in Figures 6.2 and 6.3. In Figure 6.2, the compositions are in weight % acetone and in Figure 6.3, the compositions are in volume % acetone.

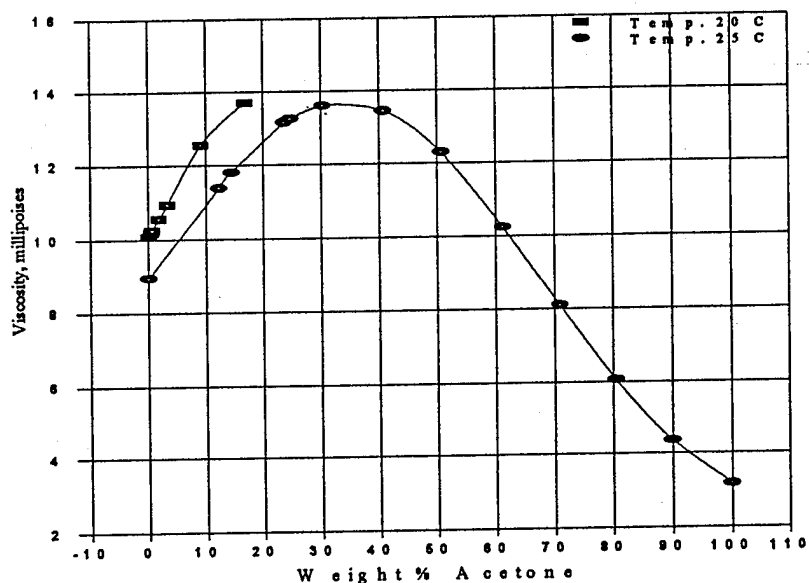


Figure 6.2. Viscosities of aqueous solutions of acetone as a function of temperature and composition.

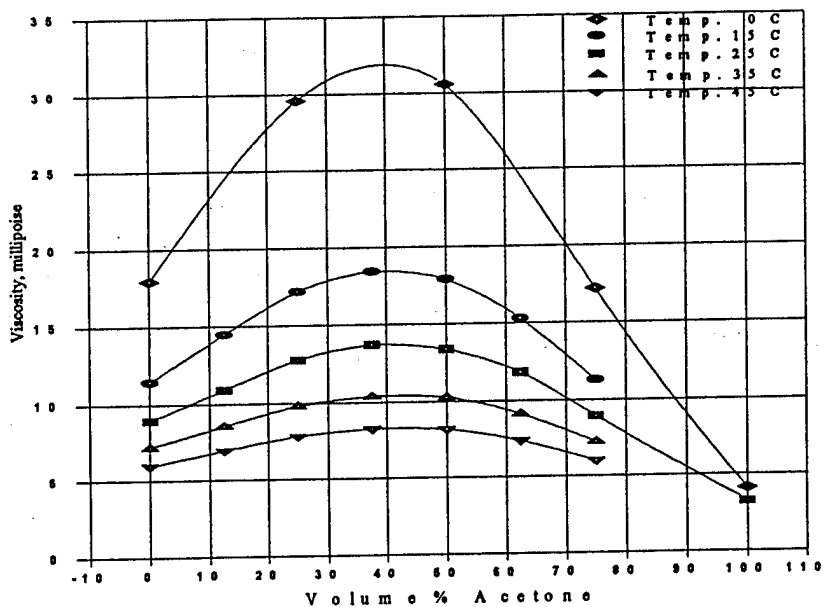


Figure 6.3. Viscosities of aqueous solutions of acetone as a function of temperature and composition.

This method of analysis cannot be used for the determination of composition of the solution because solutions with two different compositions can have the same viscosity, as can be seen from the shape of the curves in Figure 6.2. & 6.3. Thus this method is not useful for analyzing aqueous solutions of acetone.

### 6.3 GAS CHROMATOGRAPHY

Gas-Liquid Chromatography (GLC) is one of the most often used and most powerful tools available for separation and analysis. Many reasons can be given for this, but the three major factors are speed, resolving power, and extreme sensitivity (Barry, 1973).

We used GLC to determine the compositions of aqueous solutions of acetone. In order to do this, the Gas Chromatograph needs to be calibrated. The GC gives a peak for each compound in the mixture. The occurrence of the peak depends on the residence time of that particular compound in the column of the GC. The residence time, in addition depends on the molecular weight of the compound. The areas under each peak correspond to the amount of that material present in the mixture.

The calibration is done by injecting known concentrations of aqueous solutions of acetone into the GC. The gas chromatograph gives out data of area percent corresponding to each compound. This area percent is plotted against the known weight percent of the compound in the mixture. An example peak of the gas chromatograph run is shown in Figure 6.4. A calibration chart thus developed is shown in Figure 6.5. This calibration chart is then used to determine the composition of an unknown mixture of acetone and water.

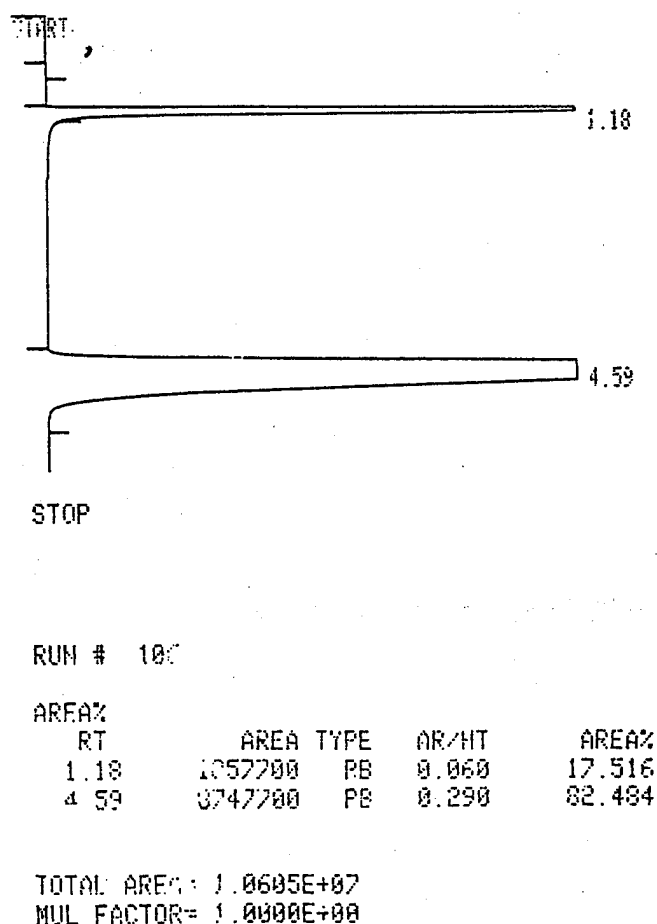


Figure 6.4. A typical gas chromatograph reading for water-acetone mixture injected into GC column.

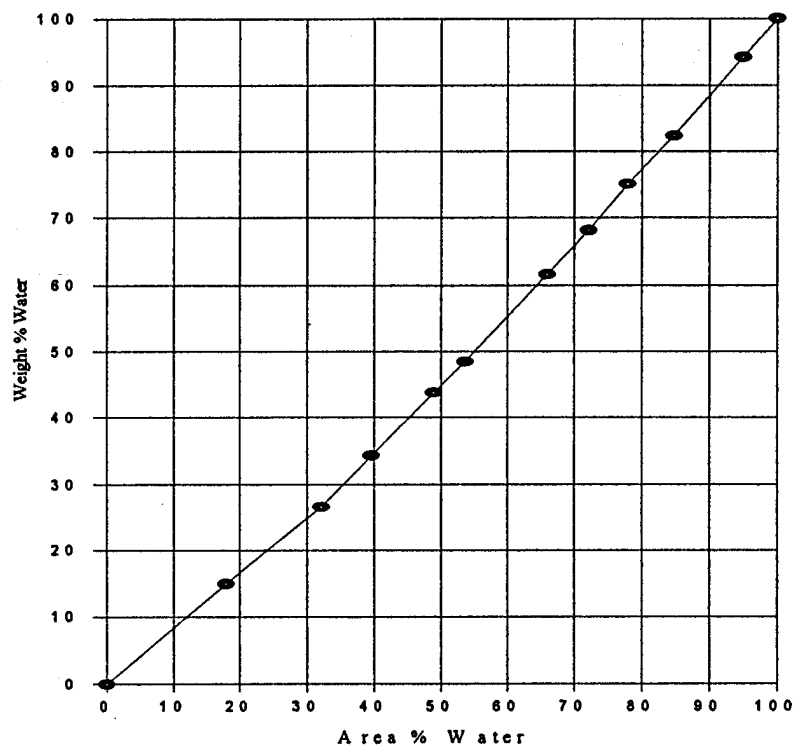


Figure 6.5. Calibration of Gas Chromatograph for the Water-Acetone Binary System.

#### 6.4 CONCLUSIONS

Density measurements are not accurate enough for small differences in concentrations. In addition, they are also temperature dependent. The viscosity measurements have an additional disadvantage that two compositions can have the same viscosity for a given temperature. The gas chromatograph is the easy, accurate, and best method available to determine the mass concentrations of acetone in water.

## SECTION 7

### CONCLUSIONS AND RECOMMENDATIONS

The most important conclusion from this work is that the flash vaporization under vacuum yields good separation of acetone from its aqueous solutions. The operating temperatures are also lowered, thus making the separation process safe with the heat sensitive energetic compounds. For a vacuum of 250 mm Hg at 40°C applied to a solution of 55% mass concentration acetone in water the final composition of 24% mass concentration acetone in the liquid was obtained. By mass balance this calculated out to a separation of 74% of initial acetone present in the liquid. By using a stronger vacuum pump, much higher separation of the solvent can be achieved.

The vacuum rating of the pump, the critical concentration of acetone in water that keeps the energetics in solution, and the temperatures that would make a safe separation process are the three important factors that will be used in the scale up of the process. The bubble pressure plot for the water-acetone binary system sets up the limits of the operating conditions of the flash vaporization process.

Freezing can be combined with the flashing process to concentrate the energetics in the organic phase, and water forming the solid phase (ice). The freezing step can be incorporated as the final step of the separation process.

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## APPENDIX

### DIFFERENTIAL SCANNING CALORIMETER PLOTS

Differential Scanning Calorimeter (DSC) instruments measure the energy change in the sample directly. (Daniels, 1925). They make quantitative measurements of heats of reaction and transition, specific heats, etc. The measurements may be made isothermally or at very low heating rates without loss of sensitivity. The sample containers used in DSC are shallow metal pans which may be open, loosely lidded or sealed. Sealed aluminium pans, capable of withstanding 30 psi ( $0.2 \text{ MN/m}^2$ ) internal pressure, are used for samples which evaporate or sublime. The sample and the reference pan are placed on individual bases thermally isolated from each other, each base containing a separately controllable heater and a thermocouple or resistance thermometer (Daniels, 1925). Sample size for the differential scanning calorimeter is approximately 25 mg or less (Zief, 1969).

A DSC curve is a plot of *differential power* (i.e. difference in rate of energy supply) against temperature or time. The peak area is directly proportional to the heat of transition, and the sample temperature increases linearly even through a transition.

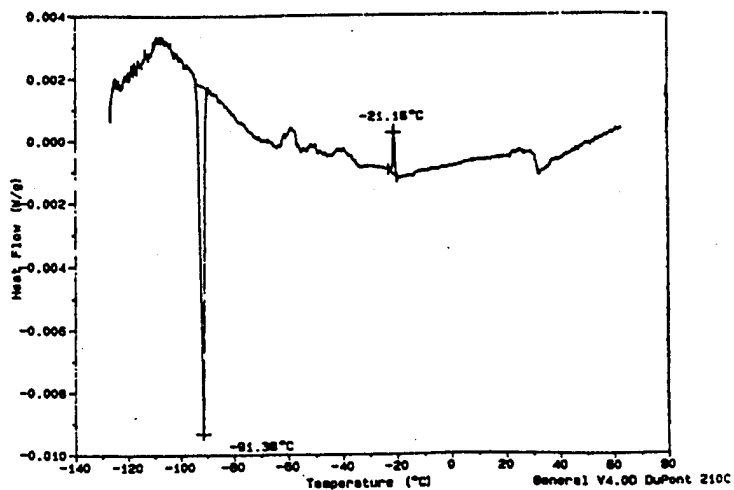
Figures A.1, A.2, and A.3 show the complete set of results obtained from the DSC. The results include the melt curves of following binary systems. (1) Acetone-Methyl Catechol in Figure A.1, (2) Acetone-Trinitrobenzene in Figure A.2, and (3) Acetone-Dinitrotoulene in Figure A.3. The mass concentrations of methyl catechol are varied from 0 to 13%, the mass concentrations of trinitrobenzene are varied from 0 to 9%, the mass concentrations of dinitrotoulene are varied from 0 to 19%.

The heating rate is same for all the experiments and is  $3^\circ\text{C min}^{-1}$ . The initial temperature is  $-150^\circ\text{C}$  and the final temperature is  $25^\circ\text{C}$  in most of the experiments.



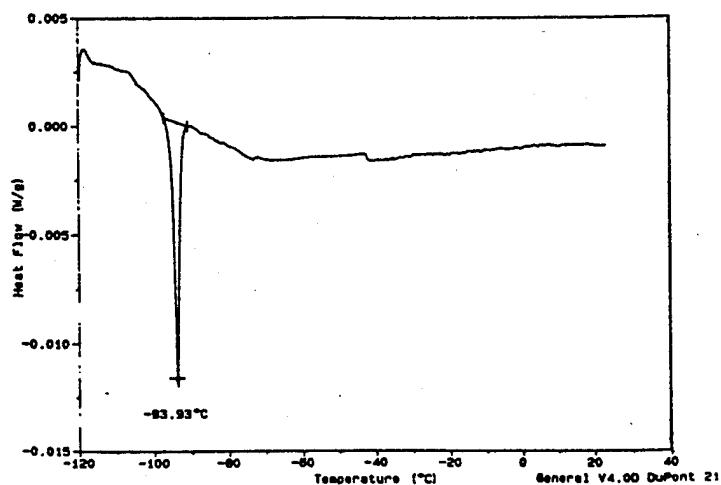
Sample: Pure Acetone  
Size: 2.4000 mg

DSC



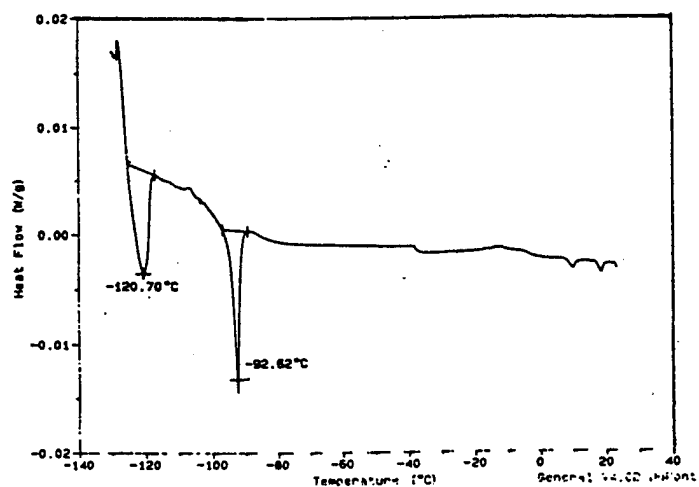
Sample: Acetone-M.Col (1X M)  
Size: 2.5000 mg

DSC



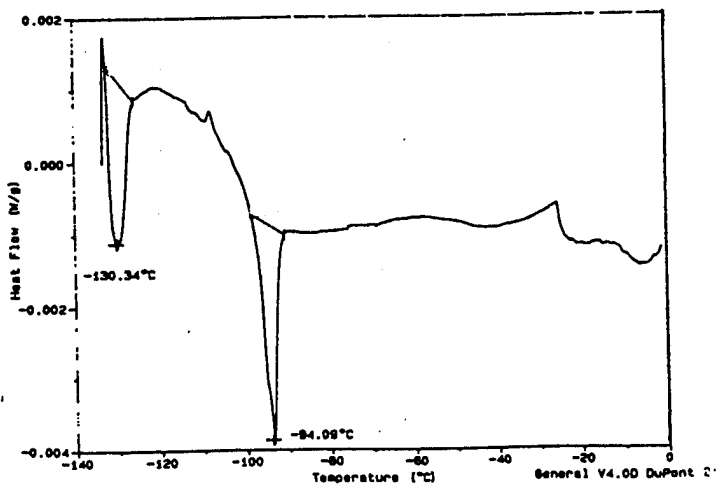
Sample: Acetone-M.Col (3X M)  
Size: 2.0400 mg

DSC



Sample: Acetone-M.Col (7X M)  
Size: 3.4000 mg

DSC



Sample: ACETONE - M.COL  
Size: 1.8000 mg

DSC

Comment: Methyl Catechol 13X By weight

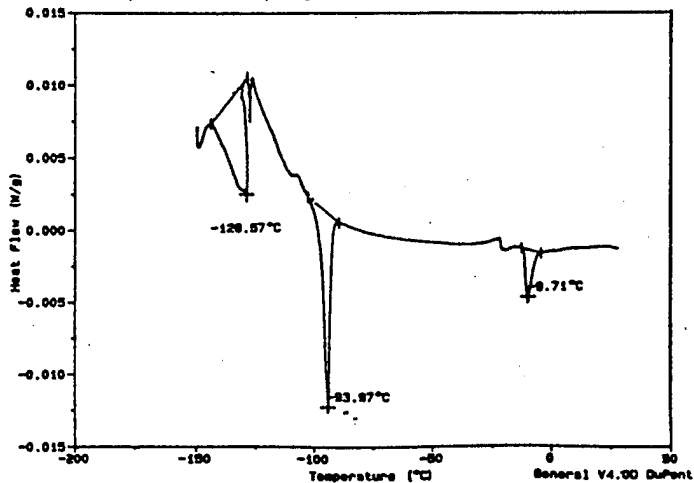
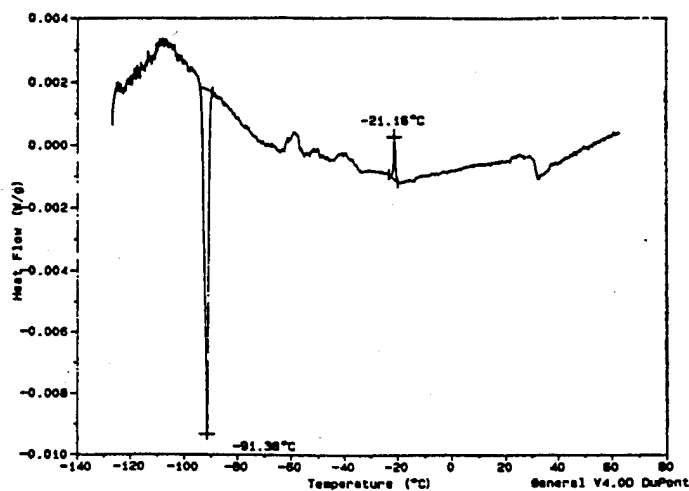


Figure A.1. DSC scans for acetone with methyl catechol for different compositions of solute.

Sample: Pure Acetone  
Size: 2.4000 mg

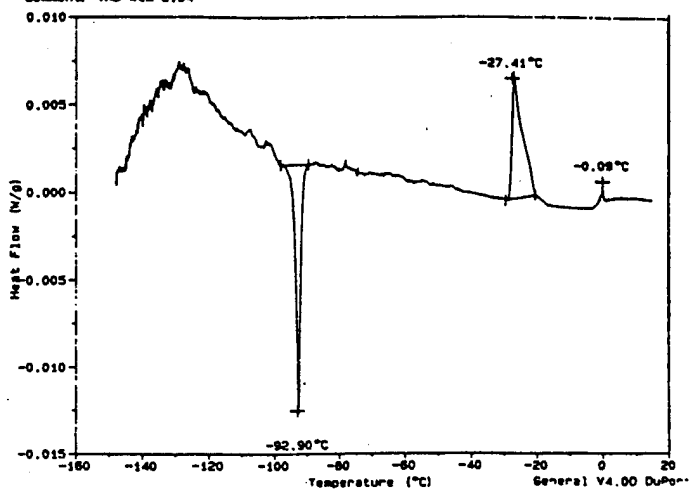
DSC



Sample: Acetone-TNB  
Size: 1.9000 mg

DSC

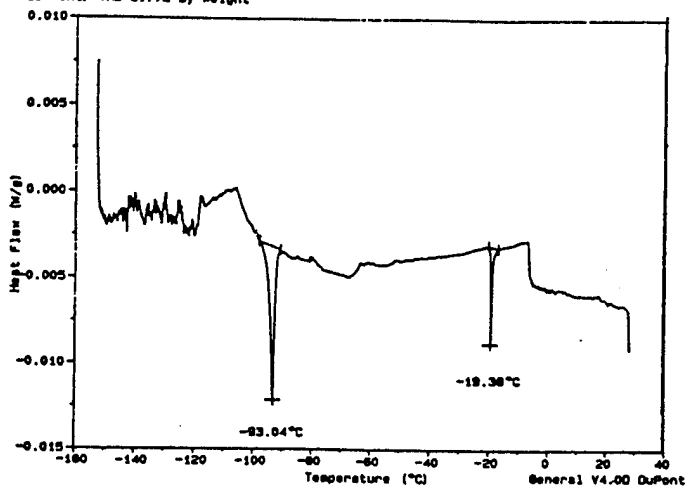
Comment: TNB wt% 2.94



Sample: TNB-Acetone  
Size: 2.3000 mg

DSC

Comment: TNB 8.77% By Weight



Sample: TNB-Acetone  
Size: 1.8000 mg

DSC

Comment: TNB 8.59% By Weight

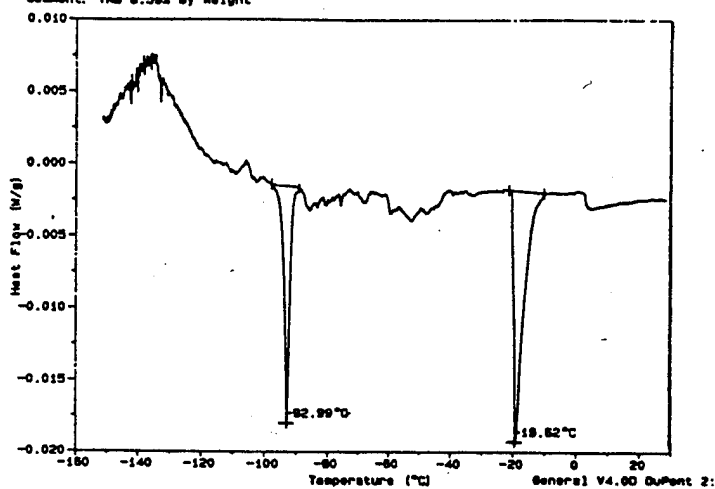


Figure A.2. DSC scans for acetone with trinitrobenzene for different compositions of the solute.

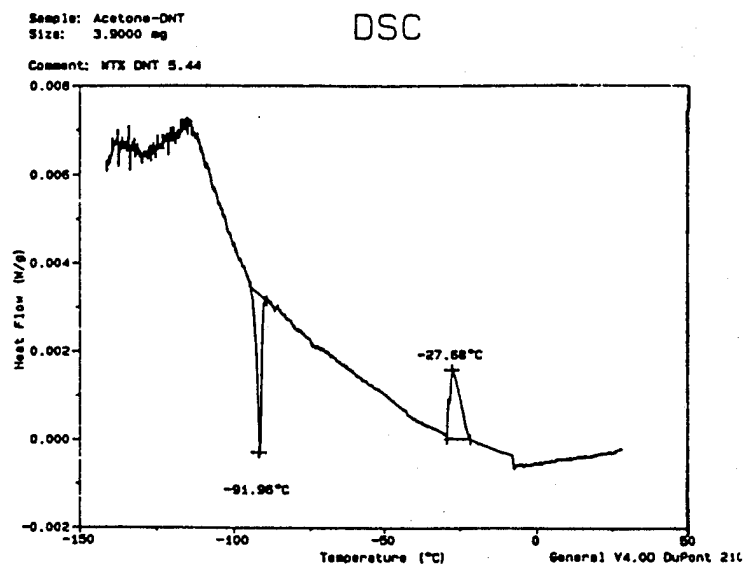
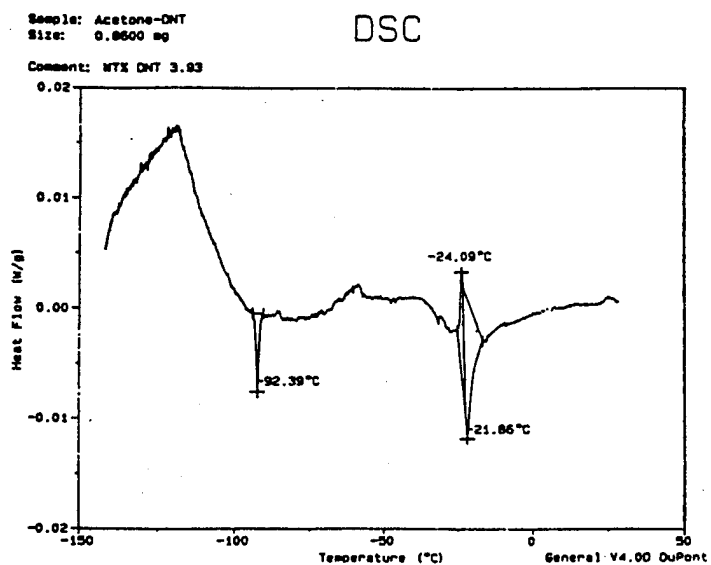
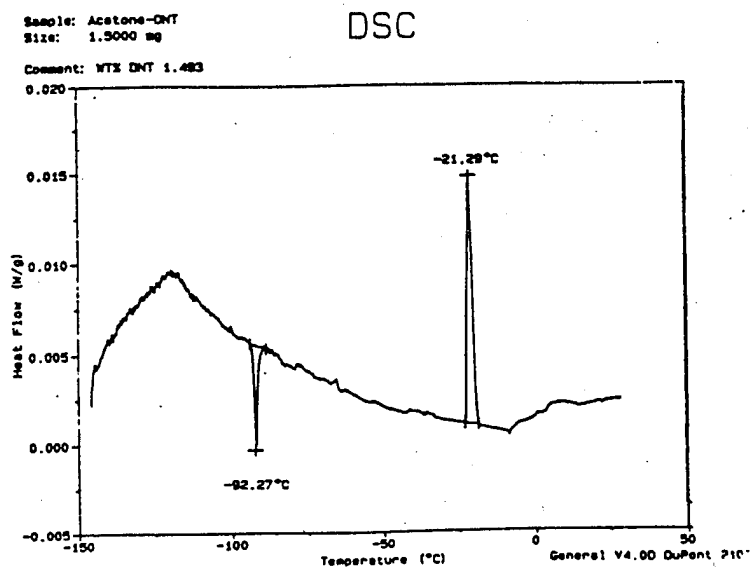
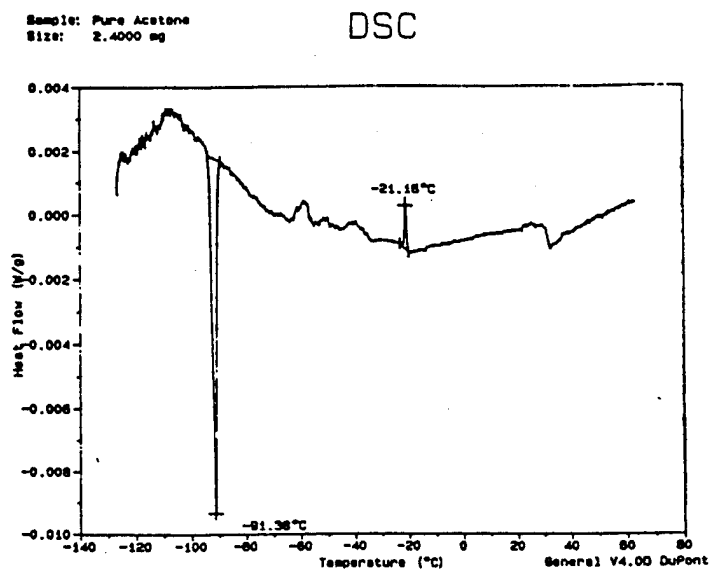


Figure A.3. DSC scans for acetone with dinitrotoulene for different compositions of the solute.

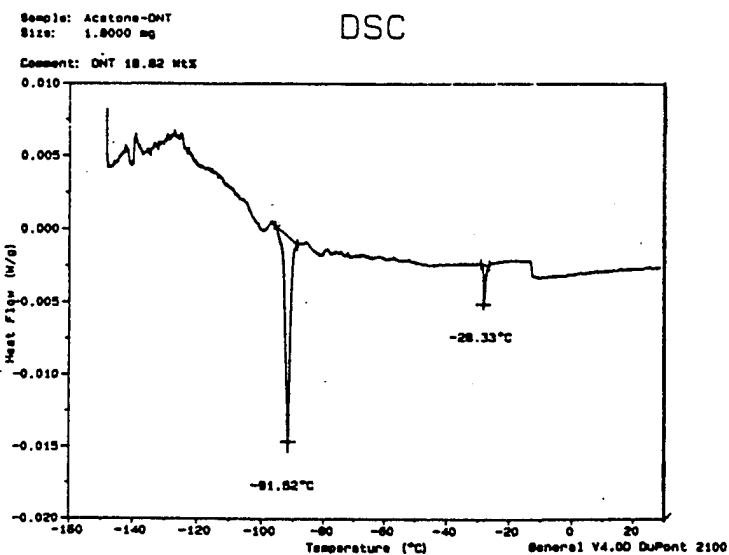
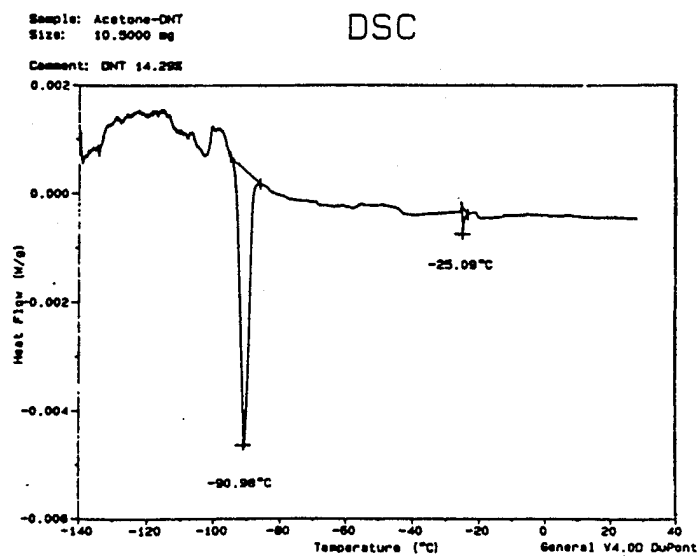
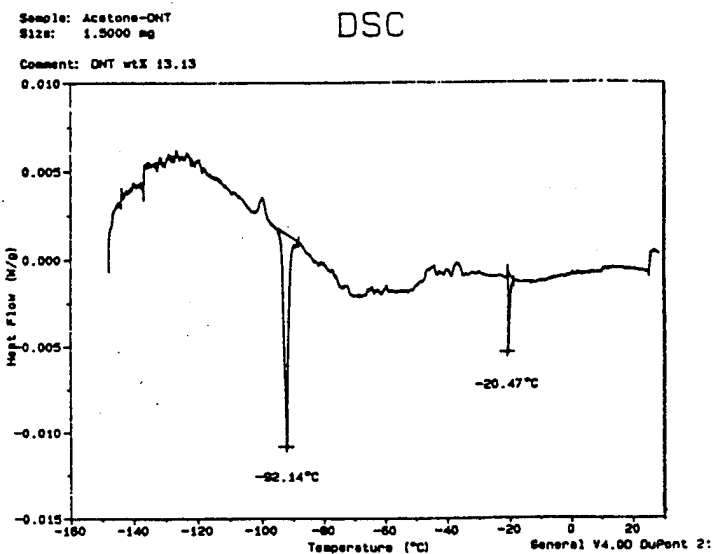
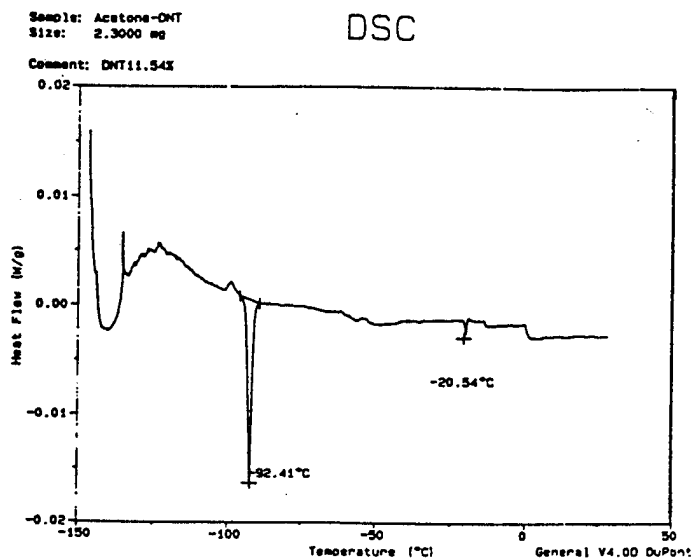
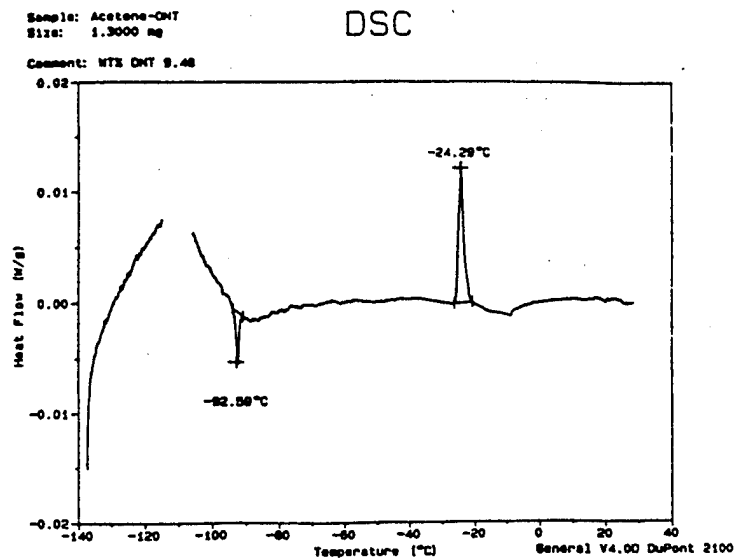
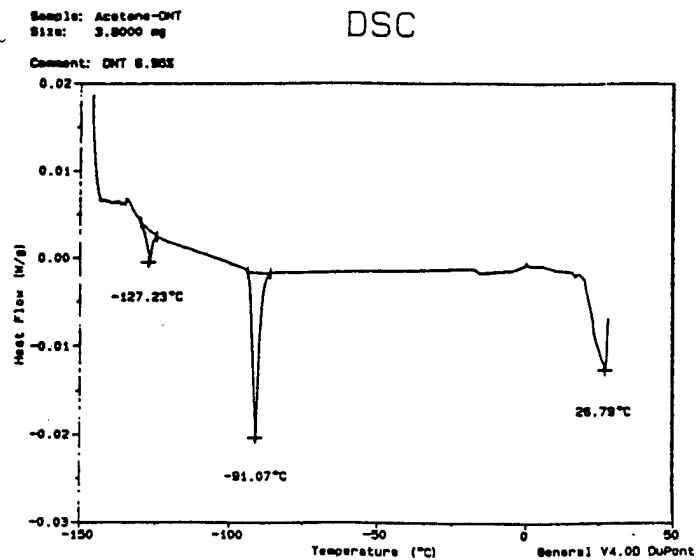


Figure A.3. (cont'd).