Separations Of Dilute Solutions By The Smooth Deposit Approach Of The In-Situ Indirect Freezing Process

Jeng-Hung Lue

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Date
SEPARATIONS OF DILUTE SOLUTIONS BY THE SMOOTH DEPOSIT APPROACH OF THE IN-SITU INDIRECT FREEZING PROCESS

BY

JENG-HUNG LUE

B.S., National Taiwan University, 1974

THESIS

Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science in Chemical Engineering

The University of New Mexico
Albuquerque, New Mexico
December, 1979
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SEPARATIONS OF DILUTE SOLUTIONS BY THE SMOOTH DEPOSIT APPROACH OF THE IN-SITU INDIRECT FREEZING PROCESS

BY

Jeng-Hung Lue

ABSTRACT OF THESIS

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SEPARATIONS OF DILUTE SOLUTIONS BY THE SMOOTH DEPOSIT APPROACH OF THE IN-SITU INDIRECT FREEZING PROCESS

Jeng-Hung Lue
B.S., Chemical Engineering, National Taiwan University, 1974
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It has been demonstrated that high degree separations of both dilute organic mixtures and aqueous solutions can be accomplished and an energy saving can be realized by a refined in-situ indirect freezing process with in-situ washing and melting operations conducted in a small conduit freezer-melter. There are two versions of the in-situ indirect freezing process; one is the dendritic approach, the other is the smooth deposit approach. The smooth deposit approach has been used in the present study. A convenient pressure-induced nucleation technique has been used to initiate a freezing step uniformly; a close control of ΔT has been used to have a close control of the morphology of the deposited solid phase. The process is useful in producing polymerization grade monomers for the synthetic fiber industries and plastic industries such as para-xylene and styrene. For example, from a feed containing 99 percent styrene a product containing 99.95% styrene has been obtained in a single stage operation. The process is also useful in desalination of brackish water. A brine containing 4600 ppm sodium chloride has been purified to produce product water containing 200 ppm sodium chloride.
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CHAPTER 1
THE REFINED IN-SITU INDIRECT FREEZING PROCESS

1-1 Introduction

The main objective of the present study is to demonstrate experimentally the feasibility of applying the smooth deposit approach of the in-situ indirect freezing process to the separations of both dilute organic mixtures and aqueous mixtures. The in-situ indirect freezing process with in-situ washing and melting operations was first introduced by C. Y. Cheng and S. W. Cheng [1].

The major contributions made in this study are as follows:

(1) Successfully incorporating the pressure-induced nucleation technique in separating dilute organic solutions by the smooth deposit approach of the in-situ indirect freezing process.

(2) Successfully incorporating the negative pressure-induced nucleation technique in separating dilute aqueous solutions by the smooth deposit approach of the in-situ indirect freezing process.

(3) Building an equipment setup that can be operated at a temperature as low as -70°C and conducted separations of dilute styrene-ethylbenzene mixtures.

With the successful implementation of these new techniques, the in-situ indirect freezing process has now been brought closer to commercial application. The present study is very timely,
because it contributes to the development of a highly efficient fractional solidification process which, in turn, contributes to great energy saving in industries.

The refined in-situ indirect freezing process of the present study is an improved process of the programmed indirect freezing process. Several innovative features have been incorporated in the process. These characteristic features are summarized as follows:

(1) An indirect freezing process with in-situ washing and melting operations is introduced to eliminate the need of transferring solids.

(2) A smooth solid deposit approach is introduced to form a small solid phase from a dilute solution under a small ΔT for heat transfer and a proper agitation to thereby facilitate separation of the solid phase from the mother liquor phase.

(3) A small conduit freezer-melter is used and an oscillatory pumping is applied to enhance rates of freezing and melting operations.

(4) A pressure-induced nucleation technique is introduced to obtain a uniform initiation of a freezing step of freezing a non-aqueous solution.

(5) A negative pressure-induced nucleation technique is introduced to obtain a uniform initiation of a freezing step of freezing an aqueous solution.
(6) A pressure-induced supersaturation technique is introduced to obtain a close control of the ΔT for heat transfer and obtain a close control of the morphology of the deposited solid phase.

The inherent advantages of fractional solidification processes and problems suffered by the conventional fractional solidification processes are reviewed in Section 1-2. The innovative features incorporated in the in-situ indirect freezing processes are described in Sections 1-3 through 1-9. Heat reuse by the two pressure zone simultaneous freeze-melt operation is described in Section 1-10; a multivoid freezer-melter to be used in accomplishing heat reuse by the two pressure zone approach is described in Section 1-11. Finally, the scope of the present study is summarized in Section 1-12.

1-2 Fractional Solidification Process

A fractional solidification process is a separation process which generally comprises three functional steps: (1) a freezing step in which a feed solution is partially frozen by removing heat of crystallization, (2) a washing step in which the solid formed in a freezing step is purified by washing the solid phase free of adhering mother liquor, (3) a melting step in which the purified solid is melted to yield a high melting product by supplying the heat of melting. The mother liquor recovered in the washing step becomes a low melting product.
Fractional solidification processes can be applied to the separation of both aqueous and nonaqueous solutions and have the following inherent advantages over distillation processes:

1. Heats of fusion are much lower than heats of vaporization (refer to Table 1).

2. Degree of separation that can be accomplished in one theoretical stage in a crystallization process is by far better than that of a distillation process.

However, the major disadvantages of the conventional fractional solidification processes, which have prevented their widespread applications, are the low actual separating efficiency, the high equipment cost, the high operation cost, and the operational difficulties encountered. The actual separation efficiency of a conventional fractional solidification process is lowered by the formation of cellular structures and dendritic structures in the deposited solid and the resulting entrapping of mother liquor within the interstices of these structures. The formation of the cellular and the dendritic structures is generally caused by the so-called constitutional super-cooling, which, in turn, is caused by the concentration polarization at the solid-liquid interface during the solidification step. The high equipment costs and the high operating costs are due to the solid handling problems of mechanically scraping the deposited solid from heat transfer surfaces and of moving the slurry of deposited solid and mother liquor, low heat transfer rate due to the added heat transfer resistance imposed by the deposited solid, and inadequate reuse of heat energy. The
Table 1. Heats of Fusion and Vaporization of Various Substances [2]

<table>
<thead>
<tr>
<th>Substance</th>
<th>Heat of Fusion (cal/g)</th>
<th>Heat of Vaporization (cal/g)</th>
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<tr>
<td>Water</td>
<td>80.0</td>
<td>540.0</td>
</tr>
<tr>
<td>Styrene</td>
<td>25.2</td>
<td>85.2</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>46.7</td>
<td>96.7</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>38.5</td>
<td>81.2</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>26.0</td>
<td>82.0</td>
</tr>
<tr>
<td>O-Xylene</td>
<td>30.6</td>
<td>82.9</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>20.6</td>
<td>95.1</td>
</tr>
<tr>
<td>Aniline</td>
<td>27.1</td>
<td>103.7</td>
</tr>
<tr>
<td>Benzene</td>
<td>30.1</td>
<td>103.6</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>36.0</td>
<td>75.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>7.6</td>
<td>85.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>23.4</td>
<td>134.7</td>
</tr>
</tbody>
</table>
operational difficulties are generally associated with handling of a solid phase and an inadequate permeability of a packed bed formed. Of these problems, the low actual separation efficiency problem is of the utmost importance. Once a solution or solutions to this problem is found, many practical fractional solidifications will emerge. The present study is addressed to these problems.

The key problems of a fractional solidification process for which solutions should be found are summarized as follows:

(1) Effective separation of the solid phase and the mother liquor phase that are formed in a fractional solidification step.

(2) Difficulties associated with handling of a solid phase.

(3) An effective utilization of the heat released in a freezing step for supplying the heat needed in a melting step.

(4) Enhancement of the rates of freezing and melting operations.

(5) Reduction of the equipment cost by designing new equipments and developing new fabrication techniques.

(6) Simplification of operational procedures and development of a simple way of controlling a freezing operation.

(7) Developing a simple way of uniformly initiating a freezing step.

Several innovative solutions to these problems have been
introduced by C. Y. Cheng [1, 3]. These solutions are described in the following sections.

1-3 The Indirect Freezing Process with In-Situ Washing and Melting Operations

The indirect freezing process with in-situ washing and melting operations is a precisely controlled cyclic crystallization process. Figures 1(a) through 1(h) illustrate various stages of each cycle conducted in a conduit of a freezer-melter. The operational steps of each cycle are explained as follows:

(1) Figure 1(a) illustrates the condition at the end of a feeding step. It shows that the narrow conduit is filled with a feed mixture.

(2) Referring to Figure 1(b), heat is removed through the heat conducting wall during a partial solidification step and a thin layer of solid phase is deposited on the surface of each conduit. Depending on the concentration of the solution, degree of agitation, thickness of deposit and the rate of solidification, the morphology of the deposited solid phase may vary from a smooth structure to a dendritic structure. The deposited solid phase is relatively solvent-rich and a solute-rich liquid phase surrounds the dendritic crystals. The spaces filled by the mother liquor will be called interstitial spaces in general and are further classified into two types of spaces: i.e., interdendritic
Figure 1. Illustration of the Programmed Indirect Freezing Process conducted in a Narrow Compartment Freezer-melter
spaces and central unfilled spaces.

As the solidification step progresses, solid deposits grow toward the center, and thus the central unfilled space in a conduit gradually diminishes. In the meantime, each dendritic crystal also grows sidewise, and therefore the interdendritic spaces also become smaller. When a fractional solidification is carried far enough the two layers of solid deposit may intermesh each other. Then it is no longer possible to distinguish central unfilled spaces from interdendritic spaces. Figure 1(c) illustrates the condition at the end of the fractional solidification step. In order to be able to carry out an effective in-situ washing step to be described, the structure of the deposited solid phase at the end of a fractional solidification step has to meet several critical conditions to be described in Sections 1-4 and 1-5.

(3) Referring to Figure 1(d), a displacing fluid is introduced from one end of the conduit to displace mother liquor from all the interstitial spaces. The figure shows that the displacing fluid has displaced the mother liquor to the left and the two liquids form an interface. It is preferable to use purified solvent as the displacing fluid in this washing operation. The displaced mother liquor constitutes the low melting product.
(4) Figure 1(e) illustrates the condition of the narrow conduit at the end of an ideal in-situ washing operation. It shows that all the interstitial spaces are now filled by the displacing fluid.

(5) After the deposited solid phase is separated from the mother liquor, it is subjected to an in-situ melting operation. Figure 1(f) illustrates a condition during the melting step during which heat is supplied to the conduit through the heat conducting surfaces. At the end of the melting step the conduit is filled with the melt of the solid phase.

(6) The melt has to be discharged from the conduit and a quantity of feed has to be introduced into the conduit to initiate the next cycle. One may use a quantity of the feed to displace the melt from the conduit. In this case, mixing of the two fluids at the interface of the two fluids has to be minimized. Another way to conduct the discharging and feeding steps is to use a gas stream (e.g., air or nitrogen) to displace the melt from the conduit (Figure 1(g)) and then introduce the feed to displace the gas from the conduit (Figure 1(h)). At the end of these displacement steps, the conduit is filled with feed mixture (Figure 1(a)). The discharged melt constitutes the high melting product.

The above described steps are repeated cyclically. Since the solid is deposited, washed in-situ and melted in-situ, there is
no need of mechanically scraping the heat transfer surfaces and mechanically transferring slurry streams.

1-4 A High Degree Separation of a Dilute Solution by Forming a Smooth Solid Phase

When a dilute solution is frozen at a slow rate with an appropriate agitation, the solid phase deposited has a smooth or a near smooth interface. The interstitial spaces consist only of central unfilled spaces and the displacement of mother liquor can be accomplished rather easily. In adopting this approach, the main concerns are the maximum freezing rate that can maintain stable solid/liquid interface, the degree of agitation that has to be applied and the power requirement for the agitation. The maximum freezing rate that can maintain the interface stability is a function of the solute concentration and degree of agitation, or

\[ \text{Maximum Allowable Freezing Rate} = f_{1} \text{ [Concentration, Degree of Agitation].} \]  \hspace{1cm} (1)

The freezing rate that can be used decreases and the degree of agitation needed increases as the concentration of the feed solution increases. It becomes uneconomical to use this smooth solid phase approach when the feed concentration exceeds a certain limit, because then the allowable freezing rate may become too low and the agitation needed may become too excessive. An appropriate way of agitating the mother liquor during a freezing step is to apply an oscillatory flow to the mother liquor.
A High Degree Separation of a Concentrated Solution by the Formation of a Dendritic Solid Bed Having an Appropriate Permeability

A dendritic solid phase is usually formed from a concentrated solution, unless it is frozen at an extremely slow rate. The interstitial spaces that surround the solid phase consist of central unfilled spaces and interdendritic spaces. To be able to attain an efficient separation, all the interstitial spaces should be accessible to the displacing fluid and the dimensions of the central unfilled spaces and interdendritic spaces should be such as to minimize dispersion and prevent preferential channeling during the in-situ washing step. Furthermore, the permeability of the bed should be reasonably high so that the in-situ washing step can be carried out at a reasonable rate and at a reasonable pressure drop. The permeability of the solid bed obtained in an indirect freezing operation is related to the concentration of the solution, freezing rate and degree of solidification, or expressed in a functional form,

permeability

\[ = f_2[\text{Brine Conc.}, \text{Freezing Rate}, \text{Degree of Solidification}] \]  

It is noted that the in-situ washing step used in the present process is somewhat similar to the liquid displacement operation used in the counterwasher of a direct contact freezing process of sea water conversion. However, the two processes differ in the ways the porous solid beds for washing are formed. While the porous
solid bed in the counterwasher of the desalination process is formed from a slurry of ice crystals and brine by a filtration operation, the porous solid bed of the present process is formed by a properly controlled indirect freezing operation.

1-6 Enhancement of Heat Transfer Rates

Reduction in the diameter of freezer and melter conduits and application of oscillatory pumping during a freezing step and a melting step are keys to increasing heat transfer rates.

The diameter of the conduits in a freezer-melter is the most important single factor in determining the economy of the process. The time taken in a freezing step is about proportional to the square of the diameter. Therefore, as the conduit diameter is reduced, the cycle time is reduced, and the overall heat transfer coefficient is increased. The use of small conduit diameter is also favorable from the standpoint of producing good quality products because when the thickness of the ice layer formed is small there is less tendency of forming enclosed spaces which are not accessible by the displacing fluid. Furthermore, as the conduit diameter is reduced, the wall thickness of a multivoid freezer-melter unit needed to sustain the high pressure required for heat reuse is reduced (refer to Section 1-11). Therefore, the amount of metal needed per square foot of heat transfer surface in constructing a multivoid freezer-melter can be reduced. It has been found in a study that it is desirable to use a conduit diameter less than 3/8 inch or preferably less than 1/4 inch [21]. It is noted, however, that in
order to be able to operate a freezer unit with a small conduit
diameter, it is essential to maintain a high degree of uniformity
in solidification along the length of each conduit and throughout
all the conduits in a freezer-melter.

1-7 Uniformity in the Degree of Solidification

For a deposit formed in a freezer conduit to be effectively
freed from its surrounding mother liquor by a displacement opera-
tion, the degree of solidification has to be uniform and the degree
of uniformity required increases as the conduit diameter decreases.
In order to maintain a uniform solidification, a freezing step has
to be initiated uniformly, mother liquor concentration has to be
uniform, and Δt for heat transfer has to be about the same through-
out. The subject of a uniform initiation of a freezing step is
described in the next section. In this section, another factor
that causes non-uniformity in degree of solidification is described.
When a solution is frozen in a long freezer conduit, a longitudinal
movement of mother liquor takes place due to the volume expansion
or contraction associated with the freezing. This longitudinal
movement of mother liquor causes a non-uniformity in mother liquor
concentration, which in turn causes a non-uniformity in degree of
solidification. A theoretical analysis has shown that this non-
uniformity is rather significant [19]. This problem can be remedied
by a gentle circulation of mother liquor.
Uniform Initiation of a Freezing Step

The use of a small $\Delta t$ for heat transfer during an indirect freezing step is the key to the success of the in-situ indirect freezing process: a small $\Delta t$ is used in the smooth solid phase approach to maintain a stable or near stable solid/liquid interface and a small $\Delta t$ is used in the dendritic solid phase approach to obtain a large dendrite spacing and consequently a high permeability of the porous bed that is formed. The use of a small $\Delta t$ for heat transfer is also advantageous from the standpoint of heat reuse. Thus, the $\Delta t$ value is usually limited to less than 5°F. With such a small $\Delta t$, a spontaneous nucleation does not take place. Therefore, there is a need to bring or form seed crystals, or bring effective nucleating agents uniformly into the freezing conduits.

Several approaches were proposed and tested earlier. These approaches are, however, not as convenient and versatile as the following two approaches:

(1) Seeded Feed Approach with Ultrasonic Nucleation

In this approach, a feed is supercooled by 1°F to 2°F in an ultrasonic cleaner tank and ultrasonic vibration is applied to the supercooled feed. Nucleation takes place and the resulting seeded feed liquor is then introduced to a freezer unit.

(2) Supercooling by Pressurization

It has been described that a small $\Delta t$ for heat transfer is used both in the smooth solid phase approach and the dendritic solid phase approach. Such a small $\Delta t$
does not cause nucleation in a freezer conduit. In the supercooling by pressurization approach, a pressure higher than a normal operating pressure is applied to freezer conduits for a short while to raise the freezing temperature so that $\Delta t$ value becomes so high as to initiate a spontaneous nucleation throughout the freezer conduits. Once the nucleation has started, the pressure applied is reduced to the normal operating pressure. Recently, a new technique, negative pressure-induced nucleation, has been developed and tested to initiate nucleation of an aqueous solution. Details of these two methods will be discussed in Chapter 2.

1-9 Pressure-programmed Indirect Freezing Operation

A pressure-programmed indirect freezing operation may be explained by referring to Figure 2. The figure shows freezing curves of a binary system at various pressures, $P_1$ through $P_4$. Referring to the figure, let us first consider an indirect freezing operation in which a feed at composition $X_1$ is partially solidified under pressure $P_1$ in a freezer conduit with wall temperature $T_w'$. The initial freezing temperature is $T_1$ and the initial $\Delta t$ for heat transfer is $T_1 - T_w'$. As the freezing progresses, the mother liquor becomes successively richer in A-component and the freezing temperature decreases. This relation is shown on Figure 2 by 1-2 on Lines $B_1E_1$ in the figure. When the mother liquor composition becomes $X_2$, the freezing temperature $T_2$ becomes equal to $T_w'$ and the freezing
Figure 2. Illustration of a Pressure-programmed
Indirect Freezing Operation
operation stops. In the pressure-programmed indirect freezing operation, the pressure applied to the freezer conduit is increased as the freezing progresses so as to maintain an appropriate $\Delta t$ value for a desired period of time. For example, the figure shows that one may increase the applied pressure to $P_2'$, $P_3'$ and $P_4'$ as the mother liquor composition becomes $X_2'$, $X_3'$ and $X_4'$ to maintain the freezing temperature at substantially constant values, $T_2'$, $T_3'$ and $T_4'$. Thus, substantially, the same $\Delta t$ value is maintained throughout the freezing operation.

It is noted that it is simple to adjust and program the pressure applied to a freezer conduit. By initiating a freezing step by the pressure-induced nucleation approach or the negative pressure induced nucleation approach and controlling $\Delta t$ for heat transfer by programming the applied pressure, both the operation and control of a freezer-melter has been greatly simplified.

1-10 Heat Reuse by the Two Pressure Zone Simultaneous Freeze-melt Operations

In the two-pressure zone simultaneous freeze-melt process, the freezing and melting steps are conducted under sufficiently different pressure so that the prevailing temperature of the melting step becomes lower than the prevailing temperature of the freezing step, and that the desired heat reuse is accomplished simply by establishing heat exchange between the two steps. It is noted that the use of a heat pump is no longer necessary in this process. Referring to Figure 3, one may accomplish the desired
heat reuse in an organic system by conducting a step of freezing an organic mixture, and a step of melting the purified solid phase in two separate pressure zones which are maintained in heat exchange relation and maintaining the freezing step under a sufficiently high pressure $P_H$ such that the freezing temperature ($T_f^H$) is higher than the melting temperature ($T_m^L$) of the purified solid.

In general, by referring to Figure 4, the pressure in the freezer and the melter, $P_f$ and $P_m$ respectively, differ by an amount $P_f - P_m$ calculated by

$$\frac{(P_f - P_m)}{\left(\frac{dP}{dT}\right)_{S/L}} = \Delta T_f + \Delta T \tag{3}$$

where $\Delta T_f$ is the freezing point depression of the solution in the freezer, $\Delta t$ is the temperature differential between the freezer and melter allowed for heat transfer and $\left(\frac{dP}{dT}\right)_{S/L}$ is the slope of the melting curve of the pure solvent. Since $\Delta T_f$ is generally a positive value and $\Delta t$ is always positive, $P_f$ is greater than $P_m$ when $\left(\frac{dP}{dT}\right)_{S/L}$
Figure 4. Illustration of Temperature Relationship in the Separation of p-xylene-m-xylene Mixtures by the Two-pressure Zone Simultaneous Freeze-melt Operations
is positive and $P_f$ is less than $P_m$ when $\left(\frac{dP}{dT}\right)_{S/L}$ is negative. The latter is the case for an aqueous system and the former is the case for a nonaqueous system.

1-11 A Multivoid Freezer-melter for the Indirect Freezing Process with Two Pressure Zone Simultaneous Freeze-Melt Operations

The indirect freezing process with two pressure zone simultaneous freeze-melt operations may be conducted in a multivoid freezer-melter illustrated by Figure 5. Referring to the figure, a multivoid unified freezer-melter has two sets of small and longitudinal conduits, denoted as A-conduits and B-conduits, which are to be alternatively and simultaneously used as a freezer and melter. The diameter of the conduits is 1/4 inch to 3/8 inch. One may use an auxiliary set of conduits or use the outer surface of each unit or module for an auxiliary refrigeration required in start-up operations, and in keeping the system under a thermally balanced condition. Referring to the figure, one may distinguish two types of separating walls, denoted respectively as $\alpha$-walls and $\beta$-walls. A wall separating an A-conduit from an adjacent A-conduit or a wall separating a B-conduit from an adjacent B-conduit is called an $\alpha$-wall, and a wall separating an A-conduit from an adjacent B-conduit is called a $\beta$-wall. A $\beta$-wall may be half as thick as that of an $\alpha$-wall because pressurization operations are to be alternatively applied to the A-conduits and B-conduits. A multivoid freezer-melter consists of a main body which is a multivoid metal block, and two headers for introducing and removing fluid streams. Since a high productivity
Figure 5. A Unified Freezer-melter Made of a Multivoid Metal Block [1]
is the key to reducing production cost, a metal extrusion process is considered to be the best way for manufacturing the multivoi
d metal blocks and an investment-casting process is probably the best way to produce the headers.

1-12 Scope of the Present Study

The present study includes the following subjects:

(1) to experimentally investigate the feasibility of purifying dilute organic mixtures such as styrene-
ethyl-benzene system and p-xylene-m-xylene system by a smooth deposit approach of the in-situ indirect freezing process. The eutectic type phase diagram of styrene-ethylbenzene is presented in Figure 6. This phase diagram was constructed by using Schroder-van Larr equation [4, 5]. The phase diagram of p-
xylene-m-xylene is also given in Figure 7 [20].

(2) to develop and test the negative pressure induced nu-
cleation for nucleating supercooled aqueous solution in desalinating brackish water.

(3) to make a review of the facts and theories reported in the literature to arrive at an acceptable mechanism for the negative pressure induced nucleation.

(4) to qualitatively study the effects of Δt for heat trans-
fer, degree of agitation and methods of mother liquor displacement to the quality of product obtained in the smooth deposit approach.
Figure 6. Eutectic Type Phase Diagram of Styrene and Ethylbenzene System
Figure 7. Eutectic Type Phase Diagram of the p-xylene and m-xylene System
CHAPTER 2
UNIFORM INITIATION OF A FREEZING STEP

2-1 Introduction

The first stage of crystallization is the formation or introduction of an appropriate minute nucleus, called a seed. In order to induce a compound to crystallize, it is often necessary to subject it systematically to a variety of treatments in the hope that one of them may lead to formation of crystal nuclei. These techniques mainly involve orienting influence, the effect of foreign particles and surfaces, or mechanical agitation and shock.

The nucleation of crystals in an undercooled melt can occur by a variety of processes. For convenience we may subdivide these processes into four categories: homogeneous nucleation, heterogeneous nucleation, nucleation by cavitation, and a fourth category which is not really nucleation but the production of new crystals by breeding from existing crystals. Homogeneous nucleation is the process by which nucleation occurs because of configurational fluctuations in an otherwise homogeneous liquid. The nuclei in this process are small, transient aggregates of atoms or molecules which form spontaneously in the melt. They do not depend on the surfaces, the container, or foreign particles for their existence. In heterogeneous nucleation, the nuclei are also formed by configurational fluctuations in a liquid, but in this case the fluctuations occur at a surface on some foreign object in the liquid. The nucleation
depends on the existence of foreign matter and is therefore termed heterogeneous. Nucleation by cavitation can occur only in liquids. Small cavities, opened in the liquid by negative pressures, produce high pressures when they collapse. These high pressures produce nuclei. The breeding of nuclei includes all those processes—fracture, partial melting, etc.—by which previously existing crystals can subdivide to produce many separate crystals.

As has been described in the indirect freezing process, the use of a small \( \Delta t \) for heat transfer is essential to a successful operation. A small \( \Delta t \) is always necessary for maintaining a stable solid-liquid interface in the smooth deposit approach; it is also needed to obtain a packed bed with high permeability in the dendritic approach and for an efficient heat reuse. With such a small \( \Delta t \) for heat transfer, a spontaneous nucleation, homogeneous or heterogeneous, does not take place. Since the freezer conduits are so small and so long, and since a precise control of degree of solidification is the key to a high degree separation of a feed solution and also the key to a trouble free operation, it is necessary to develop a convenient method for initiating each freezing step very uniformly.

Over the past few years, several methods to initiate freezing steps have been developed and tested by C. Y. Cheng and his co-workers. They are (1) residual solid phase approach, (2) local supercooling approach, (3) seeded feed approach with a gas phase nucleation, (4) seeded film approach with a gas phase nucleation, (5) seeded feed approach with ultrasonic nucleation, and (6) pressure-induced nucleation approach. Among these methods, the pressure-induced
nucleation approach is most convenient. In the present study, the pressure-induced nucleation approach which is used in the dendritic approach by J. Miles [6] is now adopted in the smooth deposit approach. Furthermore, a new technique, negative pressure-induced nucleation, is developed to initiate the freezing step of a mixture that expands on freezing, such as aqueous solution. All of the above methods are described in the following sections. A review of observed facts and proposed mechanisms are also presented in this chapter.

2-2 A Summary of the Earlier Methods

Several methods have been tested to initiate freezing steps in the earlier stage of developing the indirect freezing process by C. Y. Cheng and his co-workers. These methods are explained briefly as follows:

(1) The Residual Solid Phase Approach

In this method, some solid is prevented from melting in a melting step so that the next following freezing step can be initiated from these remaining crystals. One way of applying this approach is to have some insulated spots at properly spaced locations within a freezer conduit. Methods of adopting this approach in a commercial operation have not been explored. This approach may be adopted in a commercial operation only when a convenient way of providing insulated and protected small regions can be found.
(2) The Local Supercooling Approach

This method was used by Howard H. Y. Sung [7] and James K. P. Shou [8]. In this approach, a nucleating tube is installed in each freezer conduit. A nucleation tube is a metal tube insulated by a perforated heat shrinkable tube. The portions of the tube at the perforations are uninsulated. Prior to a freezing step, a very cold cooling medium is introduced to form crystals at the uninsulated portions of the nucleation tube. Freezing is initiated from these crystals. This method is not a practical method, because it is too costly to install a nucleating tube in each conduit and it complicates the operating procedures. This method was used to take care of the uniform initiation problem temporarily so that other aspects of the indirect freezing process could be studied.

(3) Seeded Feed Approach with a Gas Phase Nucleation

This approach consists of a step of forming small ice crystals 1μ to 20μ in a gas stream by one of the many ways developed for weather modification, a step of transferring the ice crystals from the gas stream to a quantity of precooled feed solution to form a quantity of seeded feed and a step of introducing the seeded feed to a freezer tube. With this approach, a uniform initiation can be accomplished and no local plugging of a freezer conduit has been experienced. This approach was
first developed by E. Chang [9], and later extensively used by W. Chang [10] and K. S. Lin [11].

(4) Seeded Film Approach with a Gas Phase Nucleation

This approach also has a step of forming small ice crystals in a gas stream by the cloud seeding techniques and transferring the ice crystals from the gas stream to a thin liquid film existing on the inner surface of a freezer-melter tube prior to a feeding and freezing step. It has been described that a unified freezer-melter is to be operated cyclically, and each cycle consists of a freezing step, a washing step, a melting step and a feeding step. In order to adopt this seeding method, product water formed in a melting step is displaced from each freezer-melter conduit by a gas stream. As a result, a thin layer of fresh water remains on the surface of each conduit. A gas phase seeding is made at this condition to transfer ice crystals to the liquid film. A quantity of feed brine is then introduced into the conduits and a freezing step is initiated. T. Ford [12] has developed this approach.

(5) Seeded Feed Approach with Ultrasonic Nucleation

This approach was first developed by J. P. Chiang [13] and later used by J. Miles [6]. In this approach, a feed stream is first supercooled by 1°F and 2°F and then ultrasonic vibrations are applied to the supercooled feed to cause nucleation in the feed. The resulting seeded feed liquor is then introduced into freezer conduits.
Pressure-induced Nucleation Approach Applied to Non-aqueous Solutions

In the pressure-induced nucleation approach, a high pressure is applied to freezer conduits for a short while to raise the freezing temperature so that $\Delta t$ value becomes so high as to initiate a spontaneous nucleation throughout the freezer conduits. Once nucleation has started, the pressure applied is reduced to the normal operating pressure. Figure 8 illustrates the principle of pressure-induced nucleation approach. Lines $A_1 E_1$ and $B_1 E_1$ show freezing lines at pressure $P_1$. Lines $A_2 E_2$ and $B_2 E_2$ show freezing lines at pressure $P_2$. When a feed $F$ is brought into a freezer conduit with wall temperature $T_w$ and a pressure $P_1$ is applied to the feed, the freezing temperature is $(T'_f)$ and the supercooling attainable is $(T'_f) - T_w$. Let us assume that the degree of supercooling attained is insufficient to cause a spontaneous nucleation. However, when the high pressure $P_2$ is applied to the conduit, the freezing temperature is raised to $(T'_f)$ and the degree of supercooling is increased to $(T'_f) - T'_w$ and a spontaneous nucleation results. It is expected that a very uniform initiation of a freezing step can be attained by this approach. Pressure shock waves that propagate through the freezer conduit in the pressurization operation also help lower the degree of supercooling required for a spontaneous nucleation.

Negative Pressure-Induced Nucleation in an Aqueous Solution

In the negative pressure-induced nucleation, a high pressure,
Figure 8. Illustration of the Principle of Pressure-Induced Nucleation
say 7000 psi, is applied to an aqueous solution that is maintained at a temperature slightly lower than its freezing temperature. On suddenly producing the applied pressure, a spontaneous nucleation takes place. The increased melting point theory described in Section 2-3 is not adequate to explain the nucleation of an aqueous solution in this way since its melting point is lowered as the applied pressure increases. The observed phenomenon can be explained by the negative pressure theory to be described.

In every-day experience, a liquid cannot sustain any tensile stress, because liquid in general is able to change its shape and flow in such a direction as to relieve the stress. There are, however, theoretical grounds for expecting that, when a liquid is suitably restrained so that failure must occur in the body of the liquid rather than by gross change of shape, it can sustain a tensile stress of the order $10^3$ or $10^4$ atmospheres. A liquid that is under tensile stress is said to be under a negative pressure. This may be contrasted with a normal situation in which a liquid that is under a compressive stress is said to be under positive pressure. A volume element of the liquid is subjected to positive and negative pressures when a pressure shock is induced.

It has long been recognized that nucleation of a crystal in an undercooled liquid can be induced by cavitation [14]. The cavities are small voids in the liquid which open in negative pressure regions. The negative pressure can be produced either mechanically or ultrasonically; in either case, the negative pressure is transient. When the cavities collapse, high local pressures result.
Wylie [15] proposed that extremely high negative pressures just before cavitation locally raised the melting point of ice well above 0°C, thereby yielding ice nuclei. Hunt and Jackson [16] also hypothesize that the difference in melting characteristics of benzene and water does not affect nucleation because benzene may nucleate in the positive pressure period immediately after the collapse of the cavity, while water does so during the negative pressure period. These pressures, negative or positive, change the melting temperature according to the Clausius-Clapeyron equation. The change in melting temperature produces sufficient undercooling for homogeneous nucleation [16]. Figure 9 shows melting curve for ice (I) with a possible extrapolation into the region of negative pressures.

As a high pressure is applied to an aqueous solution which is enclosed in a high pressure tubing, a sudden opening of a valve produces a fluid hammer. A fluid hammer is the term for the overall effect of pressure transients in a piping system and is fluid shock resulting from the opening or closing of a valve. It includes the effects of initial system pressure, fluid inertia, piping dimensions, pipewall elasticity, fluid bulk modulus, and valve operating time (to open or close). Elasticity of fluid and pipewall produces waves of positive and negative pressures which travel from the valve at one end, through the fluid, to the valve at the other end, and back to the original valve. An analogy to a positive-negative pressure wave is a coil spring that is extended and then released, the stresses reverse from tension to compression. During the negative
Figure 9. Melting Curve for Ice I with a Possible (Straight Line) Extrapolation into the Region of Negative Pressures. The insert (diagrammatic) shows the stable phase boundaries (solid line) in the immediate vicinity of the triple point B: low-salinity inclusions containing only ice and water follow the metastable extension of line AB (in the pure system water); along BC these inclusions show slightly superheated ice at positive pressures lower than that of the triple point B; beyond C they enter into the region of negative pressure.
pressure period, spontaneous nucleation of water may occur. Figure 10 shows a damped pressure wave produced by the opening or closing of a valve [17].

2-5 Theory of Homogeneous Nucleation from Melt

The stability of a nucleus in an undercooled liquid depends on two factors. The free energy of the liquid decreases when it transforms to solid; for too small particles of solid, the surface area is large relative to the volume and the surface energy of such a particle dominates. Small particles can decrease the total free energy of the system (liquid plus particles) by shrinking and reducing their surface area. Large particles can reduce the free energy of the system by growing and creating more crystal. A balance between these tendencies defines the critical nucleus.

The change in free energy of the system in forming a spherical solid particle of radius $r$ from a bulk liquid is

$$
\Delta F = \frac{4}{3} \pi r^3 \cdot \Delta F_v + 4\pi r^2 \cdot \sigma
$$

(4)

where $F_v$ is the difference between the volume free energy of the liquid and solid, and $\sigma$ is the specific surface free energy.

The volume free energy difference depends on the undercooling and is given by

$$
\Delta F_v = \frac{L \Delta T}{T_E}
$$

(5)

where $L$ is the latent heat of fusion, $\Delta T = T_E - T$ is the undercooling, and $T_E$ is the equilibrium temperature between the solid
Figure 10. The Damped Pressure Waves Produced by Instant Opening or Closing of a Valve
and liquid.

The radius of the critical nucleus $r^*$ is given by the following equation which is obtained by maximizing $\Delta F$ with respect to $r$ in Equation 4:

$$ r^* = \frac{2\sigma T_E}{kT} $$

(6)

The rate of formation of nuclei of critical size has been discussed by many authors. An excellent review of the theory of nucleation in condensed systems has been given by Turnbull [18].

The rate of nucleation is given approximately by

$$ I = n\nu \exp(-Q_D/kT) \exp(-F^*/kT) $$

(7)

where $n$ is the number of molecules in the system; $\nu$ is the Debye frequency, $kT/h$; $Q_D$ is the activation energy for diffusion in the liquid; and $\Delta F^*$ is the free energy of the cluster of critical size, obtained by substitution of $r^*$ from Equation 6 into Equation 4.

Equation 7 may be rewritten as

$$ I = I_0 \exp[-b/T_r(\Delta T_r)^2] $$

(8)

where

$$ I_0 = n\nu \exp(-Q_D/kT), $$

$$ b = \frac{16}{3} \pi \left( \frac{\sigma}{L} \right)^3 \left( \frac{L}{kT_E} \right)^2, $$
\( T_r \) is the reduced temperature defined by

\[
T_r = \frac{T}{T_E}
\]

and \( \Delta T_r \) is defined by

\[
\Delta T_r = \frac{T_E - T}{T_E}
\]

Several refinements could be made in the definition of \( I_o' \), such as consideration of crystal growth kinetics or time lag effects. These would have to change \( I_o \) many magnitudes to alter appreciably the experimental conclusions, because of the exponential dependence of the nucleation rate on \( \Delta T_r \): a few degrees' change in \( \Delta T \) makes a few magnitudes' change in nucleation rate for most materials.
CHAPTER 3
STRATEGIES FOR OBTAINING HIGH DEGREE SEPARATIONS

3-1 Introduction

The essential requirements for attaining an efficient, high degree separation and a trouble-free operation in the in-situ indirect freezing process are (1) that the degree of solidification be maintained substantially the same throughout in each freezing step so as to avoid local plugging and channeling during the following in-situ washing step, and (2) that the main operating variables, such as $\Delta t$ for heat transfer, degree of agitation and degree of solidification, be so controlled as to form a solid phase at the end of each freezing step from which the mother liquor phase can be effectively displaced during the following in-situ washing operation.

In order to maintain the degree of solidification substantially uniform throughout the freezer conduits, each freezing step has to be initiated uniformly and the effective $\Delta t$ for heat transfer be maintained substantially the same throughout the freezer-melter unit. Methods of uniformly initiating a freezing step are described in Chapter 2. In dealing with the problem of maintaining effective $\Delta t$ for heat transfer substantially the same throughout the freezer-melter unit, one has to be concerned with the effects of longitudinal movement of mother liquor caused by volume change associated with the freezing operation, because this longitudinal
movement of mother liquor tends to create a longitudinal variation in mother liquor concentration and a longitudinal variation of effective $\Delta t$ for heat transfer. These effects and methods of suppressing these effects are described in this chapter.

3-2 Longitudinal Movement of Mother Liquor due to the Volume Change Associated with an Indirect Freezing Operation

During an indirect freezing operation with an external agitation or pumping in a longitudinal freezer conduit, a longitudinal movement of mother liquor inherently takes place, because of the volume expansion or contraction associated with the freezing operation. This longitudinal movement causes a variation in the concentration of mother liquor, a variation in the effective $\Delta t$ for heat transfer, a variation in the rate of solidification per unit length of the freezer conduit and a variation in the degree of solidification along the longitudinal direction of the conduit. H. Y. Sung [7] has made an analytical study of the magnitudes of these variations. In his analysis, the following assumptions have been made:

(1) The longitudinal movement of mother liquor is caused solely by the volume change associated with freezing operation.

(2) Heat transfer in the longitudinal direction is neglected.

(3) Diffusion of solute in the longitudinal direction is neglected.

(4) Variation in concentration of mother liquor in the radial direction at a given longitudinal position is neglected.
Basing on these assumptions, he has reached conclusions that the effects of the longitudinal movement of mother liquor caused by volume change with a non-agitated indirect freezing process may be very significant and that this longitudinal movement of mother liquor may cause a premature local plugging and make an efficient in-situ washing impossible. A successful solution is to superimpose an oscillatory flow of a small amplitude to the longitudinal movement of mother liquor to suppress its effects throughout a freezing step.

3-3 The Morphology and Washability of a Deposited Solid Phase

The degree of purification that can be attained in the indirect freezing process depends on how effectively the mother liquor existing in the interstitial spaces, including both the interdendritic spaces and the central unfilled spaces, can be displaced by an in-situ washing operation.

Depending on the concentration of the solution, degree of agitation and the rate of solidification, the morphology of the deposited solid phase may vary from a smooth or near smooth surface to a dendritic structure. In the former case, the interstitial spaces consist only of central unfilled spaces and the displacement of mother liquor can be accomplished rather easily. In the latter case, the interstitial spaces consist both of central unfilled spaces and the interdendritic spaces. For a deposit containing dendritic crystals to be effectively purified by a displacing fluid, these interstices should not be too narrow and
should not be enclosed, and the permeability of the bed should be reasonably high. The dimensions of the central unfilled spaces and the interdendritic spaces should be such as to minimize dispersion and preferential channeling of fluid either through the central unfilled spaces or through part of the interdendritic spaces during the in-situ washing step. Therefore, the degree of solidification, defined as the fraction of the freezer volume occupied by solid phase at the end of a freezing step, should be within an appropriate range. It is generally between 40 to 60 percent [7]. In the conventional fractional solidification processes, a thick layer of deposit 1 cm or more, is formed under a rather large temperature differential, 10°C or more. Under these operating conditions, the interdendritic spaces become extremely narrow and enclosed spaces containing mother liquor are formed. In order to be able to form a solid bed of the desired characteristics, and to have a low resistance to heat transfer and to be able to accomplish an efficient heat reuse, it is considered desirable to limit Δt for heat transfer to less than 3°C and limit the thickness of deposit to less than 3 mm [7].

3-4 Smooth Deposit Approach and Interface Stability

As has been described in Section 3-4, the main concerns of a smooth deposit approach are the maximum freezing rate that can maintain stable solid/liquid interface, the degree of agitation that has to be maintained and the power requirement to maintain the agitation. To form a smooth solid phase, a stable solid/liquid interface has to
be maintained. B. Chalmer was the first in associating interface stability to constitutional supercooling [19]. He later modified his original theory to allow for a tolerable degree of supercooling, which he has called kinetic supercooling, $\Delta T_k$. According to this modification an interface stability can be maintained as long as the degree of constitutional supercooling does not exceed a certain limit. According to Chalmer, the value of $\Delta T_k$ is typically $10^{-3}$ to $10^{-4}$ degrees. Such a small supercooling is insufficient for nucleation, even if a very potent nucleant is present. However, for the smooth solid phase deposit approach to be successfully applied in the in-situ indirect freezing process, it is sufficient that the morphology of the solid phase formed in a freezing step be such as to have a sufficiently low entrapment in the solid phase and for the solid phase, to be amenable to a sufficiently effective in-situ washing operation to produce a product of a desired quality. It is, therefore, not necessary to attain the absolute stability of solid/liquid interface as required in the Chalmer's theory. Some degree of instability is therefore tolerable and the degree of instability allowable is mainly related to the feed concentration. Since the interface stability is related to the degree of constitutional supercooling, one may say that there exists a tolerable degree of supercooling for a given feed solution producing product of a given quality.

H. Y. Sung [7] has conducted some experiments to investigate the smooth solid phase approach by freezing dilute brine solutions. The significant conclusions that can be drawn from the results of
his experiments are summarized as follows:

(1) Dendrite ice-bed is obtained under a non-flow condition.

(2) A smooth or near smooth ice-bed is obtained under a flow condition.

(3) A smoother ice-bed is obtained under a higher circulation rate.

(4) Amount of brine retained per gram of ice in an ice bed after an air displacement operation increases as degree of solidification increases.

(5) Good quality product water may be obtained by a simple air displacement operation in the place of a regular washing operation using fresh water as displacing fluid.

(6) The applicability of the smooth-ice approach in producing good quality product water is probably limited to feed brine containing 5,000 ppm NaCl. For a brine of an intermediate concentration, higher than 5,000 ppm, one may still use the smooth deposit approach under a high degree of agitation and a low freezing rate. For a brine containing more than 15,000 ppm NaCl, this approach does not lead to an economical separation process.

In a freezing step of the present study, an oscillatory flow is applied within a freezer conduit to reduce concentration polarization and the freezing rate is controlled at such a rate that the tolerable degree of constitutional supercooling is not exceeded.
CHAPTER 4

EQUIPMENT SETUP AND OPERATIONAL PROCEDURES

4-1 Introduction

The equipment employed in this study was designed and built to test the technical feasibility of a high degree separation of dilute mixtures by using the smooth deposit approach of the in-situ indirect freezing process.

Referring to Figure 11, the system used comprises the coiled freezer-melter F, a circulation bath and a bath cooler, an air driven hydraulic pump J1, an oscillatory pump J2, a wash liquor precooling coil H1, a displacing air precooling coil H2, a feed bottle B1, a discharge storage bottle B2, a sample bottle B3, a wash liquor storage bottle B4, and a wash liquor measuring burette B5. There are a three way high pressure valve V1, a two way high pressure valve V2, two low pressure five way valves V3 and V4, each having four valve positions, a low pressure two way valve V5, and two low pressure three way valves V6 and V7.

In order to purify styrene whose normal melting point is -30.6°C, a Thermotron cooling chamber was used to propose a cooling medium at a proper temperature. To use the techniques of pressure-induced nucleation and negative pressure-induced nucleation, a convenient air-driven hydraulic pump supplied by Haskel Co. is used for the pressurization. An oscillation pump is adopted to maintain a stable solid/liquid interface while the freezing step is
Figure 11. Equipment Setup with the Coiled Freezer-melter
Used in the In-situ Indirect Freezing Experiments
in progress. The dilatometer is used to monitor the progress of a freezing step. A detailed description of these individual parts will be presented in the following sections.

Although the principles of heat reuse have been described in Chapter 1, heat reuse has not been included in this study.

4-2 Coiled Freezer-melter

Referring to Figure 12, the coiled freezer-melter has a coiled stainless tube and a 3-inch O.D. Plexiglass tube enclosing the coiled tube. The stainless steel tube is 0.25 inch O.D., 0.134 I.D. tube and is 19.3 feet in length and coiled to a 2-inch I.D. coil. The coiled stainless tube serves as a freezer-melter conduit and the space surrounding the coiled tube is to contain a cooling medium for freezing and a heating medium for melting. This unit would serve two useful demonstrations. In the first place, the tubing was put in a coiled form to show that a compact unit could be made. Secondly, the diameter of the tubing is the dimension to be used in the large scale applications.

Since both the entrance and the exit of the freezing tube are not cooled by cooling medium, the solution in these spaces is not frozen during the freezing step. Consequently, the washing characteristics of the bed are affected by back mixing in these spaces during the washing operation. Therefore, these spaces were made small, approximately 1.5 cc for the entrance and approximately 2.0 cc for the exit. The total volume of the freezer-melter is 53.5 cm$^3$. 

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Figure 12. Installation of Freezer-melter
There are two major advantages by using this coiled freezer-melter:

(1) A smaller and much shorter cooling medium enclosure was used; thus a more uniform temperature distribution along the length of the freezer-melter was realized. The difference between the inlet and outlet temperature could be reduced to less than 0.3°C.

(2) The working pressure of this unit after installing high pressure valves and stainless steel tubing is 7000 psi. This enables one to use nucleation for many organic systems and the negative pressure-induced nucleation for dilute aqueous solutions.

4-3 Controlled Freezing Systems

Two controlled freezing systems were constructed for different applications. One is used for the freezing of mixtures of relatively higher melting temperatures such as para-xylene-meta-xylene, and brines. The other was set up to purify styrene whose melting point is much lower (-31°C).

In the first system, refrigeration is supplied by Neslab PBC-2 refrigeration units. The Neslab TE2-9 constant temperature bath which has an internal centrifugal circulation pump is used in conjunction with the refrigeration unit to supply the cooling medium during the freezing step. The working medium used is an ethylene glycol-water mixture. The temperature of the bath is controlled by a model 71-A Y.S.I. Thermistemp temperature controller. The controller keeps the bath temperature within ±0.1°C.
of the set point. All temperatures are measured by Y.S.I. probes and are displayed on a United System Digital Thermometer (Fig. 13, Fig. 14).

In the second system, refrigeration is supplied by a Thermotron Refrigeration Chamber, Model T-31-CH-3-3 supplied by the Thermotron Company. The cooling is accomplished by Refrigerant 13, Refrigerant 502 and water cooled cascaded refrigeration system. The cascade arrangement of the system permits efficient operation throughout the full cooking range. The lowest temperature that can be attained is -73°C. Air circulation inside the chamber is provided with one propeller-type fan driven by an externally located ball bearing motor. For the present study, the working medium used is 95 percent ethylalcohol. The alcohol is contained in a closed stainless steel tank to avoid loss of the medium due to evaporation. The ethylalcohol is pumped and circulated through two sets of fin tubes and cooled by the circulating cool air in the chamber. Two circulation pumps are used in conjunction with the freezer to supply the cooling medium during freezing step. The temperature of the cooling air inside the chamber is controlled by an API TEMP TENDOR, Model 717. The temperature of the working medium can be maintained rather constant. With good insulation and fast circulation of the cooling medium, the temperature can be maintained substantially the same throughout the entire freezer-melter. The temperature of the cooling medium is indicated by a Y.S.I. TELE-THERMOMETER, model 41 SC (refer to Figure 15).
Figure 13.
Neslab PBC-2 Bath Cooler and Neslab TE2-9 Constant

Figure 14. Y.S.I. 71-A Thermistemp Temperature Controller
Figure 15. Illustration of Thermotron Cooling Chamber
4-4 Oscillatory Pumping System

Referring to Figure 16, the oscillatory pumping system comprises of a Scotch-Yoke mechanism, a double rod hydraulic cylinder and a variable speed motor. The variable speed motor activates the Scotch-Yoke mechanism, which, in turn, activates the piston rod. The hydraulic cylinder has a piston rod extending out of the cylinder body from both ends and is used as a reciprocating piston pump, with equal volume displacements in both directions. The variable speed motor is a 1/3 HP motor and the rpm of the output shaft can be varied from 0 to 250. The output shaft of the motor is connected to the Scotch-Yoke mechanism. The system forces a given amount of liquid back and forth in the freezing conduit without substantial net flows. The frequency and amplitude of the Scotch-Yoke mechanism can be adjusted by adjusting the speed of the motor and eccentricity of the Scotch-Yoke mechanism.

4-5 Dilatometer

The progress of freezing can be measured by observing the movement of the meniscus level in the dilatometer. This volume change is due to the difference in densities between the liquid and solid phases. A 10 ml capillary pipette is employed to measure the volume change associated with the freezing operation in the freezer-melter unit. One end of the pipette is connected to the freezer-melter by a three-way valve. The meniscus level in the dilatometer rises or falls as the degree of solidification increases in processing an aqueous or a non-aqueous solution.
Figure 16. An Oscillatory Pumping System
Washing System

For experiments requiring less than 90 psi pumping pressure for the displacement operation, a 100 ml burette is connected to a precooling chamber, which in turn is connected to the inlet of the freezer-melter unit. The other end of the burette is connected to compressed air and controlled by a pressure regulator which indicates the pressure used during the washing step.

Air Driven Hydraulic Pump

Referring to Figure 17-a, an air-driven hydraulic pump supplied by Haskel Co. is used for the pressurization during the nucleation step and pressure-induced freezing step. An air-driven liquid pump can convert air supply power to hydraulic energy through a simple ratio system that uses a large area piston at low pressure to produce a hydraulic pressure on a small area hydraulic piston. As the system pressure approaches the maximum, dictated by the setting of the air pressure regulator, the pumps slow down and finally cease pumping when the hydraulic force balances the air force. They will thus maintain the desired pressure while consuming no power. The pressure can be raised as high as 10,000 psi. The application of this pump enables one to use the approaches of pressure-induced nucleation and negative pressure-induced freezing. The cross sectional view of this pump is given in Figure 17-b.

Operational Procedures

The operating procedures for conducting the present experiments can be described by the following four steps:
Figure 17-a. Illustration of an Air-driven Hydraulic Pump

Figure 17-b. Cross-sectional View of a Hydraulic Pump
(1) Nucleation Step

(a) Nucleating an organic mixture such as ethylbenzene-
styrene

The feed solution is introduced into the freezer-
melter at room temperature and cooled down to a
temperature slightly lower than its freezing
temperature by the circulation of cooling medium.
Once the desired temperature is reached and remains
relatively constant, a high pressure, say 4500 psi,
is applied to the mixture to raise the freezing
temperature so that $\Delta T$ value becomes so high as
to initiate a spontaneous and uniform nucleation
throughout the freezer conduit. The pressure ap-
plied is then quickly reduced to the normal atmos-
phere after a drop of about 250 psi is observed.
Only a very small degree of solidification is
accomplished in this step.

(b) Nucleating an aqueous solution such as brine

The solution is admitted to the freezer and a
cooling medium cooled to a desired temperature is
then introduced to the surrounding space of coiled
stainless tube. A high pressure, say 7000 psi, is
applied to the solution for a while. On releasing
the pressure applied, a spontaneous nucleation oc-
curs. The spontaneous nucleation can be observed
by the pressure rise due to the expansion associated with the freezing of water. This phenomenon has been explained in Chapter 2.

(2) Freezing Step

Once the feed is nucleated, the solution is allowed to solidify slowly by maintaining a small ΔT, say 3°C, for heat transfer. An oscillatory agitation is applied by an oscillatory pump until the freezing step is completed. Due to the decrease or increase of volume in going from a liquid to a solid phase, one can control the degree of solidification by observing the volume change in the dilatometer. This step normally takes 4 to 8 minutes depending on the required degree of solidification.

(3) Washing Step

After the freezing step is completed, the cooling medium surrounding the freezer conduits is immediately drained by precooled air. A precooled washing solution followed by a precooled air is introduced to displace the mother liquor. Samples of the displaced mother liquor are collected at the outlet. The samples are numbered, weighed and analyzed.

(4) Melting Step

After the washing step is completed, the purified solid is melted by introducing a heating medium in the freezer-melter compartment. The medium is at a temperature
slightly higher than the melting temperature of the solid. After melting, the product is displaced by air or nitrogen, collected, and analyzed for impurities.

Each cycle consists of the above four steps. The operation parameters can be easily modified for various feed solutions.
CHAPTER 5
RESULTS AND DISCUSSION

5-1 Introduction

As stated earlier, there are several operating conditions which have to be carefully controlled in order to obtain an efficient separation by the smooth deposit approach of the in-situ indirect freezing process. These factors are (1) uniform initiation of a freezing step, (2) small and controlled \( \Delta T \) for heat transfer, (3) an adequate agitation during the freezing step, and (4) a proper degree of solidification. Several experiments with different operating conditions have been carried out to investigate the dependence of product quality on these factors. Also, several experiments have been conducted to demonstrate the feasibility of purifying brackish water by using the negative pressure-induced nucleation technique. Furthermore, a low temperature cooling medium has been incorporated in this unit to demonstrate the feasibility of separating styrene from ethylbenzene by using the in-situ indirect freezing process. Experimental results obtained and discussions on the results obtained are given in the following sections.

5-2 Separations of Dilute Styrene-ethylbenzene Solutions without Agitation (Series A Experiments)

5-2-1 Experimental Results

In order to investigate the dependence of product quality
on $\Delta T$ for heat transfer during freezing operation, several experiments were carried out with different $\Delta T$ without agitation. Air displacement method was used for each experiment during the washing operations. Results obtained and the key operating parameters used are summarized in Table 2. The purification factor is defined as the ratio of the key component ratio in the feed to that in the melt. The gas chromatograms of the feed solution and products obtained are shown in Figures 18, 19, 20, 21, 22 and 23, respectively.

5-2-2 Discussion

The objectives of these experiments have been successfully demonstrated. The significant results obtained are summarized as follows:

(1) Without agitation, the tendency to form a dendritic deposit cannot be suppressed.

(2) The higher the $\Delta T$ is, the worse is the quality of the product obtained.

(3) Excessive plugging has been observed, indicated that the degree of solidification is not uniform.

(4) With the same $\Delta T$, the quality of the product of Experiment #A4 is better than that of Experiment #A5. This is because the degree of solidification of Experiment #A5 is much higher than that of Experiment #A4.
<table>
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<tr>
<th></th>
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<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
<th>A6</th>
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<td>Δt for heat transfer (°C)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
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<tr>
<td>% ethylbenzene in feed</td>
<td>0.946</td>
<td>0.946</td>
<td>0.946</td>
<td>0.946</td>
<td>0.946</td>
<td>0.946</td>
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<tr>
<td>% ethylbenzene in product</td>
<td>0.327</td>
<td>0.344</td>
<td>0.396</td>
<td>0.521</td>
<td>0.658</td>
<td>0.865</td>
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<td>volume of melt phase (ml)</td>
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<td>34.5</td>
<td>38</td>
<td>32</td>
<td>43</td>
<td>50</td>
</tr>
<tr>
<td>degree of solidification</td>
<td>54%</td>
<td>52%</td>
<td>57%</td>
<td>49%</td>
<td>63%</td>
<td>78%</td>
</tr>
<tr>
<td>purification factor</td>
<td>2.89</td>
<td>2.75</td>
<td>2.38</td>
<td>1.82</td>
<td>1.44</td>
<td>1.09</td>
</tr>
<tr>
<td>pressure for displacement (psig)</td>
<td>50</td>
<td>45</td>
<td>50</td>
<td>65</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td>pressure for nucleation (psig)</td>
<td>4750</td>
<td>4600</td>
<td>4700</td>
<td>4600</td>
<td>4550</td>
<td>4500</td>
</tr>
<tr>
<td>time for freezing (sec)</td>
<td>360</td>
<td>370</td>
<td>425</td>
<td>350</td>
<td>365</td>
<td>353</td>
</tr>
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</table>
Figure 18. Gas Chromatograms Obtained for Experiment #Al
Figure 19. Gas Chromatograms Obtained for Experiment #A2
Figure 20. Gas Chromatograms Obtained for Experiment #A3
Figure 21. Gas Chromatograms Obtained for Experiment #A4
Figure 22. Gas Chromatograms Obtained for Experiment #A5
Figure 23. Gas Chromatograms Obtained for Experiment #A6
5-3 Separations of Dilute Styrene-Ethylbenzene Solutions with Agitation (Series B Experiments)

5-3-1 Experimental Results

The objective of these experiments is to investigate the dependence of product quality on degree of agitation in the smooth deposit approach. These experiments also demonstrate how well a mixture can be separated by using air displacement. The $\Delta T$ for heat transfer is controlled to be 3°C for each experiment. Results obtained and operating parameters used are summarized in Table 3. The gas chromatograms of the feed solution and the products are shown in Figures 24 through 30.

5-3-2 Discussion

The significant results obtained from these experiments are summarized as follows:

(1) The stronger the agitation is applied during the freezing operation, the better the product quality is.

(2) By keeping the liquid phase properly agitated and by maintaining a small $\Delta T$ throughout the freezing step, a stable solid-liquid interface can be maintained and a tendency to form a dendritic deposit can be suppressed.

(3) By applying agitation, the pressure required for displacement is reduced as compared with the results of the A series.

(4) No excessive pluggings have been observed, indicating that degree of solidification is rather uniform.
Table 3. Results Obtained in B-Series Experiments

<table>
<thead>
<tr>
<th></th>
<th>B1</th>
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<th>B3</th>
<th>B4</th>
<th>B5</th>
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<th>B7</th>
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<tr>
<td>% ethylbenzene in feed</td>
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<td>0.961</td>
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<td>0.961</td>
<td>0.961</td>
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<tr>
<td>% ethylbenzene in product</td>
<td>0.227</td>
<td>0.219</td>
<td>0.144</td>
<td>0.137</td>
<td>0.128</td>
<td>0.109</td>
<td>0.104</td>
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<td>degree of solidification</td>
<td>55%</td>
<td>53%</td>
<td>54%</td>
<td>50%</td>
<td>52%</td>
<td>49%</td>
<td>48%</td>
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<td>purification factor</td>
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<td>4.38</td>
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<td>7.50</td>
<td>8.82</td>
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<td>4500</td>
<td>4650</td>
<td>4550</td>
<td>4550</td>
<td>4500</td>
<td>4550</td>
</tr>
<tr>
<td>temp. of cooling medium (°C)</td>
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<td>-34</td>
<td>-34</td>
<td>-34</td>
<td>-34</td>
<td>-34</td>
<td>-34</td>
</tr>
<tr>
<td>time for freezing (sec)</td>
<td>360</td>
<td>350</td>
<td>320</td>
<td>315</td>
<td>330</td>
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<td>25</td>
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<td>frequency of oscillation (cycles/min)</td>
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<td>20</td>
<td>44</td>
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<td>79</td>
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<td>90</td>
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Figure 24. Gas Chromatograms Obtained for Experiment #Bl
Figure 25. Gas Chromatograms Obtained for Experiment #B2
Figure 26. Gas Chromatograms Obtained for Experiment #B3
Figure 27. Gas Chromatograms Obtained for Experiment #B4
Figure 28. Gas Chromatograms Obtained for Experiment #B5
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<thead>
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<th>Time</th>
<th>Value</th>
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<tr>
<td>15.43</td>
<td>Feed</td>
</tr>
<tr>
<td>16.26</td>
<td>Product</td>
</tr>
</tbody>
</table>

**Figure 29.** Gas Chromatograms Obtained for Experiment #86
Figure 30. Gas Chromatograms Obtained for Experiment #B7
(5) The best product quality which can be obtained by using air displacement seems to be about 99.89 percent.

5-4 Separations of Dilute Styrene-Ethylbenzene Solutions

5-4-1 Experimental Results

In order to have a more effective washing operation, a displacement by a small amount of precooled wash solution is followed by a displacement by a precooled air. How well a mixture is separated by using this method depends on how well the unfrozen mother liquor phase is displaced by the displacing fluids. An ideal performance is obtained when a plug-flow displacement of the liquid can be accomplished throughout the interdendritic spaces without any channeling and dispersion. A way to characterize a bed formed is to prepare a C-curve by plotting the concentration of the liquid displaced versus volume displaced. Results obtained and key operating parameters used in these experiments are summarized in Table 4. The C-curves for each experiment are shown in Figures 31, 32, and 33 respectively.

5-4-2 Discussion

The significant results obtained are summarized as follows:

(1) The technical feasibility of using pressure-induced nucleation in a smooth deposit approach is demonstrated. Product qualities in all these experiments are better than 99.9 percent.
Table 4. Results Obtained in C-Series Experiments

<table>
<thead>
<tr>
<th></th>
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<td>% styrene in feed</td>
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<td>% styrene in product</td>
<td>99.927</td>
<td>99.945</td>
<td>99.930</td>
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<td>% styrene in wash</td>
<td>99.901</td>
<td>99.901</td>
<td>99.929</td>
</tr>
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<td>purification factor</td>
<td>14.5</td>
<td>19.0</td>
<td>15.0</td>
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<tr>
<td>degree of solidification</td>
<td>55%</td>
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<td>52%</td>
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<td>temp. of cooling medium (°C)</td>
<td>-33.5</td>
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<td>pressure for nucleation (psig)</td>
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<td>(cycles/min)</td>
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<td>amount of wash used (ml)</td>
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<td>time for freezing (sec)</td>
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Figure 31. C-curve Obtained for Experiment #C-1
Figure 32. C-curve Obtained for Experiment #C-2
Figure 33. C-curve Obtained for Experiment #C-3
Figure 34. Gas Chromatograms Obtained for Experiment #C1
Figure 35. Gas Chromatograms Obtained for Experiment #C2
**Figure 36. Gas Chromatograms Obtained for Experiment #C3**
(2) Excellent C-curves were obtained. In each C-curve, there is a sharp rise, followed by a near constant concentration region, and finally followed by a sharp decrease in ethylbenzene concentration. The presence of the near straight line indicates that the mother liquor in the freezing zone is displaced in a near plug-flow fashion.

(3) As expected, there is a slow rise at the beginning of each of these curves due to the presence of an inactive freezing zone at the entrance region. The bottom flattens somewhat slowly due to the presence of an inactive region at the exit region.

5-5 Separations of Brackish Water by the Smooth Deposit Approach
Incorporating the Negative Pressure-Induced Nucleation Technique (Series D Experiments)

5-5-1 Experimental Results

Several experiments were carried out to demonstrate the technical feasibility of using the negative pressure-induced nucleation technique in separating dilute aqueous solutions. Results obtained and operating parameters used are summarized in Table 5. Analyses of samples were conducted in a Solu-Meter supplied by Beckman Instrument Co. The C-curves for the experiments are shown in Figures 37, 38 and 39, respectively.
Table 5. Results Obtained in D-Series Experiments

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D1</td>
</tr>
<tr>
<td>salinity in feed (ppm)</td>
<td>4500</td>
</tr>
<tr>
<td>salinity in wash (ppm)</td>
<td>300</td>
</tr>
<tr>
<td>salinity in product (ppm)</td>
<td>200</td>
</tr>
<tr>
<td>purification factor</td>
<td>22.5</td>
</tr>
<tr>
<td>degree of solidification</td>
<td>54%</td>
</tr>
<tr>
<td>pressure for nucleation (psig)</td>
<td>7000</td>
</tr>
<tr>
<td>temp. of cooling medium (°F)</td>
<td>28.5</td>
</tr>
<tr>
<td>pressure for displacement (psig)</td>
<td>25</td>
</tr>
<tr>
<td>time for freezing (min)</td>
<td>4</td>
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</tbody>
</table>
Figure 37. C-curve Obtained for Experiment #D1 (Brine)
Figure 38. C-curve Obtained for Experiment #D2 (Brine)
Figure 39. C-curve Obtained for Experiment #D3 (Brine)
Discussions

The objectives of these experiments have been successfully demonstrated. The significant results obtained are summarized as follows:

(1) Clearly, the technical feasibility of using the negative pressure-induced nucleation technique has been successfully demonstrated. Product qualities in all experiments were excellent.

(2) Excellent C-curves were obtained. A near plug flow displacement has been demonstrated.

(3) No operational difficulties such as plugging were encountered. This indicates uniform nucleation and uniform solidification.

Separations of Dilute Para-xylene-meta-xylene Solutions
(Series E Experiment)

Experimental Results

The experiment was carried out to separate meta-xylene from dilute paraxylene solution. In this experiment, a smaller ΔT, 2°C, was used for heat transfer and a strong agitation, 100 cycles/min, was applied during the freezing operation. During the washing operation, a displacement by a small amount of pure grade wash solution, 99.9 percent p-xylene, is followed by a displacement of precolled air. The operating parameter use is summarized in Table 6. The gas chromatograms of the feed, the refined product and the wash solvent are shown in Figure 40, and gas chromatograms
<table>
<thead>
<tr>
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<th>Experiment</th>
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<tbody>
<tr>
<td>% m-xylene in feed</td>
<td>0.485</td>
</tr>
<tr>
<td>% m-xylene in wash</td>
<td>0.090</td>
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<tr>
<td>% m-xylene in product</td>
<td>0.016</td>
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<td>purification factor</td>
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<td>degree of solidification</td>
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<tr>
<td>pressure for nucleation (psig)</td>
<td>6500</td>
</tr>
<tr>
<td>pressure for displacement (psig)</td>
<td>20</td>
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<td>time for freezing freezing (min)</td>
<td>6</td>
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<tr>
<td>frequency of oscillation (cycles/min)</td>
<td>98</td>
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</tbody>
</table>
Figure 40. Gas Chromatograms Obtained for Experiment #E
of Samples 1 through 6 obtained during the washing step are shown in Figure 41. The C-curve obtained is presented in Figure 42.

5-6-2 Discussions

The significant results obtained in this experiment are summarized as follows:

(1) A very effective purification of paraxylene has been demonstrated in a one-stage freezer-melter operation in this experiment, and no operational difficulty has been encountered.

(2) The criteria for good operation seem to be completely met in this experiment: (1) freezing step has been initiated uniformly, (2) adequate agitation and small $\Delta T$ for heat transfer have been maintained, (3) a uniform solidification throughout the entire length of freezer has been obtained.

(3) An appropriate oscillatory flow reduces concentration polarization and this helps maintain a smooth solid/liquid interface, and also suppresses longitudinal concentration variation caused by the longitudinal movement due to the volume change associated with the freezing operation.

(4) With an appropriate oscillatory flow, more uniform freezing rate can be obtained throughout the entire length of the freezer conduit and a freezing step can be conducted to a higher degree of solidification.
Figure 41. Gas Chromatograms Obtained for Successive Samples Collected in Experiment #E
Figure 42. C-curve Obtained for Experiment #E
CHAPTER 6

RECOMMENDATIONS

In order to benefit development of the in-situ indirect freezing process, the following suggestions are made:

(1) The theoretical analyses for the smooth solid phase approach and the dendritic solid phase approach require further improvements and refinements. For example, a better method of determining the tolerance limit of constitutional supercooling for maintaining a smooth solid phase for each system has to be developed. There is also a great need to obtain basic information such as rate of crystal growth, permeability of solid bed, dendritic spacing and optimum operating variables.

(2) Using the negative pressure-induced nucleation technique, tests should be made to establish the feasibility of desalinating sea water by the dendritic deposit approach.

(3) Tests have to be made on a variety of commercially significant substances such as naphthalene, benzene, P-dichlorobenzene, aniline and acetic acid, whereby technical feasibility can be demonstrated.
(4) Although the cost analysis of this process relating to sea water desalination has been made by P. T. Yang [21], a more extensive economic analysis and process analysis have to be made for systems other than sea water.

(5) An improved freezer-melter which will enable the heat reuse by the two pressure zone operations should be developed and constructed. With this new unit, the feasibility of renovating waste water should be studied.
BIBLIOGRAPHY


