



The solvent selection expert system for azeotropic and extractive distillation
by Zuyin Yang

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemical Engineering
Montana State University
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Abstract:

Azeotropes, or close-boiling mixtures often preclude conventional distillation as a method of separation. Instead, extractive or azeotropic distillations are commonly used to separate close or azeotropic boiling mixtures. For the design of these separation units, selecting suitable solvents is an indispensable step. The traditional method for solving this problem is through experimentation which is time-consuming and expensive.

A new approach is offered by combining heuristic knowledge and numerical methods for solvent screening in the form of a knowledge-based expert system. The prototype expert system takes as inputs a small amount of physico-chemical property data for pure components and mixtures, and the processes which are suitable for the separation of a close boiling or an azeotropic mixture are selected. Then the expert system proposes solvents from the solvent databases based on the requirements of the process under consideration. The heuristic knowledge and numerical knowledge from different sources for selecting solvents for mass-based separation are organized through a task-oriented framework as the representing strategy. The structured heuristic search hierarchy has been developed as the problem-solving strategy that an expert follows.

At present, the prototype expert system is limited to the preliminary selection of promising solvents for azeotropic and extractive distillation. The prototype expert system is applied to screen numerous solvents for the separation of xylene isomers and ethanol-water mixture. The result for the separation of xylene isomers agrees with experimental results to date. For the ethanol-water mixture to be separated by extractive distillation, the expert system confirms some solvents suggested in the literature and proposes more solvents for further experimental verification. For the methyl acetate-methanol mixture, the expert system can propose promising solvents based on Berg's solvent classification and Sheibel's rule, but cannot accurately rate the solvents.

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APPROVAL

of a thesis submitted by

Zuyin Yang

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Azeotropes, or close-boiling mixtures often preclude conventional distillation as a method of separation. Instead, extractive or azeotropic distillations are commonly used to separate close or azeotropic boiling mixtures. For the design of these separation units, selecting suitable solvents is an indispensable step. The traditional method for solving this problem is through experimentation which is time-consuming and expensive.

A new approach is offered by combining heuristic knowledge and numerical methods for solvent screening in the form of a knowledge-based expert system. The prototype expert system takes as inputs a small amount of physico-chemical property data for pure components and mixtures, and the processes which are suitable for the separation of a close boiling or an azeotropic mixture are selected. Then the expert system proposes solvents from the solvent databases based on the requirements of the process under consideration. The heuristic knowledge and numerical knowledge from different sources for selecting solvents for mass-based separation are organized through a task-oriented framework as the representing strategy. The structured heuristic search hierarchy has been developed as the problem-solving strategy that an expert follows.

At present, the prototype expert system is limited to the preliminary selection of promising solvents for azeotropic and extractive distillation. The prototype expert system is applied to screen numerous solvents for the separation of xylene isomers and ethanol-water mixture. The result for the separation of xylene isomers agrees with experimental results to date. For the ethanol-water mixture to be separated by extractive distillation, the expert system confirms some solvents suggested in the literature and proposes more solvents for further experimental verification. For the methyl acetate-methanol mixture, the expert system can propose promising solvents based on Berg's solvent classification and Sheibel's rule, but cannot accurately rate the solvents.

CHAPTER 1**INTRODUCTION**Techniques for Difficult-to-Separate Mixtures

Separating azeotropic or close-boiling mixtures into pure components is a task commonly encountered in the chemical industry. Sometimes, an azeotrope can be negated through an ordinary distillation by swinging pressure. However, that is not always the case. Generally, pressure-swing distillation cannot be applied to separating close-boiling mixtures because the pressure change will result in the same change in boiling points for each of the components in the mixture. If pressure-swing distillation cannot apply because the azeotrope composition does not vary much with pressure or because the required pressure leads to product degradation, there are still many separation techniques available and some of them are being used widely in chemical industry to accomplish the tasks mentioned above. The most commonly used are the following:

- azeotropic distillation
- extractive distillation
- solvent extraction

- reactive distillation
- "salt" distillation

These techniques have in common the addition of a third component. The application of azeotropic and extractive distillation depends on how much the relative volatility of the two constituents in the mixture is altered by adding a third component. In solvent extraction, a mixture of two or more components is treated by adding a component that preferentially dissolves one or more of the components in the mixture. Reactive distillation involves the reversible and preferential reaction of the added component with one of the components in the mixture. In "salt" distillation, the added component dissociates ionically in the solution and changes the azeotrope composition. Among them, azeotropic distillation, extractive distillation and solvent extraction have drawn the greatest attention in industry for separating azeotropic or close-boiling mixtures.

Sucksmith[1] has pointed out that extractive distillation is worth considering even when the conventional distillation is feasible for some close-boiling mixtures. Using conventional distillation to separate some close-boiling mixtures usually requires many stages, which means a high fixed cost for the process, and a high reflux ratio, which results in a high operating cost for the process. Extractive distillation often uses less energy than conventional distillation does for many close-boiling mixture separations.

Significance of Selection of Solvents

The development of a separation process for the difficult-to-separate mixture consists of several steps[2] as shown in Figure 1. After establishing the need for one of the aforementioned techniques for a tough separation task in industry, screening the promising solvents (also called entrainers) becomes an inevitable step in the whole development process.

The initial phase of designing a separation process consists of three principal steps: First, a separation technique is determined based on a given separation problem; second, potential solvents are screened, then a separation sequence is synthesized for each selected solvent. Once the separation technique is chosen, the second step becomes critical for the process design, as pointed out by Laroche et al.[3], because an economically optimal design made with an average solvent can be much more costly than an average design using the best solvent.

The selection of potential solvents for azeotropic or extractive distillation and solvent extraction has been largely empirical and experimental, and thus is very time-consuming and expensive. Over the years, the criteria, or rules for selection of promising solvents or entrainers have been established, and the knowledge about predicting the behavior of liquid solutions has been accumulated in the

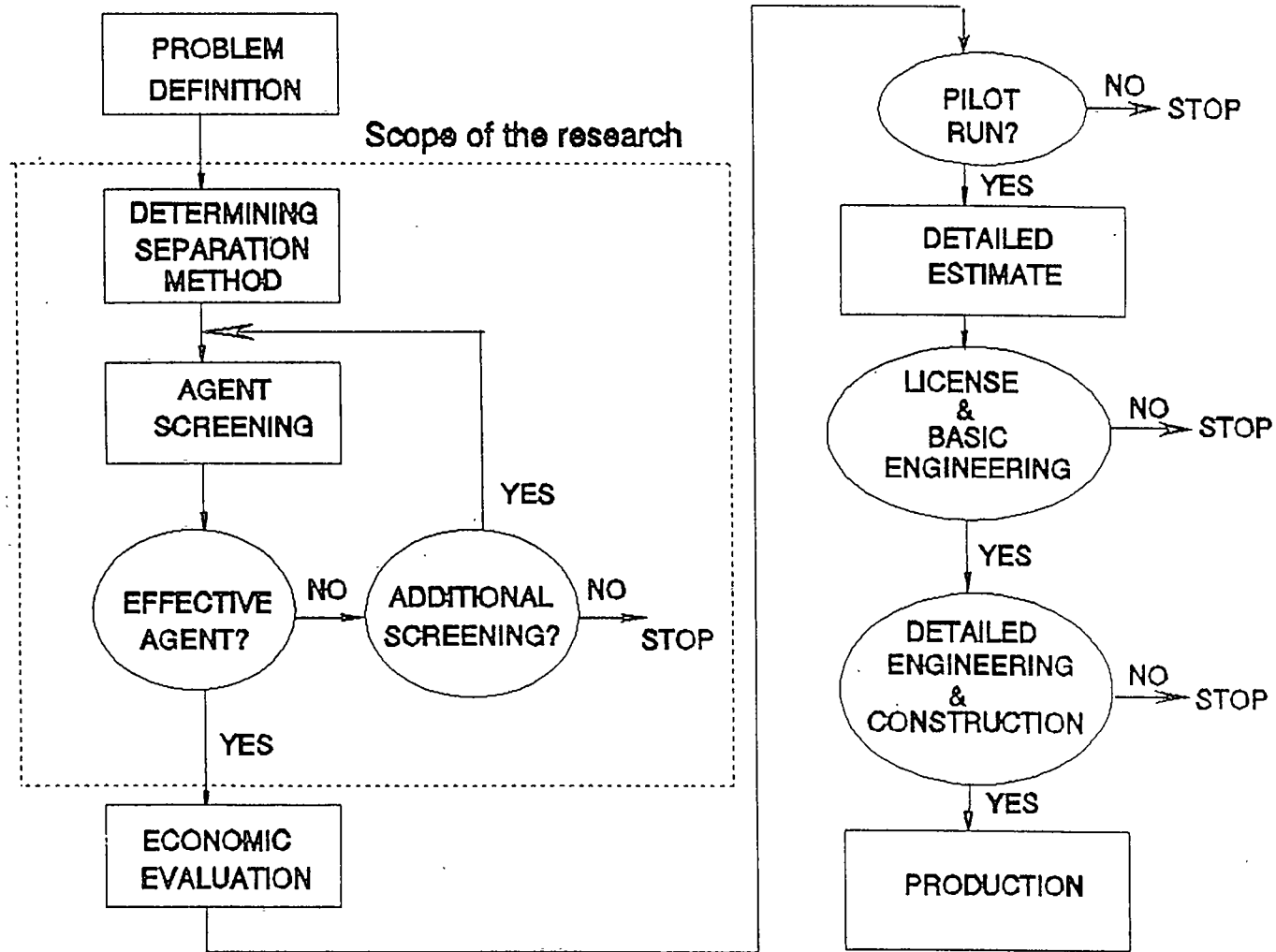


Figure 1 Process development steps for the mass-based separation and the scope of this research [2]

literature. But the knowledge is represented as both empirical rules and procedural algorithms, it is not complete, and there are sometimes contradictions within this problem domain knowledge.

Expert System Approach

The 1980's and the beginning of 1990's witnessed the emergence of artificial intelligence (AI), which has led to knowledge-based system (also called expert system) application to many disciplines. The main advantage of a knowledge-based system approach lies in the fact that it can make use of qualitative models based on the available knowledge about the system and heuristics proposed by the experts who work in the field. As pointed out above, the knowledge for the selection of promising entrainers for azeotropic and extractive distillation is both qualitative and quantitative. This work took advantage of a knowledge-based system approach to combine these two kinds of knowledge to establish an expert system capable of identifying potential solvents.

Problem Specification

The development of an expert system for the selection of proper solvents for azeotropic and extractive distillation is an interdisciplinary endeavor, combining aspects of both

chemical engineering and artificial intelligence (AI). These two diverse fields contribute very different, but deeply interrelated, perspectives to the problem of the selection of solvents for azeotropic distillation and extractive distillation. In a broad sense, the problem of the selection of solvents for azeotropic and extractive distillation can be defined generally as follows:

Given (1) an azeotrope, a close-boiling mixture, or other difficult-to-separate mixture such as dilute acetic acid aqueous solution, (2) physical property data of the mixture, and (3) a portfolio of solvents with their physical property data; first, find an appropriate separation method between azeotropic distillation and extractive distillation; second, choose solvents for effectively negating the azeotrope or markedly enhancing the separation of the close-boiling mixture; third, predict their effectiveness or rate their separation-enhancing ability.

The Objectives and the Scope of Research

We are concerned here with speeding the preliminary solvent screening process for the separation of azeotropes or close-boiling mixtures that are often encountered in chemical industry using knowledge available from various sources. We developed and illustrated a prototype expert system that deals with selecting a proper separation technique based on the

characteristics of the mixture to be separated. We then focus on the solvent selection process for the separation of a binary azeotrope or binary close-boiling mixture by azeotropic or extractive distillation.

CHAPTER 2

HISTORICAL BACKGROUND

Terminologies for Azeotropic and Extractive Distillation

In this section, some terminologies and concepts related to the selection of solvents for azeotropic and extractive distillation are introduced as the basis for further discussion.

Azeotrope and Close-boiling Mixtures

Difficult-to-separate mixtures can be generally classified into two types: azeotropes and close-boiling mixtures.

Azeotrope, from the Greek "to boil unchanged," literally means that the vapor boiling from a liquid has the same composition as the liquid. An azeotrope forms because the mixture comprises structurally dissimilar compounds and its vapor-liquid equilibrium behavior deviates considerably from Raoult's law. Azeotropic systems may be classified broadly in relation to the characteristics of the azeotrope (maximum- or minimum-boiling), number of components in the system (binary,

ternary, or quaternary), and whether one or more liquid phases are formed (homogeneous or heterogeneous). In line with deviations from Raoult's law, azeotropes can be divided into positive azeotropes and negative azeotropes. Positive azeotropes are characterized by a minimum-boiling temperature at constant pressure, i.e., a maximum in the total vapor pressure at constant temperature. Acetone and methanol form a typical positive azeotrope system and its vapor-liquid equilibrium (X-Y curve), temperature-composition at constant pressure plot (T-X or T-Y curve), and pressure-composition at constant temperature plot (P-X or P-Y curve) are shown in Figures 2, 3, and 4, respectively. Negative azeotropes have a maximum boiling temperature and a minimum total vapor pressure. A representative system forming a negative azeotrope (maximum boiling) is chloroform and acetone; its X-Y curve, T-X or T-Y curve, and P-X or P-Y curve are given in Figures 5, 6, and 7, respectively. The term azeotrope gives no indication of whether one, two, or more liquid phases are formed. To make it clear, the terms "homoazeotrope" and "heteroazeotrope" were introduced[6]. Typical vapor-liquid equilibrium data for binary homoazeotropes are represented in Figures 2 to 7. A typical heteroazeotrope is the water-n-butanol system for which an X-Y curve, T-X (or Y) curve, and P-X (or Y) curve are represented in Figures 8 and 9, respectively. It should be noted that most azeotropes commonly encountered in industry are binary, minimum-boiling azeotropes, though many

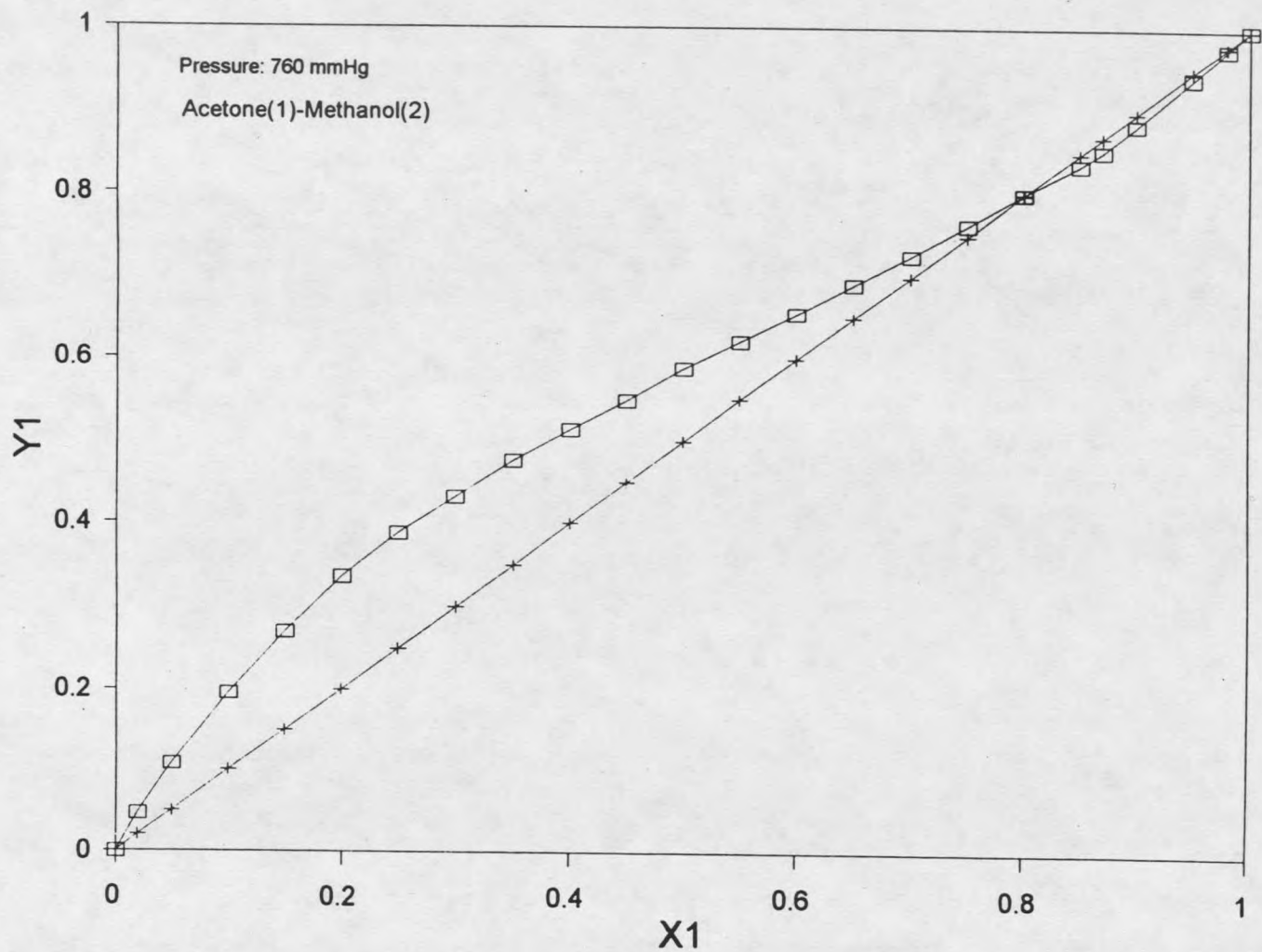


Figure 2 Liquid mole fractions and vapor mole fractions for minimum-boiling mixtures of acetone and methanol[4]

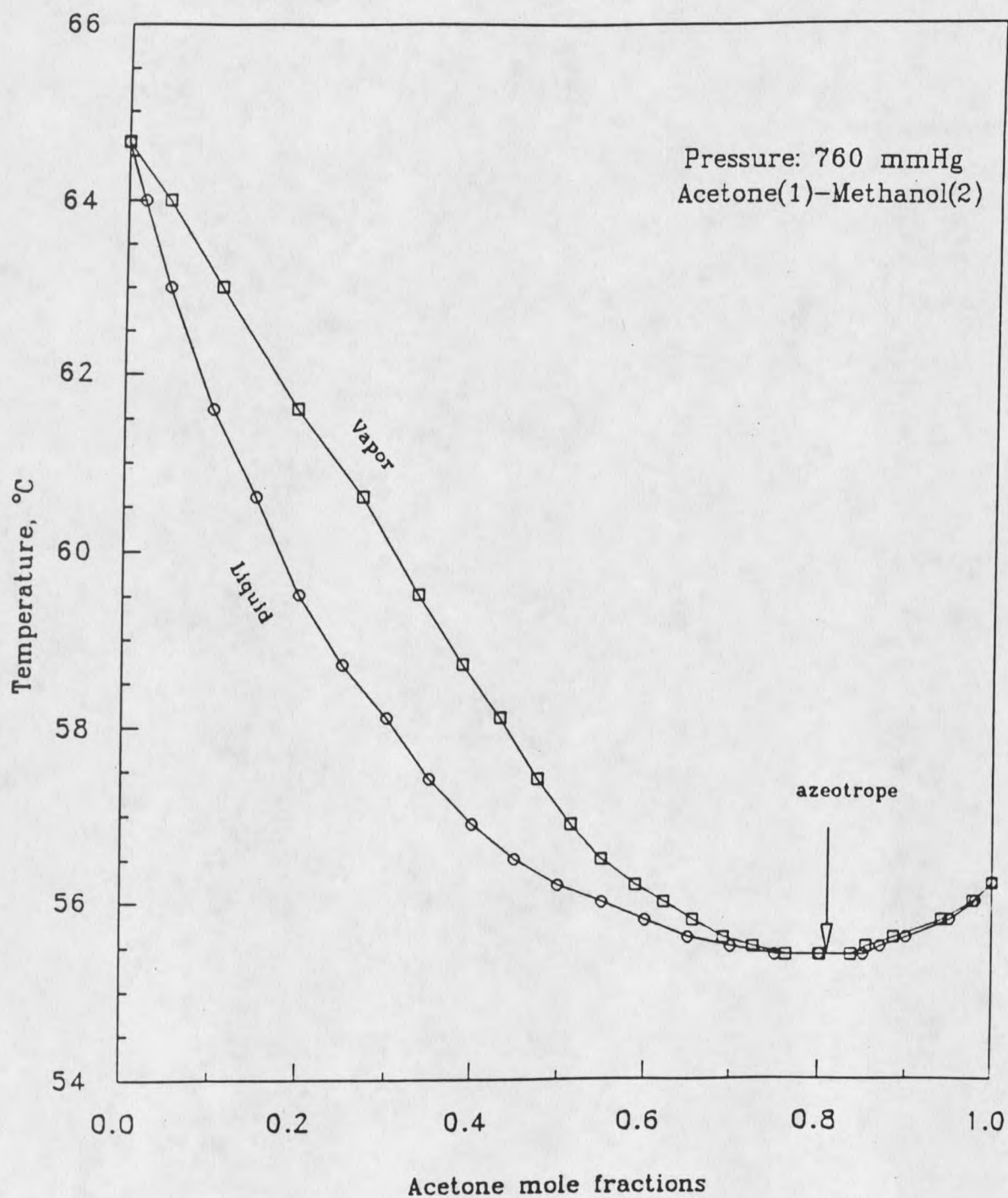


Figure 3 Liquid boiling points and vapor condensation temperatures for minimum-boiling azeotropic mixture of acetone and methanol[4]

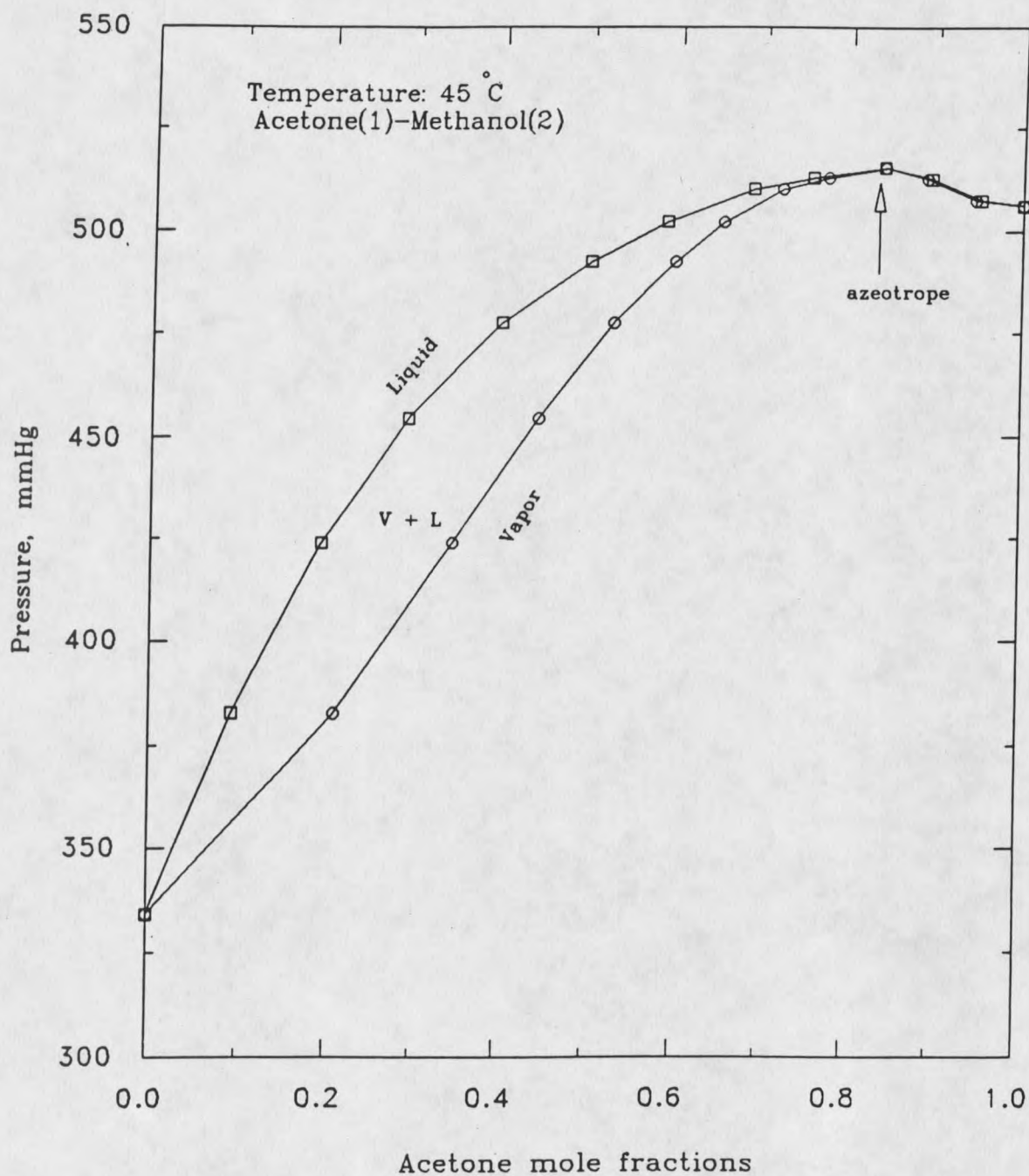


Figure 4 Pressure and Liquid Compositions for Minimum-Boiling Azeotropic Mixture of Acetone and Methanol[4]

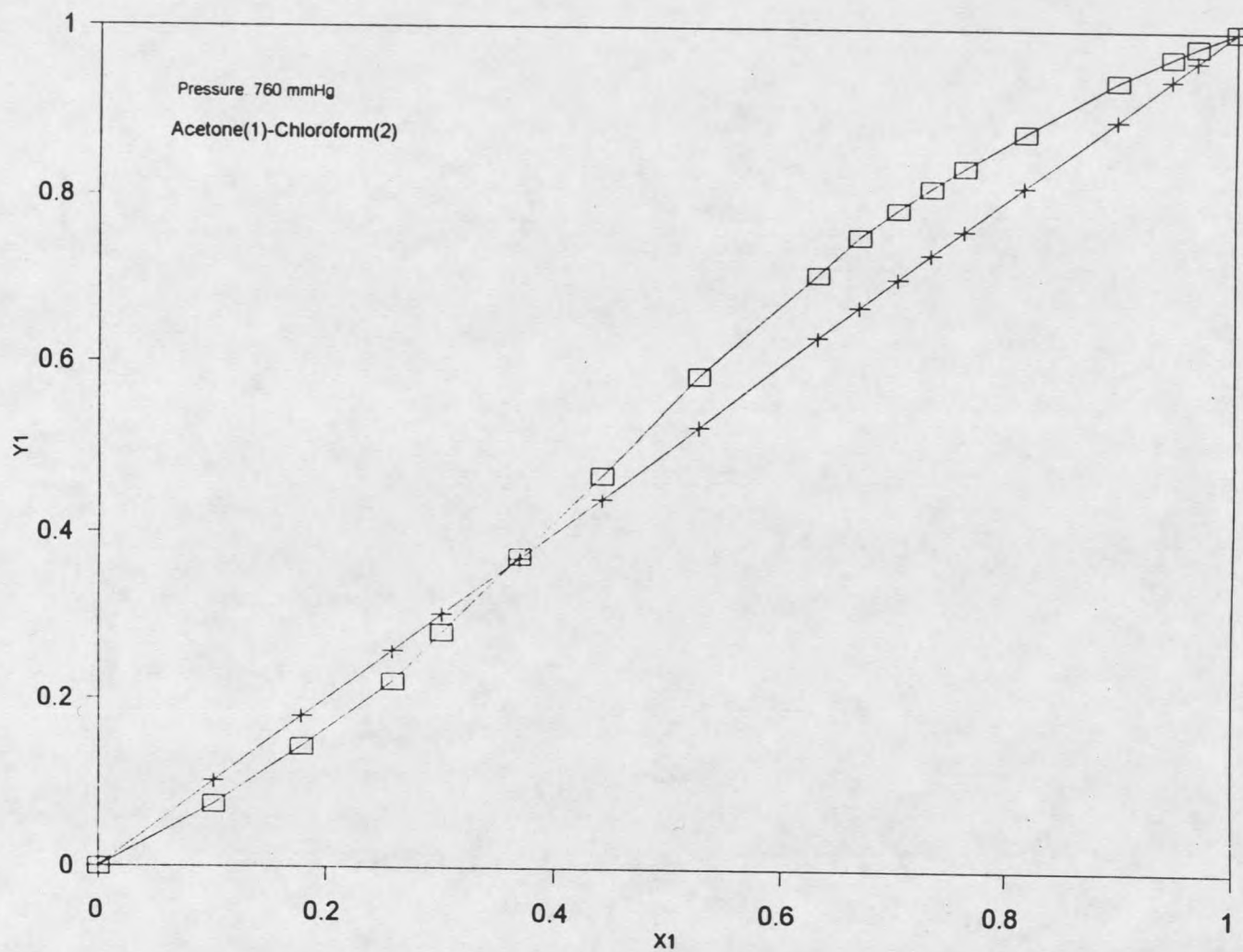


Figure 5 Liquid mole fractions and vapor mole fractions for maximum-boiling azeotropic mixture of acetone and chloroform[4]

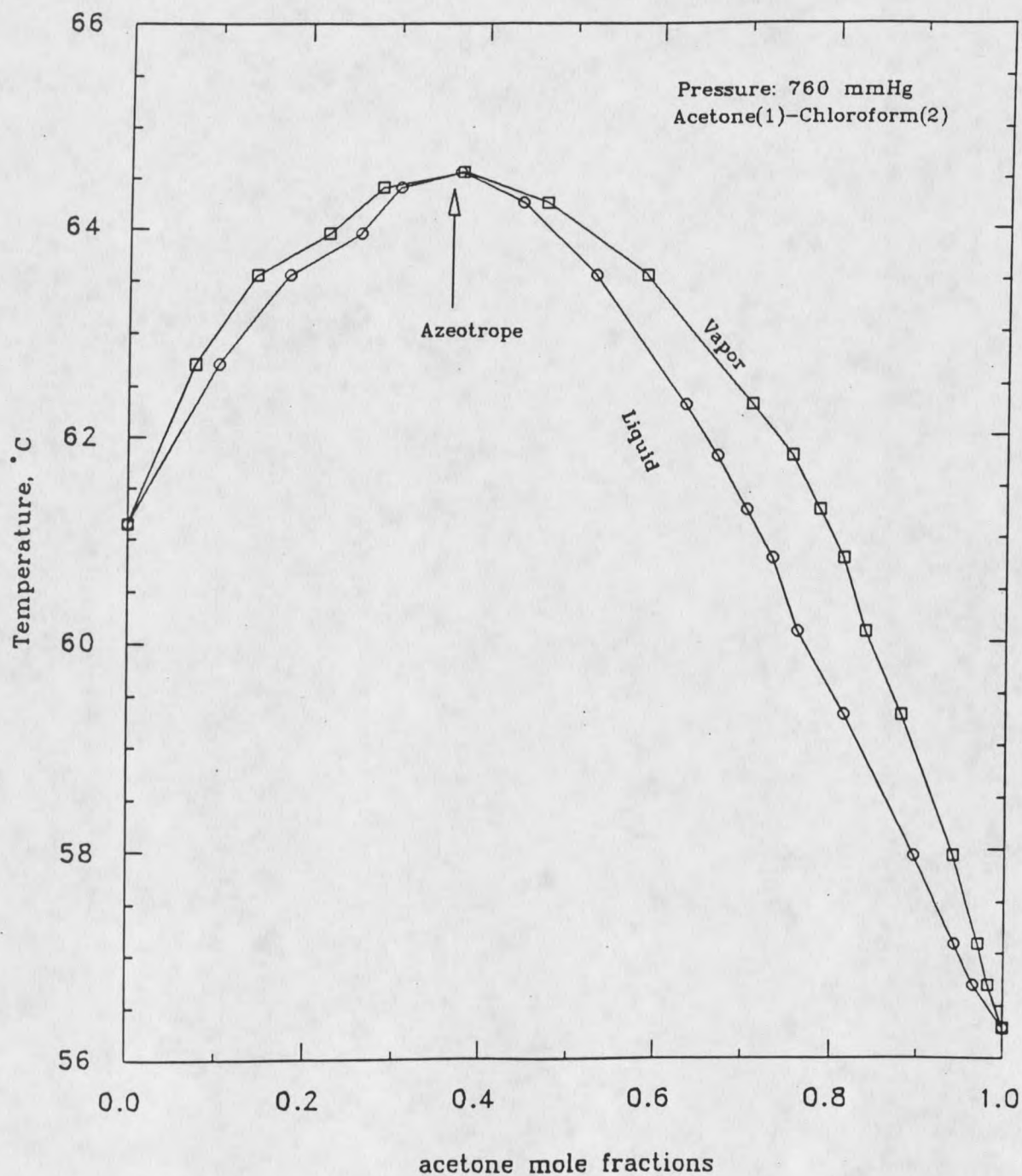


Figure 6 Liquid boiling point and vapor condensation temperatures for maximum-boiling azeotropic mixture of acetone and chloroform[4]

