MONTANA STATE UNIVERSITY

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 ac 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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of the requirements for the degree

of

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in

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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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TABLE OF CONTENTS

Page

APPROVAL..... ii

STATEMENT OF PERMISSION TO USE..... iii

ACKNOWLEDGEMENTS..... iv

TABLE OF CONTENTS..... v

LIST OF TABLES..... viii

LIST OF FIGURES..... x

ABSTRACT.....xiii

1. INTRODUCTION..... 1

Techniques for Difficult-to-Separate Mixtures 1
Significance of Selection of Solvents..... 3
Expert System Approach..... 5
Problem Specification..... 5
The Objectives and the Scope of Research..... 6

2. HISTORICAL BACKGROUND..... 8

Terminologies for Azeotropic and Extractive Distillation..... 8

Azeotropes and Close-Boiling Mixtures..... 8
Azeotropic and Extractive Distillation Processes..... 18

The Brief History of Azeotropic and Extractive Distillation..... 27
An Overview of Solvent Selection Methods..... 28

For Azeotropic Distillation..... 29
For Extractive Distillation..... 36

The Selection of Azeotropic or Extractive Distillation..... 42

TABLE OF CONTENTS--Continued

	Page
3. SOLVENT SELECTION CRITERIA	47
Separation Enhancement Characterization	47
Separation Factor	47
Relative Volatility	49
Selectivity	52
Activity Coefficients at Infinite Dilution	56
Thermodynamic Models for the Estimation of ACID	59
Easy Reversibility	66
4. EXPERT SYSTEMS AND SELECTION PROBLEMS	67
Introduction to Expert Systems	67
Expert System Shell -- LEVEL 5 OBJECT	70
Expert System Applications in Chemical Engineering	71
The General Theory of Selection Problems	73
Selection-related Expert Systems in Chemical Engineering	75
5. KNOWLEDGE BASE	79
Knowledge Acquisition	79
Knowledge Involved in the Solvent Selection Problem	79
Knowledge Used in the Current Expert System	82
Types of Knowledge	86
Knowledge Representation Strategy	89
Implementation Language -- Object-oriented Programming	90
Features of an Object	92
Procedural Knowledge -- Rules and Methods Representation	96
Search Space -- Solvent Database and Related Objects	98
Structuring Knowledge	106

TABLE OF CONTENTS--Continued

Page

6. EXPERT SYSTEM IMPLEMENTATION..... 109

Selection Hierarchy..... 109

Hydrocarbon Branch..... 114
Aqueous System Branch..... 118
Nonaqueous Nonhydrocarbon Branch..... 120
Azeotropic Branch..... 122

Application Examples..... 124

Example 1. Selection of Solvents for Separation of Xylene Isomers..... 124
Example 2. Selection of Solvents for Separation of Water from Ethanol..... 131
Example 3. Selection of Solvents for Separation of Methyl acetate from Methanol..... 136

7. SUMMARY..... 140

Conclusions..... 140
Recommendations for Further Studies..... 141

NOMENCLATURE..... 143

ABBREVIATIONS..... 146

LITERATURE CITED..... 148

APPENDICES..... 158

APPENDIX A. INDUSTRIAL SOLVENTS FOR THE EXPERT SYSTEM DATABASE..... 159
APPENDIX B. SOLVENTS RECOMMENDED BY DR. LLOYD BERG..... 164
APPENDIX C. QBASIC PROGRAM FOR CALCULATING ACID FOR THE EXPERT SYSTEM..... 166
APPENDIX D. RULES AND THERMODYNAMIC MODELS FOR THE EXPERT SYSTEM..... 171

LIST OF TABLES

Table		Page
1.	Solvent Selection Based on Scheibel's Rules	37
2.	Heuristics and Rules for Selection of Separation Methods	44
3.	Experimental Methods for Determining ACID	59
4.	Binary Activity Coefficient Correlations at Infinite Dilution	60
5.	Models for Estimation of Activity Coefficients at Infinite Dilution Using Solubility Parameters	62
6.	Deviation Between Experimental and Predicted Activity Coefficients at Infinite Dilution	64
7.	Predicted Infinitely Dilute Activity Coefficients by UNIFAC for Aqueous Systems	65
8.	The Basic Features of LEVEL 5 OBJECT	72
9.	Application Areas of ES and Their Functions	73
10.	Progress of the Knowledge for Solvent Selection for Azeotropic and Extractive Distillation	83
11.	Rules Used in the Current Expert System	85
12.	The Physico-Chemical Properties of Solvent Methanol	103
13.	Critical Temperatures Estimated by Group Methods	103
14.	Solvent Classes Based on Chemical Function Groups	104
15.	Correlations for Calculating Induction Parameter	116

LIST OF TABLES--Continued

Table		Page
16.	Correlations for Calculating the Nonpolar Solubility Parameter	117
17.	Physical Properties of Xylene Isomers	125
18.	The Selected Solvents by SSS with Their Selectivities	131
19.	Properties of Components and Azeotrope at 1 Atm for Ethanol and Water	133
20.	Activity Coefficients at Infinite Dilution for Water-Ethanol with Different Solvents	134
21.	Solvents for Water-Ethanol Based upon Selectivity	135
22.	Solvents for Water-Ethanol Based upon Relative Volatility	136
23.	Properties of Components and Azeotrope at 1 Atm for Methanol and Methyl Acetate	136
24.	Partial Solvent List Selected for Separating Methanol from Methyl Acetate	137

LIST OF FIGURES

Figure		Page
1.	Process Development Steps for the Mass-based Separation and the Scope of This Research	4
2.	Liquid Mole Fractions and Vapor Mole Fractions for Minimum-Boiling Mixtures of Acetone and Methanol	10
3.	Liquid Boiling Points and Vapor Condensation Temperatures for Minimum-Boiling Azeotropic Mixture of Acetone and Methanol	11
4.	Pressure and Liquid Compositions for Minimum-Boiling Azeotropic Mixture of Acetone and Methanol	12
5.	Liquid Mole Fractions and Vapor Mole Fractions for Maximum-Boiling Azeotropic Mixture of Acetone and Chloroform	13
6.	Liquid Boiling Point and Vapor Condensation Temperatures for Maximum-Boiling Azeotropic Mixture of Acetone and Chloroform	14
7.	Pressure and Liquid Mole Fractions for Maximum-Boiling Azeotropic Mixture of Acetone and Chloroform	15
8.	Liquid Mole Fractions and Vapor Mole Fractions for Heteroazeotropic Mixture of Water and n-Butanol	16
9.	Liquid Boiling Point and Vapor Condensation Temperatures for Minimum-Boiling Heteroazeotropic Mixture of Water and n-Butanol	17
10.	Liquid Mole Fractions and Vapor Mole Fractions for Close-Boiling Mixture of Propylene and Propane	19
11.	Liquid Mole Fractions and Vapor Mole Fractions for Close-Boiling Mixture of n-Hexane and Benzene	20

LIST OF FIGURES--Continued

Page

12. Liquid Mole Fractions for Low Relative Volatility Mixture of Water and Acetic Acid..... 21

13. Simplified Flow Diagram for an Extractive Distillation Process to Separate Toluene and Methyl Cyclohexane..... 23

14. Azeotropic Distillation Process for Separating Ethanol and Water by Using Pentane as the Entrainer..... 25

15. A Typical Residue Curve Map Showing a Distillation Boundary..... 32

16. The Algorithm for Determining the Residue Curve Map and the Selection of Azeotropic Entrainers..... 34

17. Procedure for the Selection of Extractive Solvents Based on UNIFAC and UNIQUAC Models..... 41

18. Relative Volatility Required for Different Separations with Equal Cost..... 46

19. Vapor-Liquid Equilibrium Curves for the Methanol Acetone System with Solvents and with No Solvent..... 48

20. NTP Requirements for Different Relative Volatilities..... 51

21. NTP and Column Cost vs. Relative Volatility..... 53

22. Effect of Ratio of Solvent to Mixture on Selectivity..... 54

23. Effect of Temperature on Selectivity..... 55

24. Effect of Solvent Selectivity on Cost for Low Selectivity..... 57

25. Effect of Solvent Selectivity on Cost for High Selectivity..... 58

26. Integration of Expert System Components..... 68

LIST OF FIGURES--Continued

Page

27. Knowledge Involved for Solvent Selection Problems..... 81

28. Knowledge Components and Classification..... 88

29. Illustration of Object Concept..... 94

30. Object "Domain" for the Driving Module..... 95

31. An Example of Creating a Rule..... 99

32. An Illustration of Creating a Method..... 100

33. An Example of Inheritance..... 107

34. Selection Hierarchy for Solvent Selection..... 111

35. The Flowsheet of the Expert System..... 113

36. Selection Procedure and Results for p-Xylene and m-Xylene..... 129

37. Selection Procedure and Results for o-Xylene and m-Xylene..... 132

38. Selection Procedure and Results for Methyl Acetate and Methanol..... 138

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

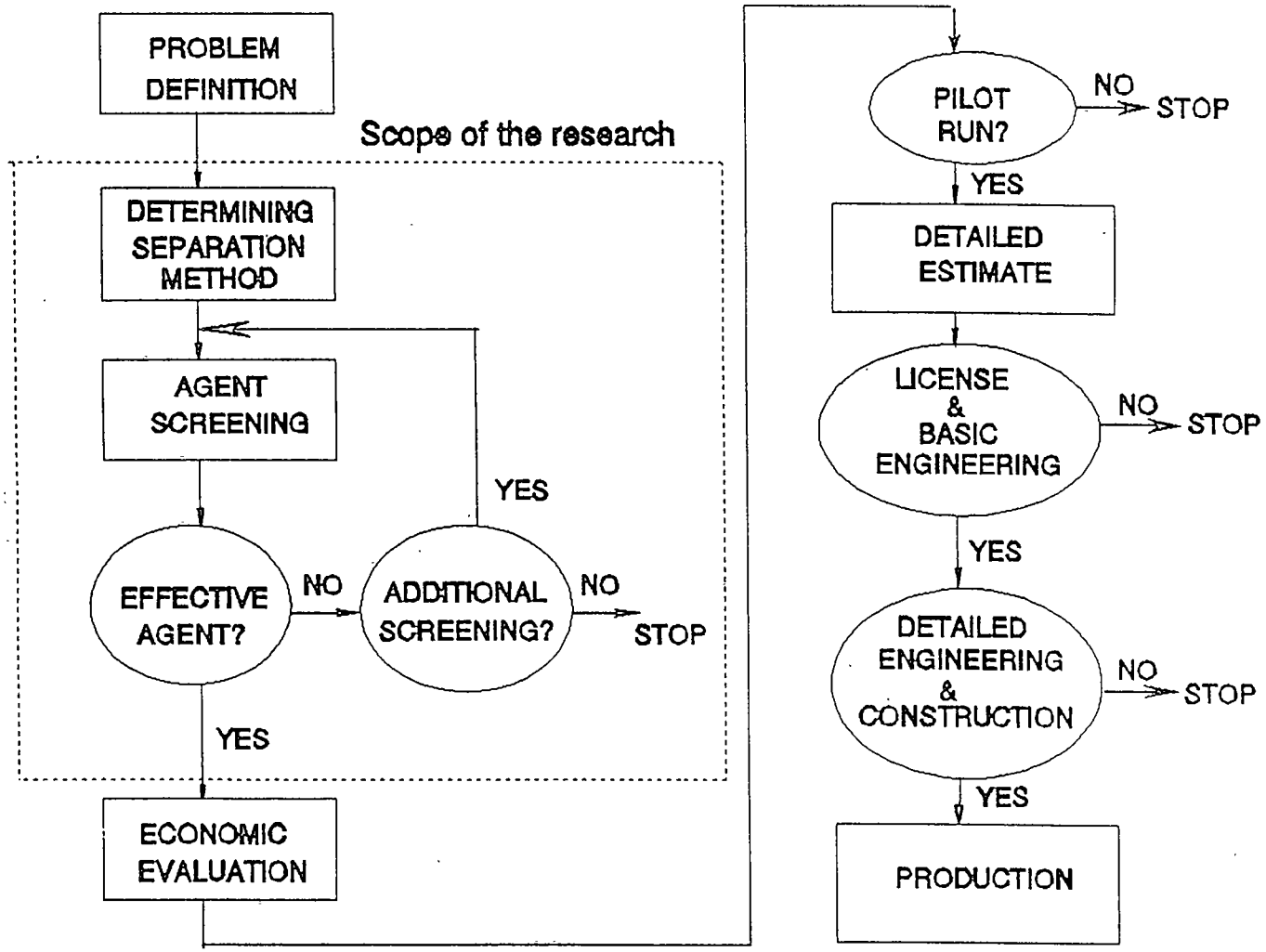

Figure 1 Process development steps for the mass-based separation and the scope of this research [2]

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

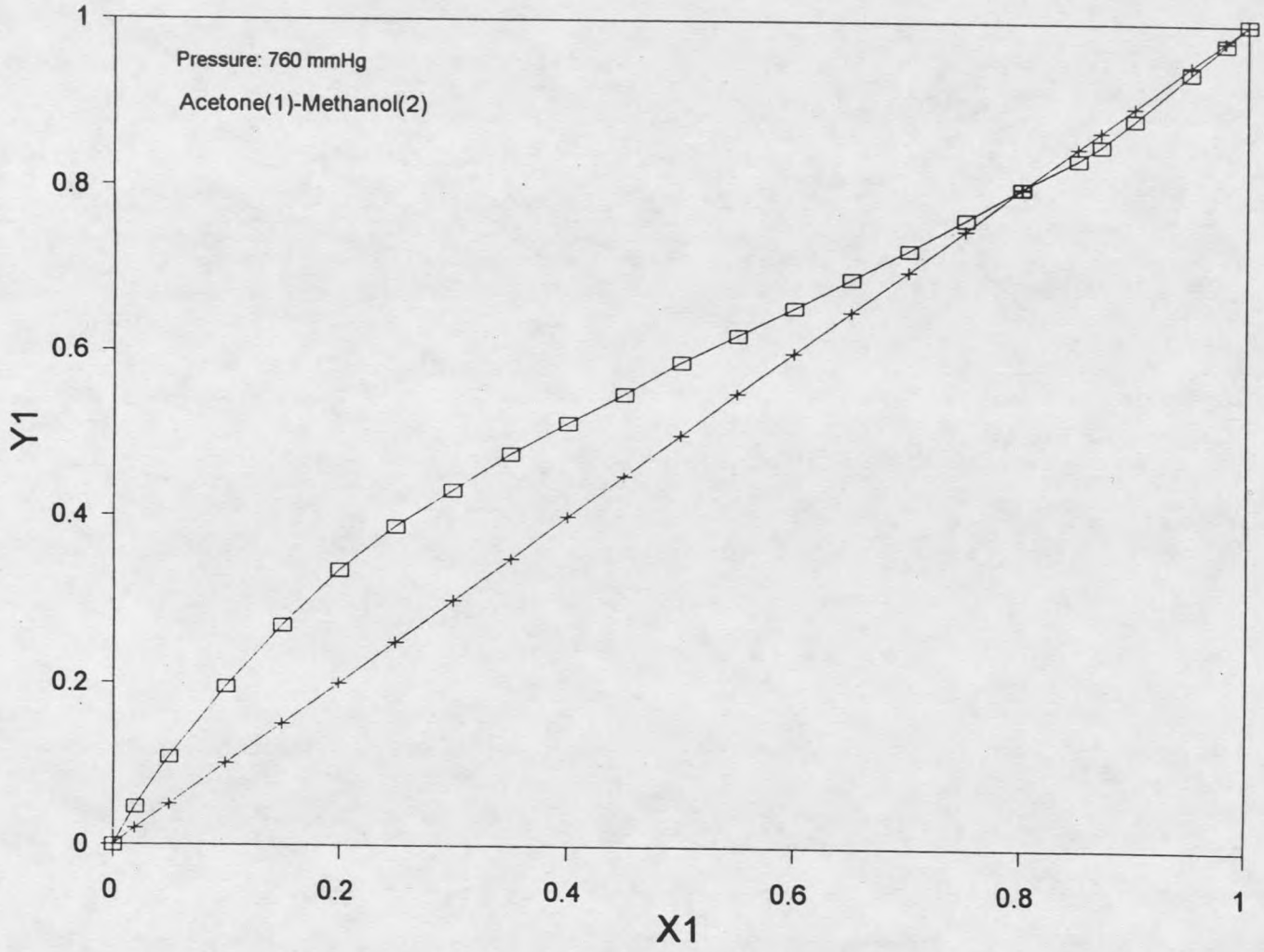

Figure 2 Liquid mole fractions and vapor mole fractions for minimum-boiling mixtures of acetone and methanol[4]

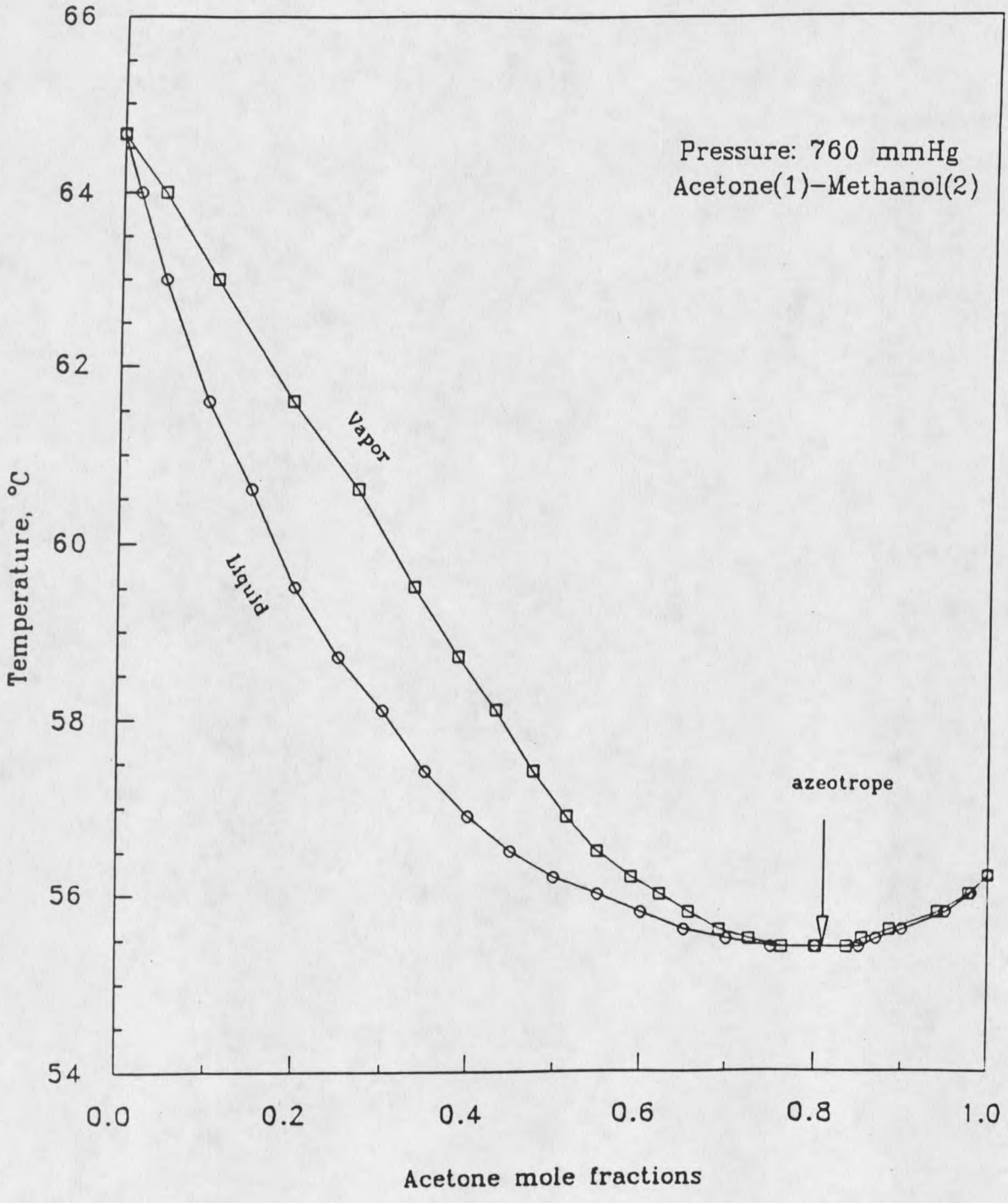

Figure 3 Liquid boiling points and vapor condensation temperatures for minimum-boiling azeotropic mixture of acetone and methanol[4]

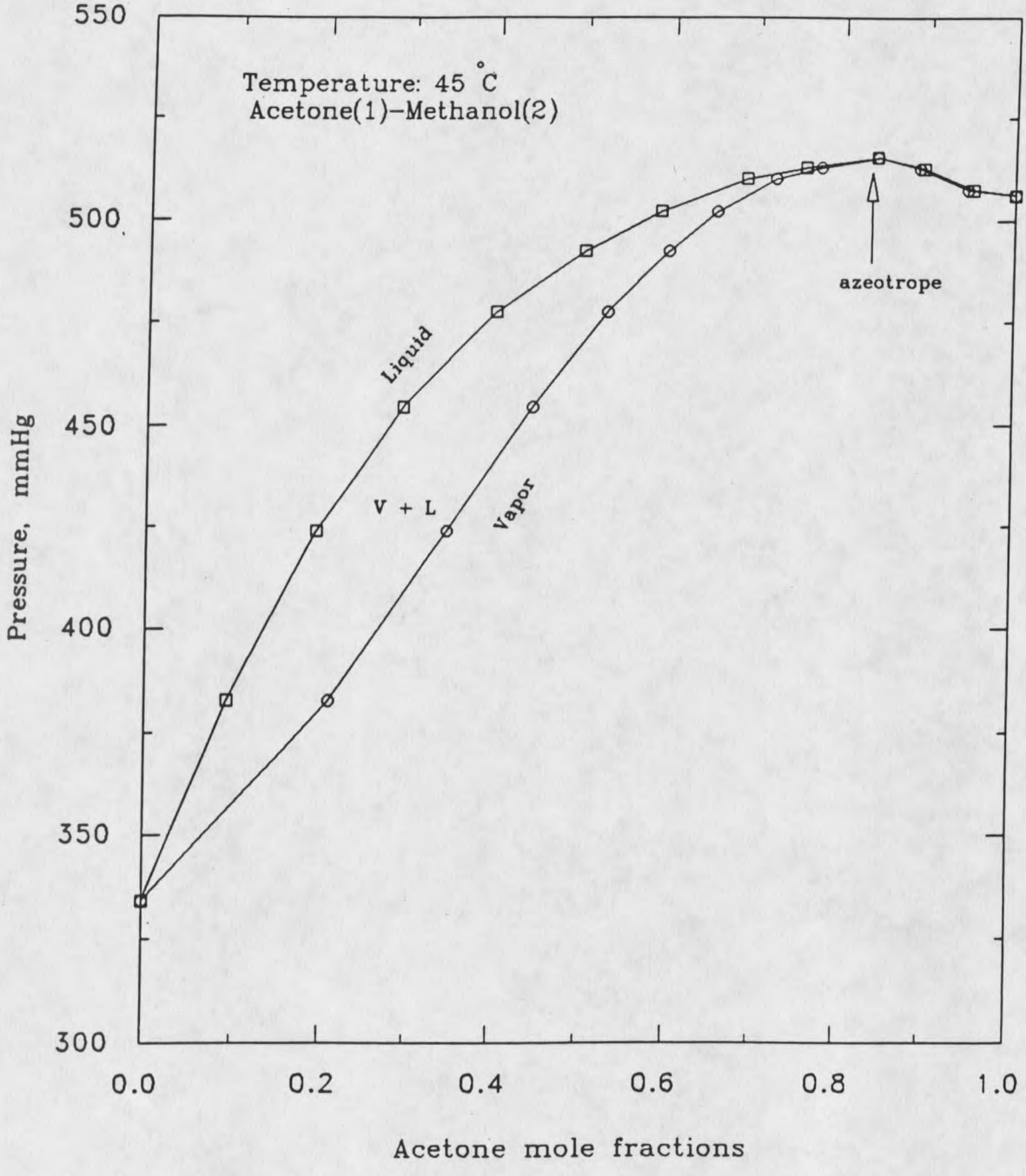

Figure 4 Pressure and Liquid Compositions for Minimum-Boiling Azeotropic Mixture of Acetone and Methanol[4]

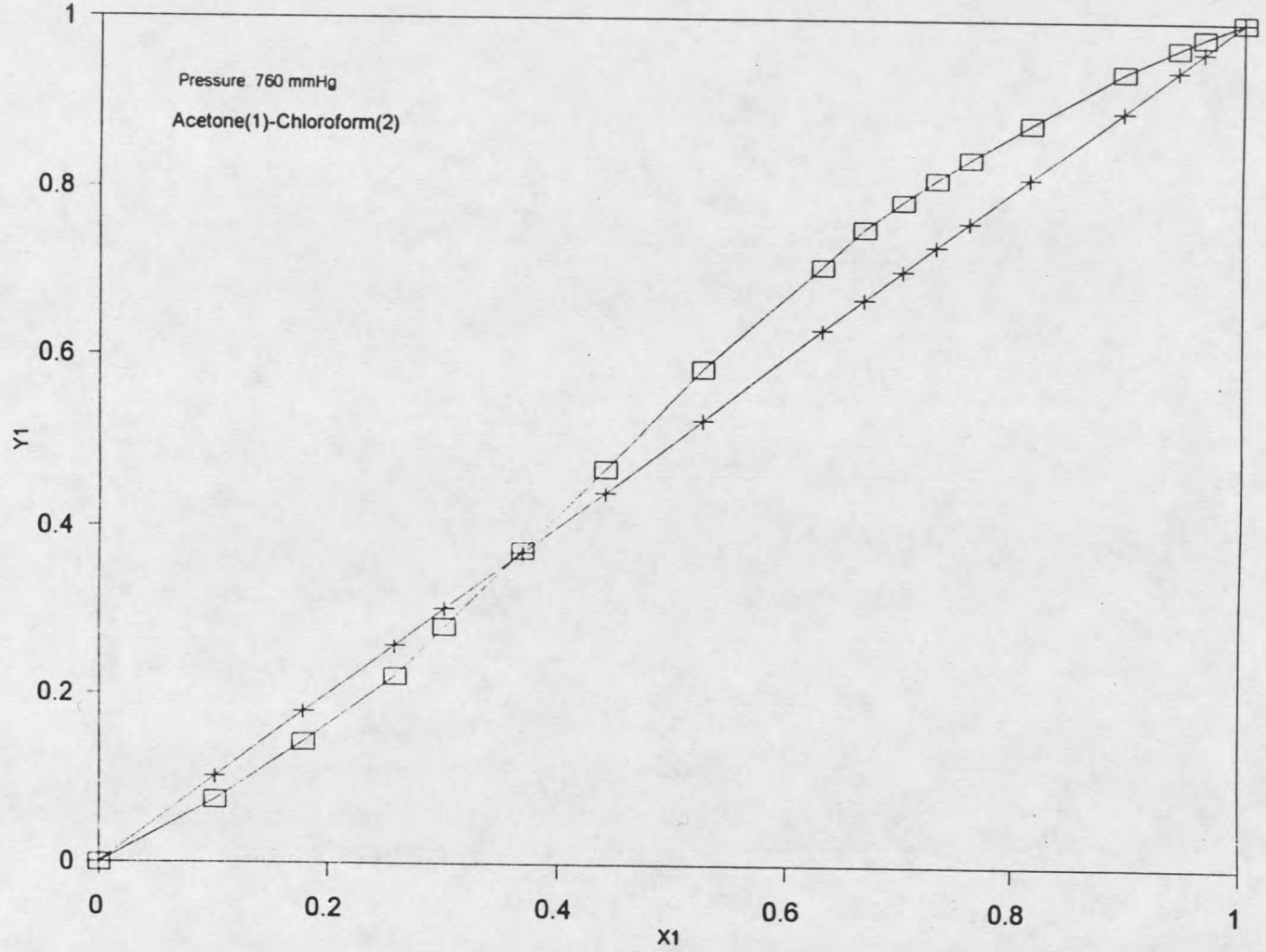

Figure 5 Liquid mole fractions and vapor mole fractions for maximum-boiling azeotropic mixture of acetone and chloroform[4]

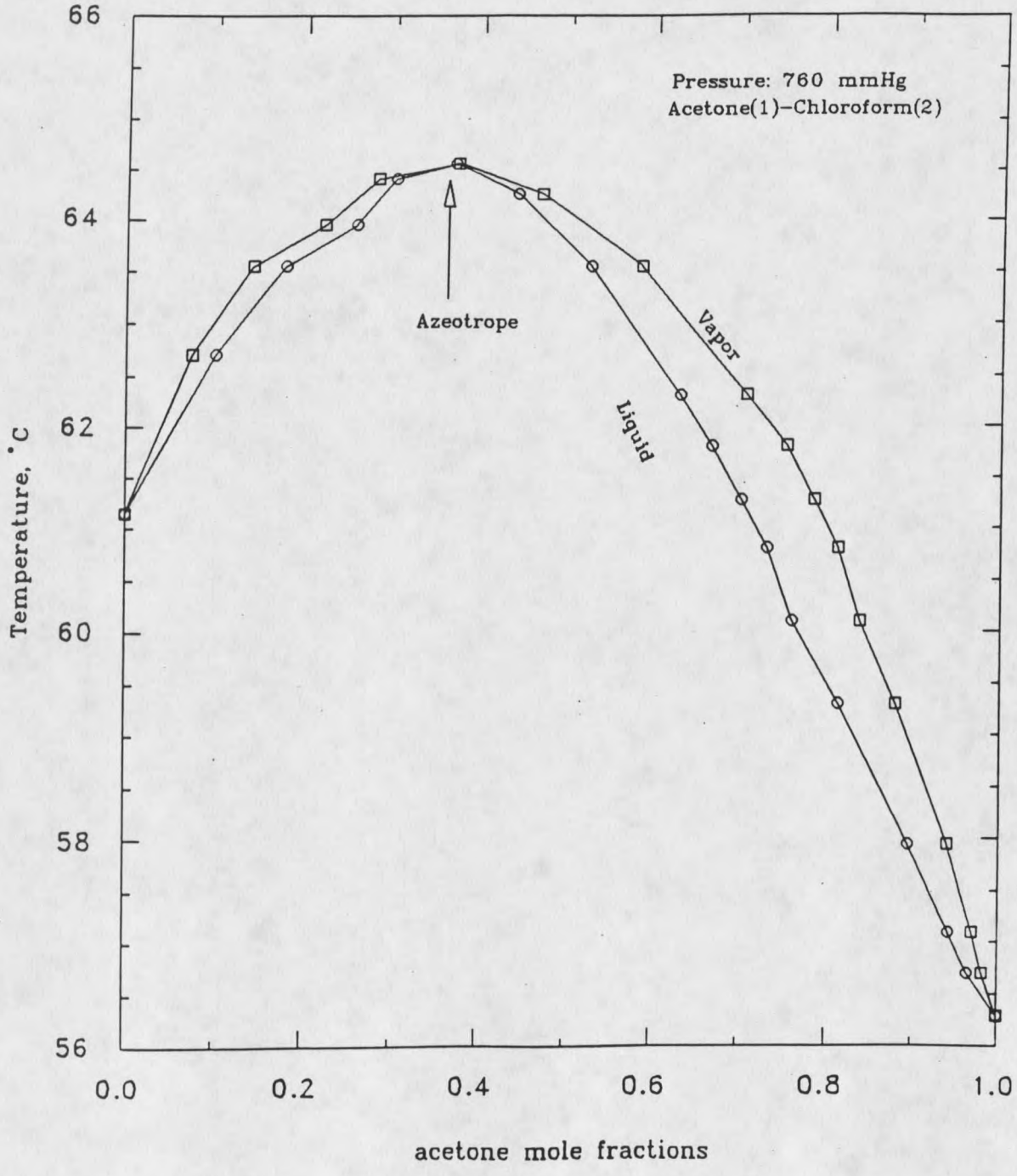

Figure 6 Liquid boiling point and vapor condensation temperatures for maximum-boiling azeotropic mixture of acetone and chloroform[4]

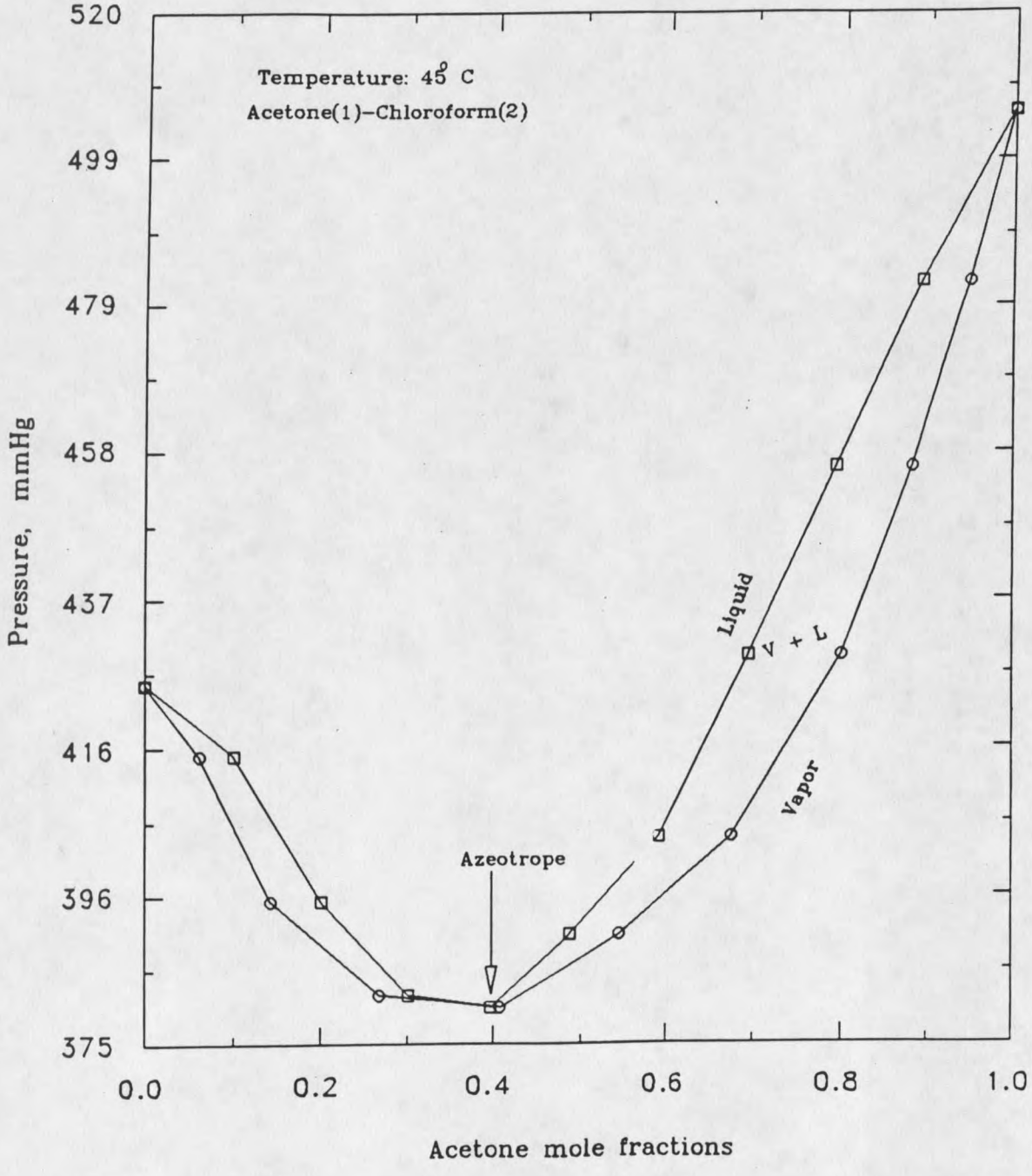

Figure 7 Pressure and liquid mole fractions for maximum-boiling azeotropic mixture of acetone and chloroform[4]

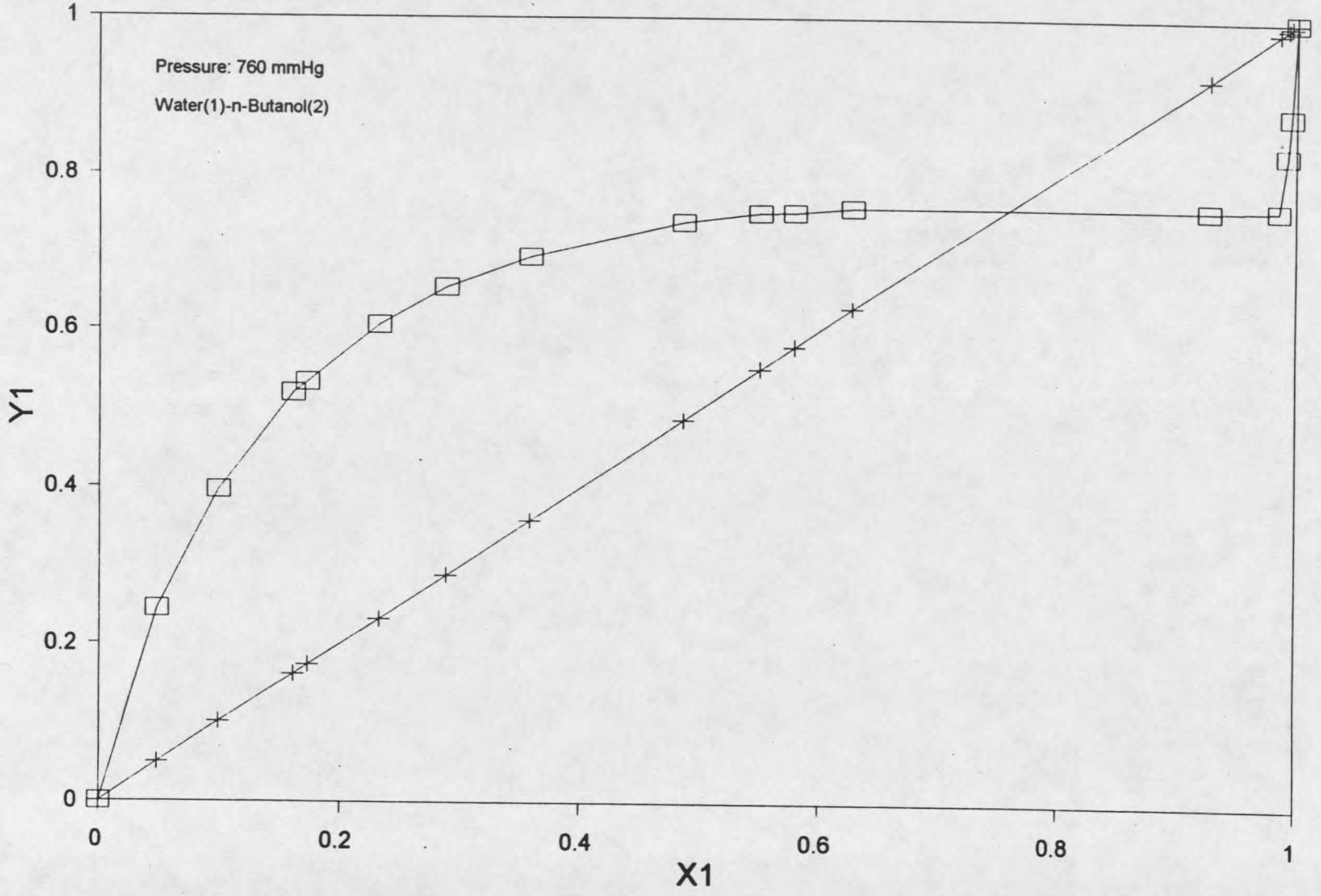

Figure 8 Liquid mole fractions and vapor mole fractions for heteroazeotropic mixture of water and n-butanol[4]

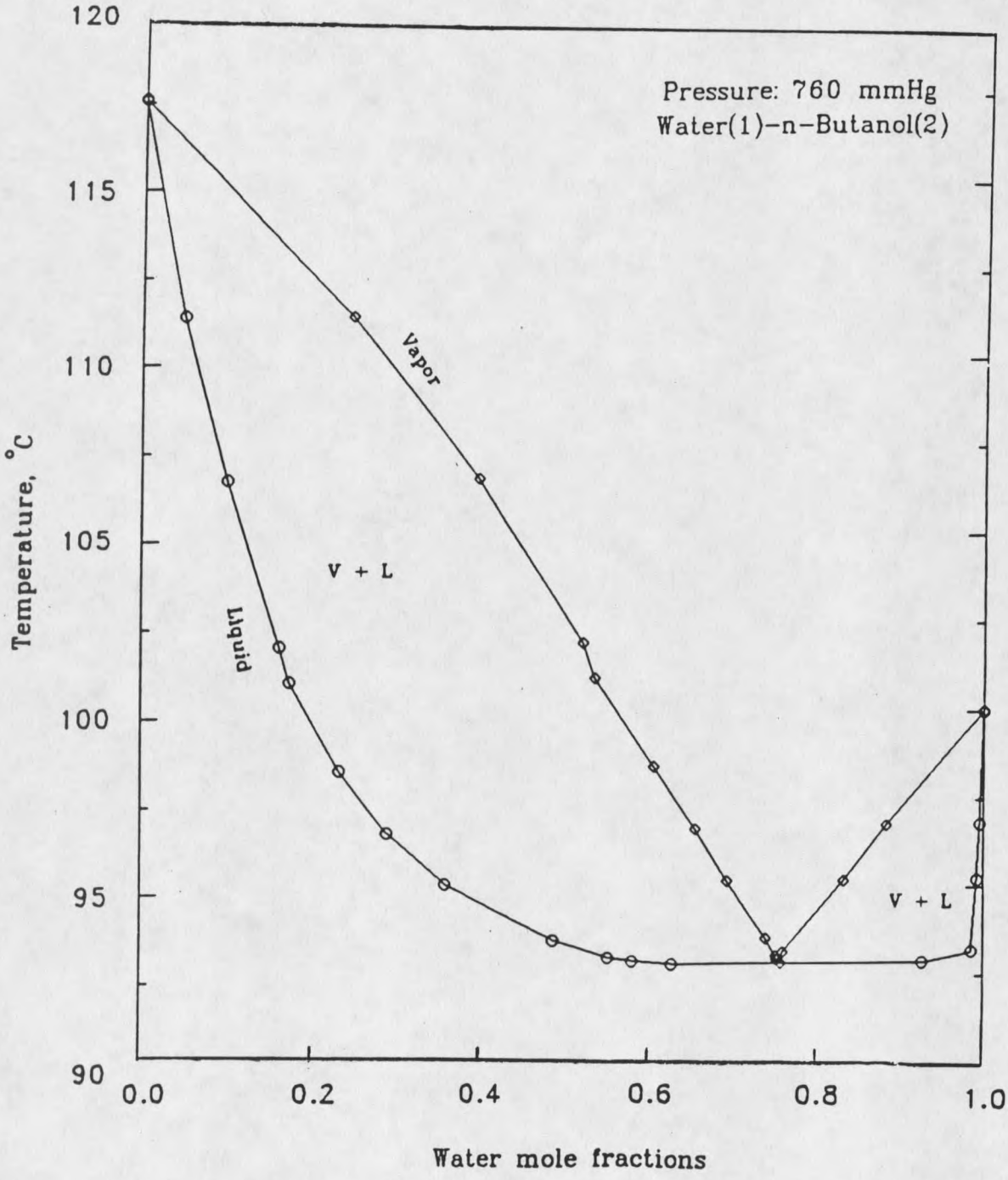

Figure 9 Liquid boiling point and vapor condensation temperatures for minimum-boiling heteroazeotropic mixture of water and n-butanol [4]

maximum-boiling binary, ternary and even quaternary ones are known to exist.

A close-boiling mixture is difficult to separate by conventional distillation because components in the mixture have very similar physical properties and boil very closely together. Examples of such systems include the propylene-propane system or aromatic-paraffinic hydrocarbons. These close-boiling mixtures have relative volatilities close to unity. Figures 10 and 11 present the typical vapor-liquid behavior of these kinds of solutions. Other solutions that form regions of very low relative volatility (such as acetic acid and water) can fall into this category even though the pure-component boiling points of the components in the solution vary quite widely. Vapor-liquid equilibrium for acetic acid and water is shown in Figure 12 (Vapor-liquid equilibrium data for Figures 2 through 12 is adapted from [4]).

From Figures 2 through 12, it can be seen that the separation of these mixtures by means of ordinary distillation is either impossible (for azeotropes) or needs so many theoretical plates (for close-boiling mixtures) that the capital investment for equipment is prohibitively high.

Azeotropic and Extractive Distillation Processes

Azeotropic and extractive distillation are separation processes in which a third separating entrainer (also called

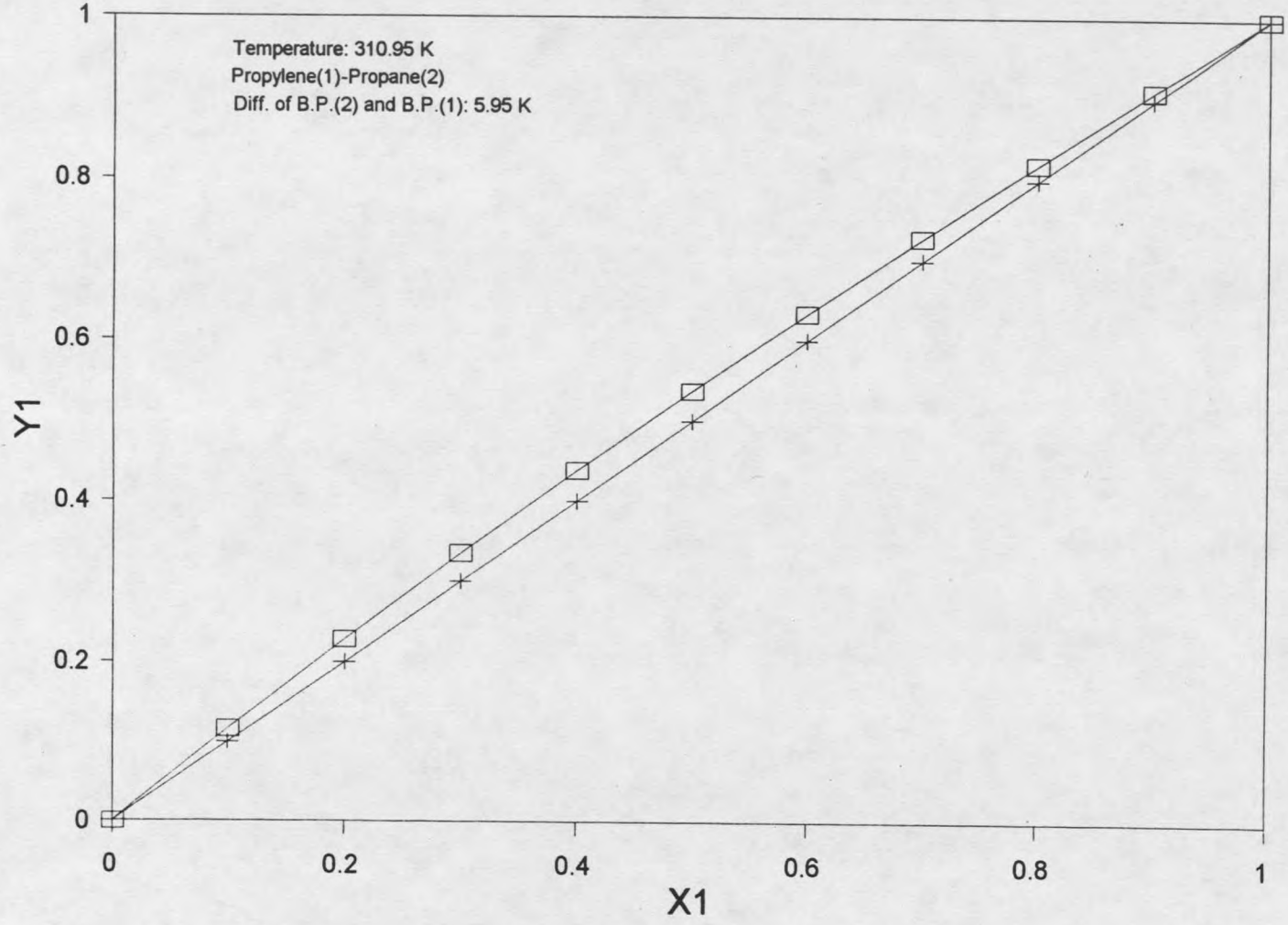

Figure 10 Liquid mole fractions and vapor mole fractions for close-boiling mixture of propylene and propane [4]

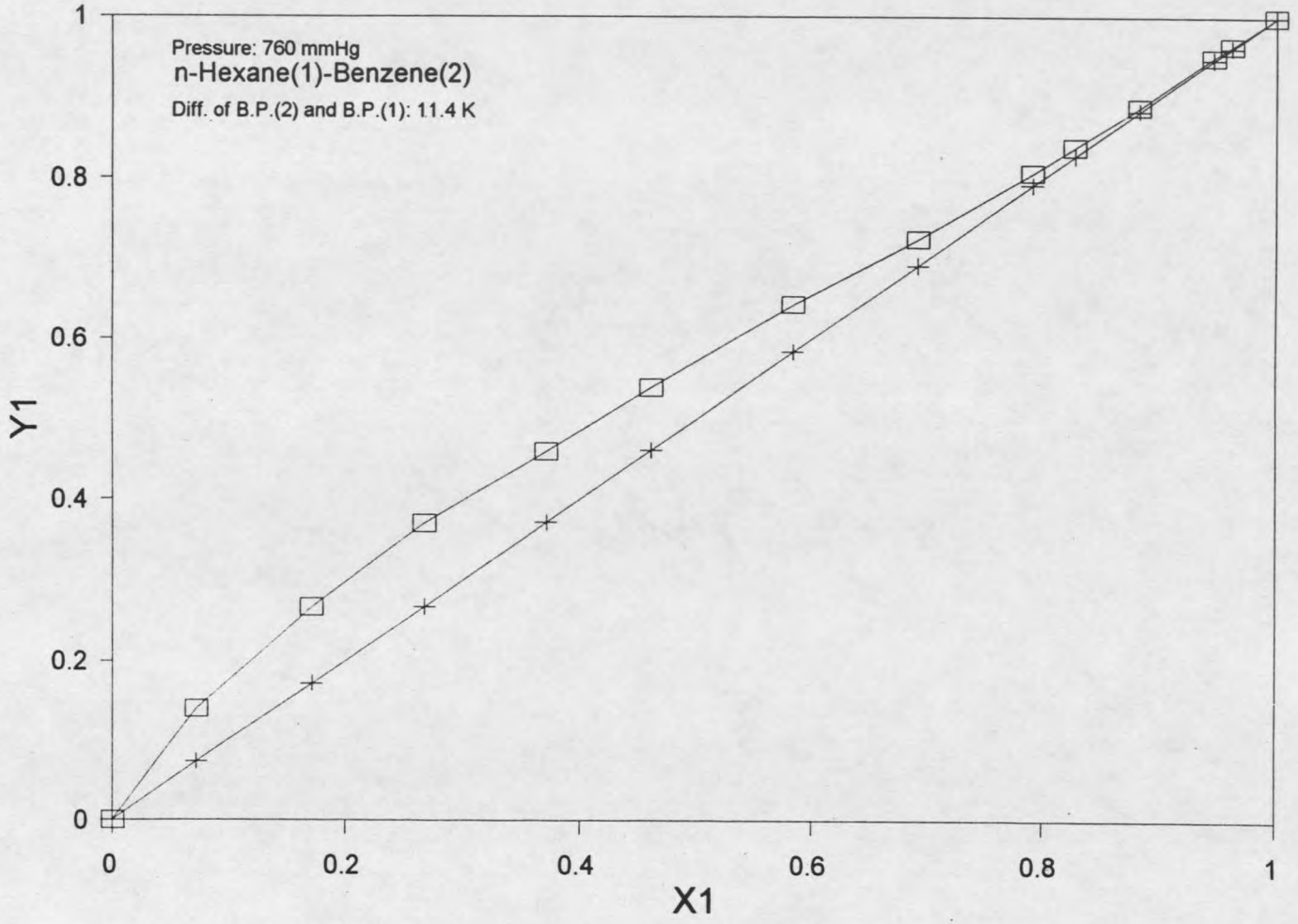

Figure 11 Liquid mole fractions and vapor mole fractions for close-boiling mixture of n-hexane and benzene [4]

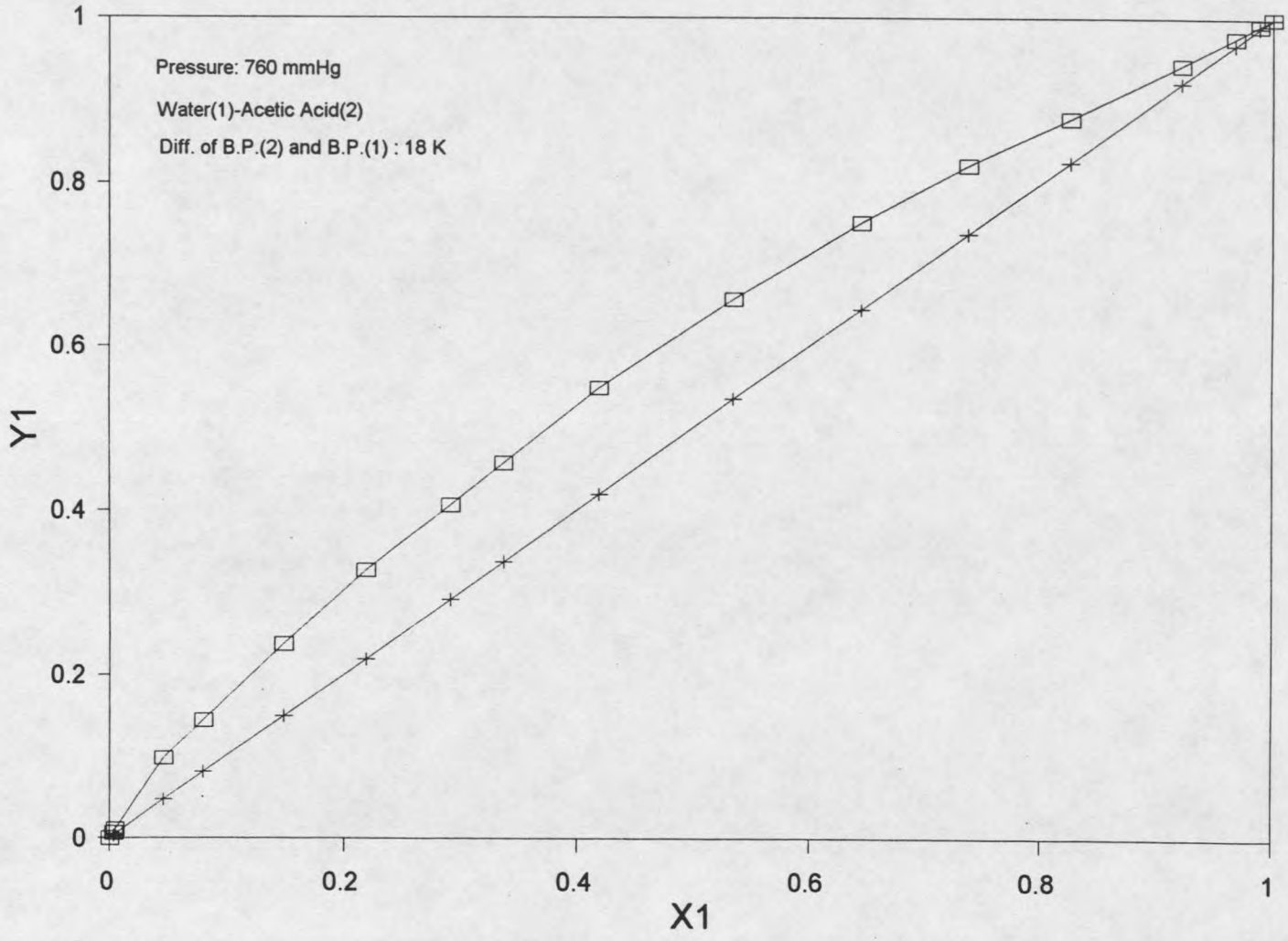

Figure 12 Liquid mole fractions for low relative volatility mixture of water and acetic acid [4]

a solvent or an agent) is deliberately added to the distillation column to improve the relative volatility of the feed components.

Extractive distillation refers to those processes in which a high-boiling solvent is added to a tray in a column to alter the relative volatilities of components in the main feed to the column. The solvent is generally selected such that it boils at a temperature so far above the boiling points of the feed components that the formation of a new azeotrope is impossible. Also, any troublesome azeotropes present in the untreated feed disappear in the presence of a well-chosen solvent. The absence of azeotropes plus the fact that the solvent can be recovered by simple distillation makes extractive distillation a less complex and more widely useful process than azeotropic distillation. The generally accepted definition of extractive distillation is given by Benedict and Rubin[5]:

> Distillation in the presence of a substance that is relatively non-volatile compared to the components to be separated and, therefore, is charged continuously near the top of the distilling column so that an appreciable concentration is maintained on all plates of the column.

The typical configuration for an extractive distillation process is shown in Figure 13, in which methyl cyclohexane and toluene are to be separated[6]. These two components do not form an azeotrope, but their relative volatility is less than 1.01 at low concentrations of toluene. The volatility of methyl cyclohexane relative to toluene is enhanced by the

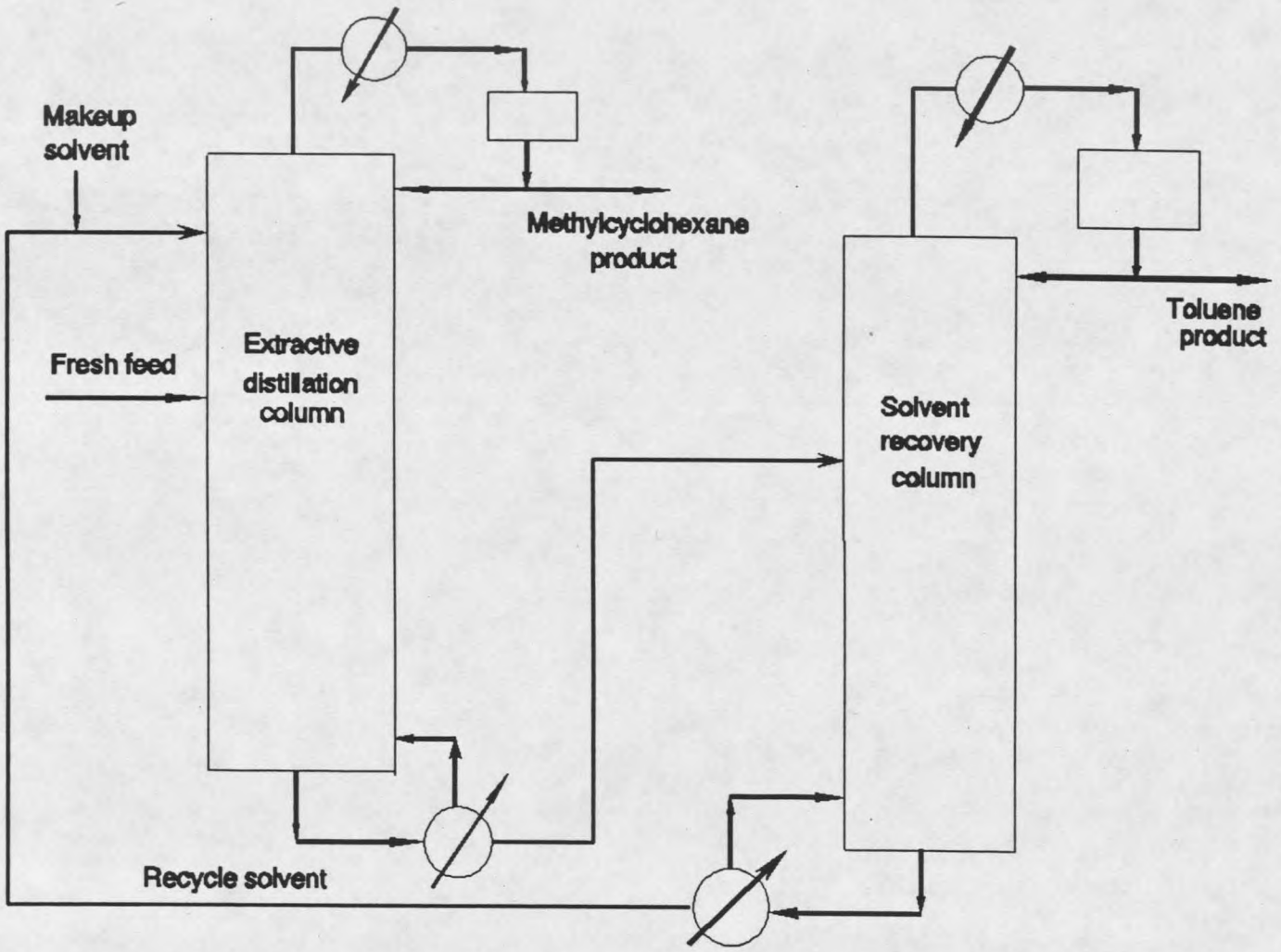

Figure 13 Simplified flow diagram for an extractive distillation process to separate toluene and methyl cyclohexane[6]

addition of a solvent. This allows separation of these two components with fewer stages than would be required in simple distillation. The solvent chosen is less volatile than the two components and, in order to maintain a high concentration of solvent throughout most of the column, must be introduced to the extractive distillation column above the fresh-feed stage. It is usually introduced near the top stage. Recovery of the solvent is relatively simple for extractive distillation as compared with azeotropic distillation. The solvent chosen does not form an azeotrope with non-solvent material in the bottom product from the extractive distillation tower, and solvent recovery can be accomplished by simple distillation.

Azeotropic distillation refers to those processes in which a component (called solvent or entrainer) is added above the main feed tray to form (or nearly form) an azeotrope with one or more of the feed components. The azeotrope is then removed as either a distillate or a bottom product. Azeotropic distillation can also refer to a process in which a solvent is added to break an azeotrope that otherwise would be formed by components in the feed. Here, the process is distinguished from extractive distillation because the solvent appears in the distillate, from which it must be separated and recycled back to the top section of the column. A representative flowsheet for azeotropic distillation of an ethanol-water mixture using pentane is shown in Figure 14[6]. Nearly pure ethanol [78.3°C] cannot be obtained from a dilute mixture with

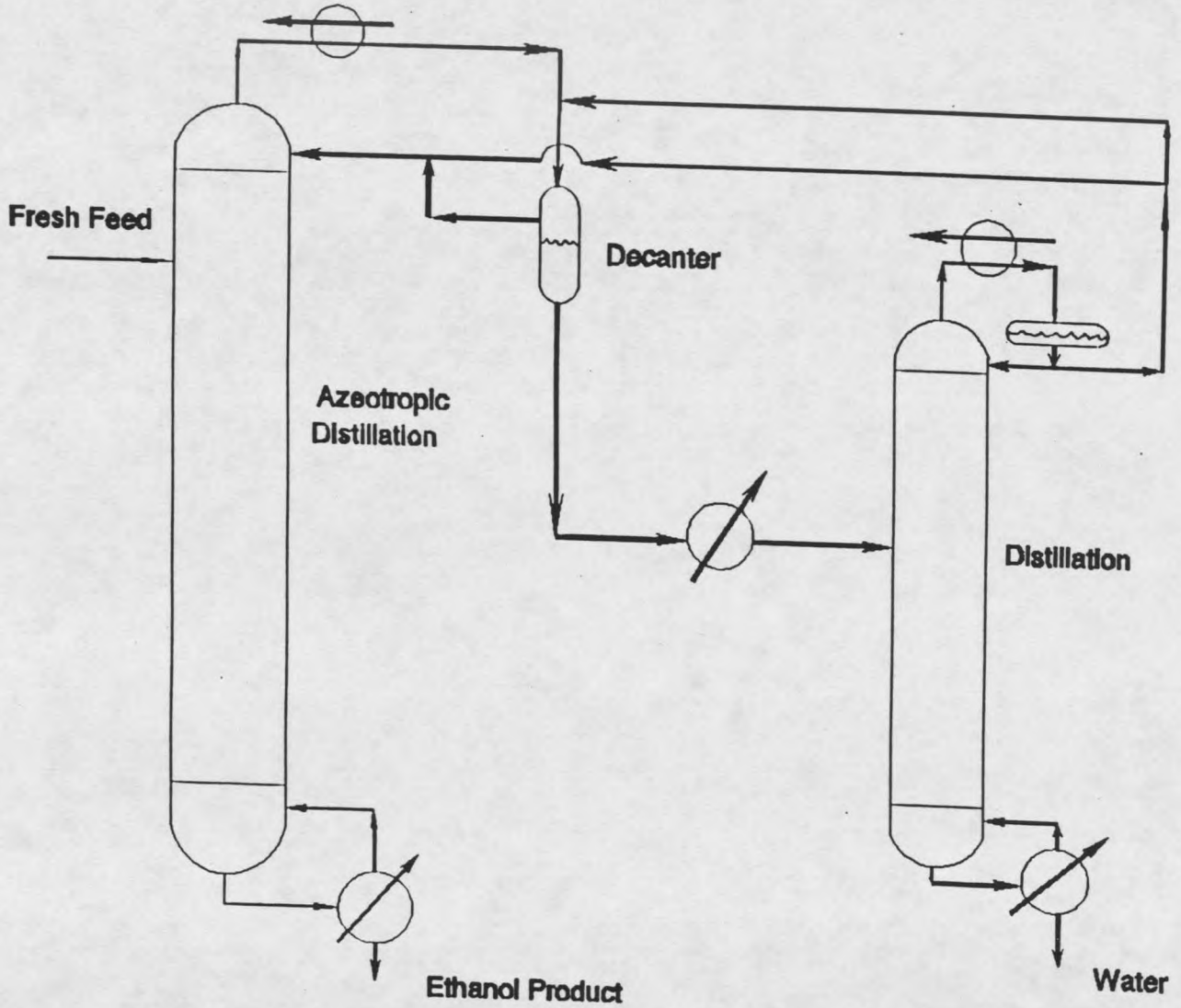

Figure 14 Azeotropic distillation process for separating ethanol and water by using pentane as entrainer[6]

water [100°C] by simple distillation at 1 atm. because a minimum-boiling homogeneous azeotrope [78.15°C] is formed. As discussed by Black et al.[7], the separation can be made by low-pressure [<0.1135 atm] simple distillation, extractive distillation with gasoline or ethylene glycol, or azeotropic distillation with n-pentane, benzene, or diethyl ether. Figure 14 shows the azeotropic distillation process with n-pentane as the entrainer. In the azeotropic column, nearly pure ethanol is taken as a bottom product and a heterogeneous minimum-boiling azeotrope is taken as a distillate, condensed, and decanted into a pentane-rich reflux stream and an aqueous ethanol stream that is separated by distillation to produce a bottom product of nearly pure water and a distillate that is combined with the reflux from the decanter.

It should be noted that either extractive distillation or azeotropic distillation can be used to separate both close-boiling mixtures and azeotropes.

Heterogeneous azeotropic distillation vs. homogeneous azeotropic distillation. Doherty et al.[8] classified azeotropic distillation into the homogeneous, in which the added solvent or entrainer alters the relative volatility of the two azeotropic constituents without inducing liquid-liquid separation, and the heterogeneous, in which the added solvent alters the relative volatility of the two azeotropic constituents and induces liquid-liquid separation. Homogeneous azeotropic distillation covers the traditional extractive

distillation for the separation of an azeotrope. Laroche et al.[1] argued that heterogeneous azeotropic distillation suffers from a major drawback: Operating such a column can be very difficult because upsets can induce phase separation inside the column, leading to severe efficiency losses. Thus homogeneous azeotropic distillation which does not have the above disadvantage is easier to operate, can outperform heterogeneous azeotropic distillation while separating the same azeotrope, and represents an economically attractive way of separating azeotropes.

The Brief History of Azeotropic and Extractive Distillation

The first successful distillation of an azeotropic mixture is credited to Young(1902)[9], who in 1903, received a patent for his batch distillation process for making anhydrous alcohol. Young's invention can be regarded as a landmark event in the history of the chemical processing industry. In 1908 Guillaum[10] patented an extractive distillation process for the removal of fusel oil from fermentation alcohol. Since then, research on azeotropic and extractive distillation has received periodic attention, usually as the result of some crisis in world history. For example, World War I caused a tremendous increase in demand for butanol that was met by the introduction of an azeotropic distillation process. Acetic acid demand also climbed, and

engineers found that substantial savings in energy and increased production rates could be realized by converting from a conventional distillation process to an azeotropic distillation process. Then again during World War II, the greatly increased demand for rubber was met by the development of a synthetic rubber industry. This industry relied heavily on the use of azeotropic and extractive distillation for the recovery of high-grade butenes and butadiene.

Currently, azeotropic and extractive distillation are used for such widely diverse applications as dehydration of acetic acid, formic acid, ethanol, isolation of isoprene from a C_5 hydrocarbon cut, 2-propanol production, vinyl acetate production, deemulsification of oil, and separation of aliphatic and aromatic hydrocarbons or alkanes and alkenes[16].

An Overview of Solvent Selection Methods

Over the years, theoretical methods, empirical heuristic rules and experimental methods have been developed for the selection of promising solvents or entrainers for azeotropic and extractive distillation to separate azeotropes or close-boiling mixtures. The following gives only a brief description of the empirical guidelines and some thermodynamic bases for the selection process.

For Azeotropic Distillation

For azeotropic distillation, Berg[11] has proposed the general heuristic criteria to screen entrainers based on the liquid classifications using hydrogen bonding ability and polarity as attributes of liquids:

1. To separate a closely boiling pair or a maximum azeotrope, choose an entrainer such that:

a) The entrainer forms a binary minimum azeotrope with only one component, or

b) The entrainer forms a binary minimum azeotrope with each component but one minimum azeotrope boils at a significantly lower temperature than the other, or

c) The entrainer forms a ternary minimum azeotrope that boils at a significantly lower temperature than any binary azeotrope. The ratio of compositions of the original components in the ternary must be different from their ratio before the entrainer is added.

2. To separate a minimum azeotrope, choose an entrainer such that:

a) The entrainer forms a binary minimum azeotrope with one component that boils at a significantly lower temperature than the original minimum azeotrope, or

b) The entrainer forms a ternary minimum azeotrope that boils at a significantly lower temperature than any binary minimum azeotrope and in which the ratio of compositions of the original components is different from their ratio in the

binary minimum azeotrope.

Berg has also listed the following desirable properties of a solvent or entrainer for hydrocarbon separations[11]. The entrainer:

1. Should boil within a limited range (0-30°C) of the pure-component boiling points of the hydrocarbon mixture to be separated.

2. Should form, on mixing with the hydrocarbon, a large positive deviation from Raoult's law to give a minimum azeotrope with one or more of the hydrocarbon types in the mixture.

3. Should be soluble in the hydrocarbon.

4. Should be easily separable from the azeotrope.

5. Should be inexpensive and readily obtainable.

6. Should be stable at the temperature of the distillation.

7. Should be non-reactive with the hydrocarbon being separated and with the materials of construction of the equipment.

To make recovery easy, the ideal solvent or entrainer will usually boil 10°C to 30°C below the hydrocarbon mixture providing a large temperature difference between the hydrocarbon-entrainer azeotrope and the unaffected hydrocarbon.

In addition, Treybal[12] has listed the following attributes expected for a promising solvent or entrainer:

1. If the entrainer forms a new azeotrope with only one of the constituents of the binary mixture to be separated, it should preferably be the constituent present in the minority to reduce the heat requirements of the process.

2. The new azeotrope should preferably be lean in entrainer content, to reduce the amount of vaporization necessary in the distillation.

3. The new azeotrope should preferably be of the heterogeneous-liquid type, which then greatly simplifies the recovery of the entrainer.

4. Should be nontoxic.

5. Should be of low latent heat of vaporization.

6. Should be of a low freezing point to facilitate storage and outdoor handling.

7. Should be of low viscosity to provide high tray capacity.

Doherty et al.[13] have introduced a method for screening solvents for homogeneous azeotropic distillation based on the so-called simple distillation residue curve map analysis. A residue curve map is a triangular diagram (with the pure components at each vertex) which shows the locus of the liquid phase composition as it varies with time during a simple distillation process. For illustration, the residue curve map for the acetone-chloroform-benzene system is shown in Figure 15. The sketching procedure for the residue curve map needs only a knowledge of binary and/or ternary azeotropes along

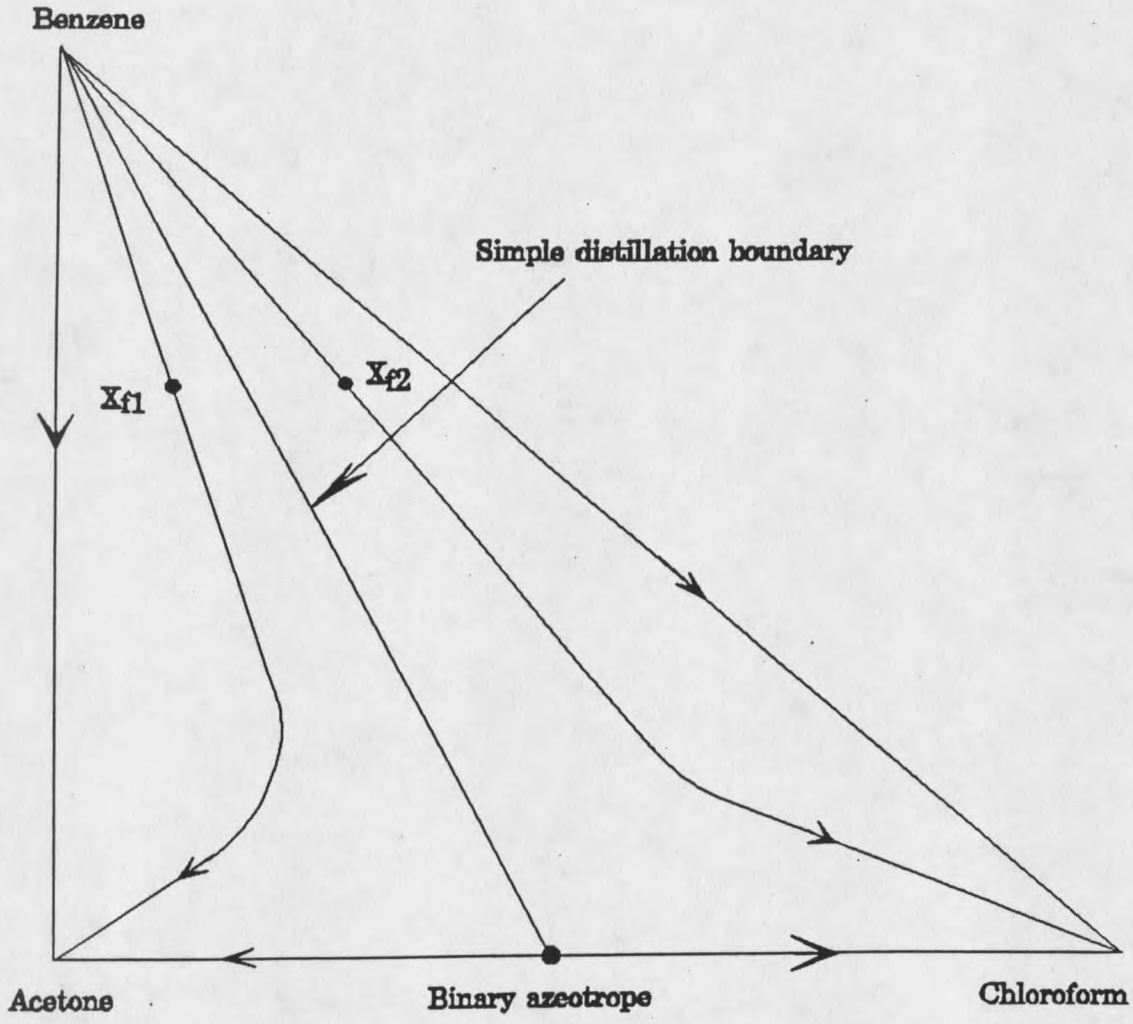

Figure 15 A typical residue curve map showing a distillation boundary[13]

with their respective boiling point temperatures and compositions, and was described by Doherty et al.[14][15]. According to Doherty and Caldarola's criterion[16], based on the analysis and classification of the residue curve maps, in the case of a minimum boiling azeotrope, any component "which does not produce an internal distillation boundary between the two components to be separated" can be used as an entrainer. Based on the results from directed graph theory and an adjacency matrix representation, Foucher et al.[16] described the extended rules and an automatic procedure for the determination of the structure of the simple distillation residue curve maps for ternary mixtures as shown by Figure 16. Their procedure requires only a knowledge of boiling temperatures and approximate compositions of any azeotropes in the mixture. They have claimed that their procedure enables the rapid identification of feasible entrainers, but their approach is limited to homogeneous azeotropic distillation.

Stichlmair et al.[18] have also tackled the entrainer selection problem and his results were given as follows:

1. If the binary mixture exhibits a maximum boiling azeotrope, the entrainer must a) be a high-boiling substance or b) form new maximum boiling binary azeotropes.

2. If the binary mixture exhibits a minimum boiling azeotrope, the entrainer must a) be a minimum boiling substance or b) form new minimum boiling binary azeotropes.

By examining homogeneous azeotropic distillation, Laroche

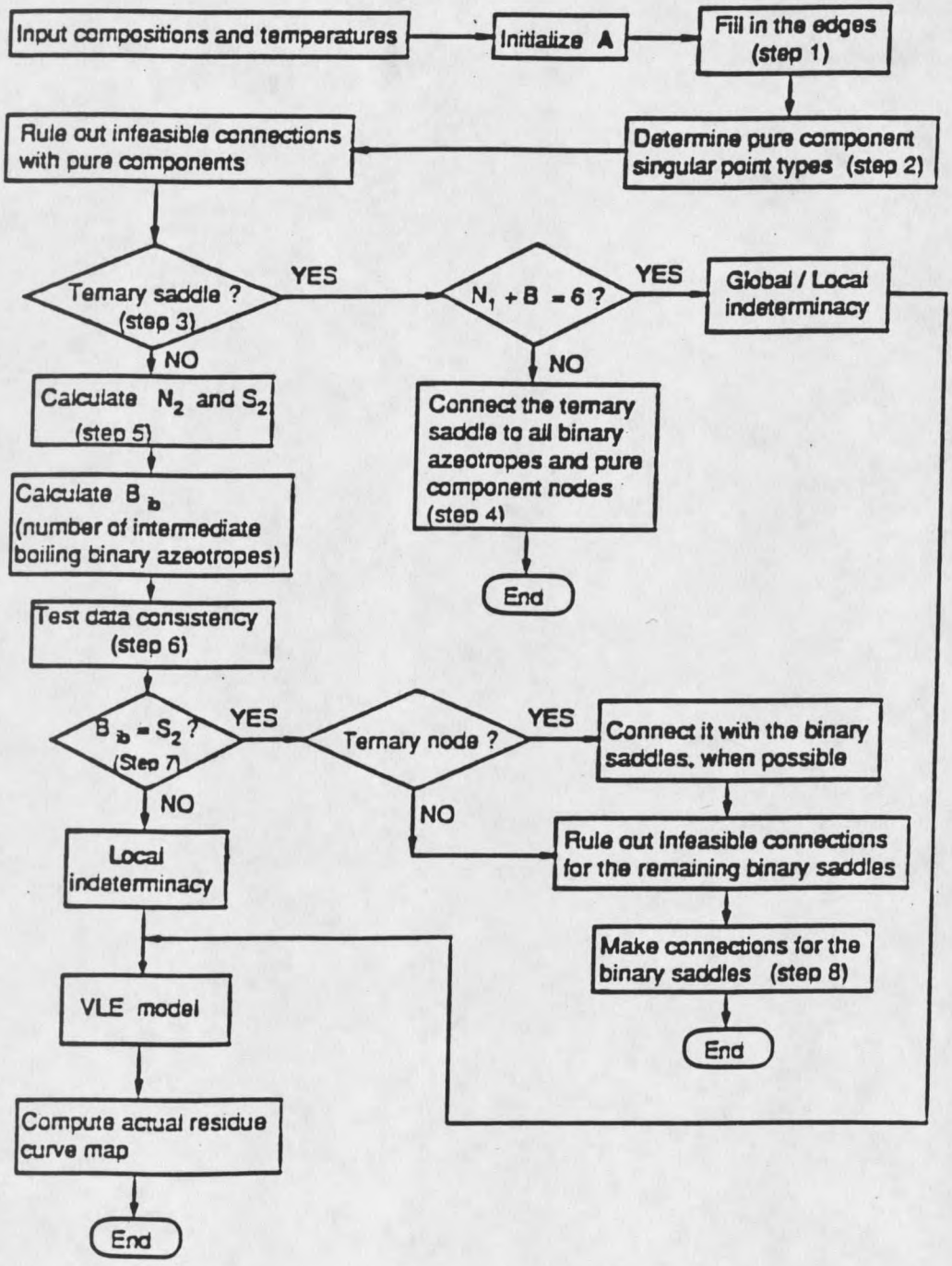

Figure 16 The algorithm for determining the residue curve map and the selection of azeotropic entrainers[16]

et al.[19] have found that homogeneous azeotropic distillation can behave in a very unusual manner. The following lists some strange features for homogeneous azeotropic distillation:

1. Increasing reflux in a given column does not always increase separation. In fact, in many cases, there is no separation at all at infinite reflux.

2. Meeting the same specifications with a large number of trays sometimes requires higher internal flows.

3. Sometimes, the separation is feasible, but neither the direct nor the indirect sequence is possible. Indeed, there are cases where we can recover the intermediate boiler as a pure distillate product, but not the light boiler. There are also cases where we can recover the intermediate boiler as a pure bottom product, but not the heavy boiler.

On the basis of the above observations, they have analyzed the assumptions behind Doherty et al.'s rules and Stichlmair et al.'s rules, and they have found that the existing entrainer selection rules for the minimum boiling azeotrope are conflicting. Thus, they proposed the following entrainer selection procedure for homogeneous azeotropic distillation:

1. Eliminate all chemicals that introduce additional azeotropes.

2. By comparing the corresponding equivolatility curve diagrams, select the best (or best few) candidates in each of the following classes:

a) Heavy entrainers that send the lighter azeotropic component to the top of the extractive column;

b) Heavy entrainers that send the heavier azeotropic component to the top of the extractive column;

c) Light entrainers that send the lighter azeotropic component to the bottom of the extractive column;

d) Light entrainers that send the heavier azeotropic component to the bottom of the extractive column.

3. Keep all intermediate entrainers.

4. Design, cost and optimize the feasible separation sequence(s) corresponding to the remaining candidate entrainers. The best entrainer yields the lowest total annualized cost.

For Extractive Distillation

Scheibel[20] has pointed out that

1. The entrainer must not form an azeotrope with either of the components of the mixture to be separated.

2. The entrainer must be sufficiently less volatile than either of the components.

3. The entrainer must have a different effect on the partial pressure of each of these components in the solution at a given concentration. This means that selectivity is different from unity.

4. The following well-known properties of mixtures can be made use of for selecting a solvent, first, members of a

homologous series show little or no deviations from Raoult's law; second, when two compounds show deviation from Raoult's law, one of these compounds shows the same type of deviation from any member of the homologous series of the other component. Thus, any member of the homologous series of either component of an azeotrope might be used to separate the azeotrope.

It is only necessary to choose such an entrainer that satisfies the above conditions (1), (2), and (3).

These principles are best illustrated in Table 1 for the selection of solvents for separation of the acetone-methanol azeotrope.

The solvents listed in the left-hand column of Table 1 are in the homologous series with acetone and deal with it while those in the right-hand column are in homologous series with methanol and probably deal with methanol.

Table 1. Solvent Selection Based on Scheibel's Rules. (Adapted from [20])

Acetone B.P. 56.4 °C		Methanol B.P. 64.7 °C	
Solvent	B.P.°C	Solvent	B.P.°C
Methyl-ethyl ketone	79.6	Ethanol	78.3
Methyl n-propyl ketone	102.0	Propanol	97.2
Methyl isobutyl ketone	115.9	Butanol	117.8
Methyl n-amyl ketone	150.6	Amyl alcohol	137.8
		Ethylene glycol	197.2

Berg[12] has suggested that all solvents can be divided into five classes based on their potentialities for forming hydrogen bonds. The criteria proposed by Berg for successful extractive distillation solvents are that they boil considerably higher than the components being separated, form no minimum azeotropes with the components, and be highly hydrogen-bonded liquids, that is, Class I or Class II of the hydrogen bond classification. (See Appendix C, part C for the classification in detail).

For hydrocarbons, Tassios[21] has proposed a procedure as follows:

1. Compare the molar volumes of the close-boiling hydrocarbons to be separated, and prepare a list of potential entrainers:

   a) If the difference amounts to 5% or more, consider the entrainers with high polar cohesive energy; and assume that the optimum entrainers will also have a high polar cohesive energy;

   b) If the molar volumes are too close, select as potential entrainers those having high electron affinity.

2. Consult the literature to see whether experimental data might be available on some systems under consideration;

3. If any of the close-boiling hydrocarbons belong in the three groups: saturated hydrocarbons, olefins, or aromatics; use the Weimer-Prausnitz method to estimate the selectivity of

the potential entrainers.

4. For generally more reliable values, and for hydrocarbons not included in the classes, use the Pierotti-Deal-Derr(PDD) method to calculate entrainer selectivity.

5. Compare the potential entrainers for temperature and concentration effects.

Treybal[13] has stated that the general requirements of a satisfactory extractive-distillation solvent or entrainer are:

1. High selectivity, or ability to alter the vapor-liquid equilibria of the original mixture sufficiently to allow its easy separation, with only small quantities of entrainer.

2. High capacity, or ability to dissolve the components in the mixture to be separated. It frequently happens that substances that are incompletely miscible with the mixture are very selective; yet if sufficiently high concentrations of an entrainer cannot be obtained in the liquid phase, the separation ability cannot be fully developed.

3. Low volatility in order to prevent vaporization of the entrainer with the overhead product and to maintain high concentration in the liquid phase.

4. Separability; the entrainer must be readily separated from the mixture to which it is added, and particularly it must form no azeotrope with the original substances.

5. The same considerations of cost, toxicity, corrosive character, chemical stability, freezing point, and viscosity

apply to entrainers as to agents for azeotropic distillation.

Tassios[22] has also pointed out that the entrainer has physical and chemical effects on the constituents of the binary mixture. The chemical effect is due to the formation of a complex of loosely bound aggregates. This phenomenon, called solvation, is considered the result of a Lewis acid-base interaction. Usually, the physical effect is larger than any chemical effects, and usually, the physical and chemical effects complement one another.

Kolbe et al.[23] have proposed a procedure for the selection of entrainers for extractive distillation using both the UNIFAC model and UNIQUAC as shown in Figure 17.

Yeh[24] has applied the polarity diagram to compare the affinity of an entrainer for key components in binary and ternary mixtures, and used this chemical effect to explain the behavior of DMFA and DMSO in alcohols. Furthermore, the MOSCED model developed by Eckert et al.[25] was used to predict selectivity of entrainers and then entrainers were ranked based on predicted selectivity, but the MOSCED model cannot be applied to aqueous systems.

The selection of solvents or entrainers for extractive distillation by their capacity is another important issue. Knapp et al.[26] used minimum entrainer flows in extractive distillation to second-tier rate a set of entrainers. Their approach depends upon analyzing bifurcations of the finite difference equations describing the middle section of the

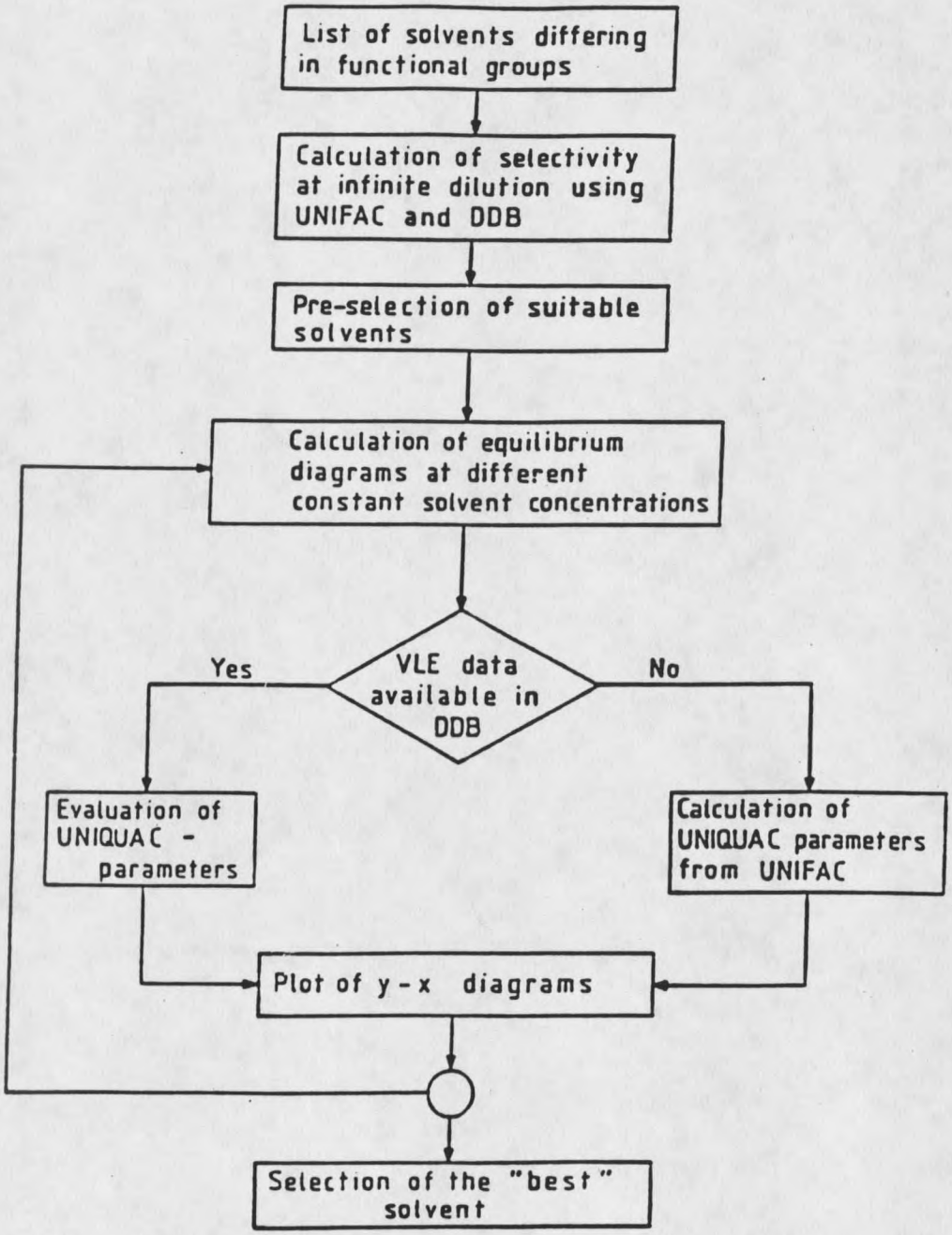

Figure 17 Procedure for the selection of extractive solvents based on UNIFAC and UNIQUAC models [23]

column for a mixture with a given VLE model.

In summary, selecting entrainers and ranking them for azeotropic and extractive distillation is a complex and inexact activity, based to some extent on experience and experimentation. Furthermore, the underlying theory for entrainer selection is not adequate to allow the prediction of unique, complete and certain answers.

Selection of Azeotropic and Extractive Distillation

In many industrial mixtures the key components under consideration can be separated by extractive distillation and azeotropic distillation by the selection of a proper solvent or entrainer, and an economic comparison of the processes is usually required for the final decision. Another important consideration in the selection of a process is the thermal stability of the components, particularly that of the heavy key component and heavier key component which boils at a higher temperature than the heavy key component. Van Winkle[27] has pointed out that if one of these components is unstable or tends to decompose, polymerize, or otherwise react at a higher temperature level, it is better to use azeotropic distillation to keep the bubble-point temperature of the bottom product at its lowest point. A heavy solvent would increase the bubble point above this temperature and could have a deleterious effect on the components in the bottom product.

Gerster[28] has indicated that if the feed is a close-boiling hydrocarbon pair, the differences in the physical properties of the feed components is usually comparatively small, so that an agent is required to improve the relative volatility over the entire height of the column; this is achieved best in extractive distillation where the agent enters at, or near the top of the column, and is discharged at the bottom of the column. He has also noted that azeotropic distillation is particularly useful when the feed component selected to come overhead as an azeotrope with the solvent is present in the feed in small amounts since in such an instance the amount of solvent or entrainer needed to be circulated is small, resulting in only small additional steam costs because of the presence of the solvent, and in a low solvent recovery cost.

Barnicki et al.[29] have classified the separations of liquid mixtures into two types: dilute and bulk. A separation is considered dilute when the total distillate or bottoms of a potential distillation operation is less than 5% of the feed, such as the recovery of acetic acid from dilute acetic acid-water mixtures. In addition, a large distillate-to-bottom (D/B) ratio has a greater effect on the economics of a distillation than small (D/B) ratio. Mixtures composed of mostly low-value, low-boiling components to be separated from a small amount (less than 10-15%) of low value, high-boiling component require a relatively large amount of energy to

Table 2. Heuristics and Rules for the Selection of Separation Methods.

Favored method	Conditions
Extractive distillation	generally favored; close-boiling mixtures.
Azeotropic distillation	very high-boiling azeotropes or close-boiling mixtures (above 170 °C); a low concentration (<10-15%) of the component that forms a minimum boiling azeotrope with the solvent; in this case, the minimum boiling azeotrope will go overhead[29].
Solvent extraction	a dilute solution (between 1% and 5%) of a high boiling, polar compound; extractive or azeotropic distillation would require vaporization of large amounts of the feed; temperature sensitive components in the feed; the separation of aliphatic or olefin hydrocarbon from aromatics[29].

vaporize the 85-90% of the feed that will appear in the distillate. In these cases, extractive and azeotropic distillation can be eliminated as potential methods, solvent extraction is favored.

Some components may decompose or react unfavorably at the temperature needed for distillation. Moreover, the freezing point of a component may be too high for distillation to be carried out at an acceptable temperature and pressure. In these cases, extractive, or azeotropic distillation cannot be used. Again, solvent extraction is favored.

Treybal[12] has shown that extractive distillation is generally considered more desirable than azeotropic distillation since (1) there is a greater choice of agents because the process does not depend upon the accident of

azeotrope formation and (2) smaller quantities of an agent must be vaporized.

Figure 18 gives the relative volatility for azeotropic distillation, extractive distillation, and solvent extraction that are required to give equal plant cost[30]. This comparison is based on the assumptions of 67% solvent concentration and four times as much liquid in extractive distillation and in solvent extraction as in ordinary distillation. The ordinate represents the relative volatility required in extractive distillation or in solvent extraction and the abscissa the relative volatility for ordinary distillation.

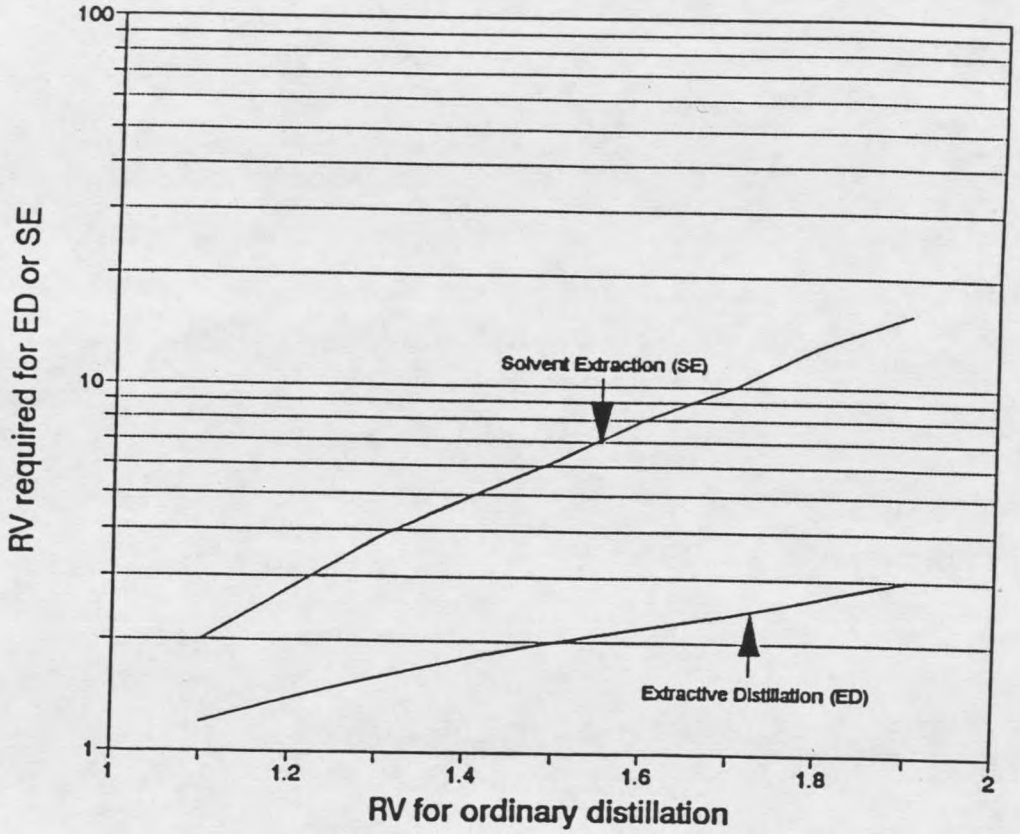

Figure 18 Relative volatility required for different separation with equal cost[30]

CHAPTER 3

SOLVENT SELECTION CRITERIA

Although the final selection of solvents must be determined by means of an economic evaluation in which all variables and criteria are considered for the whole process including the recovery process, screening solvents at the preliminary stage should consider two aspects: separation enhancement and easy reversibility.

Separation Enhancement Characterization

The separation enhancement is a major concern for the separation aided by adding a solvent. Figure 19 shows that the successful separation of acetone-methanol azeotrope can be carried out through distillation by modification of its vapor-liquid equilibrium by adding DMSO and MEK[24]. The degree of separation enhancement can be expressed by either relative volatility or selectivity.

Separation Factor

The degree of separation that can be obtained with any

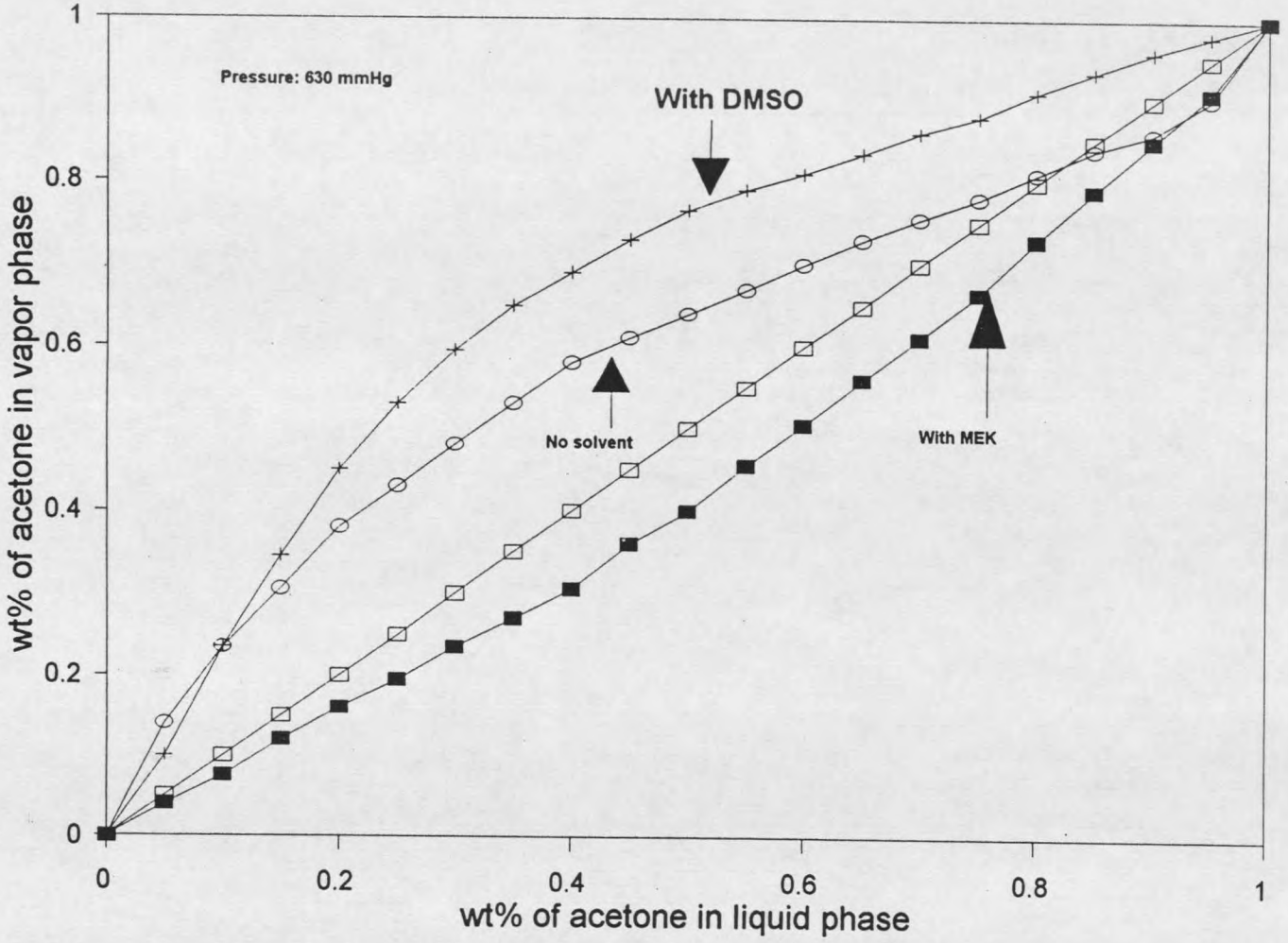

Figure 19 Vapor-liquid equilibrium curves for the methanol-acetone system with solvents and with no solvent [24]

particular separation process is indicated by the separation factor:

$$\alpha^{s}_{ij} = \frac{x_{i1}/x_{j1}}{x_{i2}/x_{j2}} \qquad (1)$$

The separation factor α^{s}_{ij} between components i and j is the ratio of the mole fractions of those two components in product 1 divided by the ratio in product 2. An effective separation is accomplished to the extent that the separation factor is significantly different from unity. If $\alpha^{s}_{ij} = 1$, no separation of components i and j has been accomplished. If $\alpha^{s}_{ij} > 1$, component i tends to concentrate in product 1 more than component j does, and component j tends to concentrate in product 2 more than component i does. On the other hand, if $\alpha^{s}_{ij} < 1$, component j tends to concentrate preferentially in product 1 and component i tends to concentrate preferentially in product 2. By convention, components i and j are generally selected so that α^{s}_{ij}, defined by Equation (1), is greater than unity.

Relative Volatility

For a vapor-liquid system, the separation factor is written as

$$\alpha_{ij} = \frac{y_{i1}/x_{j1}}{y_{i2}/x_{j2}} = \frac{\gamma_i P_i^{\circ}}{\gamma_j P_j^{\circ}} \qquad (2)$$

where α is the relative volatility, x is the liquid phase mole fraction, y is the vapor phase mole fraction, γ is the

activity coefficient, and P° is the pure component vapor pressure. The goal of the selection of solvents is to change the relative volatility, α_{ij}, as far away from unity as possible. The initial design phase for distillation involves determining the number of theoretical plates (NTP at finite reflux) required because of its impact on the column cost. The connection between the minimum number of theoretical plates N_{min} (at infinite reflux) required for a specified separation purity and relative volatility is established through the Fenske equation[27],

$$N_{min}=\frac{\log[(x_i/x_j)_d]/(x_i/x_j)_b]}{\log\alpha_{ij}} \qquad (3)$$

where d means the distillate product while b means the bottom product. The value of N_{min} includes the reboiler as an equilibrium stage. It should be noted that the relative volatility, α_{ij}, may be approximated as the geometric means of the relative volatility values at the top and bottom of the column:

$$\alpha_{av}=(\alpha_d\alpha_b)^{1/2} \qquad (4)$$

If there is a wide variation of relative volatility between top and bottom, an additional value, α_F, can be used in the average:

$$\alpha_{av}=(\alpha_d\alpha_F\alpha_b)^{1/3} \qquad (5)$$

where F represents the feed. Figure 20 shows the relationship between the minimum number of theoretical plates required for

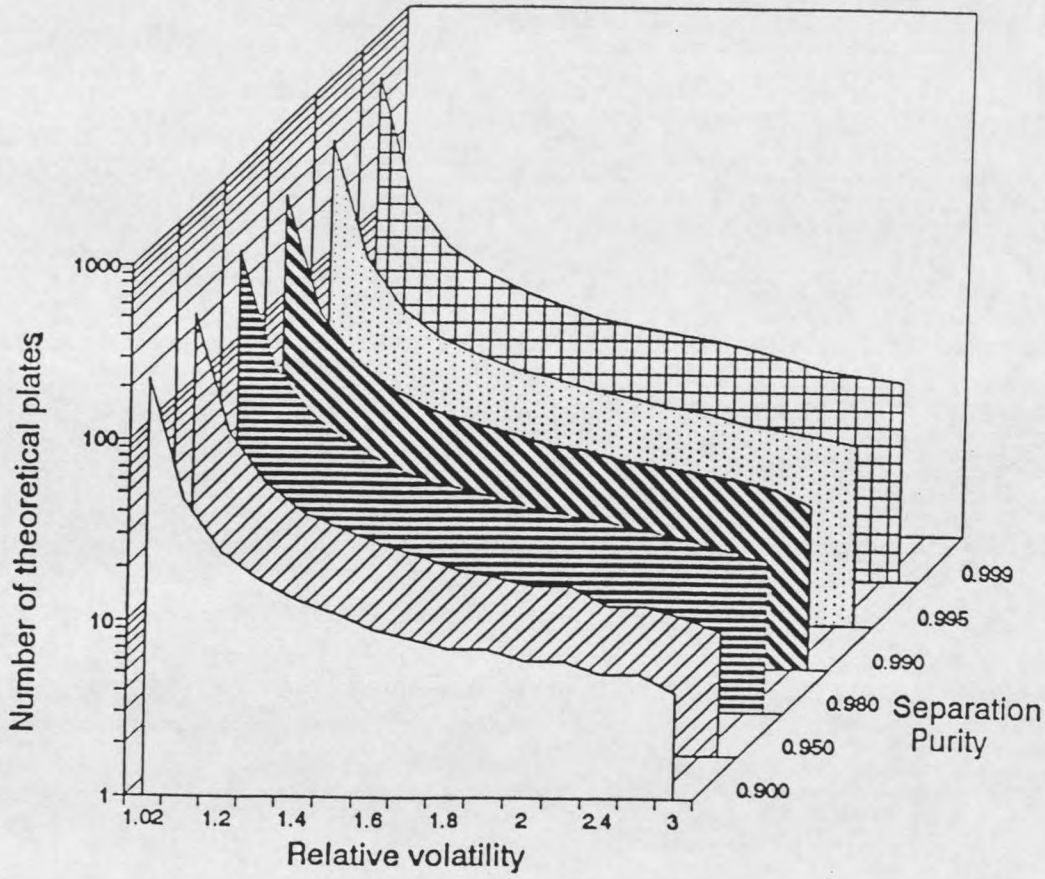

Figure 20 NTP requirements for different relative volatilities [27]

different separation purity and relative volatility at total reflux. It can be seen that the number of theoretical plates approaches infinity as the relative volatility becomes closer to unity. That is the situation for the presence of an azeotrope or close-boiling mixture. The number of theoretical plates decreases rapidly when the relative volatility increases to about 1.25. Figure 21 presents the number of theoretical plates and column cost as functions of relative volatility. It can be seen that the column cost has a similar relation to relative volatility as does the number of theoretical plates.

Selectivity

Since the ratio (P_i°/P_j°) is nearly constant for small temperature changes, the only way the relative volatility is affected is by introducing a solvent which changes the ratio (γ_i/γ_j). This ratio, in the presence of the solvent, is called the selectivity (S_{ij}):

$$S_{ij}=[\gamma_i/\gamma_j]_{solvent} \qquad (6)$$

The activity coefficients of the components at finite concentrations in the solvent depend on the mixture composition. A high selectivity gives a high relative volatility, making an easier separation possible. S_{ij} increases with increasing solvent concentration as shown in Figure 22, usually becoming a maximum at 100% solvent[21], and falls with rising temperature as Figure 23 shows. The preliminary

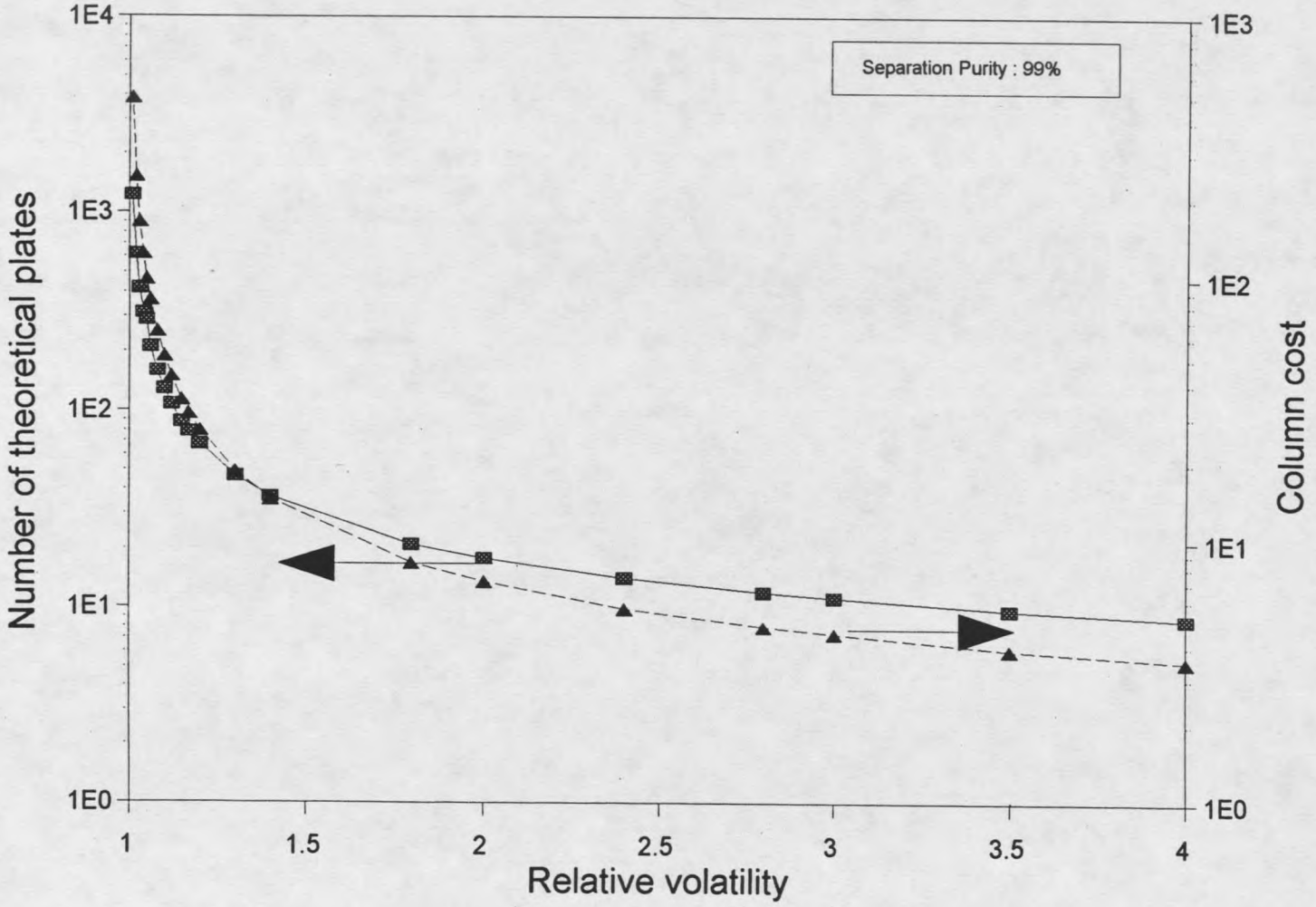

Figure 21 NTP and column cost vs. relative volatility[24]

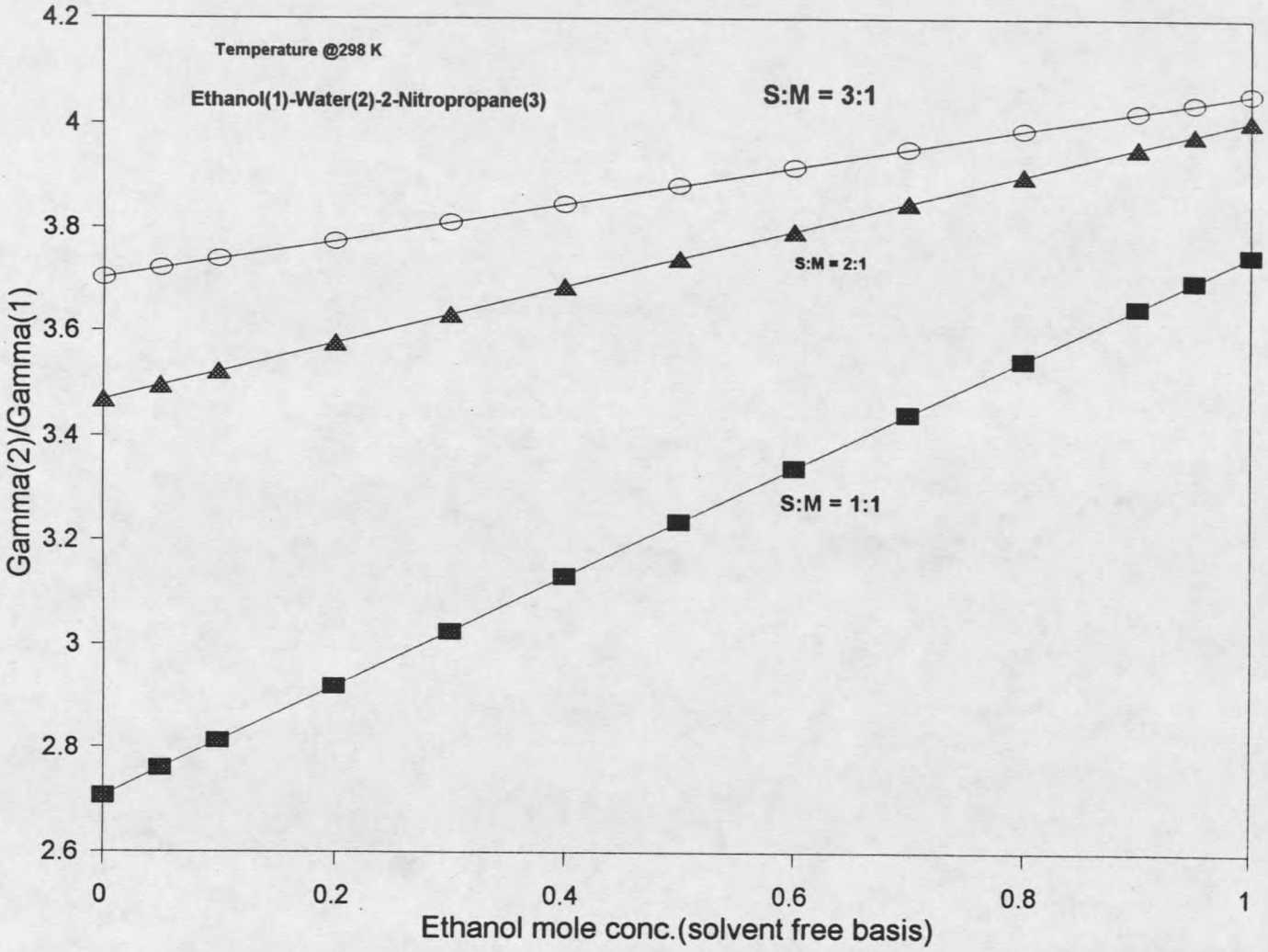

Figure 22 Effect of ratio of solvent to mixture on selectivity

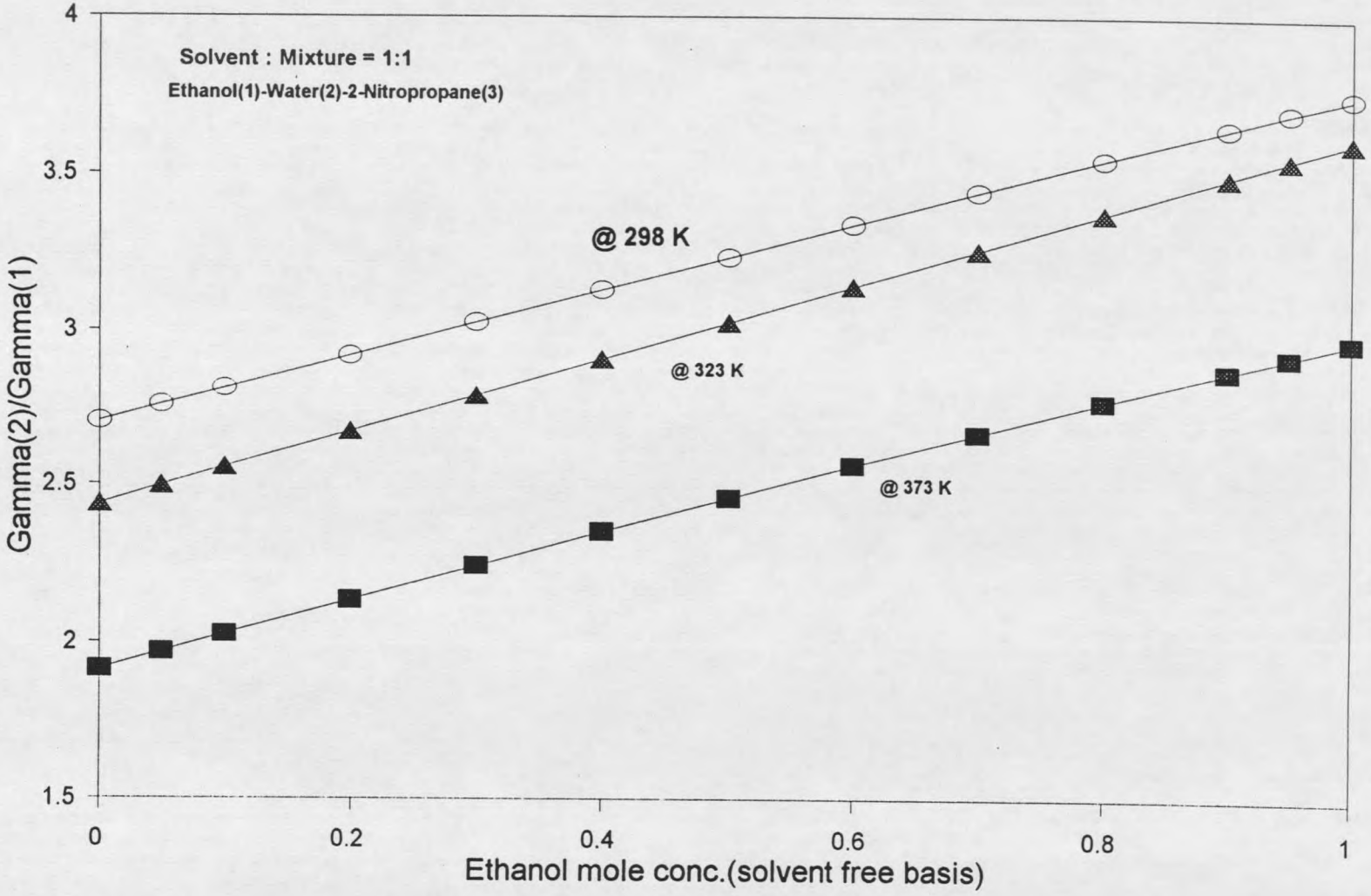

Figure 23 Effect of temperature on selectivity

selection of solvents can be based upon the limit selectivity, which is defined as the ratio of the activity coefficients of the key components when each alone is present in the solvent at infinite dilution,

$$S^{\infty}=\gamma^{\infty}_{i}/\gamma^{\infty}_{j} \qquad (7)$$

Kumar and Prausnitz[31] have discussed the annual process cost for the separation of propylene-propane system based on the limit selectivity at infinite dilution. As Figures 24 and 25 show, the annual cost falls with increasing selectivity, and the total extractive distillation process cost is approximately the same as that for binary distillation for propylene-propane at a selectivity of 2.6. A further increase of the limit selectivity makes extractive distillation process more economically attractive than conventional distillation.

Activity Coefficients at Infinite Dilution

Comparing the limit selectivity of different solvents according to Equation 7 depends upon activity coefficients at infinite dilution (ACID). ACID can be obtained from experiment, or estimated using semi-empirical and semi-theoretical thermodynamic models, or compiled ACID data in text[32] or database[33] form. Table 3 lists several good experimental techniques available for determining ACID.

The references listed in Table 3 contain experimentally measured ACID values for some binary systems.

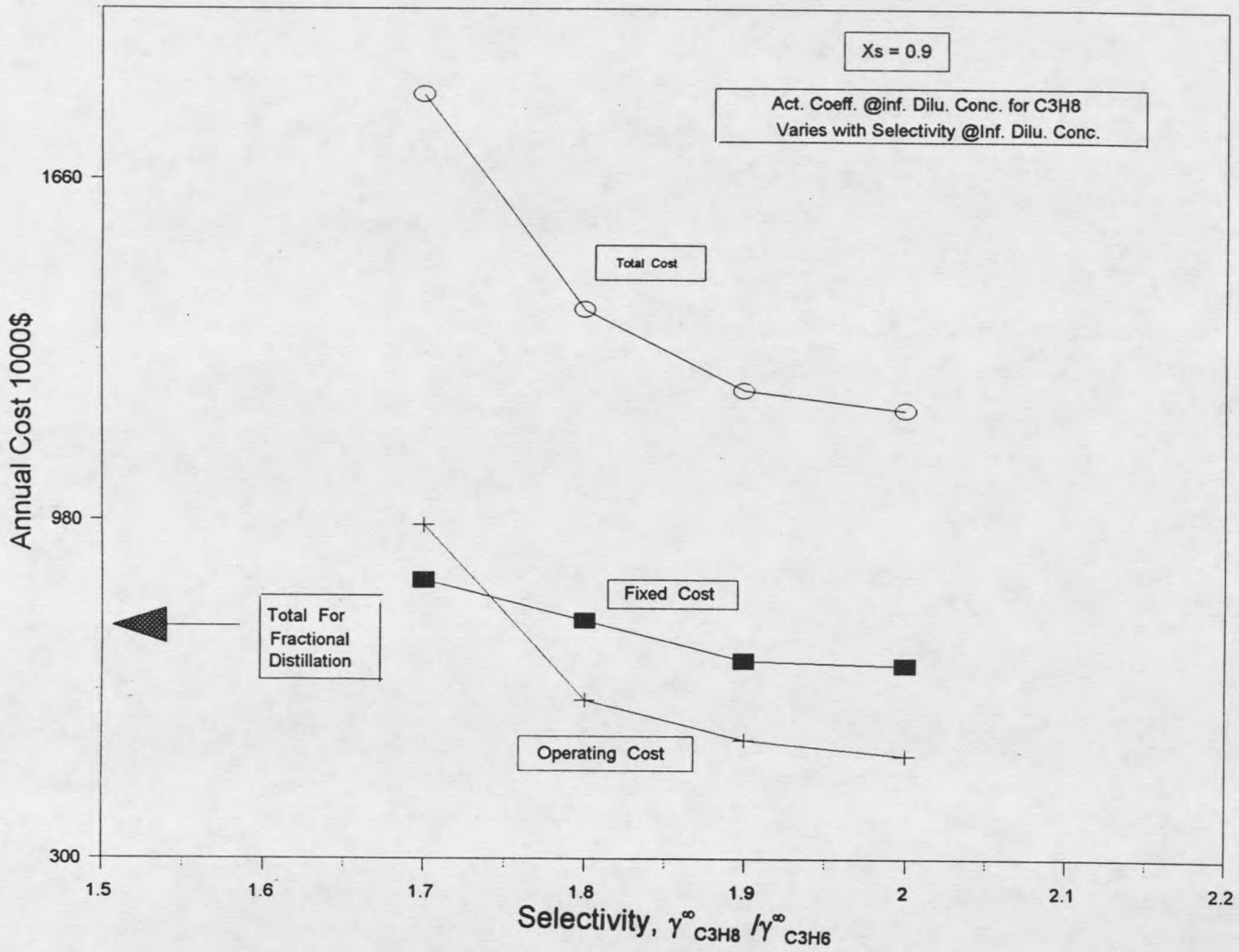

Figure 24 Effect of solvent selectivity on cost for low selectivity [31]

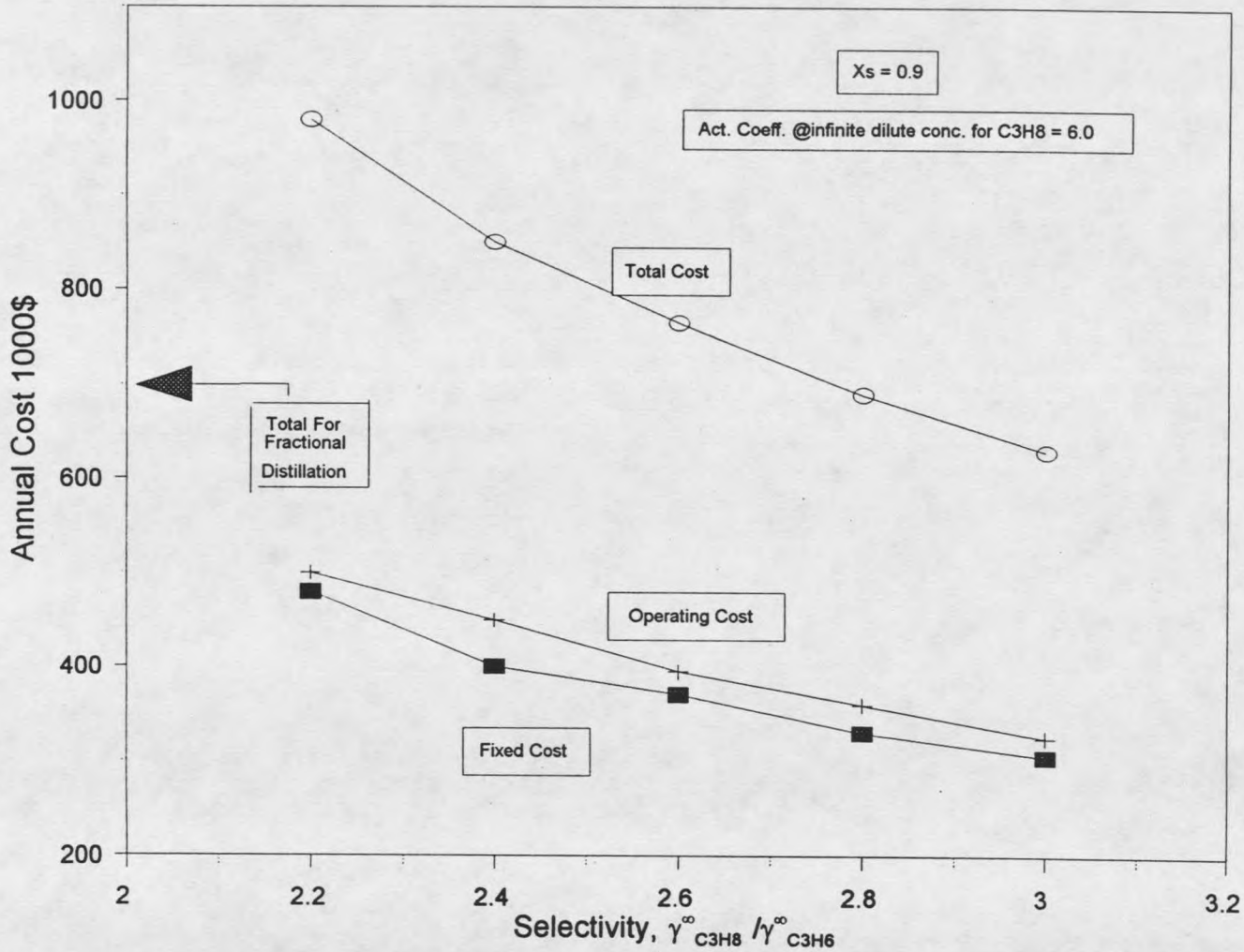

Figure 25 Effect of solvent selectivity on cost for high selectivity [31]

Table 3. Experimental Methods for Determining ACID.

Method	Author	Reference
Dew Point Measurement	Trampe and Eckert	[34]
Dynamic Gas Chromatography	Pescar and Martin	[35]
	Shaffer and Daubert	[36]
Gas Stripping	Leori et al.	[37]
	Richon et al.	[38]
Differential Ebulliometry	Scott	[39]
	Trampe and Eckert	[40]
Headspace Chromatography	Hassam and Carr	[41]

Thermodynamic Models for the Estimation of ACID

Activity coefficients at infinite dilution are so valuable in solvent evaluation for mass-aided separations that many efforts, empirical and theoretical, have been made to address this problem. Their application can frequently save extensive experimental or computational effort.

Many equations proposed for correlating activity coefficients with composition and temperature can be extended to the infinite dilution situation. The correlations applicable to binary systems at infinite dilution are listed in Table 4.

These types of equations require empirical interaction parameters between two components that can be found in the DECHEMA Vapor-Liquid Data Collection for many binary systems. Unfortunately, much such information is not available for solvent selection applications.

The importance of a knowledge of γ^{∞} has led to the development of different prediction methods. The solubility parameter approach developed by Scatchard-Hildebrand[47] has

Table 4. Binary Activity-Coefficient Correlations at Infinite Dilution.

TYPE of equation	$\ln \gamma^{\infty}_1 = \ldots\ldots$ $\ln \gamma^{\infty}_2 = \ldots\ldots$
Margules[42]	A_{12} A_{21}
van Laar[43]	A_{12} A_{21}
Wilson[1)][44]	$1-\ln \Lambda_{12}-\Lambda_{21}$ $1-\ln \Lambda_{21}-\Lambda_{12}$
NRTL[2)][45]	$\tau_{12}\ \exp(-\alpha_{12}\tau_{12})+\tau_{21}$ $\tau_{21}\ \exp(-\alpha_{12}\tau_{21})+\tau_{12}$
UNIQUAC[3)][46]	$\ln r_1/r_2+q_1[(z/2)\ln(q_1r_2/q_2/r_1)-\ln\tau_{21}+1-\tau_{12}]+l_1-r_1l_2/r_2$ $\ln r_2/r_1+q_2[(z/2)\ln(q_2r_1/q_1/r_2)-\ln\tau_{12}+1-\tau_{21}]+l_2-r_2l_1/r_1$

1) $\Lambda_{ij} = V_j/V_i \exp[-(\lambda_{ij} - \lambda_{ii})/RT]$
V_i molar volume of pure liquid component i
λ_{ij} interaction parameter between component i and j; $\lambda_{ij}=\lambda_{ji}$

2) $\tau_{ij} = (g_{ij} - g_{jj})/RT$
g_{ij} interaction parameter between component i and j; $g_{ij}=g_{ji}$
α_{ij} nonrandomness parameter; $\alpha_{ij}=\alpha_{ji}$

3) $\tau_{ij} = \exp[-(u_{ij} - u_{jj})/RT]$
u_{ij} interaction parameter between component i and j; $u_{ij}=u_{ji}$
r_i relative van der Waals volume of component i
q_i relative van der Waals surface area of component i
$l_i = z/2(r_i-q_i)-(r_i-1)$
z coordination number; z = 10

been widely used; and modifications, improvements and extensions have been proposed by many authors. Yeh[24]

summarized all the models developed along this line to 1986. Modifications continue to be proposed. Table 5 lists all the expressions established so far based on solubility parameters.

The most accurate prediction method for γ^{∞} according to solubility parameter approach is the MOSCED model proposed by Thomas and Eckert[56], which gives an average error of 9.1% for 3357 values of γ^{∞}. The original MOSCED model contains three adjustable parameters. Among them, acidity/basicity parameters are difficult to obtain or estimate. Also, the MOSCED is limited in application now to monofunctional species for which certain pure component data are available. Moreover, the MOSCED cannot apply to aqueous systems. An improved model using solvatochromic parameters for estimating the MOSCED acidity/basicity parameters, developed by Howell et al.(1989) [57], has reduced the number of adjustable model parameters from 3 to 1 + (one per compound, plus two per class). Nevertheless, this is achieved at the price of increasing the overall average error from 9.1% to 11% (fitted data) and from 13% to 15% (predicted data). An empirical modification of the MOSCED model with the addition of three adjustable constants per class was proposed by Wu et al.[58] as follows:

$$\ln \gamma^{\infty}_1 = V_1/RT[(\lambda_1-\lambda_2)^2+q_1^2q_2^2(\tau_1-\tau_2)^2/\varsigma_2+ (\alpha_1-\alpha_2)(\beta_1-\beta_2)/\xi_2+C_1(\lambda_1-\lambda_2)+C_2(\tau_1-\tau_2)(\alpha_1-\alpha_2)+C_3] +\ln(V_1/V_2)^{aa}+1-(V_1/V_2)^{aa} \quad (8)$$

Where C_1, C_2, and C_3 are empirical constants for one type of system and are obtained by regression from experimental γ^{∞}

Table 5. Models for Estimation of Activity Coefficient at Infinite Dilution Using Solubility Parameters.

Scatchard-Hildebrand[1] [47]

$$\ln \gamma^{\infty}_1 = V_1/RT(\delta_1-\delta_2)^2$$

Scatchard-Hildebrand-Flory-Huggins [48]

$$\ln \gamma^{\infty}_1 = V_1/RT(\delta_1-\delta_2)^2+\ln(V_1/V_2)+1-V_1/V_2$$

Prausnitz-Anderson-Weimer[2] [49]

$$\ln \gamma^{\infty}_1 = V_1/RT[(\lambda_1-\lambda_2)^2+\tau_2^2-2\Psi_{12}]+\ln(V_1/V_2)+1-V_1/V_2$$
$$\Psi_{12} = c\tau_2^2$$

Helpinstill-Van Winkle[50]

$$\ln \gamma^{\infty}_1 = V_1/RT[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2-2\Psi_{12}]+\ln(V_1/V_2)+1-V_1/V_2$$
$$\Psi_{12} = c(\tau_1-\tau_2)^2$$

Hsieh-Newman[51][52]

$$\ln \gamma^{\infty}_1 = V_1/RT[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+(\sigma_1-\sigma_2)(\tau_1-\tau_2)]+\ln(V_1/V_2)+1-V_1/V_2$$

Hansen[53]

$$\ln \gamma^{\infty}_1 = V_1/RT[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+(\alpha_1\beta_1-\alpha_2\beta_2)^2]+\ln(V_1/V_2)+1-V_1/V_2$$

Tijssen-Billet-Schoenmakers[54]

$$\ln \gamma^{\infty}_1 = V_1/RT[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+2(\alpha_1-\alpha_2)(\beta_1-\beta_2)]+\ln(V_1/V_2)+1-V_1/V_2$$

Karger-Snyder-Eon[55]

$$\ln \gamma^{\infty}_1 = V_1/RT[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+2(\alpha_1-\alpha_2)(\beta_1-\beta_2)+2(\alpha_1-\alpha_2)(\tau_1-\tau_2)]$$

Thomas-Eckert's MOSCED model[56]

$$\ln \gamma^{\infty}_1 = V_1/RT[(\lambda_1-\lambda_2)^2+q_1^2q_2^2(\tau_1-\tau_2)^2/\varsigma_2+(\alpha_1-\alpha_2)(\beta_1-\beta_2)/\xi_2]+\ln(V_1/V_2)^{aa}+1-(V_1/V_2)^{aa}$$

data. The difficulty in obtaining constants makes this modification less useful to general systems although they claim that the average correlation and prediction relative

deviations were reduced from 7.97% (original MOSCED model) to 4.62% (Equation(8)). The difficulty of application of the original MOSCED to aqueous systems is not overcome by the empirically modified MOSCED model.

There is another approach based on the so-called group contribution to predict activity coefficients at infinite dilution. In the 1960's Pierotti et al.[59] suggested the use of the molecular structure as a basis for making quantitative estimates of activities in mixtures of nonelectrolytes. Starting from these considerations, Deal and Derr in 1969 [60] proposed the ASOG method for VLE calculations. Several modifications have been introduced by various authors (e.g. Kojima and Tochigi[61]). Similar approaches have been developed by Fredenslund et al.[62] who in 1975 presented the UNIFAC method. From 1975 onwards various modifications and improved tables of the interaction parameters have been published. The UNIFAC model is a convenient tool for the prediction of VLE; however, when the method is used for predicting γ^{∞}, results of poor quality are obtained[56].

This insufficiency and the incapability of the original UNIFAC method to provide quantitative and reliable estimates of heats of mixing have led to new modifications of the UNIFAC expression in which temperature is fitted to VLE, γ^{∞} and h^{E} data simultaneously. At present, there are two modified versions of the UNIFAC expression, developed in Dortmund by Weidlich and Gmehling [63], and developed in Lyngby, Denmark,

by Larsen et al.[64], respectfully. Table 6 shows a comparison of γ^{∞} results predicted by the Dortmund modified version of UNIFAC to the results of the original UNIFAC, as well as to several other thermodynamic models.

Table 6. Deviation Between Experimental and Predicted Activity Coefficients at Infinite Dilution. (Adapted from [32])

group contribution method	$\Delta\gamma^{\infty *}$†	$\Delta\gamma^{\infty}_{rel}{}^{\#}$† (%)	$\Delta\gamma^{\infty}$‡	$\Delta\gamma^{\infty}_{rel}$‡ (%)
ASOG	1.30	26.29	1.56	26.69
UNIFAC	1.42	26.03	1.85	25.82
Modified UNIFAC (Dortmund)	0.82	13.92	0.99	13.35
Modified UNIFAC (Lyngby)	1.53	21.72	1.68	21.15

Note: * $\Delta\gamma^{\infty} = |\gamma^{\infty}_{expt} - \gamma^{\infty}_{calc}|$;
$\Delta\gamma^{\infty}_{rel} = |(\gamma^{\infty}_{expt} - \gamma^{\infty}_{calc})/\gamma^{\infty}_{expt,max}| \times 100(\%)$;
† 10,000 data points.
‡ 9,900 data point.

From Table 6, it is obvious that the Dortmund modified UNIFAC version is superior to other group contribution methods. UNIFAC has an advantage that MOSCED does not have, namely, that UNIFAC has the ability to predict activity coefficients at infinite dilution for aqueous systems. Table 7 shows that the deviation between experimental and predicted activity coefficients at infinite dilution by UNIFAC (Dortmund version) are small and in the range acceptable for engineering applications.

Table 7. Predicted Infinitely Dilute Activity Coefficients by UNIFAC (Dortmund modification) for Aqueous Systems.

Solvent	Solute	Temp K	γ^{∞} Measured	γ^{∞} Predicted	%Difference*
Acetone	Water†	307.9	6.02±0.13	6.61	9.80
		318.1	5.68±0.1	6.18	8.80
		328.5	0.30±0.02	5.78	9.06
DMFA	Water†	353.7	0.96±0.12	1.05	9.38
		363.0	0.99±0.05	1.09	10.1
		367.7	1.02±0.03	1.12	9.80
		383.0	1.33±0.07	1.19	-10.5
Isopropanol	Water†	318.4	3.5±0.4	3.27	-6.57
		328.2	3.39±0.07	3.20	-5.60
		338.0	3.0±0.16	3.12	4.00
Methanol	Water†	307.8	1.6±0.2	1.63	1.88
		317.9	1.8±0.2	1.67	-7.22
		327.9	1.7±0.25	1.69	-0.59
		337.1	0.76±0.05	1.71	-2.84
Nitromethane	Water†	314.3	13.3±0.2	13.68	2.86
		322.5	11.8±0.5	12.13	2.80
		331.1	11.8±0.8	10.73	-9.07
		343.4	8.6±0.4	9.07	5.47
Water	DMFA†	323.2	0.89±0.4	0.79	-11.2
		333.1	0.35±0.26	0.92	-31.9
Water	Methanol‡	323	1.93	1.94	0.52
		373	2.75	2.46	-10.5
Water	Ethanol‡	323	5.42	5.32	-1.85
		373	5.21	5.93	13.8
Water	n-Propanol‡	313	20.9	14.58	-30.2
		333	16.8	15.13	-9.94
		369	14.3	15.30	7.00
Water	sec-Butanol‡	333	39.7	36.74	-7.46
		367	32.1	34.53	7.57

* %Difference = (Pred. - Meas.)/Meas.× 100.
† Measured data is from Ref.[65], ‡ Measured data is from Ref.[66].

Easy Reversibility

Easy reversibility in this case means low distillation energy requirements and ease of producing a solute-free solvent that can be recycled to the primary extractive or azeotropic distillation column. A low latent heat of vaporization of the solvent will reduce the reboiler heat load. It is desirable that the solvent-solute system introduced into the solvent-recovery column do not form an azeotrope or a close-boiling mixture.

For the recovery of the entrainer from azeotropic distillation process, Berg made the following comments[12]:

> Pressure-swing rectification offers a simple means of recovering the entrainer from its azeotrope, provided the vapor pressure-temperature relation is such that the azeotrope composition varies considerably with pressure. If a solvent can be found capable of affecting a complete separation by extraction alone and which is readily separated from the extract, solvent extraction is an attractive method of recovering the original entrainer.

The classical process of recovering the entrainer from azeotropic distillation is a decantation unit plus a conventional distillation column. Stripping, absorption, and solvent extraction are the alternative techniques for recovery.

CHAPTER 4

EXPERT SYSTEMS AND SELECTION PROBLEMS

Introduction to Expert Systems

Experts, as used here, are people who have become proficient at something from long-term experience, and whose knowledge is therefore valuable within its specific domain. Using decision-making heuristics, experts can make skillful judgements at crucial moments, even in situations where the information on which such decisions ought ideally to be based is insufficient.

An expert system is an advanced computer program that attempts to emulate human expert decision making. Waterman[67] defined an expert system as:

> A computer program that uses expert knowledge to attain high levels of performance in a narrow problem area. These programs typically represent knowledge symbolically, examine and explain their reasoning processes, and address problem areas that require years of special training and education for a human to master.

By capturing and manipulating the knowledge of human experts, expert systems provide advantages of availability, consistency, and testability. The key components of expert systems and their relationships are shown in Figure 26. An

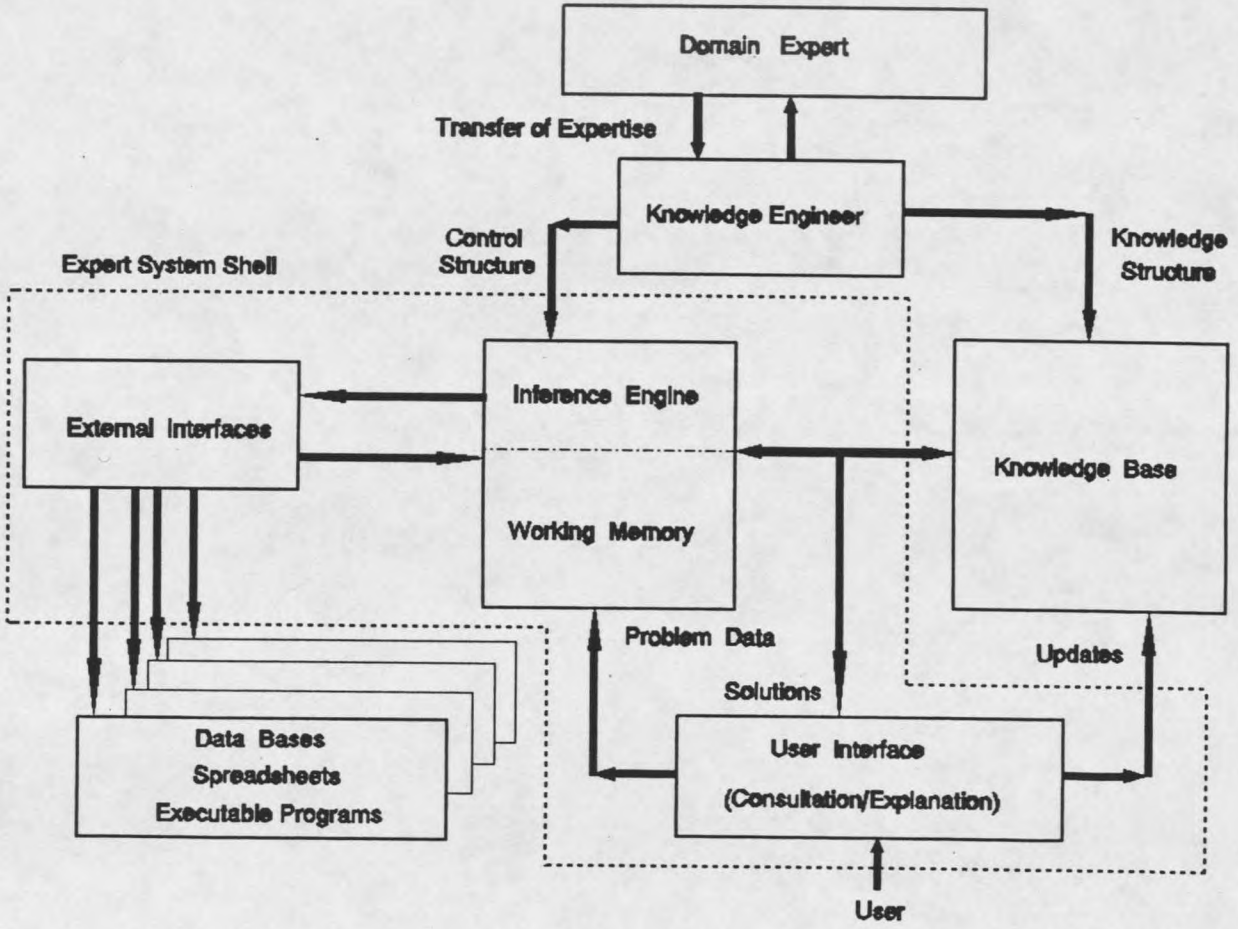

Figure 26 Integration of expert system components[67]

expert system itself usually contains:

(1) a knowledge base;

(2) an inference engine;

(3) a user interface;

(4) external interfaces; and

(5) data bases.

The knowledge base contains specific, in-depth information about the problem at hand. That knowledge consists of facts, rules, heuristics, semi-empirical models, etc.

To utilize the knowledge, an expert system relies on its inference engine. The inference engine uses inference mechanisms to process the knowledge and draw conclusions.

The user interface provides smooth communication between the program and the user.

The external interfaces provide the facilities to connect an inference engine with databases and external executable programs.

The database is a repository of some facts for the domain problem.

The knowledge, extracted from the domain expert, is obtained through the process of knowledge acquisition by the system developer, the so-called knowledge engineer among AI researchers. This knowledge provides the system with its expert reasoning capabilities. The developer then utilizes AI programming languages or software to construct the knowledge base, create the user interface, write external

executable programs if needed, establish the database, and combine them to make everything function as an integrated system. During the earlier stages of AI research, two programming languages, LISP and PROLOG, were developed to deal with the symbolic representation and reasoning for AI research work, including expert system development. This was done because conventional programming languages such as FORTRAN and PASCAL lack the abilities to efficiently handle qualitative knowledge. Then, the expert system developer who was equipped with LISP and PROLOG often devoted too much time to organizing and constructing the inference engine. Later on, AI researchers realized that the inference part of an expert system is independent of the domain knowledge and therefore can be separated from the knowledge base. Therefore, a variety of software tools that contain the inference engine and other facilities aimed at speeding up expert system development have become commercially available for meeting the needs of the expert system building. Depending on the capabilities of the development tools, the developer may also construct or modify the inference engine. Usually, this step is not necessary because modern expert system shells provide the developer with strong inference facilities.

Expert System Shell--LEVEL 5 OBJECT

As shown in Figure 26, expert systems use a combination

of user interface, inference mechanisms, and external interfaces, together called the expert system shell, for handling knowledge. The expert system shell, in which the specific domain knowledge is removed, can facilitate the construction of an expert system in any domain justified for the expert system development by providing the basic control structure, knowledge representation methodologies, and constructs for the user interface creation. In this work, the expert system shell, called LEVEL 5 OBJECT® developed by Information Builders, Inc. was used as a development environment for our prototype expert system. LEVEL 5 OBJECT is an application development environment that combines expert system technologies, object-oriented programming (OOP), relational database models, and graphical development and debugging tools. To provide a graphics-based user interface, LEVEL 5 OBJECT is run under Microsoft Windows. Table 8 shows the basic features of LEVEL 5 OBJECT.

Expert System Applications in Chemical Engineering

Expert systems have been successfully applied to financial management and planning, marketing, patient diagnoses, prospecting ore deposits, and military operations.

Expert systems have begun to penetrate chemical engineering. With the growing availability of powerful and inexpensive hardware, using an expert system is now within the