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

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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APPROVAL

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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

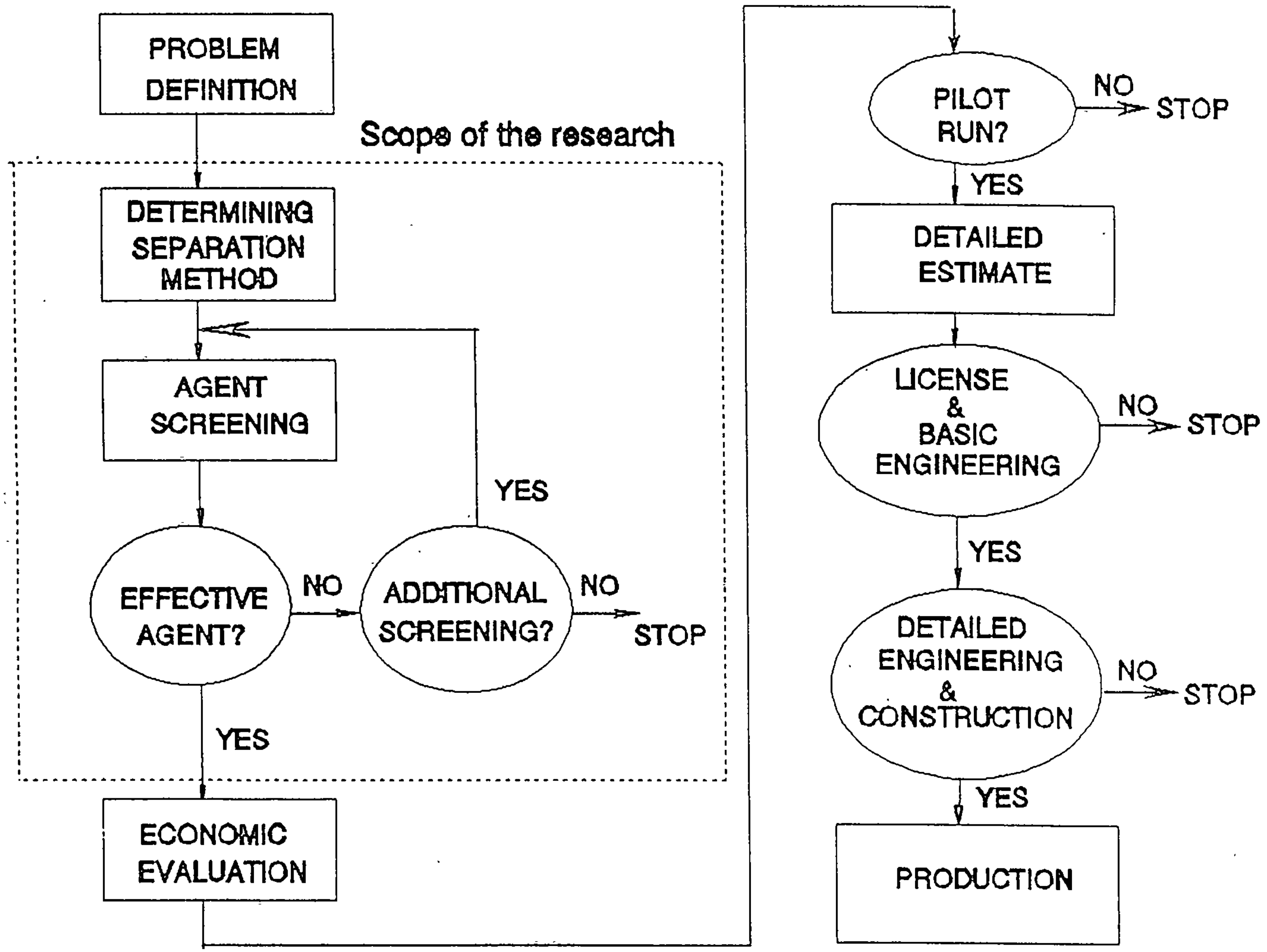


Figure 1 Process development steps for the mass-based separation and the scope of this research [2]

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

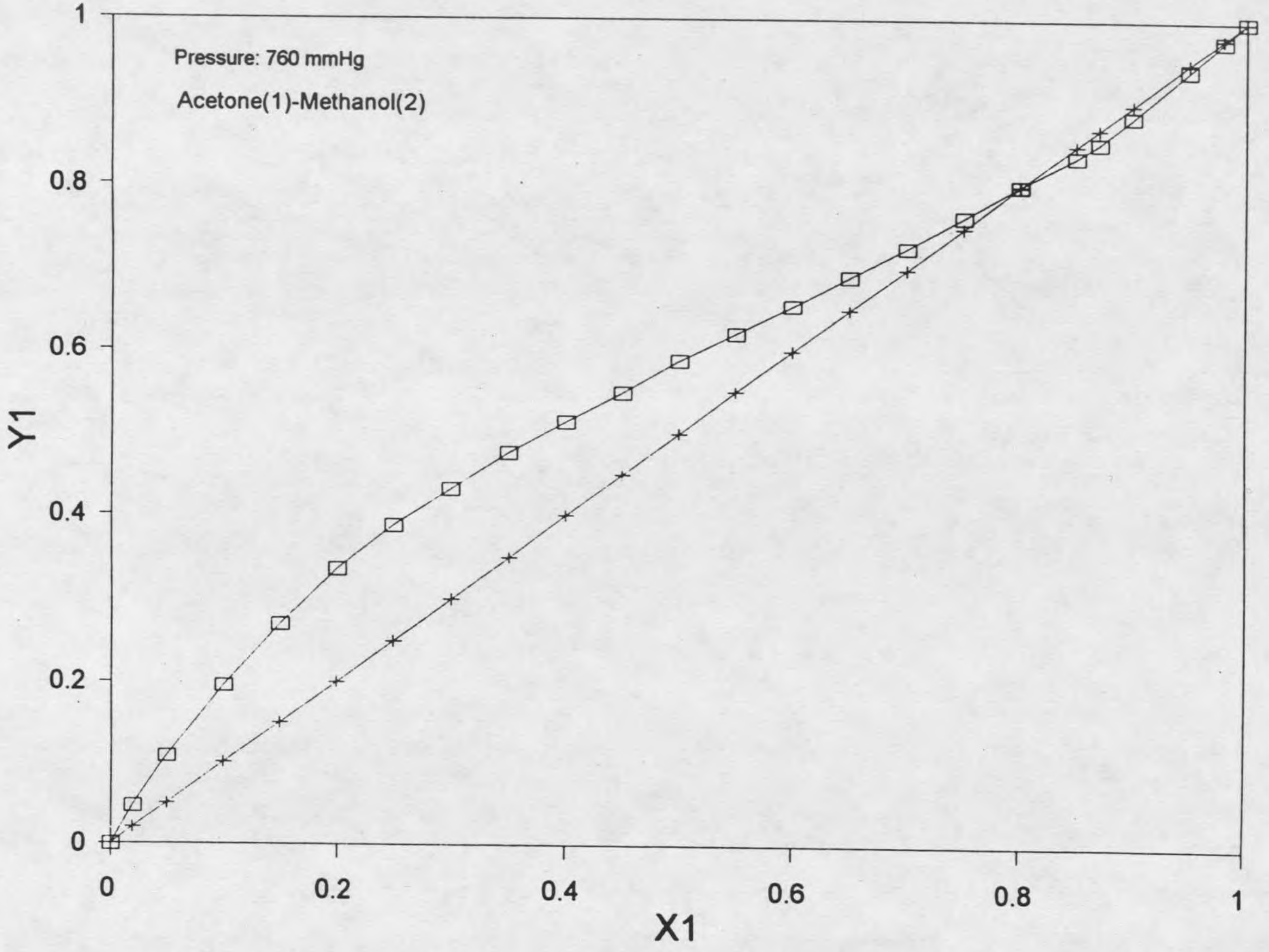


Figure 2 Liquid mole fractions and vapor mole fractions for minimum-boiling mixtures of acetone and methanol[4]

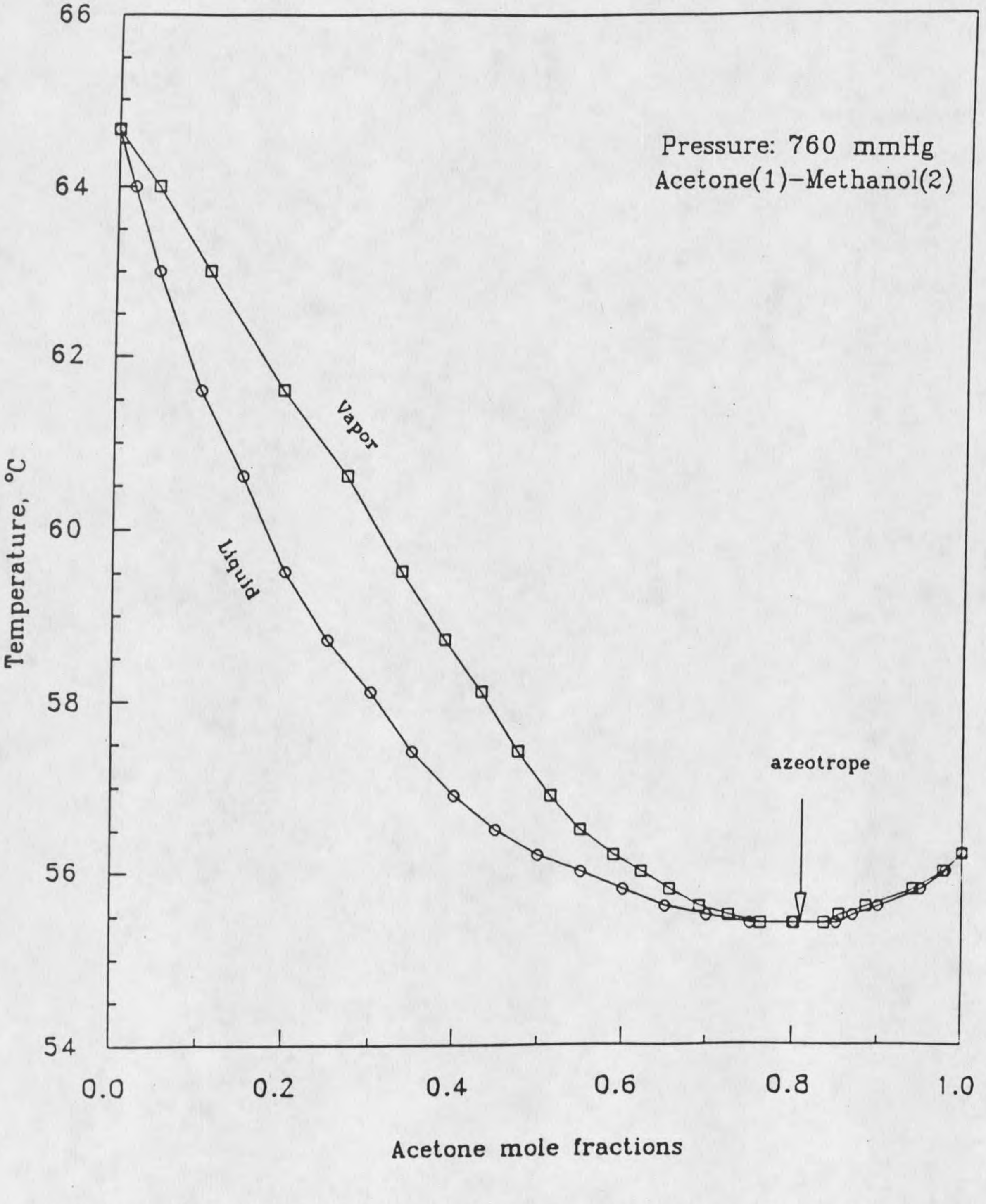


Figure 3 Liquid boiling points and vapor condensation temperatures for minimum-boiling azeotropic mixture of acetone and methanol[4]

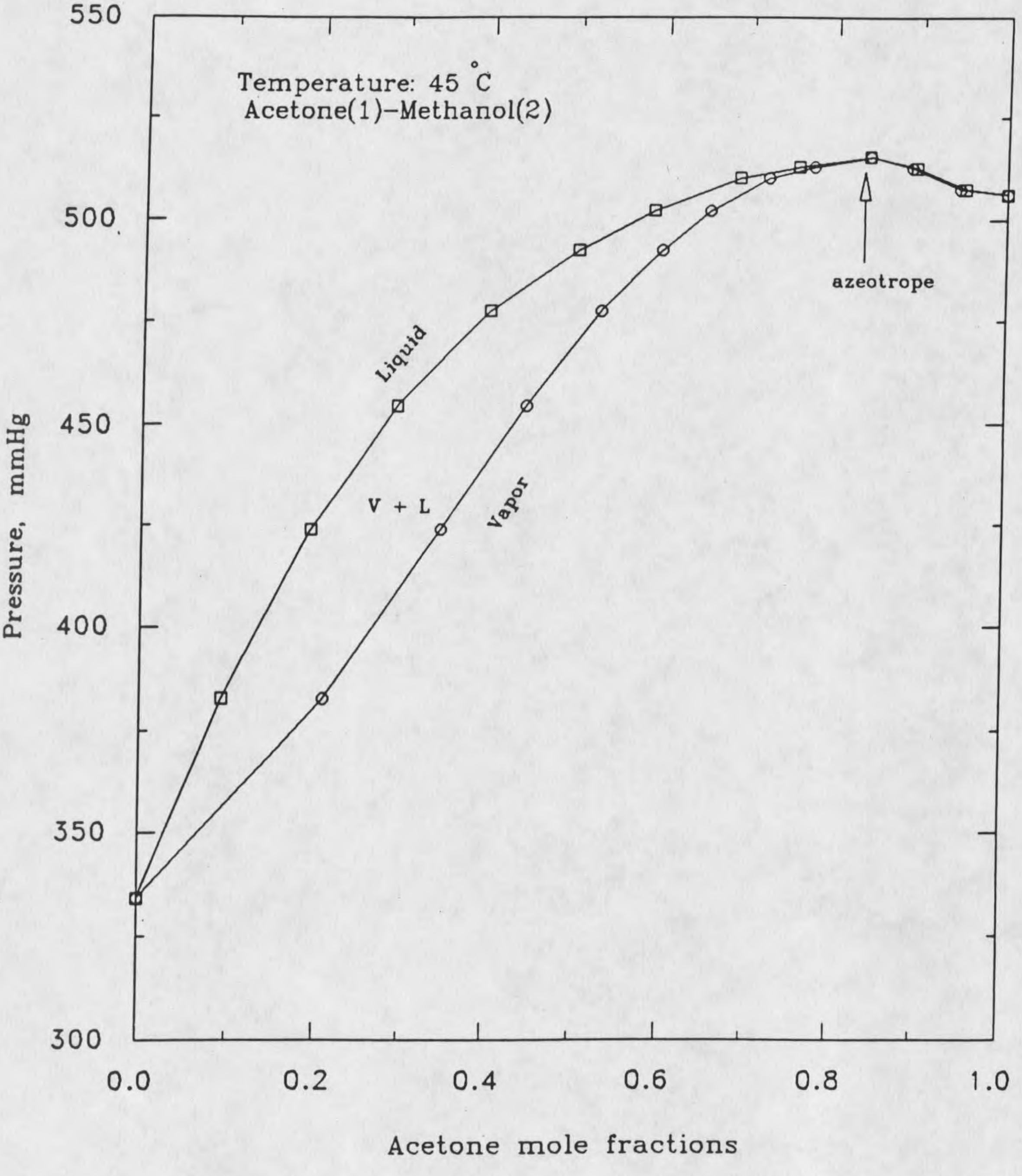


Figure 4 Pressure and Liquid Compositions for Minimum-Boiling Azeotropic Mixture of Acetone and Methanol[4]

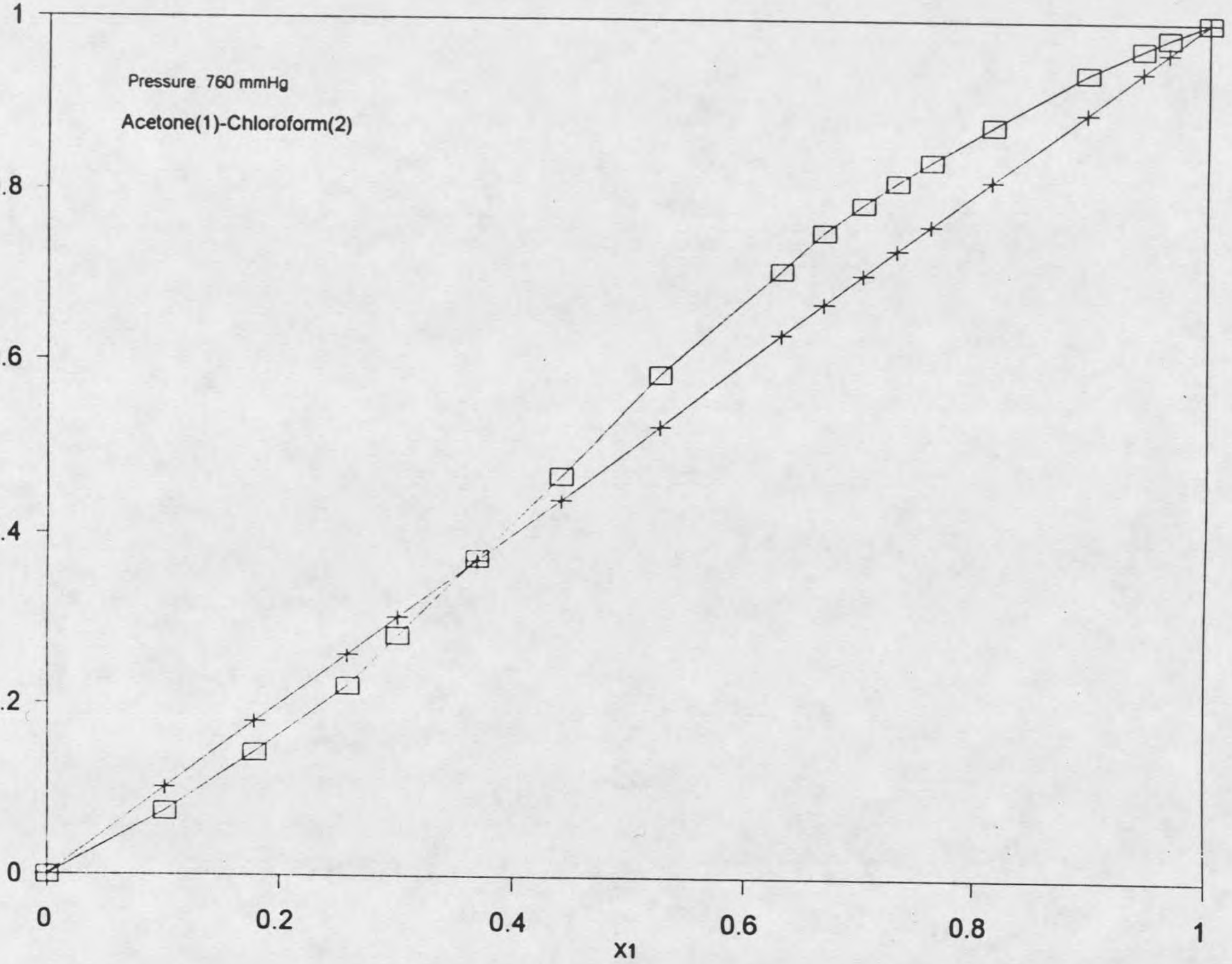


Figure 5 Liquid mole fractions and vapor mole fractions for maximum-boiling azeotropic mixture of acetone and chloroform[4]

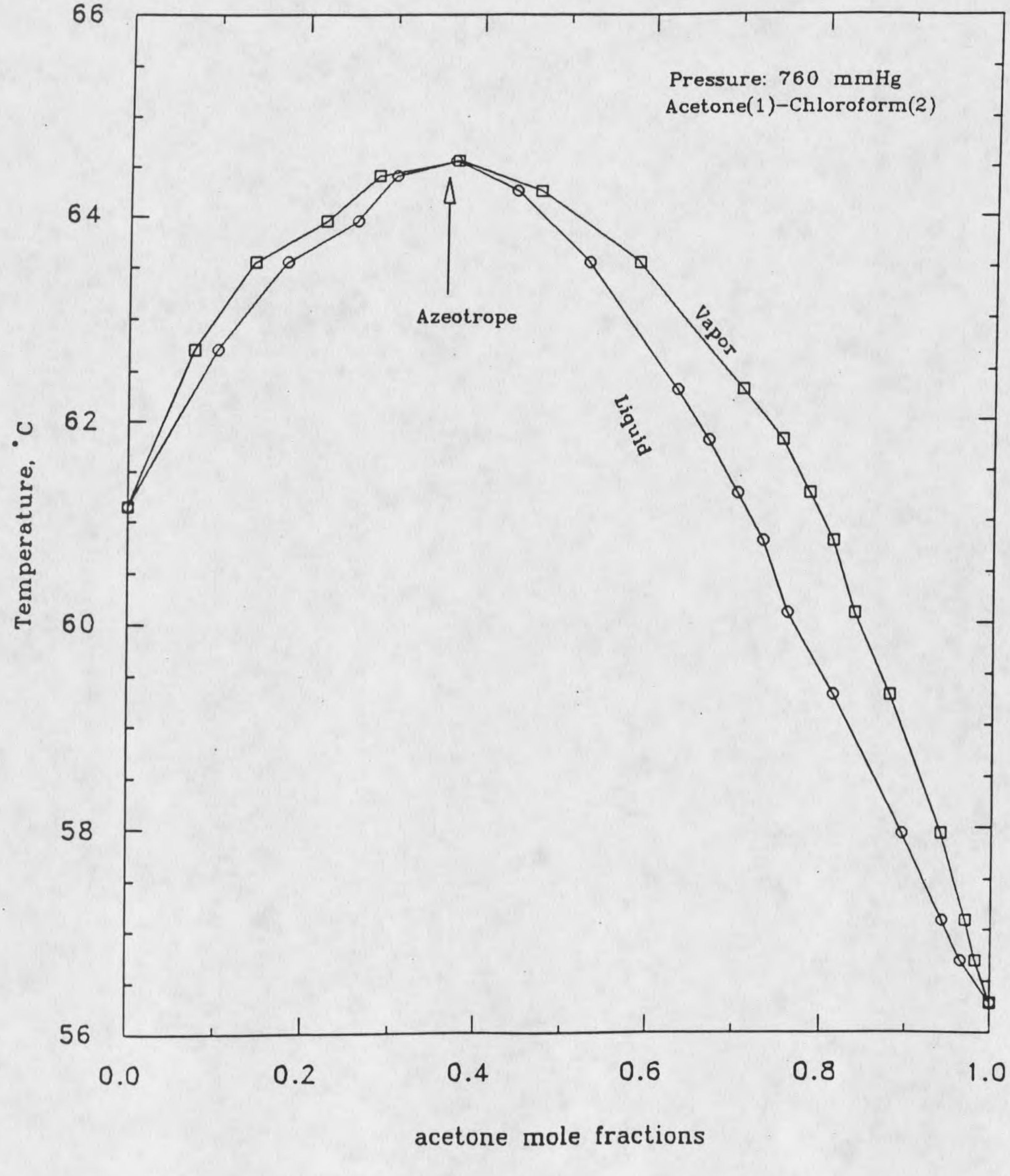


Figure 6 Liquid boiling point and vapor condensation temperatures for maximum-boiling azeotropic mixture of acetone and chloroform[4]

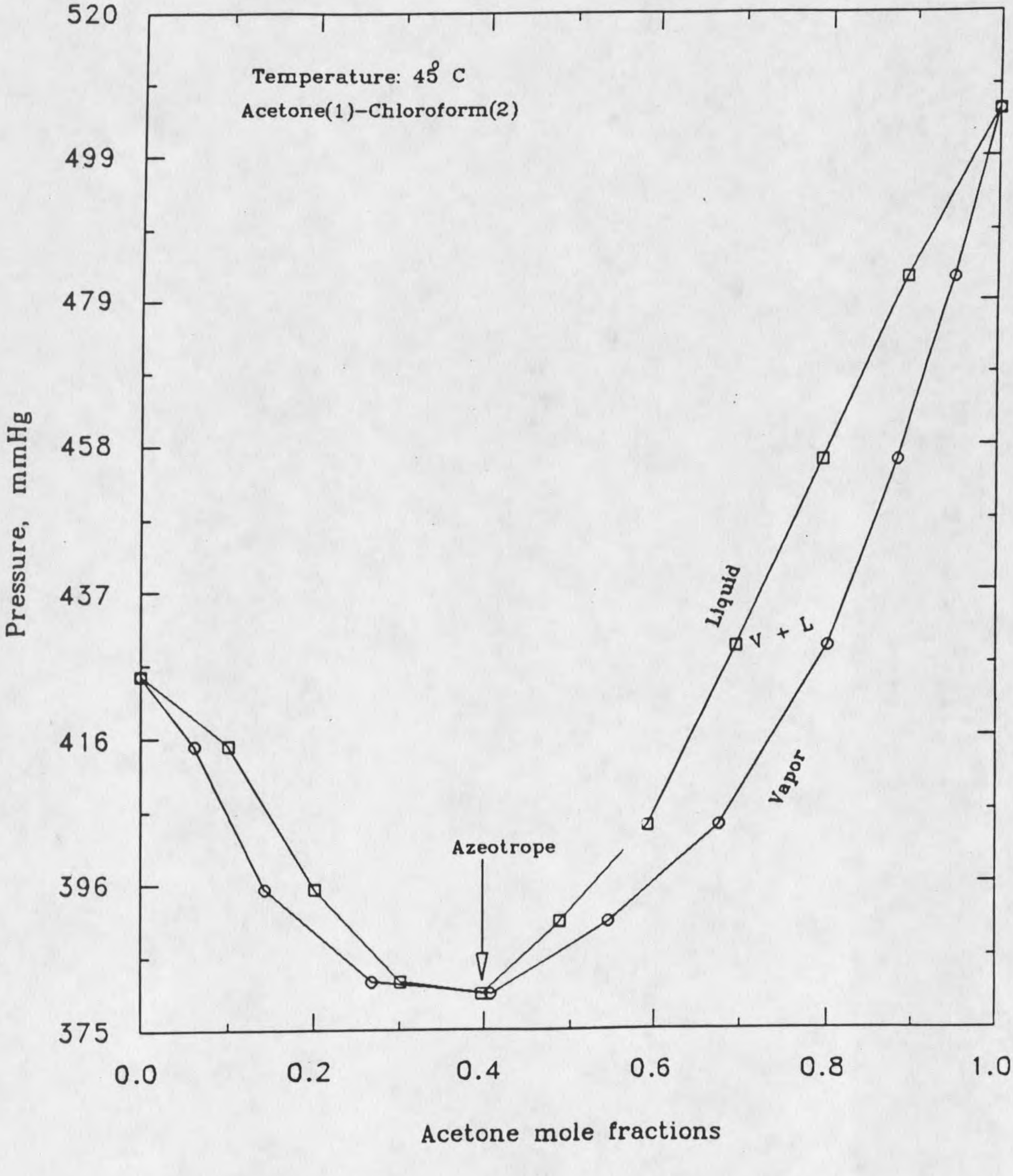


Figure 7 Pressure and liquid mole fractions for maximum-boiling azeotropic mixture of acetone and chloroform[4]

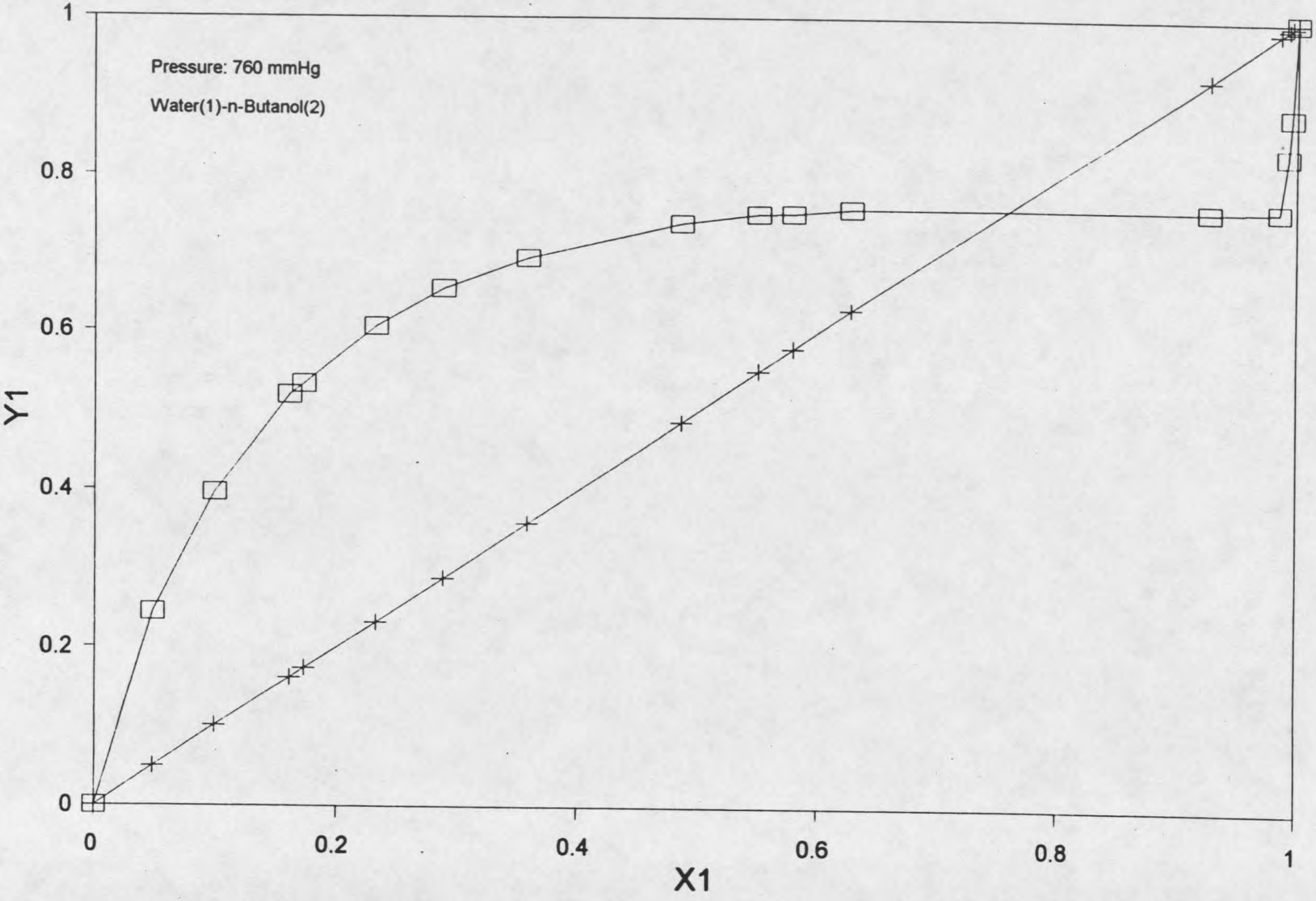


Figure 8 Liquid mole fractions and vapor mole fractions for heteroazeotropic mixture of water and n-butanol[4]

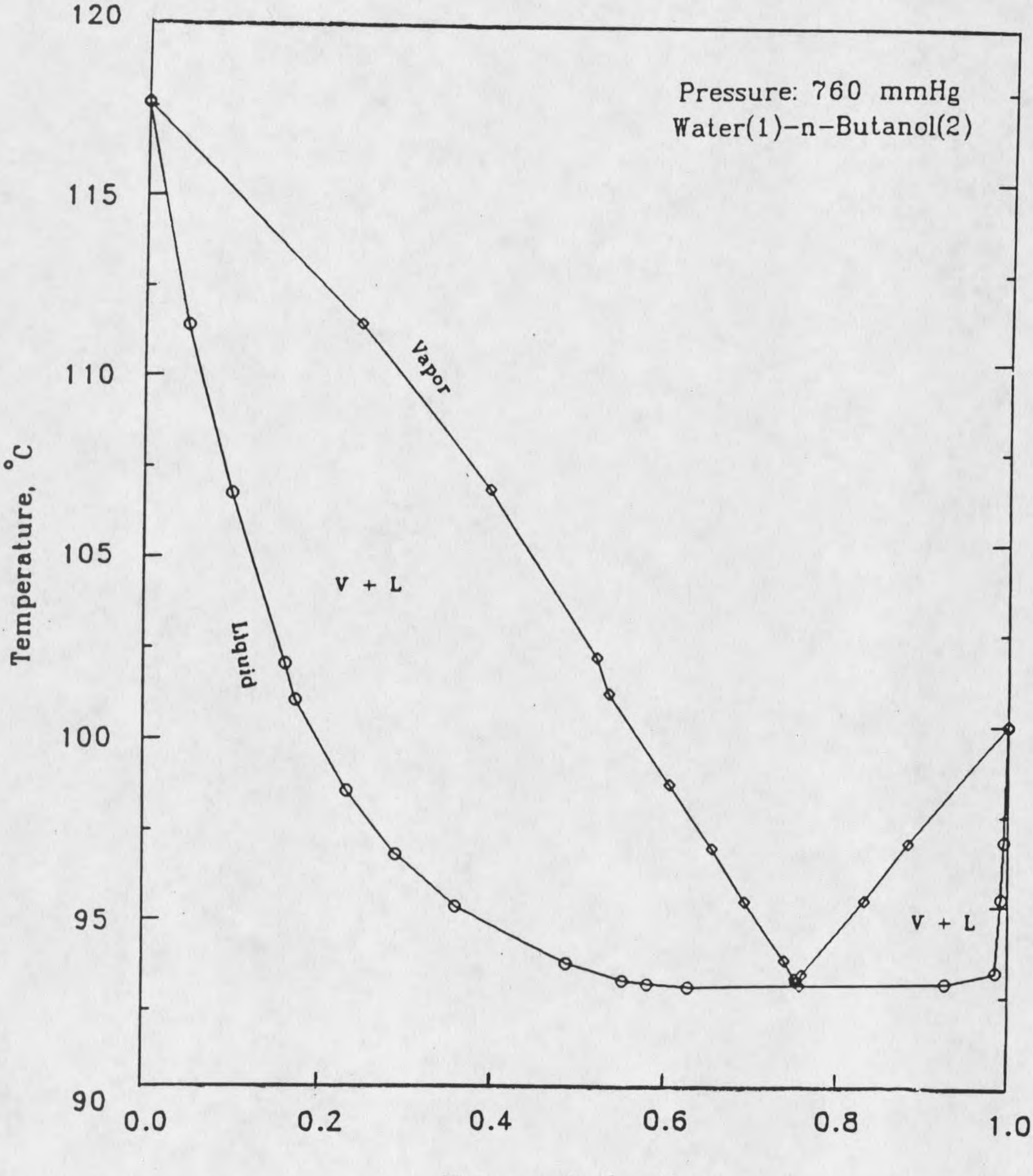


Figure 9 Liquid boiling point and vapor condensation temperatures for minimum-boiling heteroazeotropic mixture of water and n-butanol [4]

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

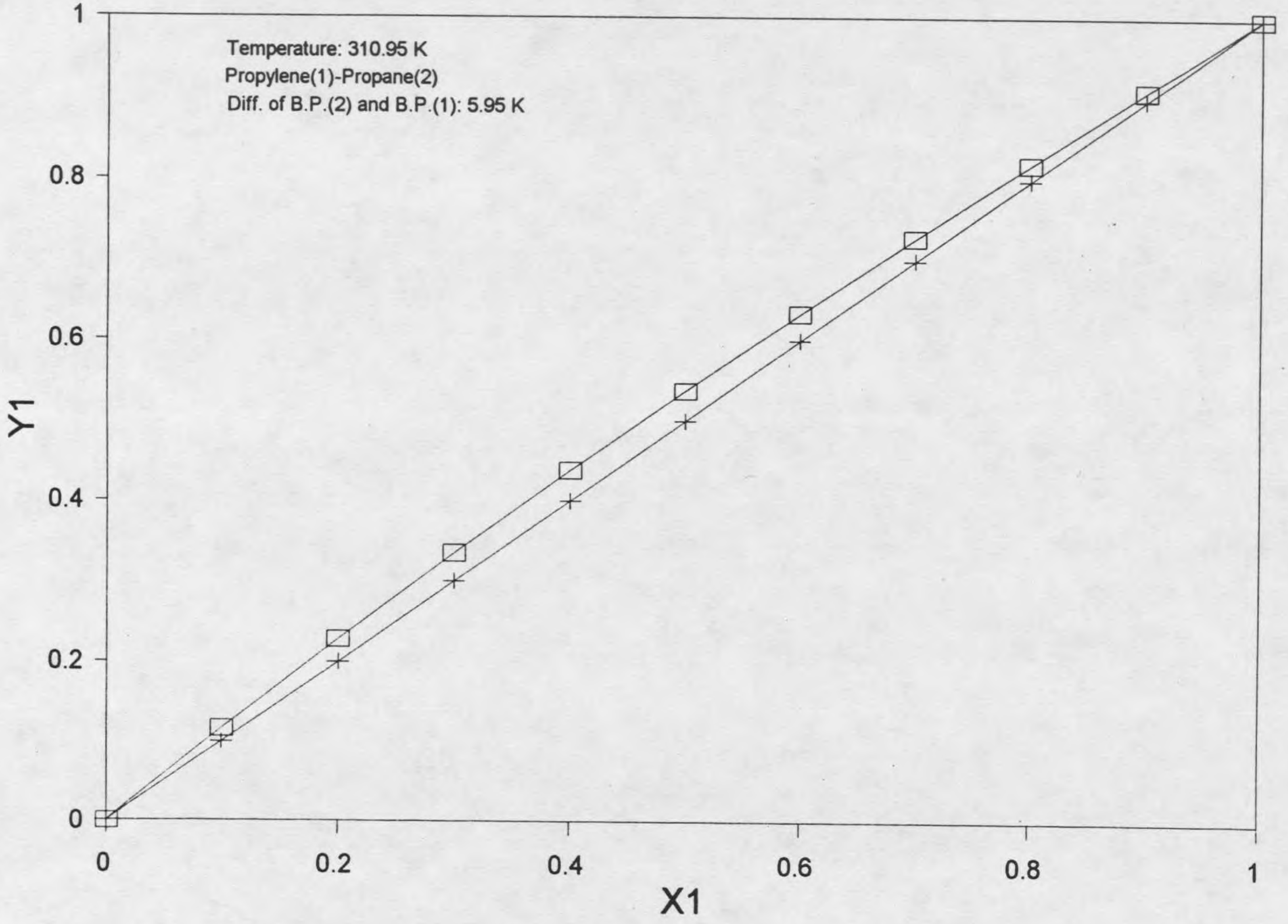


Figure 10 Liquid mole fractions and vapor mole fractions for close-boiling mixture of propylene and propane [4]

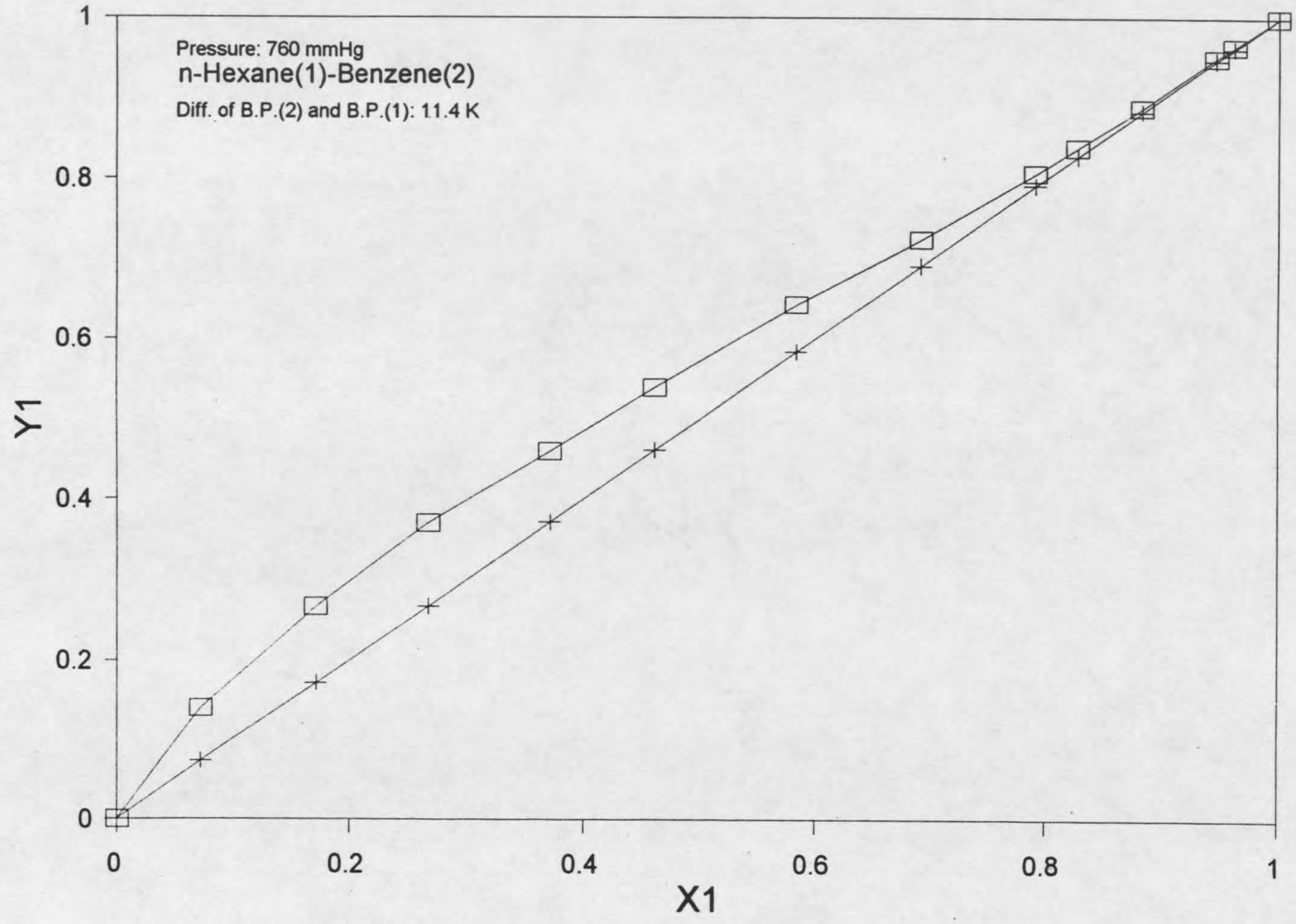


Figure 11 Liquid mole fractions and vapor mole fractions for close-boiling mixture of n-hexane and benzene [4]

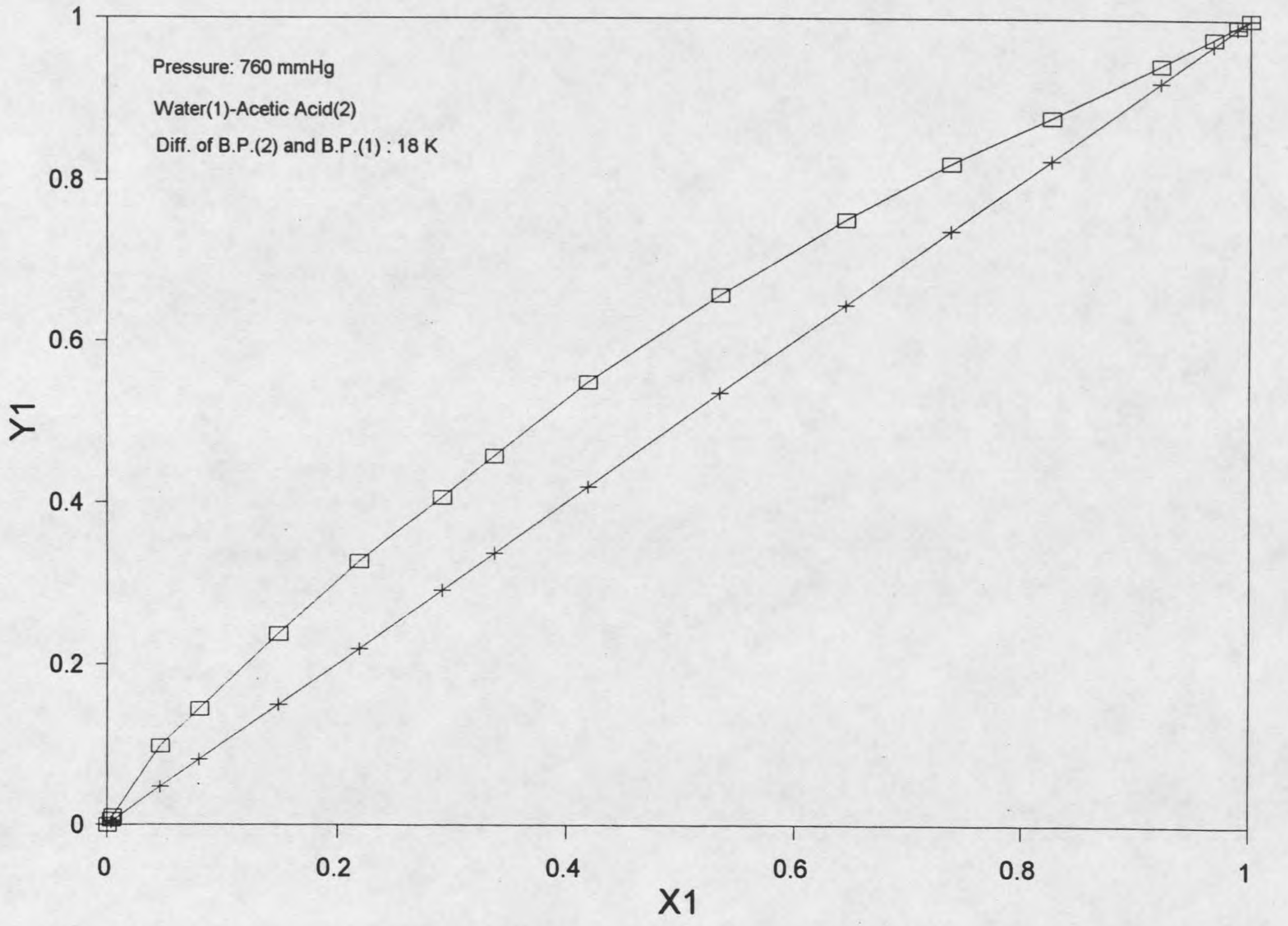


Figure 12 Liquid mole fractions for low relative volatility mixture of water and acetic acid [4]

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

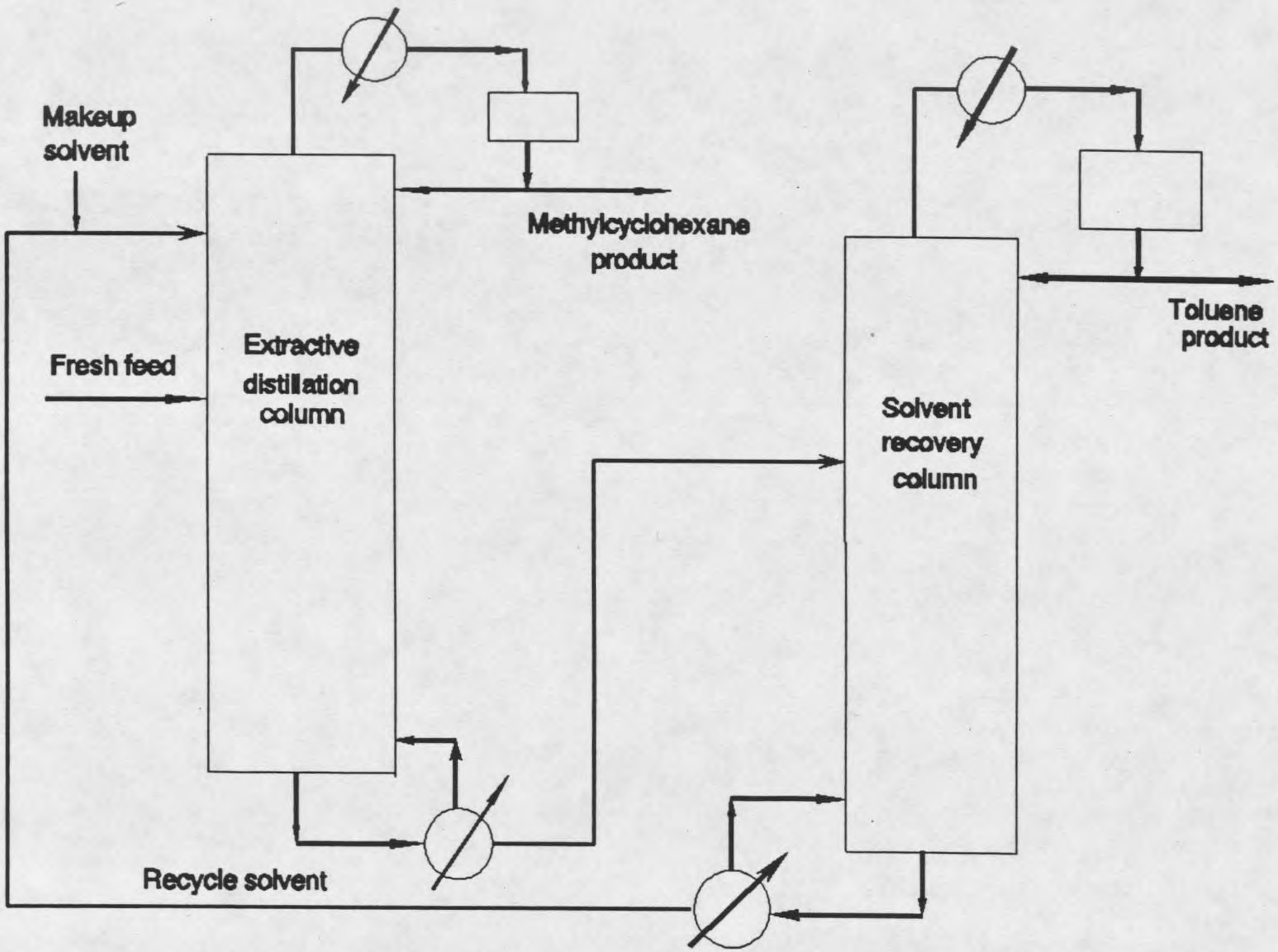


Figure 13 Simplified flow diagram for an extractive distillation process to separate toluene and methyl cyclohexane[6]

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

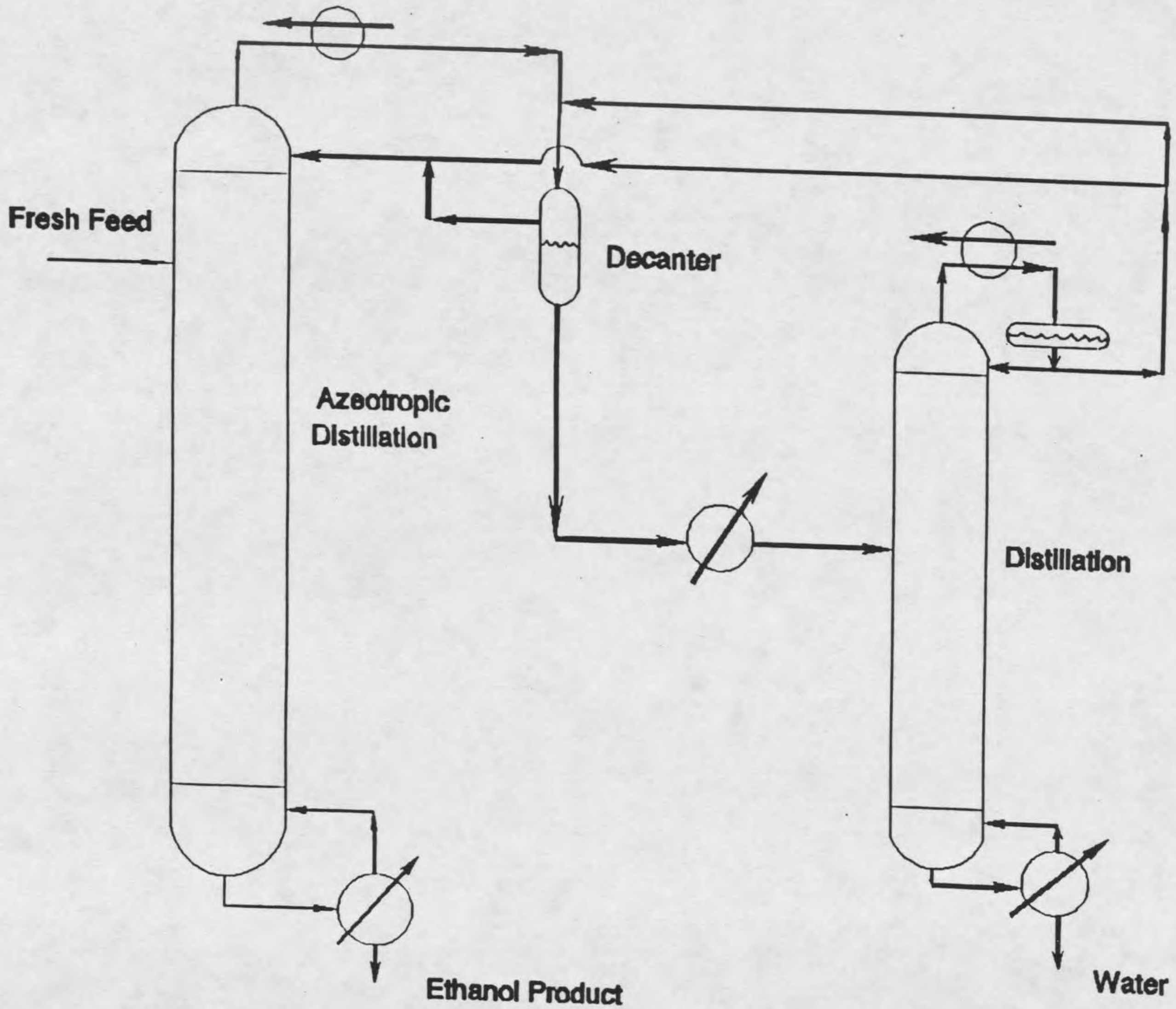


Figure 14 Azeotropic distillation process for separating ethanol and water by using pentane as entrainer[6]

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

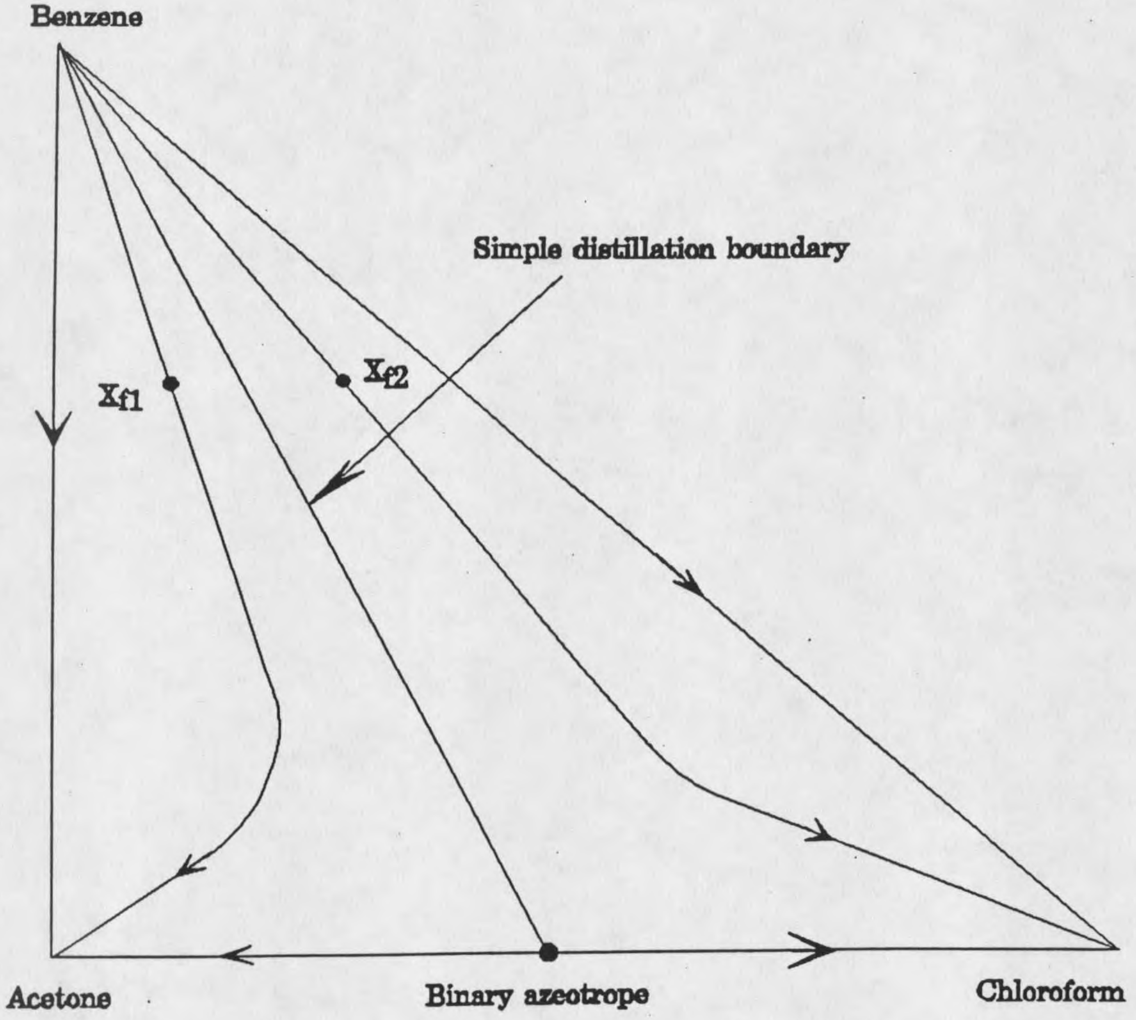


Figure 15 A typical residue curve map showing a distillation boundary[13]

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

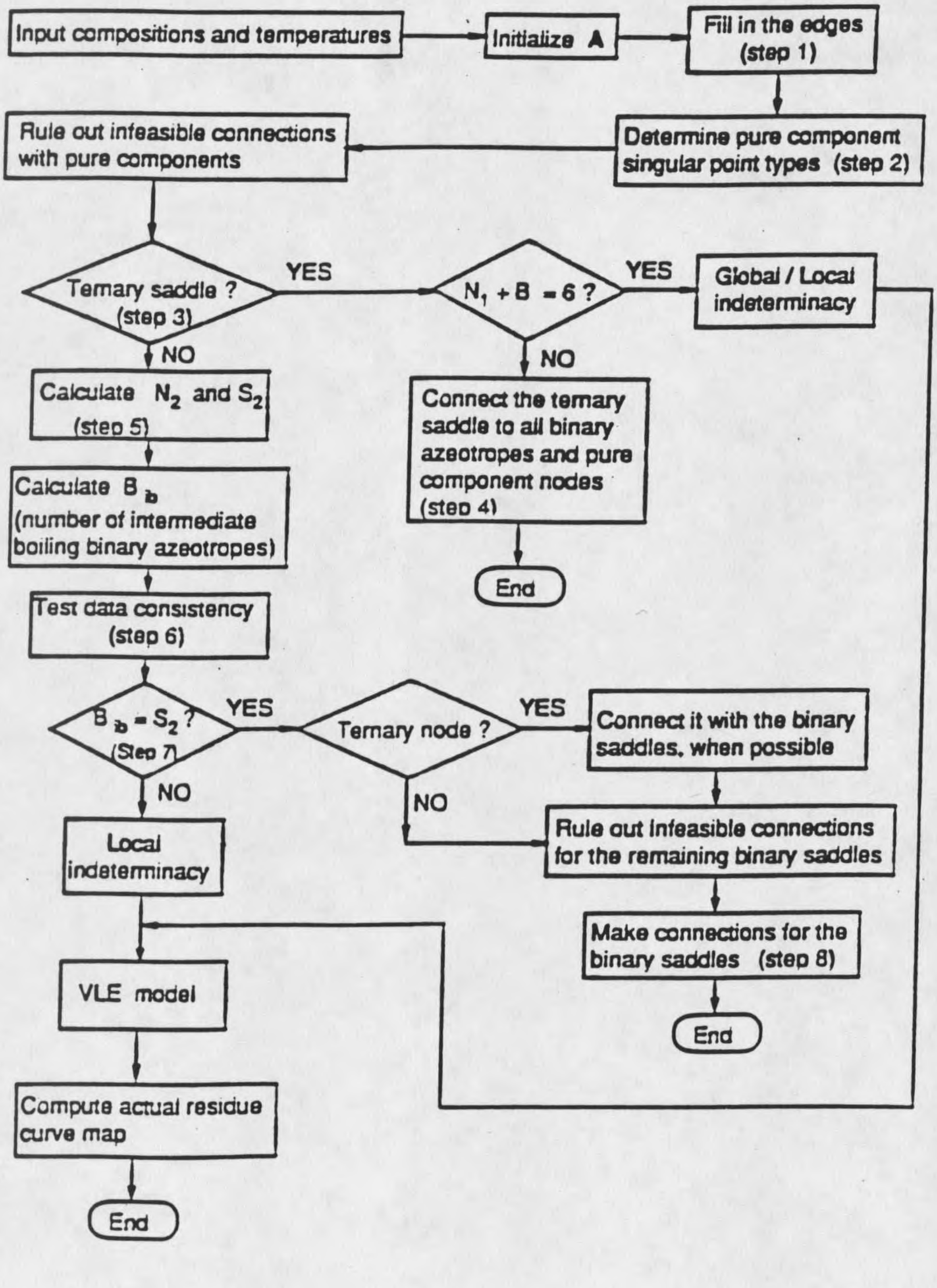


Figure 16 The algorithm for determining the residue curve map and the selection of azeotropic entrainers[16]

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

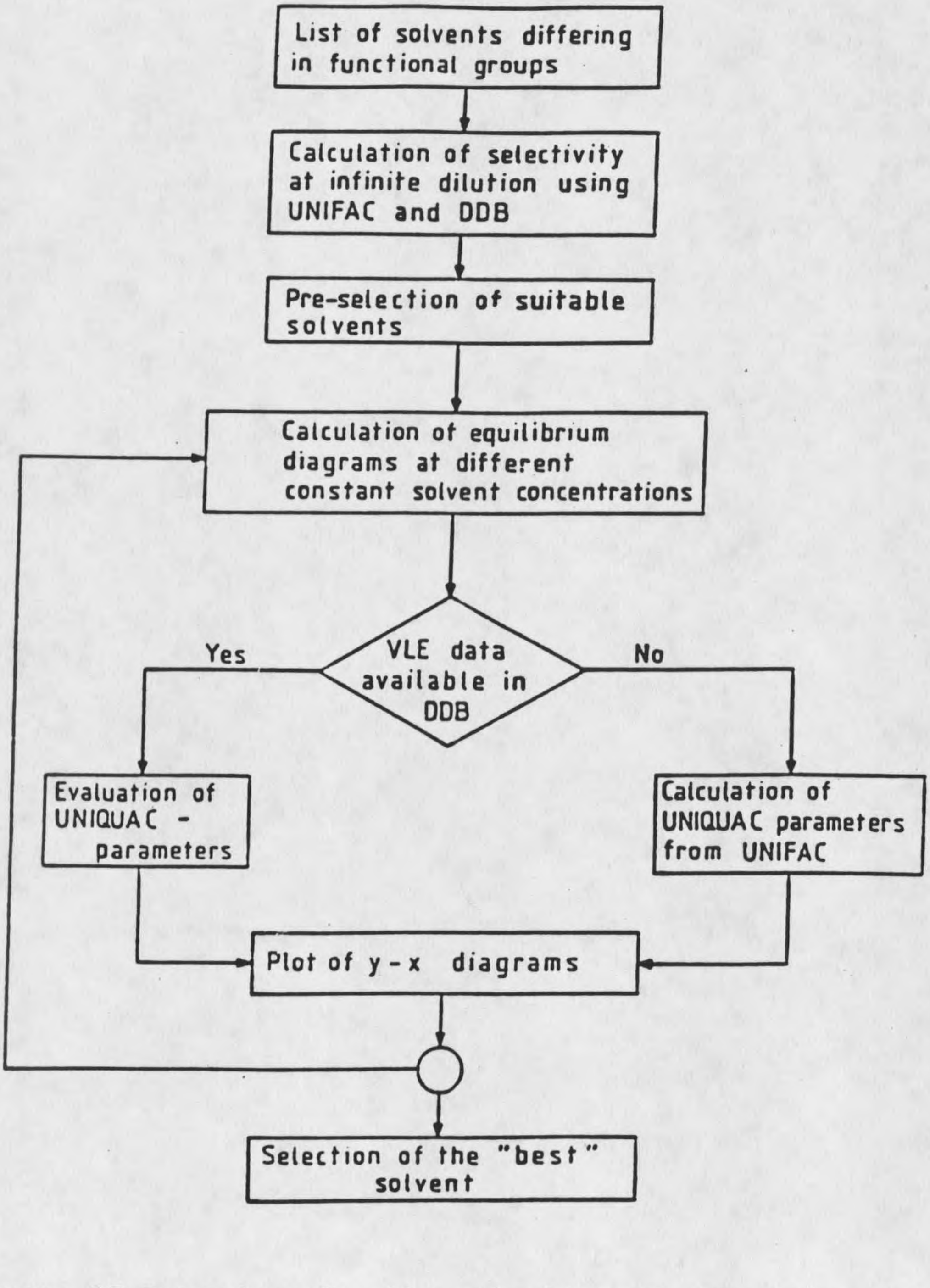


Figure 17 Procedure for the selection of extractive solvents based on UNIFAC and UNIQUAC models [23]

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.

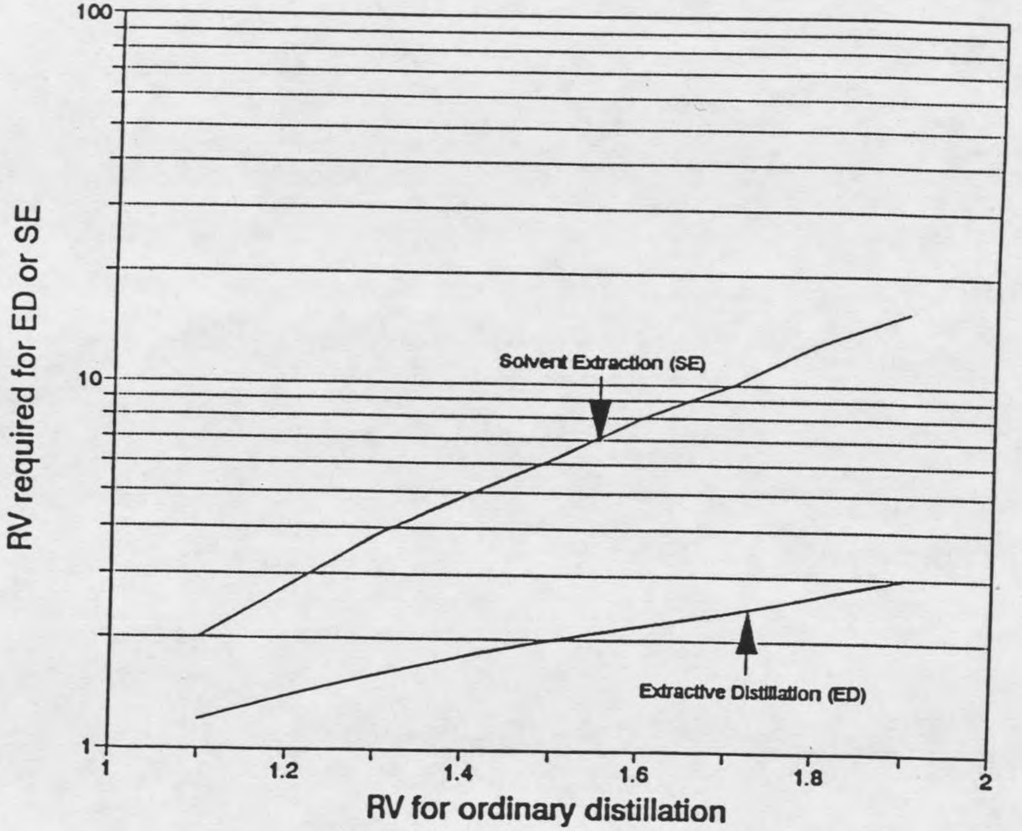


Figure 18 Relative volatility required for different separation with equal cost[30]

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

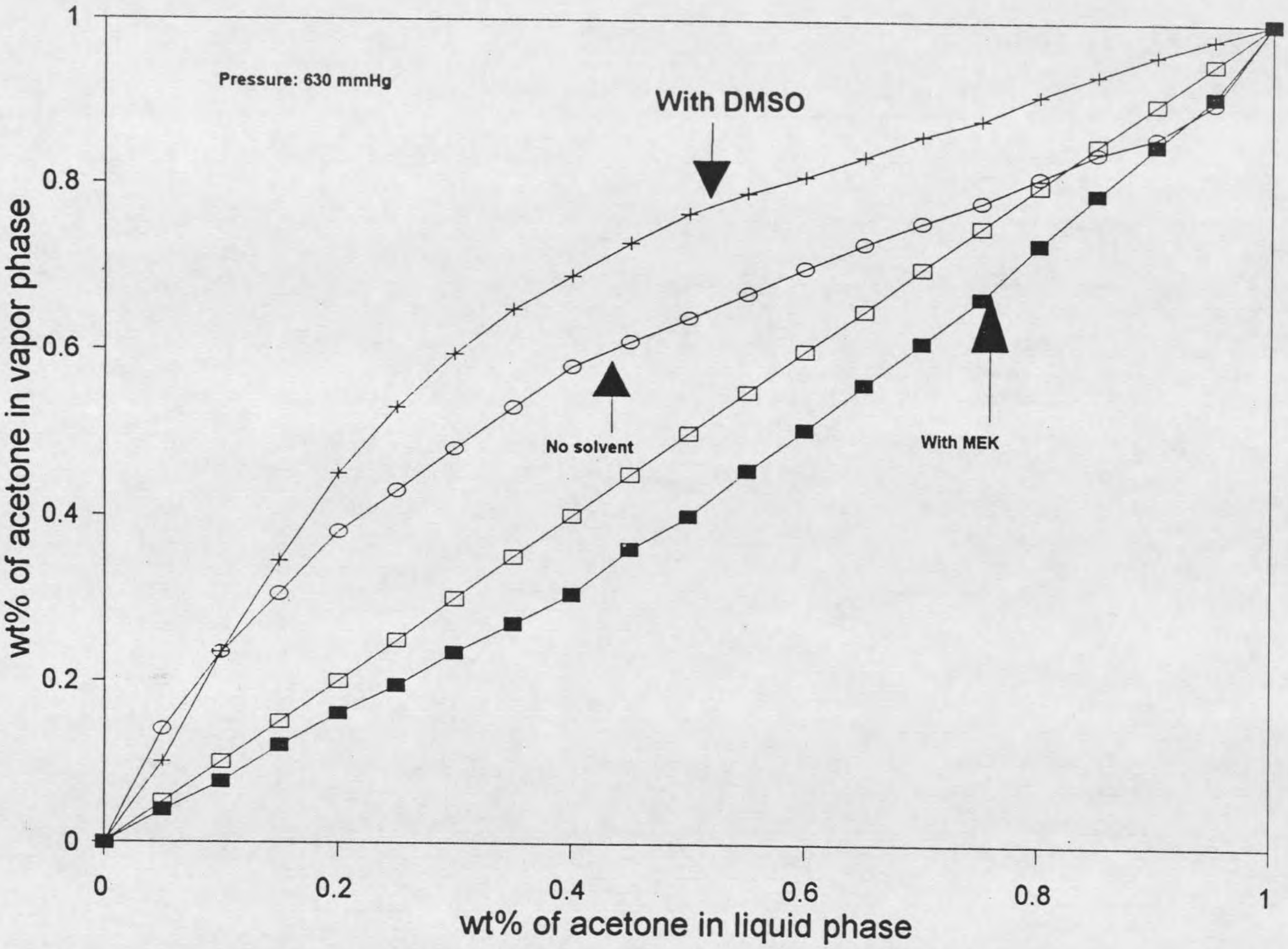


Figure 19 Vapor-liquid equilibrium curves for the methanol-acetone system with solvents and with no solvent [24]

particular separation process is indicated by the separation factor:

$$\alpha^{S}{}_{ij}=\frac{x_{i1}/x_{j1}}{x_{i2}/x_{j2}} \tag{1}$$

The separation factor $\alpha^{S}{}_{ij}$ 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 $\alpha^{S}{}_{ij}$, defined by Equation (1), is greater than unity.

Relative Volatility

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

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

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],

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

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:

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

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

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

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

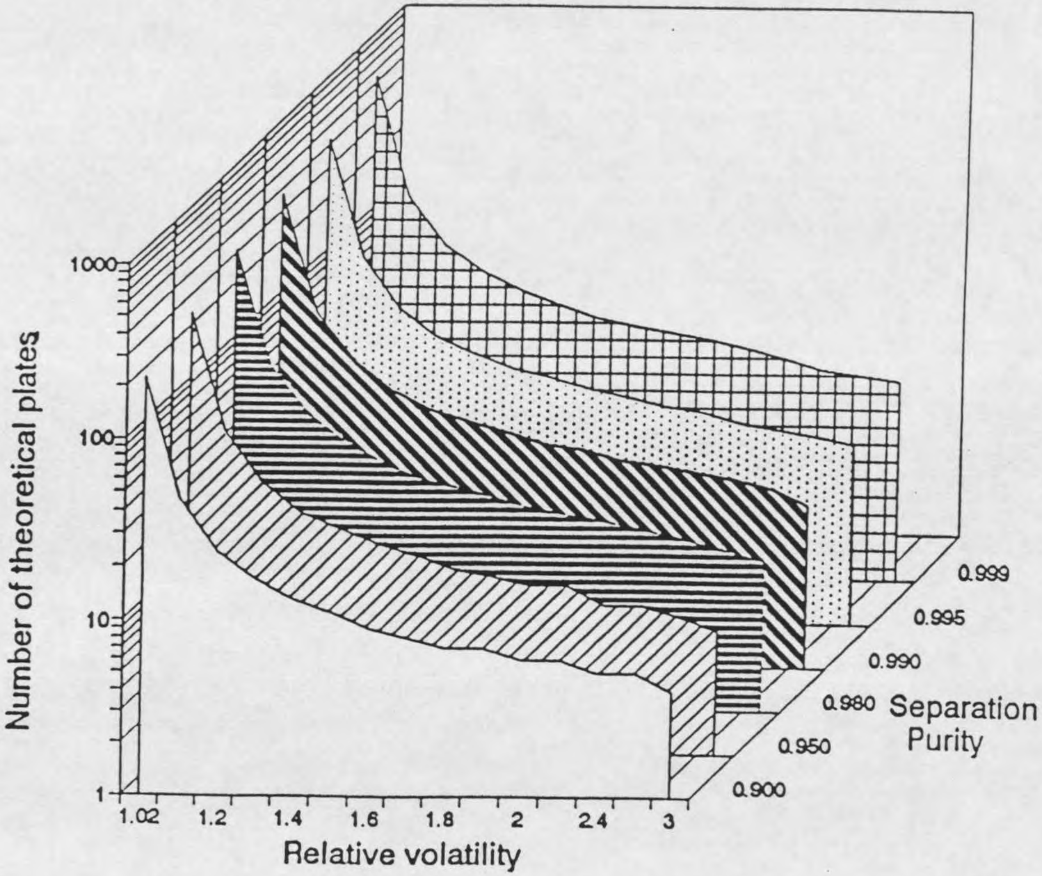


Figure 20 NTP requirements for different relative volatilities [27]

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}):

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

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

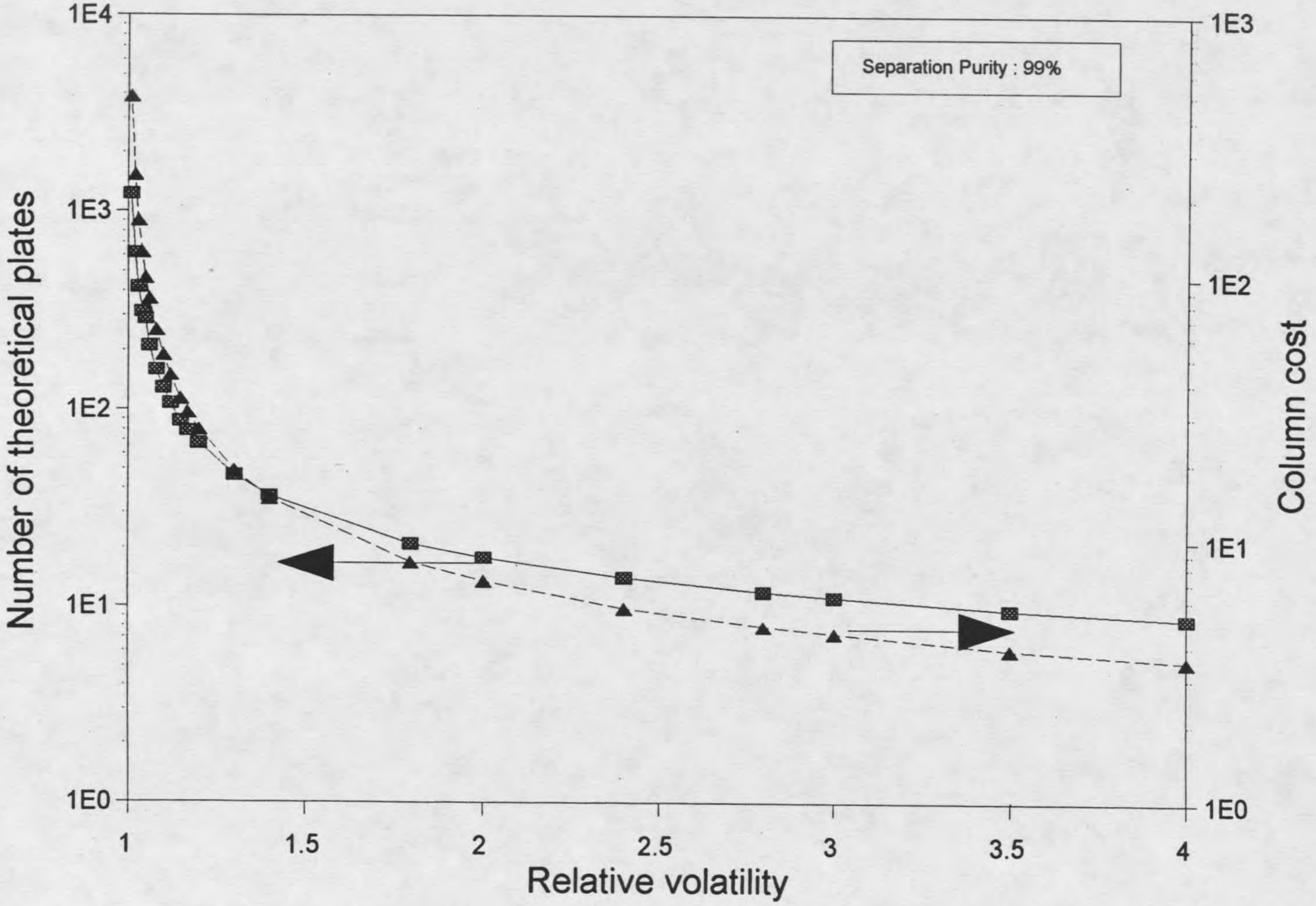


Figure 21 NTP and column cost vs. relative volatility[24]

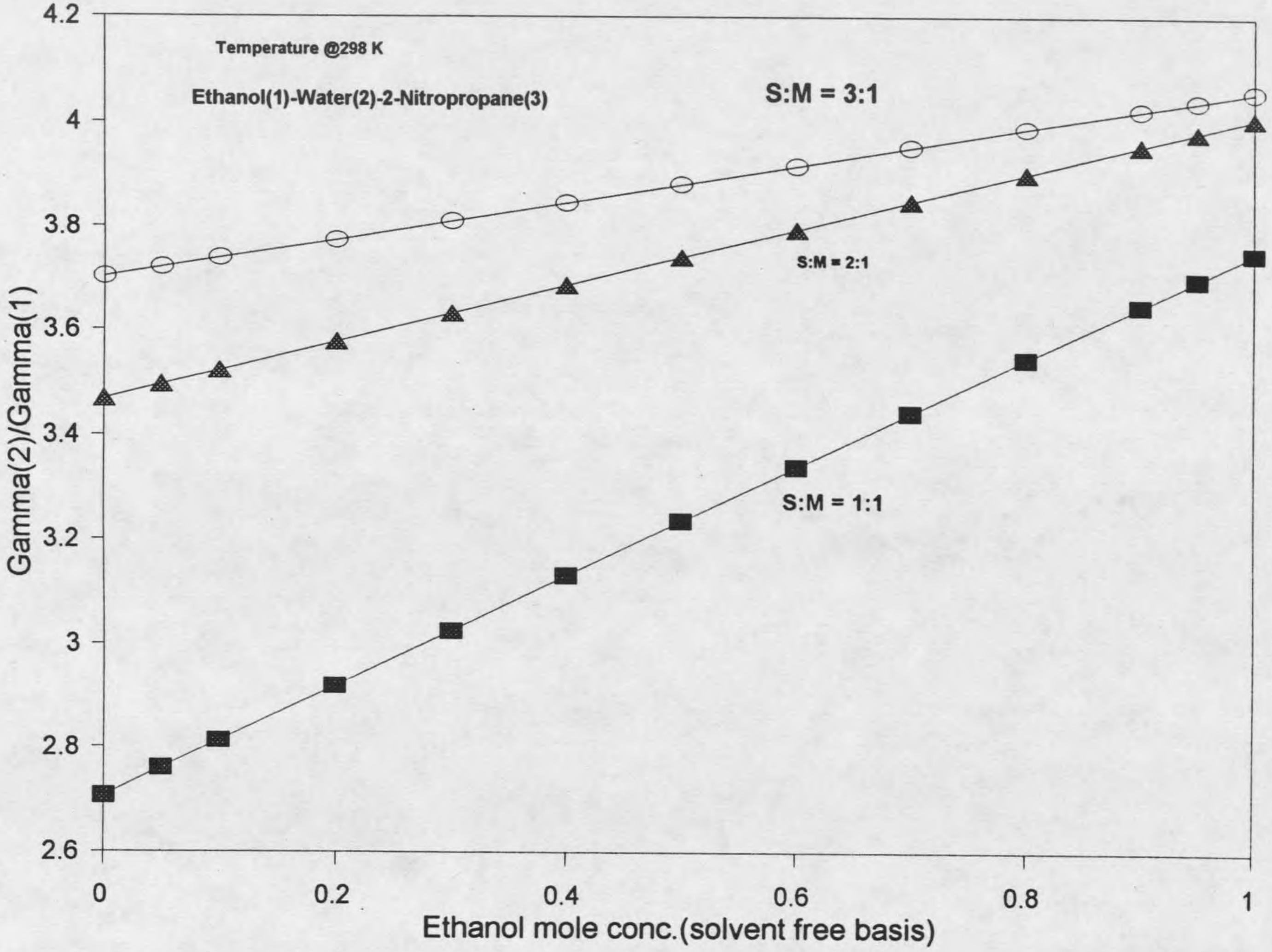


Figure 22 Effect of ratio of solvent to mixture on selectivity

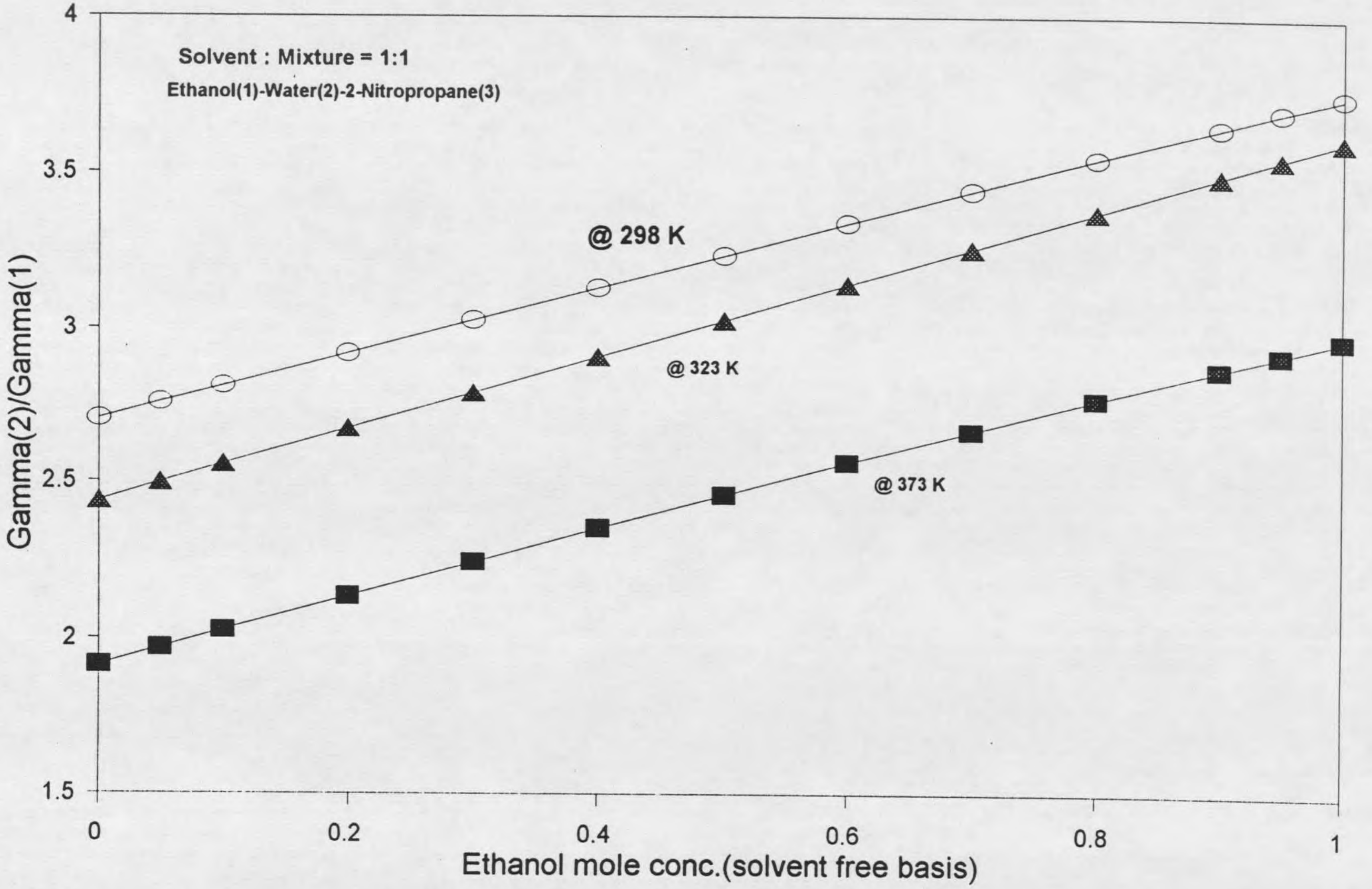


Figure 23 Effect of temperature on selectivity

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,

$$S^{\infty}=\gamma^{\infty}{}_{i}/\gamma^{\infty}{}_{j} \tag{7}$$

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.

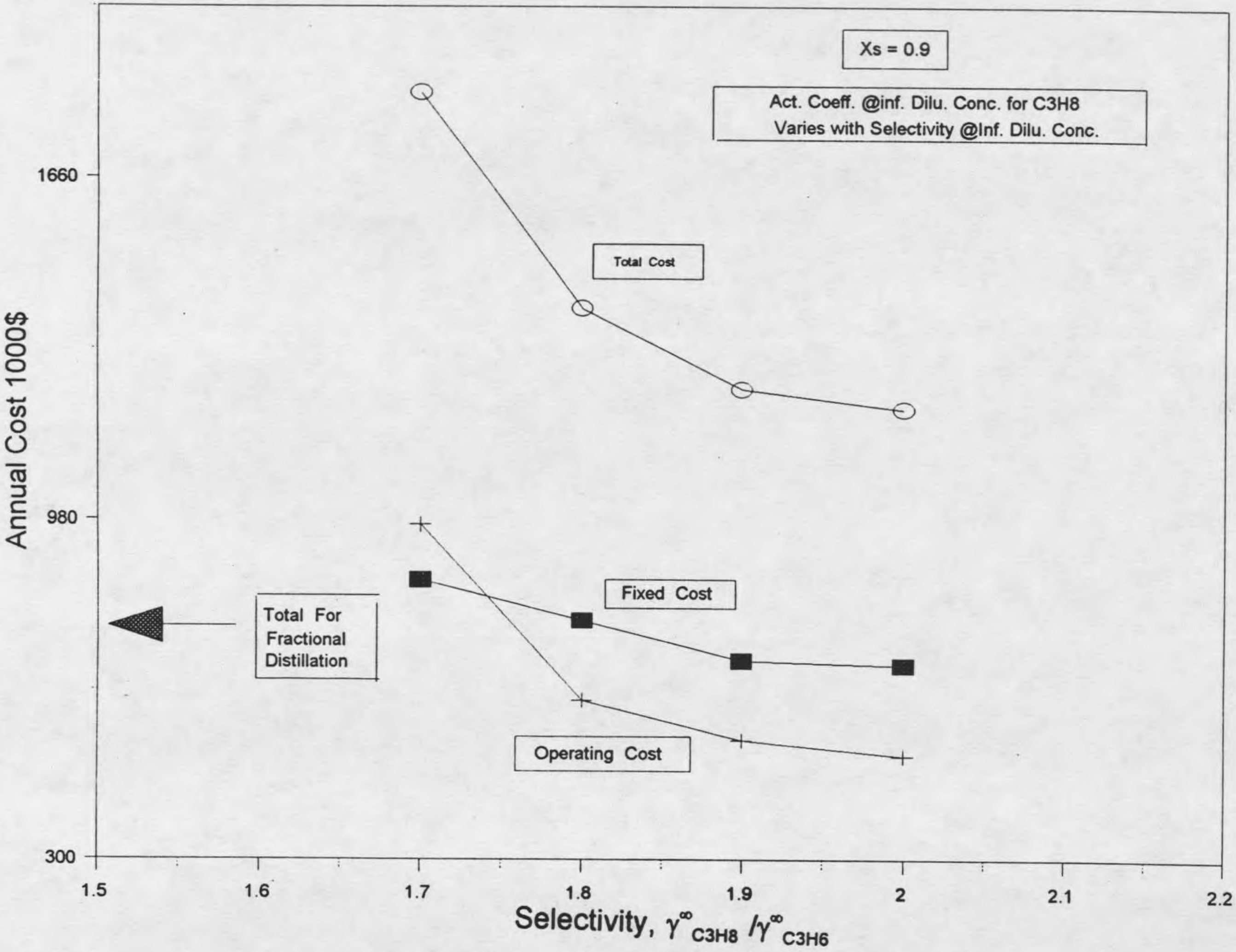


Figure 24 Effect of solvent selectivity on cost for low selectivity [31]

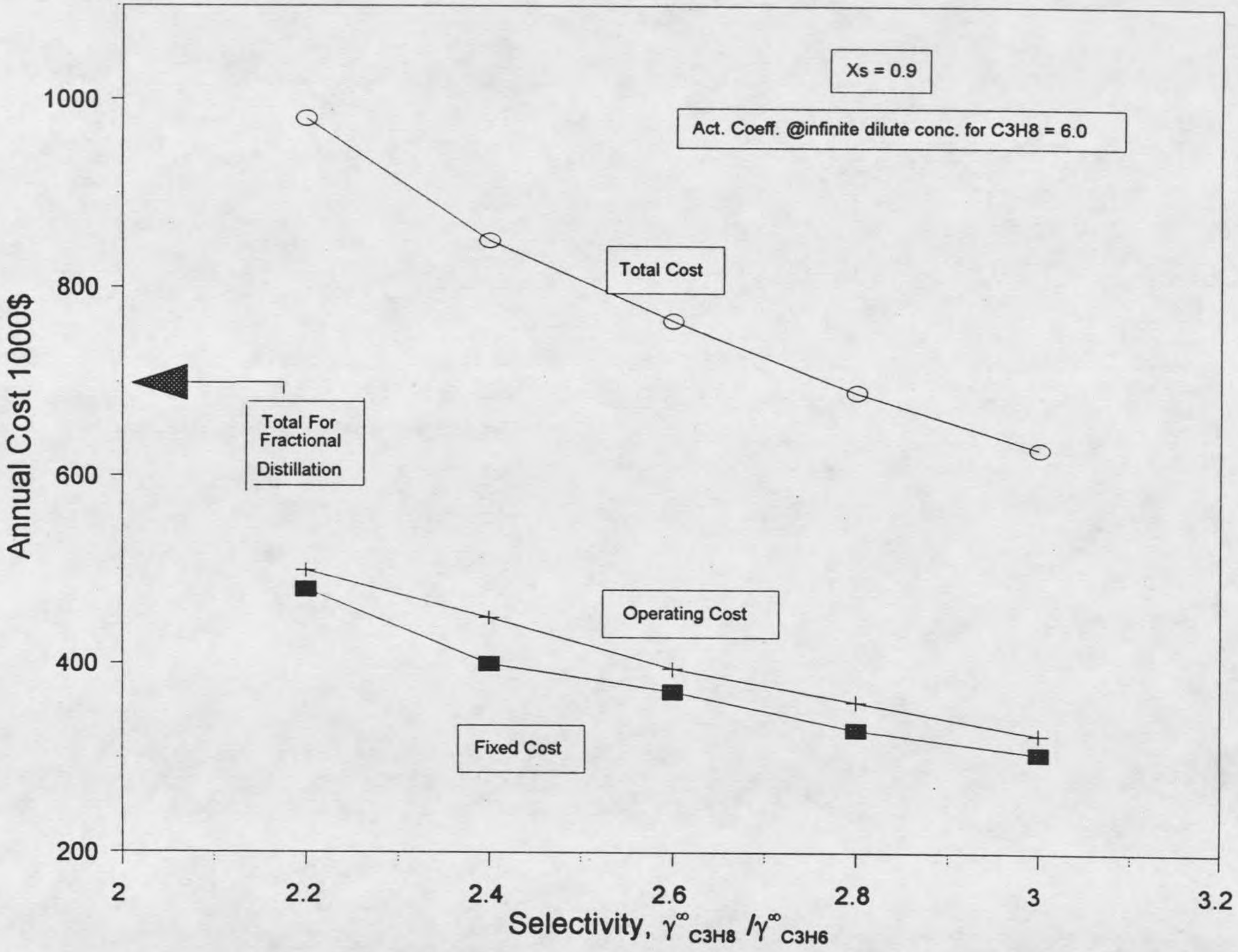


Figure 25 Effect of solvent selectivity on cost for high selectivity [31]

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

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; $z = 10$

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:

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

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-Hildebrand¹⁾ [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-Weimer²⁾ [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

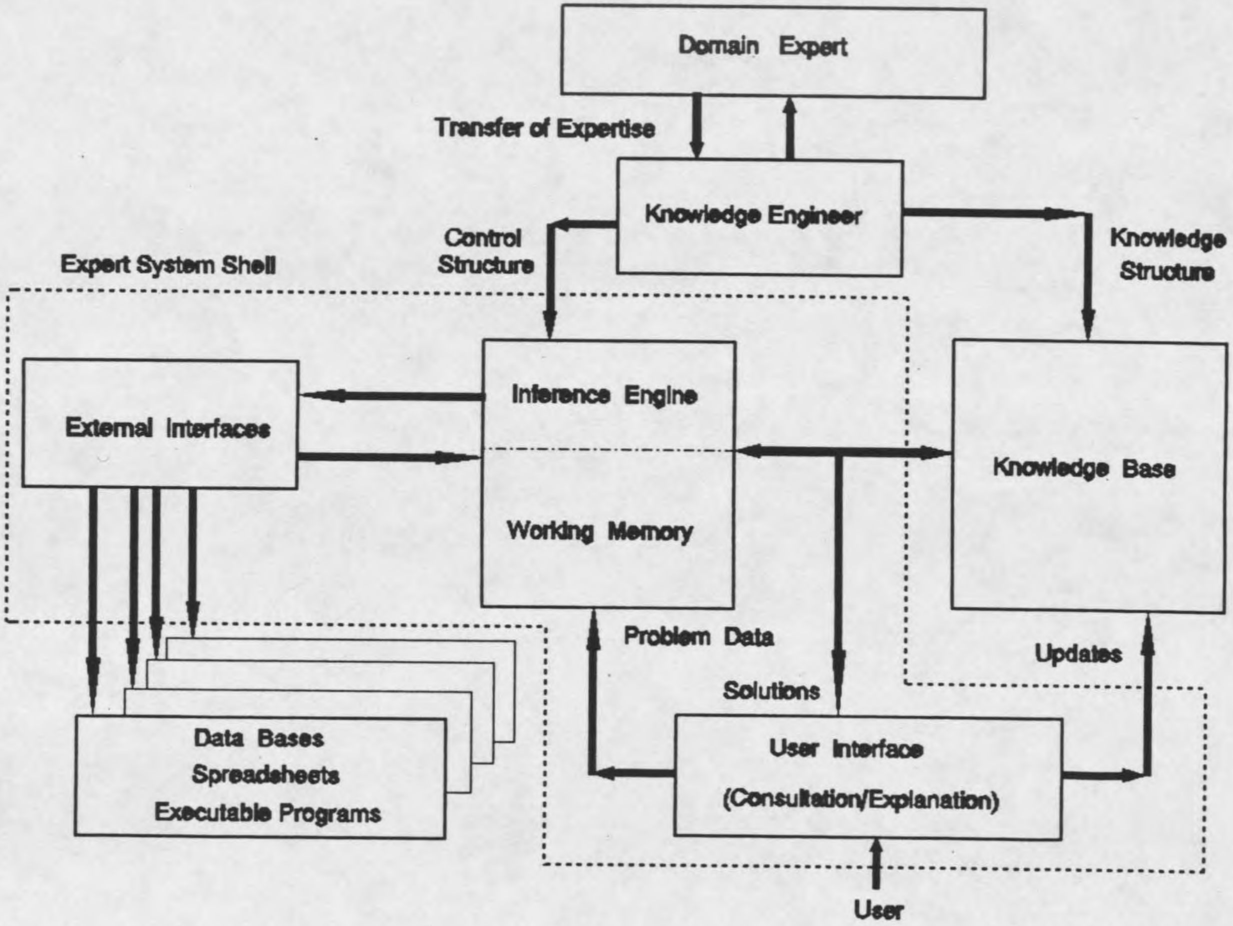


Figure 26 Integration of expert system components[67]

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

Table 8. The Basic Features of LEVEL 5 OBJECT.

1. Platforms

   IBM PC (WINDOWS)

2. Knowledge base components

   Data types:

   Compound; Color; Interval;
   Multicompound; Numeric;
   Picture; Rectangle;
   Simple; String; Time

   Knowledge representation:

   Rules; Object-oriented data structure

3. Inference Engine

   Reasoning mechanisms:

   Forward chaining; Backward chaining;
   Mixed-mode; Procedural; Object-oriented;

   Uncertainty:

   Confidence factors

grasp of the practicing engineer. Compared to typical chemical engineering computing, expert systems are unique. Instead of "crunching numbers," they contain chemical engineering knowledge, i.e., facts, rules, and heuristics. Having this knowledge, they have the ability to reason and solve problems.

Table 9 lists six main application areas of expert systems in chemical engineering identified by Quantrille et al.[68] and their individual functions. It can be seen that many applications are involved with the selection task.

Table 9. Application Areas of ES and Their Functions.

Main area	Application characteristics
Fault diagnosis	Process troubleshooting, i.e., determining the origins of process problems and recommending solutions.
Process control	Monitoring processes and improving process control.
Process design	Designing processes, developing flowsheets, specifying equipment, ensuring process safety, assessing process flexibility, estimating cost, selecting and estimating physical and thermodynamic properties.
Planning and operations	Scheduling, developing procedures, assessing safety concerns, executing complex interrelated procedures, and aiding maintenance.
Modeling and simulation	Using qualitative reasoning and symbolic computing to model and simulate chemical processes.
Product design, development, and selection	Recommending chemical formulations, compositions, materials, process procedures, selecting new or existing products that achieve specified objectives.

The General Theory of Selection Problems

Selection problems are of interest for chemical engineers and appropriate for expert-system development. Selection itself is a complex problem-solving activity that incorporates varieties of knowledge and problem-solving tasks. The selection process involves searching in an object space and testing objects using some constraints. The object space and the initial requirements, which also form the constraints for the selection process, can be very large. So, exhaustively testing attributes of each object for all the constraints is computationally intensive and can become intractable for a complex, real world selection problem.

The result of a selection activity is a set of objects which satisfy both the goals and constraints that are associated with the definition of the objects and their specifications. The inputs to the problem are constraints, information about the attributes of the objects and knowledge to be used to control the selection process.

Selection problems can range from simple to very complicated depending on the problem-solving techniques employed. For a simple selection problem such as selecting a proper wrench from a wrench set to tighten a nut, table-look-up may be an adequate strategy. But for a complex selection problem such as selecting promising solvents or entrainers among a large set of solvents for azeotropic and extractive distillation based on both thermodynamic principles and expert experiences, such a table-look-up strategy becomes inefficient.

Actually, selection processes are not well-defined problems from an AI viewpoint. A subset of selection problems are the so-called routine selection problems that are discussed thoroughly by Gandikota and defined as follows[69]:

> A routine selection problem has clearly stated goals and well-structured selection procedures to achieve the goals. The object space and the necessary knowledge for making appropriate decisions to select from the object space are well-defined.

The overall task of routine selection can be decomposed into two subtasks. The first subtask, called preliminary selection uses a hierarchy of conceptual categories. At each stage of the preliminary selection there is knowledge available to decide if a particular conceptual category can satisfy some broad initial requirements. The result of preliminary selection is a set of abstract categories that are used as inputs in the second subtask. The second subtask called critical selection involves refining the set of abstract categories using a selection critic. The selection critic consists of a set of conceptual nodes corresponding to the tip nodes of the preliminary selection hierarchy. These conceptual nodes contain knowledge to test the suitability of each abstract category to satisfy the full range of general to very specific initial requirements. The output of the critical selection is a set of selected categories ranked by some order.

Selection-related Expert Systems in Chemical Engineering

Generally speaking, the function of a selection expert system is to help end users choose products, processes, or something else, often from large or complex sets of alternatives. One of the characteristics of selection applications is the extensive use of data entry forms and the need for flexible access to databases. The object information is often stored in an inventory database, and the end user is prompted for desired features and constraints. The knowledge base is then responsible for matching the constraints to the possible alternatives in the database.

It can be seen from the following brief summary that selection processes gain much attention in chemical engineering.

Separation design. Separation sequence syntheses have gained much attention among chemical engineers as AI applications. The well-known systems for separation sequence synthesis such as EXSEP developed by Liu et al.[70], an adaptive heuristic system developed by Huang et al.[71] , and SAD developed by Barnicki and Fair [72] [73] have in common the need to select a proper separation method such as distillation, adsorption or crystallization at the initial stage of sequencing.

Thermodynamic model selection. CONPHYDE (CONsultant for PHYsical property Decisions), developed at Carnegie-Mellon University by Banares-Alcantara [74], is the first expert system that selects the appropriate physical property model for vapor-liquid equilibrium calculations. It uses an interactive "question and answer" session to acquire the information necessary to recommend a model. CONPHYDE uses rules and statistical inference techniques to draw conclusions and make recommendations. What CONPHYDE lacks, however, is depth in its knowledge base. Gani and O'Connell[75] have also developed a knowledge-base system for the selection of thermodynamic models. Their system contains deeper knowledge than CONPHYDE does. In addition, they use a different problem-solving approach from that of CONPHYDE. Gani and O'Connell's system gathers the knowledge about model selection and employs a large index table, in which the best model is simply to be looked up. Chen and Chang have also developed an expert system (ESPEM) [76] for assisting in selecting suitable vapor-liquid equilibrium thermodynamic models. In addition to giving advice on the selection of proper thermodynamic models, ESPEM supplies an intelligent database manager and provides numerical calculation facilities to give the thermodynamic properties needed for subsequent applications such as process design.

<u>Product or equipment selection</u>. CAPS [77] is an expert system for plastic selection. The user is questioned about the intended use of the final product, and CAPS recommends classifications of polymers to consider. CAPS is a forward-chaining rule-based system. DECADE (Design Expert for Catalyst Development)[78][79] is a prototype expert system developed at Carnegie-Mellon University for catalyst selection by Banares-Alcantara. On the chemical engineering side, DECADE's

knowledge base is limited. PASS (Pump Application Selection System), by Venkatasubramanian[80], is an expert system for the selection of a pump from one of the following categories: rotary-screw pumps, rotary-gear pumps, positive displacement diaphragm pumps, displacement-plunger pumps, displacement-piston pumps, and dynamic centrifugal pumps. PASS is a forward-chaining rule-based expert system. It uses production rules that "fire" when a given set of information exists. Hanratty et al.[81] developed an expert system for the selection of an appropriate laboratory reactor for collecting the experimental data for such diverse purposes as catalyst screening, scale-up, troubleshooting, and kinetic modeling.

CHAPTER 5

KNOWLEDGE BASE

An expert system, named SSS (Solvent Selection System) was designed to utilize some of both the qualitative and quantitative knowledge described in Chapters 2 and 3 to select promising solvents for extractive and azeotropic distillation.

SSS is intended to give both the expert and nonexpert quick answers to the problem of solvent selection. The first phase for the development of an expert system involves the knowledge acquisition, that is, garnering the information related to the problem domain at hand from both the literature and experts in the field. The second phase is concerned with the knowledge representation approaches which are based on knowledge characteristics and reasoning strategies applied in the system. This chapter discusses these two phases in detail.

Knowledge Acquisition

Knowledge Involved in the Solvent Selection Problem

The knowledge acquisition in this work was conducted in two parts: (1) general knowledge acquisition in order to obtain an understanding of the problem domain and (2) specific knowledge acquisition to determine the solvent classes on which the selection is based and obtain detailed knowledge about each solvent.

The objective of the general knowledge acquisition was to obtain an overview of the problem domain. With this understanding, a knowledge structure for the selection process was developed leading to a system knowledge hierarchy that is shown in Figure 27. The information for the general knowledge acquisition phase was obtained mainly from the literature (textbooks and publications) and through interviews and discussions with Dr. Lloyd Berg who has worked in this field for several decades.

The knowledge related with the selection of solvents falls into four categories:

1) Separation methods. From the foregoing overview, it is known that the procedure and rules for the selection of solvents vary for different separation methods such as azeotropic distillation, extractive distillation, and solvent extraction.

2) The specific problem knowledge -- the characteristics of the mixture to be separated. The separation method which should be used usually depends upon the characteristics of the mixture to be separated. Also, the solvent selection process is based upon both the characteristics of the mixture and the physico-chemical properties of each component in the

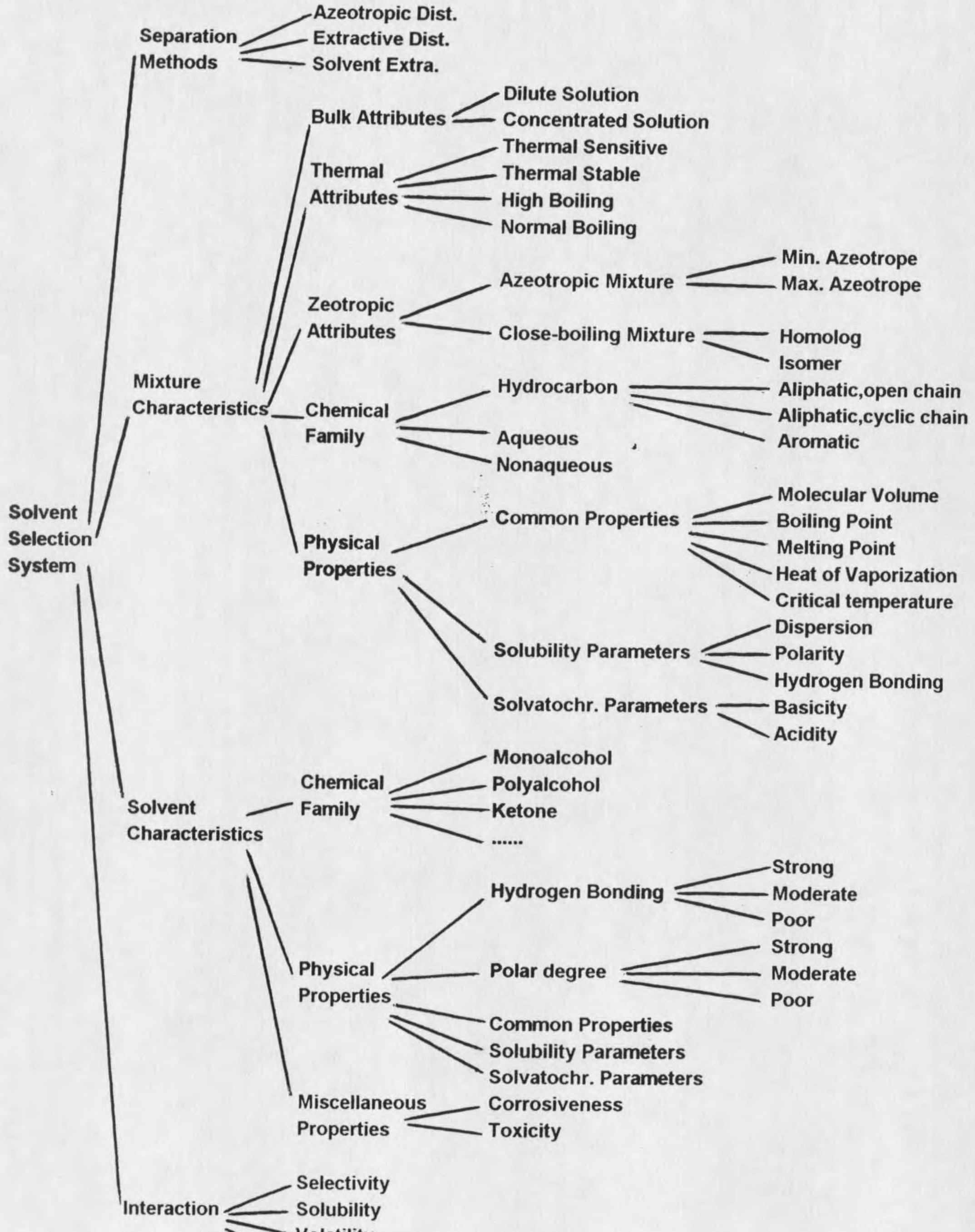


Figure 27 Knowledge involved for solvent selection problems

mixture.

3) Physico-chemical properties of solvents. The preferred solvent (from a solvent database) should be selected for a specific separation problem, and is largely justified by its physico-chemical properties such as hydrogen bonding ability, polarity, melting points, boiling points, and so on.

4) The interaction of the solvents and solutes. The goal of adding a solvent into the mixture to be separated is to change the vapor-liquid equilibrium behavior of the mixture. The changes made in the vapor-liquid equilibrium by adding the solvent are good criterion for the selection of a solvent.

During the second part of the knowledge acquisition process, the knowledge about the search space was gathered. The search space for this problem consists of solvents and specific information needed for the selection of solvents, including some physico-chemical properties and practical experience. This knowledge comes mostly from the public literature[82-86]. When particular physico-chemical properties are not available, the group contribution method is utilized to obtain an estimate.

Knowledge Used in the Current Expert System

The knowledge involved in the solvent selection problem as described in the above section contains a large amount of information. If energy saving or economic factors are taken into account, much more knowledge may be needed for tackling the problem.

Table 10 shows the progress of the knowledge for solvent selection for azeotropic and extractive distillation based on the information provided in chapter 2.

Table 10. Progress of the Knowledge for Solvent Selection for Azeotropic and Extractive Distillation.

Azeotropic Distillation	Extractive Distillation
Sheibel's rules(1948)	Ewell's heuristics(1944)
Berg's heuristics(1969)	Berg's criteria(1969)
Tassio's procedure(1972)	Treybal's criteria(1980)
Kolbe's procedure(1979)	Stichlmair'sheuristics(1989)
Treybal's criteria(1980)	Doherty's residue curve(1991)
Yeh's polarity plot(1986)	Laroche's procedure(1992)

It should be noted that not all the knowledge described in Figure 27 and Table 10 is built into the knowledge base in the current prototype expert system.

In SSS, the rule proposed by Dr. Lloyd Berg (described below) is used to select a separation method.

If the boiling point of any component in the mixture to be separated is above 170°C, then prefer azeotropic distillation. Otherwise, the end user inputs either azeotropic distillation or extractive distillation as a separation method.

This rule was also suggested by Van Winkle[27]. The reasoning behind using this rule is that we can lessen thermal decomposition, polymerization, or other chemical reactions that might happen at a higher temperature.

For azeotropic distillation, only Berg's two rules[11] are used for illustration. Those rules govern selecting solvents to separate a close-boiling mixture, a maximum azeotrope, and a minimum azeotrope by forming a new binary azeotrope. At present, the knowledge for azeotropic distillation has not been exploited very deeply due to time limitations.

For extractive distillation, it is well known that the solvent should be highly selective, and of low volatility. As described in chapter 2, authors have proposed different criteria for selecting solvents. In SSS, we use different combinations of rules and procedures according to the characteristics of the mixtures to be separated. For hydrocarbon mixtures, Berg's boiling point rule (or less volatile), Tassios's procedure, high solvency criterion (or high capacity), and high selectivity criterion are used for solvent selection. For aqueous systems, chemical families with high polarity are chosen, then Berg's boiling point rule is applied, Kolbe's procedure is used to select solvents with high selectivity. For a nonhydrocarbon, nonaqueous mixture, we use Berg's rule to classify solvents into 5 classes, of which four classes with high or medium hydrogen bonding ability are chosen. Members of homologs of each component in the mixture are chosen (Sheibel's rule). After that, Berg's boiling point rule is applied. Then solvents are selected based on a high selectivity criterion.

Table 11 lists the rules and procedures used in the current expert system.

Table 11. Rules Used in the Current Expert System.

1. Rule for method selection
   Berg's recommendation (also Van Winkle heuristic)
2. Azeotropic distillation
   Berg's two rules (form a new binary azeotrope)
3. Extractive distillation
   A. Hydrocarbon mixtures
      Berg's boiling point rule (less volatile)
      Tassios's procedure
      High solvency (high capacity)
      High selectivity
   B. Aqueous mixtures
      Chemical families (high hydrogen bonding ability)
      Berg's boiling point rule (less volatile)
      Kolbe's procedure
      High selectivity
   C. Nonhydrocarbon nonaqueous mixtures
      Berg's 5 classes of solvents
        (select solvents with high hydrogen bonding ability)
      Members of homologs (Sheibel's rule)
      Berg's boiling point rule (less volatile)
      High selectivity

The high capacity criterion proposed by Treybal is not always used in the current system because, for many mixtures, calculation of solubility is often time consuming and inaccurate. Treybal also listed the additional attributes required for solvents such as low cost, low toxicity, low corrosiveness, chemical stability, low freezing point, and low viscosity. In the present expert system, these criteria have not been considered because data for the above properties are not available for many solvents in the database.

One of Sheibel's rule requires that the selected solvent not form an azeotrope with any component in the mixture. If a solvent boils 20°C higher than components do, the chances of forming an azeotrope are rare.

Types of Knowledge

There is a difference between theoretical and real-world knowledge. We acquire the former by studying the relevant theory, which is under the form of general laws and axioms. The latter is not completely acquired through theory; one also needs to gain insight into problems that may arise in actual situations and so acquire problem-solving capabilities in order to become an expert in a given real-world domain. Therefore, knowledge has been broadly classified into two types in knowledge engineering field: Deep and Shallow Knowledge.

With Deep Knowledge, we mean the set of theoretical laws and axioms that form the basis for abstraction capability, and mathematical models developed to describe the behavior of the domain system. It is the same kind of knowledge we learn at school.

Shallow Knowledge defines all other knowledge. Such knowledge will not be acquired from books, but will need mentors to provide insightful suggestions, experience to acquire problem-solving capabilities, and intuition to tackle unknown situations. Shallow Knowledge is also called expertise, referring to the unique skills of an expert in a given domain. The outcome of Shallow Knowledge (or expertise) is also generally referred to as heuristics (or heuristic knowledge). This term refers to the so-called rules of thumb, meaning the judgment capabilities of the expert to grasp the meaning of a given situation and to foresee the consequences even when lack of data or the complexity of the domain do not permit a correct or complete theoretical analysis of the problem. Figure 28 sums up the knowledge components.

Knowledge, whether shallow or deep, must be extracted and encoded into usable forms in order for an expert system to solve problems. Knowledge extraction is performed to produce the organized, indexed deep knowledge and heuristics from experiences. These are then encoded into the AI program. Before encoding, knowledge may be subdivided into two categories[87]: declarative knowledge and procedural knowledge. Each kind of knowledge has one or more associated knowledge representation techniques.

Declarative knowledge refers to facts and assertions while procedural knowledge refers to sequences of actions and consequences. Declarative knowledge is associated with knowing

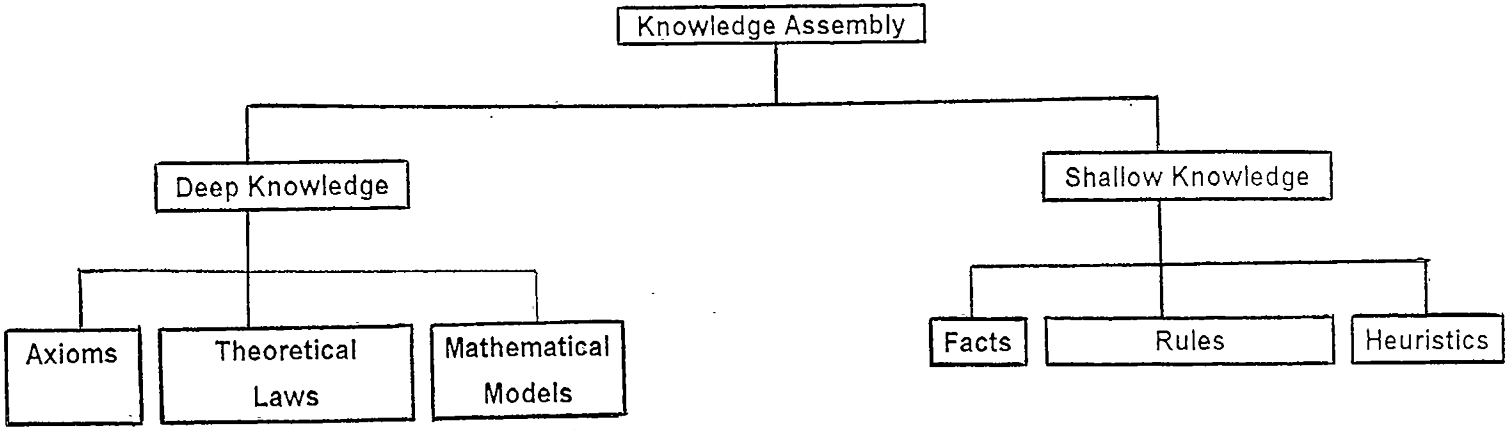


Figure 28 Knowledge components and classification

what is involved in solving a problem. Procedural knowledge isassociated with knowing how to apply appropriate problem-solving strategies to solve a given problem.

Knowledge Representation Strategy

The representation of knowledge is a basic issue in the development of Expert Systems (ESs) for applications. In fact, the performance of an ES relies heavily on the adequacy of its knowledge base.

AI researchers have developed several different knowledge representation techniques to represent the knowledge acquired from the expert in expert systems while preventing ambiguities in the problem solving procedures. Some techniques are suitable for a majority of problems typically encountered by expert systems. There are, however, some problems that require unique knowledge representation approaches. The major knowledge representation techniques[87] are (1) Semantic networks, (2) Frames, (3) Production rules, (4) Predicate logic, (5) Scripts, and (6) Object-oriented. Since the expert system shell which we have chosen as our developing tool provides us with the application development environment through both rules and object-oriented programming (OOP), we focus our discussion on knowledge representation by the object-oriented approach and rules.

Implementation Language--Object-oriented Programming

Object-oriented programming has recently emerged as a programming methodology that can assist in software development. The object-oriented approach has been gaining acceptance in the software community in part because of its representational capabilities. In traditional programming approaches, a program is made of a collection of functions that act upon data; this data may be organized into data structures. A problem is solved by repeatedly applying these functions. By contrast, the object-oriented approach models a domain as a collection of computational entities, referred to as objects. These objects define operations that are invoked as a result of the interaction of these objects with each other. In other words, these objects contain not only a list of properties (data), but also the required procedures to manipulate them. In this approach, a problem is solved through the interaction of the objects that makes up the problem domain.

One better-known prototype research program in chemical engineering application that takes an object-oriented approach is DESIGN-KIT by Stephanopoulos et al.[88]. DESIGN-KIT is a software-support tool developed to aid process-engineering activities such as: flowsheet development, control-loop configuration, and operational analysis. It is written in Common LISP, and is built on Intellicorp's software package, KEE (Knowledge Engineering Environment).

Another application in chemical engineering that takes an object-oriented approach is the expert system developed by Constantinou et al.[89] for estimation of physico-chemical properties from molecular structure.

It should be noted that application areas that have the following characteristics can benefit from an object-oriented knowledge-based system development[90]:

> Highly complex -- Applications that have many interrelated and interdependent rules or constraints that are typically beyond the scope of conventional programming systems, or those that require very large maintenance efforts.
>
> Frequently changing -- Applications where policies, information, and regulations change frequently. These type of applications can cause major maintenance problems if built with conventional tools.
>
> Requiring consistency -- Applications where the rules used to address cases are subject to inconsistent interpretation. Codifying the rules ensures that they will be interpreted consistently throughout the problem domain.
>
> Requiring expert knowledge -- Applications that deliver expertise to people who do not have it. These applications make an expert's opinion and knowledge available to a wide audience and provide tracking of the decision-making process.
>
> Time-critical -- Applications, such as process control, which must rapidly apply decision-making knowledge or rules, or quickly identify patterns due to on-line, time-critical constraints.

Basic application areas that possess some of the above characteristics include decision management, intelligent documentation, diagnosis/troubleshooting, scheduling/constraint analysis, configuration/design, process monitoring and control, and selection/classification. Our application falls into selection/classification category.

Features of an Object

Although no formal definition is available, an object in a full-fledged, object-oriented, multiparadigm programming environment is often found to exhibit the following features [91]:

1. Objects are divided into two categories: class and instance. A class is a description of one or more similar objects sharing attributes; an instance is a specific example or instance of a class.

2. An object class or instance is uniquely identified by a name.

3. An object manifests itself as a frame, accommodating slots as the frame's attributes. Slots in an object are not ordered.

4. The domain of a slot is specified by facets (slot's attributes). The value for a slot could be an atomic value, a list, or a variable pointing to another data structure, depending on the domain being defined.

5. Slots are usually defined in a class; they will be inherited across the class-subclass and class-instance hierarchies. Various inheritance mechanisms can be specified by slot facets.

6. Procedures, known as methods, can be defined in an object to manage the data stored in slots. Objects interact by

calling each other's methods through the mechanism of message sending.

7. Additional computations may be activated when a slot is created or deleted or when its data are fetched or stored by attaching active values, or demons, to the slot.

It should be emphasized that the object-oriented programming technique is a discipline tedious to master. Fortunately, LEVEL 5 OBJECT provides a user-friendly interface to facilitate the manipulation of information in a complex object world.

Figure 29 delineates the structural breakdown of a LEVEL 5 object. The LEVEL 5 class declaration provides a template for classifying and organizing knowledge within an application. A class describes the structure and behavior of an object within an application, similar to how a record structure, file, or table defines the basic structure of a database. A class is defined by a collection of characteristics called attributes, which are similar to database fields or columns. Behavior, defined by facets, rules, demons, and methods, is bound to the attributes. An object-oriented system therefore binds structure and behavior in a single object in order to facilitate maintenance and promote rapid development.

Both classes and their attributes are declared from the Objects Editor provided by LEVEL 5. For example, the Object Editor screen in Figure 30 shows the class **domain** with the

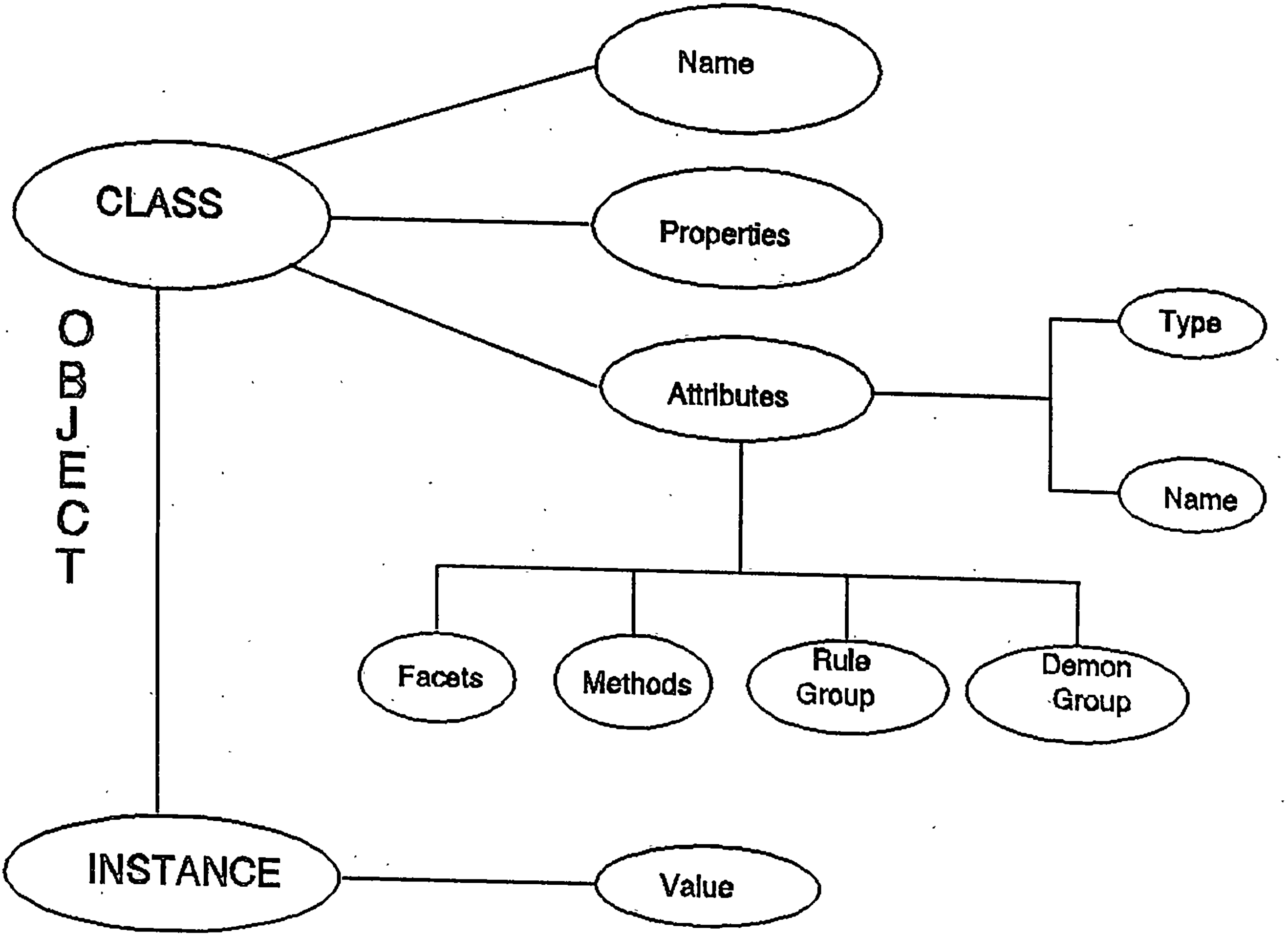
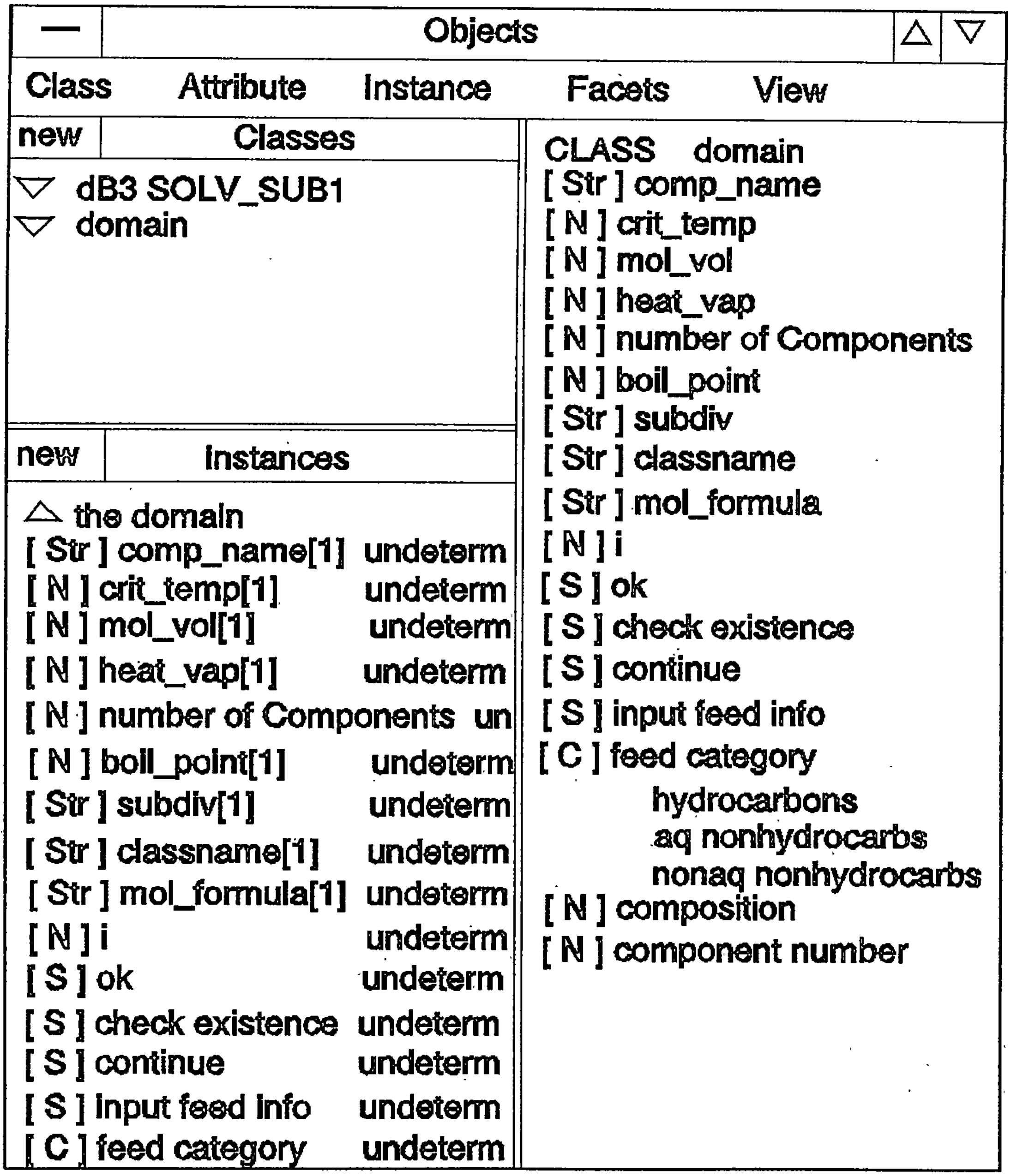


Figure 29 Illustration of object concept[90]



dB3 SOLV_SUB1
domain

the domain

[Str] comp_name[1]	undeterm
[N] crit_temp[1]	undeterm
[N] mol_vol[1]	undeterm
[N] heat_vap[1]	undeterm
[N] number of Components	un
[N] boil_point[1]	undeterm
[Str] subdiv[1]	undeterm
[Str] classname[1]	undeterm
[Str] mol_formula[1]	undeterm
[N] i	undeterm
[S] ok	undeterm
[S] check existence	undeterm
[S] continue	undeterm
[S] input feed info	undeterm
[C] feed category	undeterm

CLASS domain
[Str] comp_name
[N] crit_temp
[N] mol_vol
[N] heat_vap
[N] number of Components
[N] boil_point
[Str] subdiv
[Str] classname
[Str] mol_formula
[N] i
[S] ok
[S] check existence
[S] continue
[S] input feed info
[C] feed category
  hydrocarbons
  aq nonhydrocarbs
  nonaq nonhydrocarbs
[N] composition
[N] component number

Figure 30 Object "domain" for the driving module attributes **comp_name, crit_temp, mol_vol, heat_vap, number of components, boil_point, subdiv, classname, mol_formula, i, ok, check existence, continue, input feed info, feed category, composition, component number** in MAIN.KNB that is a drive program for the whole system. A class declaration remains an empty structure until values are added to its attributes. In order to add values, specific occurrences of the class must be created. An occurrence of a class is called an **object instance.**

Using the database analogy, if a class is similar to the file structure or table that defines a database, then instances are similar to records in the file or rows in the table. LEVEL 5 creates both temporary and permanent instances. A temporary instance occurs during a knowledge base session when the values of attributes are pursued, as, for example, during rule processing. The lower left part of Figure 30 also shows a temporary instance for **domain** class. When the session ends, any temporary instances no longer exist. A permanent instance can occur during development time as a result of an instance declaration. Instances can be declared and edited in the Objects Editor of LEVEL 5 OBJECT.

Procedural Knowledge -- Rules and Methods Representation

Procedural knowledge is compiled knowledge related to the performance of some tasks. The algorithmic knowledge to rank the entrainers and heuristic knowledge for the selection of entrainer will be utilized in our system. Heuristic is the knowledge used to make good judgements, or the strategies, tricks, or "rules of thumb" used to simplify the solution of problems. Heuristic is usually acquired with much experience. The guidelines for selection of entrainers, reviewed in the section of History of Entrainer Selection Methods, have been used largely as procedural knowledge. Those guidelines have been converted into the IF...THEN rule format for the expert system. The most common form of architecture used in expert systems is rule-based knowledge. This type of system uses knowledge encoded in the form of production rules, that is, IF...THEN rules. The rules have an antecedent or condition part, the left-hand side, and a conclusion or action part, the right-hand side. Each rule represents a small chunk of knowledge relating to the given domain of expertise. A number of related rules collectively may correspond to a chain of inferences that lead from some initially known facts to some useful conclusions. When the known facts support the conditions in the rule's left side, the conclusion or action part of the rule is then accepted as known.

As shown in Figure 29, values can be assigned to attributes of an object by rules, methods, and demons that are means for the representation of procedural knowledge. LEVEL 5 OBJECT provides us with flexible utilities to edit rules and methods. The general form of a LEVEL 5 OBJECT rule is as follows:

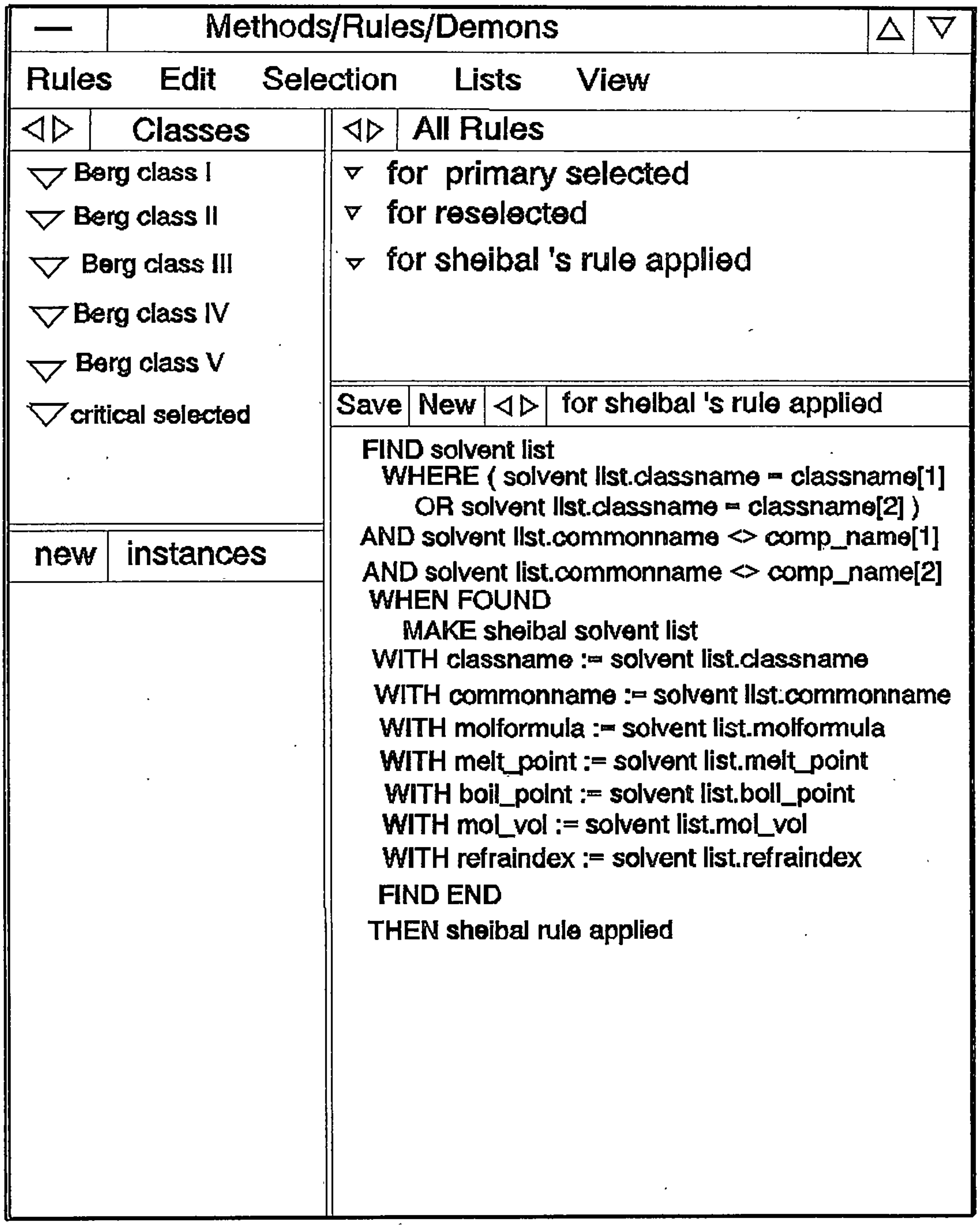
```
RULE <name>
IF   <condition>
     AND <condition>
     OR  <condition>
THEN <condition>
ELSE <alternate conclusion>
```

LEVEL 5 OBJECT's conditions are connected with the keywords **AND** or **OR**. All conditions joined by **AND** must be true for the rule to fire. **OR** can be used to combine several rules with the same conclusion into a single rule. Figure 31 displays a representative rule in our system using LEVEL 5 OBJECT syntax.

Procedural knowledge can also be represented by WHEN NEEDED methods (for backward reasoning) or by WHEN CHANGED methods (for forward reasoning). A WHEN NEEDED (or WHEN CHANGED) method contains a block of developer-defined procedural statements which the backward-chaining (or forward-chaining) inference engine uses to determine an attribute's value. Figure 32 gives an example of a WHEN CHANGED method for this system.

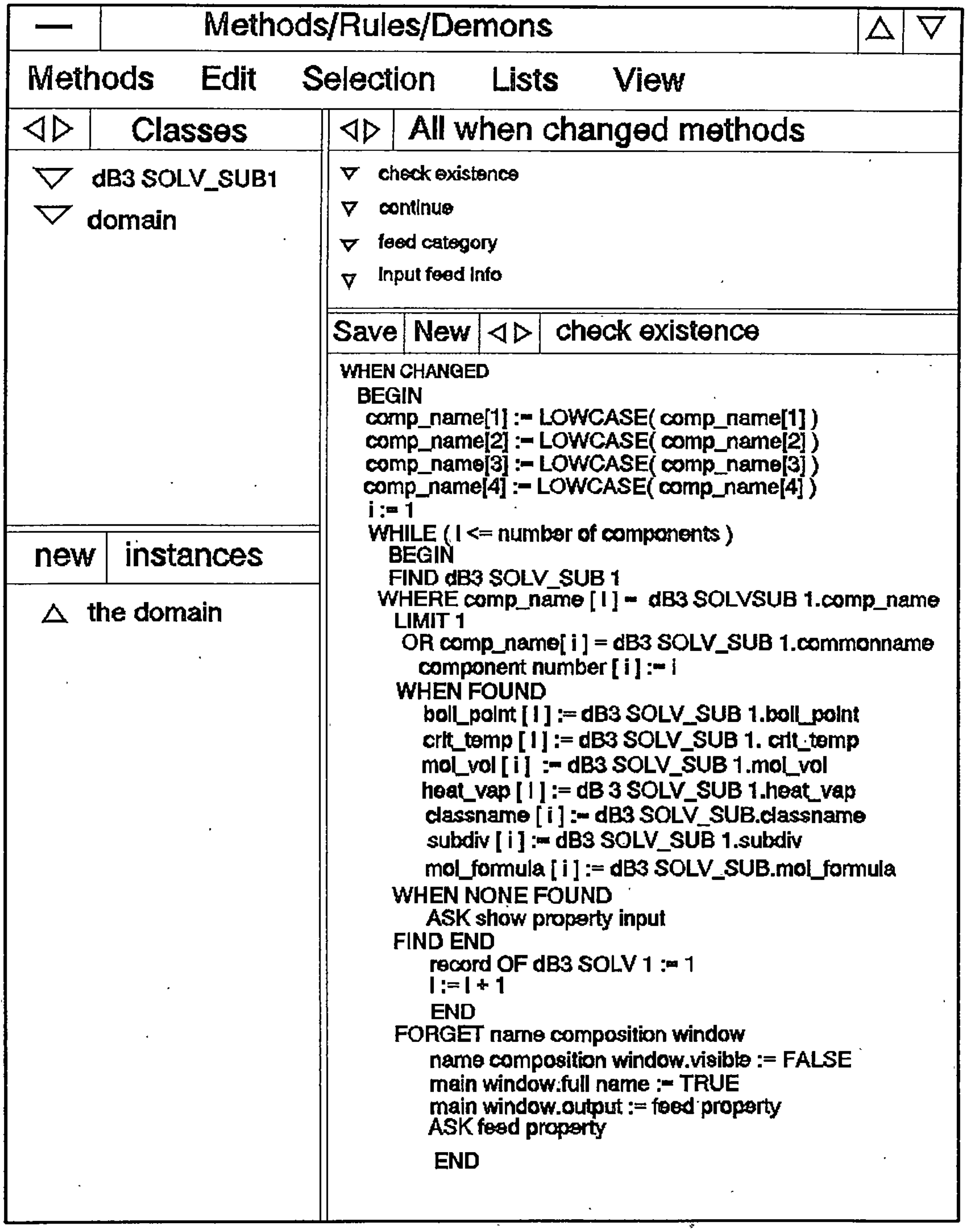
Search Space -- Solvent Database and Related Objects

The selection process involves searching in an object space and testing objects by using some constraints. The object space and the initial requirements, which also form the constraints for the selection process, can be very large. Therefore, the object space should be established first for the selection problem.



```
FIND solvent list
  WHERE ( solvent list.classname = classname[1]
     OR solvent list.classname = classname[2] )
AND solvent list.commonname <> comp_name[1]
AND solvent list.commonname <> comp_name[2]
 WHEN FOUND
    MAKE sheibal solvent list
 WITH classname := solvent list.classname
 WITH commonname := solvent list.commonname
  WITH molformula := solvent list.molformula
  WITH melt_point := solvent list.melt_point
  WITH boil_point := solvent list.boil_point
  WITH mol_vol := solvent list.mol_vol
  WITH refraindex := solvent list.refraindex
 FIND END
THEN sheibal rule applied
```

Figure 31 An example of creating a rule



```
WHEN CHANGED
  BEGIN
   comp_name[1] := LOWCASE( comp_name[1] )
   comp_name[2] := LOWCASE( comp_name[2] )
   comp_name[3] := LOWCASE( comp_name[3] )
   comp_name[4] := LOWCASE( comp_name[4] )
   i := 1
   WHILE ( i <= number of components )
     BEGIN
     FIND dB3 SOLV_SUB 1
    WHERE comp_name [ i ] = dB3 SOLVSUB 1.comp_name
      LIMIT 1
       OR comp_name[ i ] = dB3 SOLV_SUB 1.commonname
         component number [ i ] := i
      WHEN FOUND
         boil_point [ i ] := dB3 SOLV_SUB 1.boil_point
         crit_temp [ i ] := dB3 SOLV_SUB 1. crit_temp
         mol_vol [ i ]  := dB3 SOLV_SUB 1.mol_vol
         heat_vap [ i ] := dB 3 SOLV_SUB 1.heat_vap
          classname [ i ] := dB3 SOLV_SUB.classname
          subdiv [ i ] := dB3 SOLV_SUB 1.subdiv
          mol_formula [ i ] := dB3 SOLV_SUB.mol_formula
     WHEN NONE FOUND
          ASK show property input
     FIND END
          record OF dB3 SOLV 1 := 1
          i := i + 1
          END
     FORGET name composition window
          name composition window.visible := FALSE
          main window.full name := TRUE
          main window.output := feed property
          ASK feed property
           END
```

Figure 32 An illustration of creating a method

As a matter of fact, hundreds of thousands of solvents and their combinations exist which are suitable for extractive and azeotropic distillation applications. Nonetheless, there are just a few solvents that are promising for a specific separation task from the viewpoint of both separation feasibility, and economic optimization.

If solvents are selected for a special extractive or azeotropic distillation task through experimentation, one should have many solvent alternatives to try. Similarly, for an expert system to work, first, we need a database of solvents upon which the selection task is based. For a prototype expert system, it is unwise to include too many solvents in the database since manipulating the database will consume a great deal of computer resources and slow the reasoning process. Too few solvents, however, would inadequately test the expert system and give no solution for many problems. One should, then, make a compromise regarding the number of solvents to be included in the database. The choice of which solvents and what kind of properties of a solvent should be included in the solvent database was based, in this work, upon whether the solvent is used often in the chemical industry, whether the physical properties of the solvent are easy to find from the literature or to estimate by available methods, whether those physical properties are needed for the solvent-solute interaction models in the system, and the suggestions given by experts who have experience in this field.

Appendix A lists part of the solvent list for the separation of hydrocarbon mixtures by extractive distillation selected from Industrial Solvents Handbook[82]. Appendix B gives the solvent list recommended by Dr. Lloyd Berg for extractive distillation. The solvent list in the database for azeotropic distillation is from Horsely's Azeotropic Data-III[92]. The number of the solvents and the scope of azeotropic systems is very limited in the present prototype, since creating a large database is a time-consuming and routine task. The current objective is to create a prototype system as a template. The extension of the small solvent database to a large one will be a part of future work.

The physico-chemical properties of a solvent form some constraints on which the solvent selection process is based. Therefore, these properties should be contained in the solvent database. Table 12 gives a typical physico-chemical property list for methanol. Most of these properties come from the physical property handbooks, and published articles[82-86].

The Joback modification of Lydersen's method[86] was utilized for the estimation of critical properties of some solvents that cannot be found in the literature. The estimated critical temperatures of some solvents are listed in Table 13.

The solvents are classified into ten major categories based on their functional groups. Subdivisions are made according to the nature of the hydrocarbon residue such as saturated, aromatic, unsaturated; open chain, cyclic chain; the number of times the characteristic atom or group occurs; and the primary, secondary, or tertiary nature of amines. Table 14 shows the solvent classification in detail.

Table 12. The Physico-Chemical Properties of Solvent Methanol.

Class name:	monoalcohol
Molecular formula:	CH_4O
Molecular weight:	32.04
Melting point: (°C)	-97.68
Boiling point: (°C)	64.70
Molecular volume: (cm^3/mol)	40.70
Refractive index at 20 °C:	1.32841
Critical temperature: (°C)	239.43
Heat of vaporization: (kcal/mol)	8.4330
Subdivision:	aliphatic, open
Antoine constants:	
A	7.25164
B	1608.39
C	-31.070
Solubility parameters:	
Dispersion ($MPa^{1/2}$)	15.10
Polarity ($MPa^{1/2}$)	12.30
Hydrogen bonding ($MPa^{1/2}$)	22.30
Acidity	0.62

Table 13. Critical Temperatures Estimated by Group Methods.

Compound	V_m at 25°C (cm^3/mol)	T_b (°C)	T_c (°C)
Sulfolane	94.9	287.2	581.80
Dimethyl Sulfoxide	71.0	189.0	444.96
2-Pyrrolidinone	76.9	250.5	519.26
1-Methyl-2-Pyrrolidinone	96.4	202.0	425.16
Benzyl Alcohol	103.6	205.0	384.42
Methyl Salicylate	129.1	233.3	436.00
1,3-Butanediol	90.9	207.5	336.65
Propionic Anhydride	131.5	169.0	339.08
Ethyl Benzoate	144.4	212.4	391.60
Propyl Benzoate	160.5	231.2	399.30
Benzyl Benzoate	189.8	323.5	495.60
Benzyl Acetate	143.0	215.5	395.80

Table 14. Solvent Classes Based on Chemical Function Groups.

1. Water
2. Hydrocarbons
    - 2.1 saturated aliphatic
        - 2.1.1 open chain
        - 2.1.2 cyclic chain
    - 2.2 aromatic
    - 2.3 unsaturated aliphatic
        - 2.3.1 open chain
        - 2.3.2 cyclic chain
3. Hydroxy compounds
    - 3.1 monohydric
        - 3.1.1 aliphatic
            - 3.1.1.1 open chain
            - 3.1.1.2 cyclic chain
        - 3.1.2 aromatic
        - 3.1.3 phenols
        - 3.1.4 unsaturated
            - 3.1.4.1 open chain
            - 3.1.4.2 cyclic chain
    - 3.2 polyhydric
4. Ethers
    - 4.1 monogroup
        - 4.1.1 aliphatic open chain
        - 4.1.2 aliphatic cyclic chain
        - 4.1.3 aromatic
    - 4.2 polygroup
        - 4.2.1 acetal
        - 4.2.2 dioxane
        - 4.2.3 ether alcohol
5. Carbonyls
    - 5.1 aldehydes
        - 5.1.1 saturated aliphatic aldehydes
        - 5.1.2 aromatic aldehydes
        - 5.1.3 unsaturated aldehydes
    - 5.2 ketones
        - 5.2.1 aliphatic ketone
        - 5.2.2 aromatic ketone
6. Acids
    - 6.1 aliphatic acids
        - 6.1.1 saturated acids
        - 6.1.2 unsaturated acids
    - 6.2 acid anhydrides
    - 6.3 aldehyde ethers

Table 14. Solvent Classes Based on Chemical Function Groups--continued.

7. Esters
   7.1 monocarboxylic acid
      7.1.1 saturated aliphatic
      7.1.2 unsaturated aliphatic
      7.1.3 aromatic
   7.2 dicarboxylic acid
   7.3 polybasic acids
   7.4 hydroxy acids

8. Halohydrocarbons
   8.1 monochlorinated
      8.1.1 aliphatic
      8.1.2 aromatic
   8.2 polychlorinated
      8.2.1 aliphatic
      8.2.2 aromatic
      8.2.3 unsaturated
9. Nitrogen compound
   9.1 nitroparaffins
   9.2 nitriles
      9.2.1 aliphatic
      9.2.2 aromatic
      9.2.3 unsaturated
   9.3 amines
      9.3.1 primary monoamines
         9.3.1.1 primary aliphatic
         9.3.1.2 aromatic
         9.3.1.3 primary unsaturated
      9.3.2 primary polyamines
      9.3.3 secondary monoamines
      9.3.3 tertiary monoamines
      9.3.4 amino ethers
   9.4 amides
10. Sulfur compounds

The solvent database files are built based on dBASE III Plus. LEVEL 5 OBJECT is able to access these solvent database files by the database management system that controls the interaction between all objects in the knowledge base. This is implemented through a built-in object called "<u>dB3</u>" in LEVEL 5 OBJECT that can extract the information from the dBASE III

Plus files and transfer it into a hybrid object that contains the built-in attributes and developer-assigned attributes. In other words, LEVEL 5 OBJECT has an interface to communicate between dBASE III plus and the knowledge base. Figure 33 shows the relationship between the built-in object "dB3" and the hybrid object "dB3 solv_sub". This type of relationship is called inheritance in the object-oriented programming environment. In the above example, the child class object, "dB3 solv_sub", inherits all the attributes which the parent class object dB3 possesses.

Structuring Knowledge

The solvent selection problem consists of the search and selection of components. The important questions from an AI/knowledge engineering viewpoint are (1) can the search-selection problem be decoupled or decomposed into tractable subproblems and (2) what is the most effective way to represent and structure the knowledge required to select suitable solvents.

When designing the structure of the expert system, the goal is to mimic as much as possible the problem-solving strategy of the expert, although other strategies are possible. Experts employ many different strategies and variations in problem-solving. Even when the problem-solving strategy is decided upon, there are still many different ways

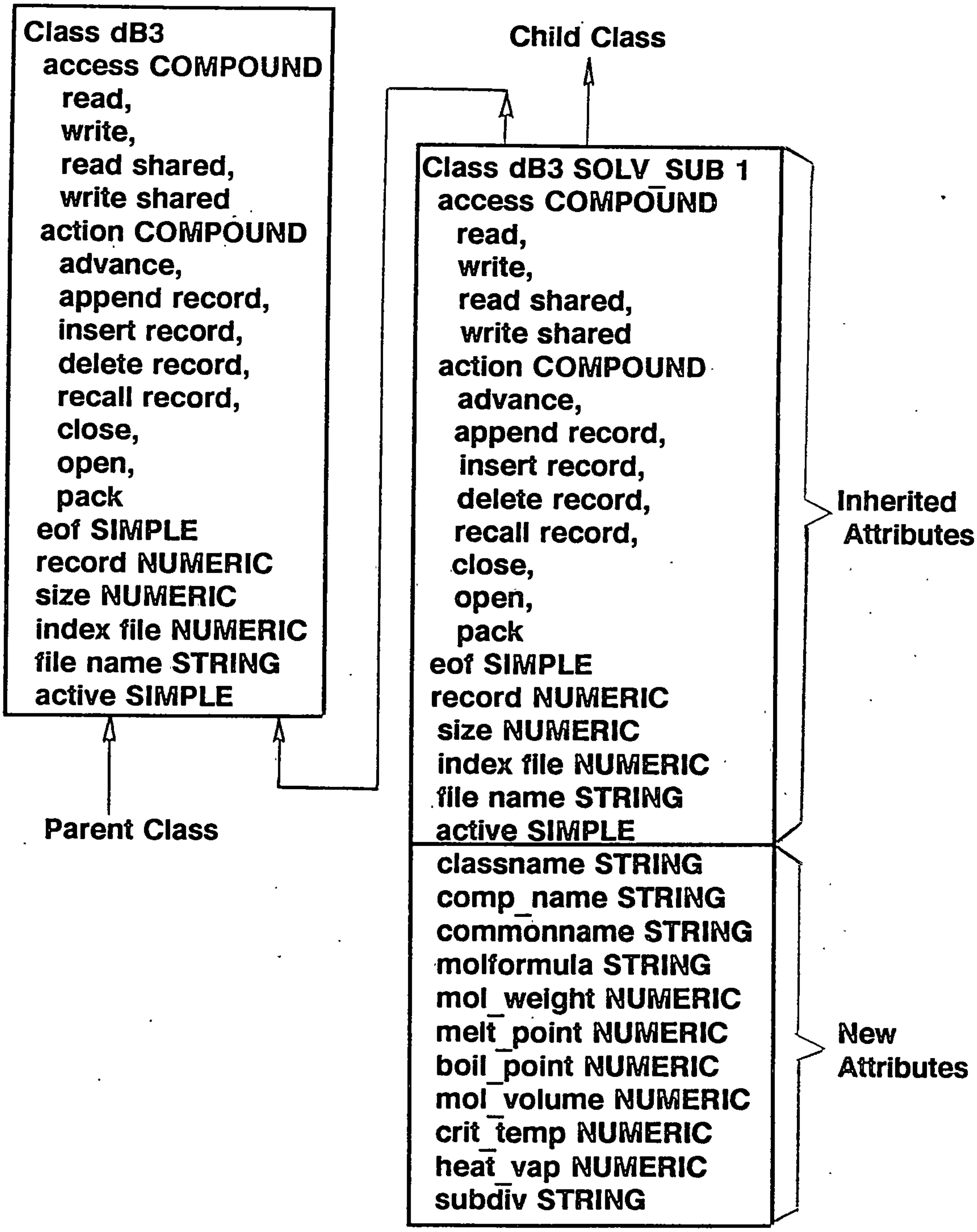


Figure 33 An Example of Inheritance

to approach the design of the structure for the knowledge base. In our system, a task-oriented expert system design is adopted. The task-oriented approach to expert system design represents a strategy of explicit knowledge organization. This method is based on the following premises stated by Chandrasekaran[93]:

(1) A complex problem can be decomposed in terms of "generic tasks." A large problem may be composed of scores of interrelated tasks.

(2) The domain knowledge is available to encode into blocks of knowledge, each of which solves a single task.

(3) The tasks can be built into a structured hierarchy that solves the overall complex problem.

A problem decomposed in this manner can be thought of as a group of "specialists", each working on a separate task. Tasks at the upper levels of hierarchy are more abstract in nature, while those at the lower levels are more concrete. The behavior is reflected in the expert who focuses first on broader issues in the problem and delays consideration of the low level details until later. The task-oriented method has proven useful in malfunction diagnosis[94][95], equipment design[96], and equipment selection problems[97] in chemical engineering.

CHAPTER 6

EXPERT SYSTEM IMPLEMENTATION

Selection Hierarchy

The key to the task-oriented approach is problem decomposition and knowledge structuring. From the overview section, it is clear that an extensive body of information on the selection of solvents is available, although much of it in a form unsuitable for directly coding into tasks.

For extractive distillation, the goal of the selection is to find solvents in order to achieve the desired separation based on criteria such as selectivity or relative volatility, heat capacity, etc.

We faced an important challenge when addressing the accuracy of an expert system for solvent selection. Without carrying out rigorous multicomponent thermodynamic equilibrium calculations, how do we determine selectivity or relative volatility for a specific solvent? Another challenge associated with the developing expert system is the incorporation of quantitative or "deep" knowledge into the systems. Systems using only qualitative or "shallow" knowledge tend to be inaccurate, and in the presence of new situation, may be unreliable. However, systems using deep knowledge often require numerical models, which are cumbersome and run too slowly to be practical. In this work, we demonstrate that a proper compromise between accuracy and efficiency in an expert system for solvent selection can be made through simplified thermodynamic models. Specifically, in order to quantitatively evaluate the selectivity, we use

- the Helpinstill-van Winkle model to estimate the selectivity for hydrocarbon mixtures;
- the extended solubility parameter approach with the solvatochromic parameters to estimate the selectivity for nonaqueous nonhydrocarbon mixtures;
- UNIFAC with UNIQUAC to estimate selectivity and relative volatility for aqueous mixtures.

Figure 34 presents the selection hierarchy in its present form. The form of the hierarchy is guided by two principles. First, as few calculations are performed as possible. Most decisions in the upper levels of the hierarchy are based solely on qualitative relationships. Second, detailed quantitative information is used primarily for final comparisons.

The hierarchy structure consists of four levels, namely,

(1) obtaining basic data for the separation problem;

(2) selection of suitable process;

(3) determination of selectivity and solvency by using

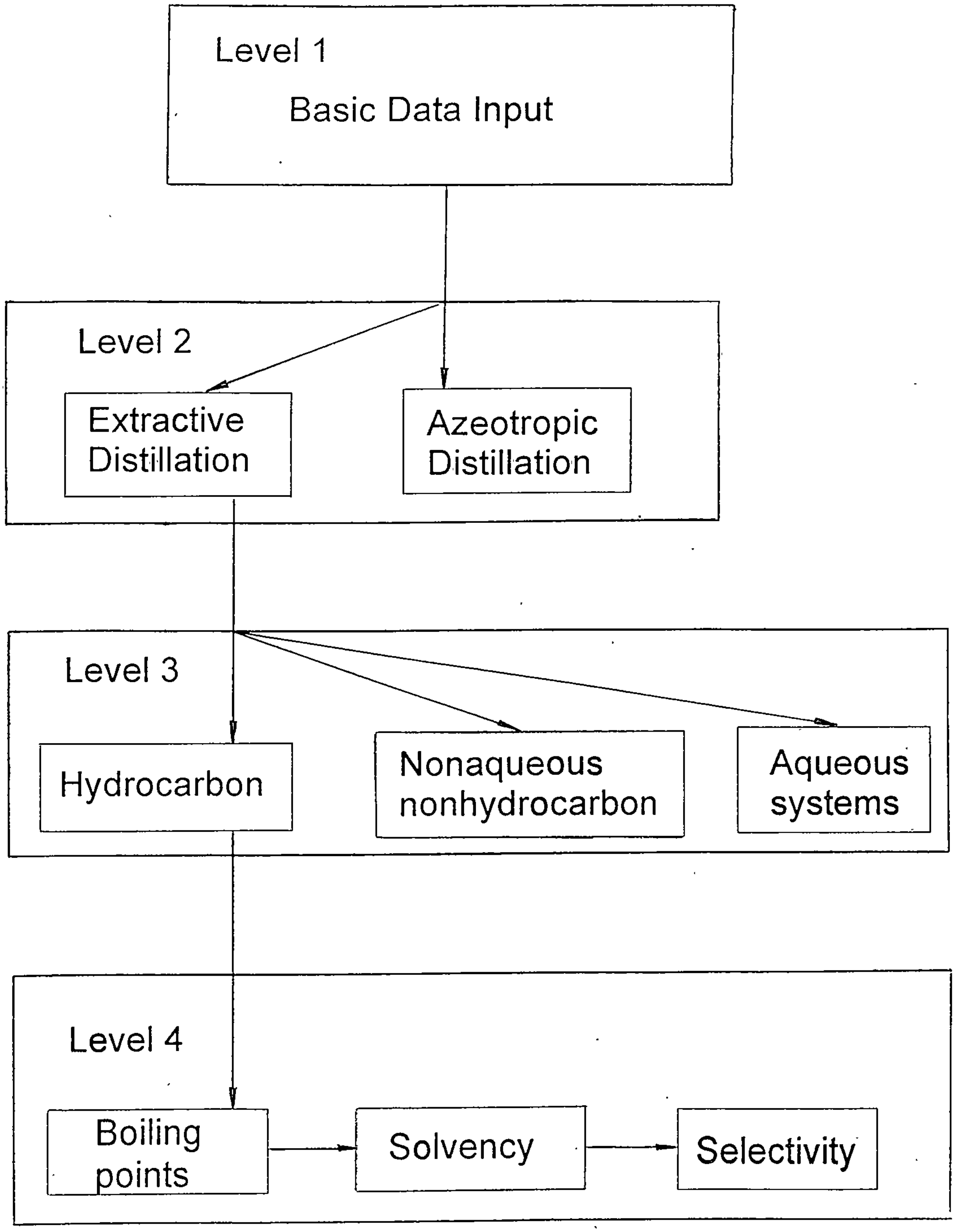


Figure 34 Selection hierarchy for solvent selection

proper thermodynamic models based on the mixture information.

(4) identifying the promising solvents based on polarity and boiling points, ranking potential solvents by using solvency and selectivity criteria.

Figure 35 gives the detailed description of all the branches in the expert system in the present form.

At the start point, the basic information needed is the number, names, and normal boiling points of components in the mixture to be separated. The end-user is prompted by the expert system to enter the information about the mixture.

Then the separation method is determined based on the given information by using the following heuristic:

If the boiling point of one of the components in the mixture is higher than 170°C, then prefer azeotropic distillation; if the boiling points of all components in the mixture are lower than 170°C, then ask an end-user to specify whether extractive distillation or azeotropic distillation is used to separate the mixture. We use this heuristic in our expert system according to Dr. Lloyd Berg's recommendation.

Next, when extractive distillation is specified as the separation method, the end-user will be prompted by the expert system to enter into one of the following three branches: *Hydrocarbon*, *Nonaqueous nonhydrocarbon*, and *Aqueous system*.

If all the components in the mixture are hydrocarbons, then *Hydrocarbon* branch should be entered. If one of the

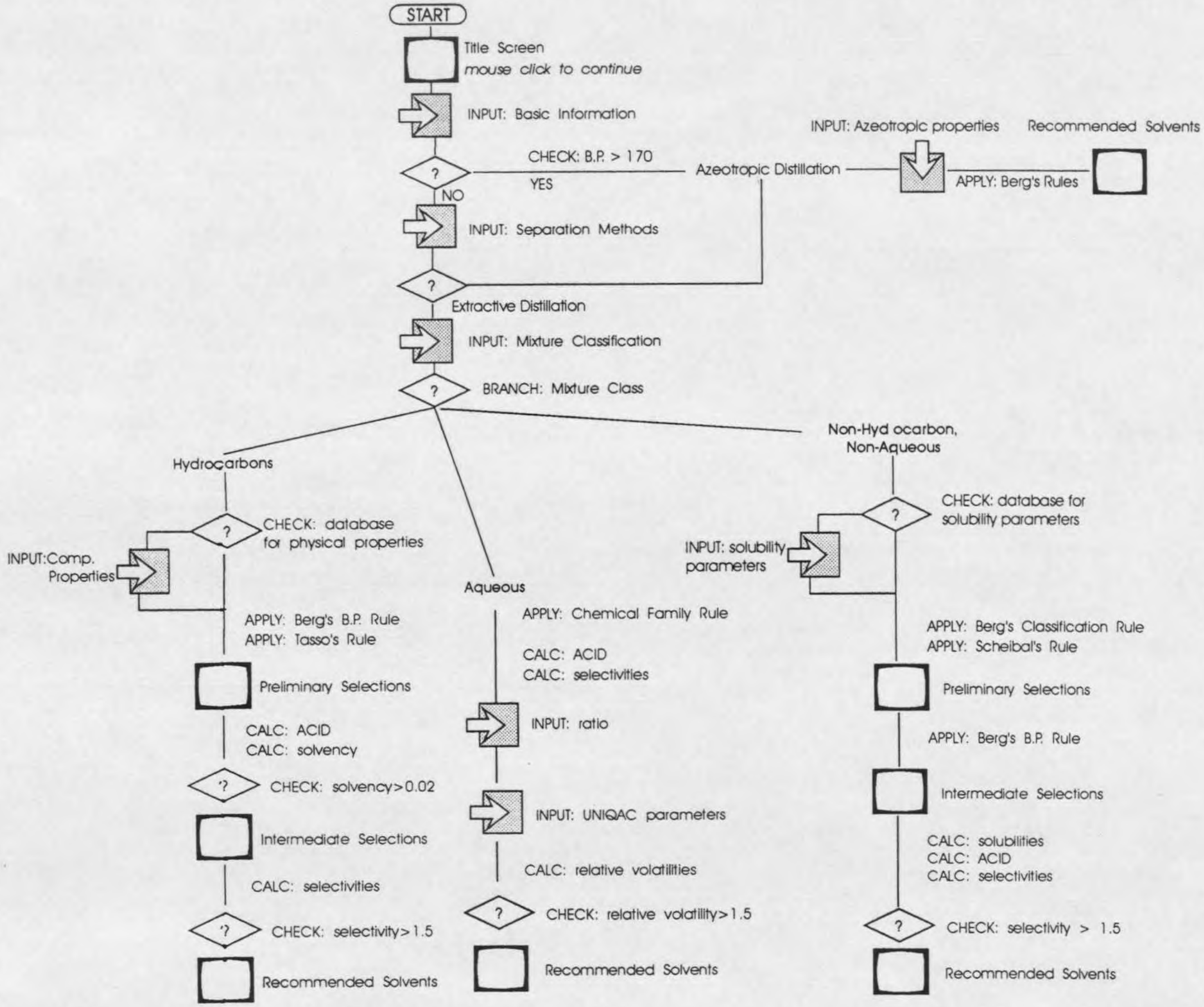


Figure 35 The flowsheet of the expert system

components in the mixture is water, then enter into *Aqueous system* branch. Otherwise, enter into *Nonaqueous nonhydrocarbon* branch.

The reason for this type of classification is that no general thermodynamic model can be successfully applied to all cases. The solubility parameter approach developed by Helpinstill-Van Winkle[50] gives satisfactory results for estimating ACID for hydrocarbon systems. Therefore, for the time being, Helpinstill-Van Winkle model is used in the expert system to calculate the selectivity for comparing solvents.

When the mixture contains water, the system will be highly nonideal. The solubility parameter approach gives very poor results for aqueous systems. So, at present, we use UNIFAC, which is an external program written in QBasic (see Appendix C), to calculate ACID, then enter the ACID values into the database created in LEVEL 5 OBJECT.

For nonaqueous nonhydrocarbon systems, at the time this work was proceeding, the most accurate method to estimate ACID was the MOSCED model[56] proposed by Thomas et al. The limitation of this model is that many parameters in the model are unavailable. Because of this we chose to implement the Karger-Snyder-Eon model [55] to calculate ACID.

Hydrocarbon Branch

If the mixture is hydrocarbons, then the expert system checks to see if the components of the mixture exist in the database for the hydrocarbon branch. If so, no physico-chemical properties need to be entered by the end-user. If not, then the end-user needs to enter the properties listed below for each component in the mixture by following the instructions on the screen:

1. class name
2. molecular formula
3. melting point (°C)
4. molar volume at 25°C (cm^3/mol)
5. critical temperature (°C)
6. heat of vaporization at 25°C (Kcal/mol)
7. refractive index at 25°C
8. subdivision

We classify hydrocarbon compounds into saturated, unsaturated, and aromatic hydrocarbons as subdivisions.

Phase 1. When all needed physico-chemical properties are available, the expert system proceeds to select solvents from the database based on 1) the polarity criterion and 2) boiling point criterion as follows:

1) Select highly polar solvents.

The solvents in the classes of monoalcohols, polyalcohols, acids, aldehydes, esters, amines, organic sulfur compounds, phenols, nitriles, and nitroparaffins in the database are considered to be highly polar solvents.

2) If the boiling points of solvents are 20°C higher than the maximum of boiling points of the components in the mixture, then the solvents satisfy the boiling point criterion. If not, the solvents are not selected.

At this point, the expert system will show the number of selected solvents and the name of each selected solvent.

Phase 2. The Helpinstill-Van Winkle model (shown below) is used to calculate ACID for each component in the mixture with each solvent.

$$\ln\gamma_1^\infty = v_1[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\psi_{12}]/RT + \ln(v_1/v_2) + 1 - v_1/v_2 \qquad (9)$$

$\lambda_{1,2}$: The nonpolar solubility parameters of the solute and solvent;

$\tau_{1,2}$: The polar solubility parameters of the solute and solvent;

$v_{1,2}$: The molar volume of the solute and solvent;

ψ_{12} : Induction parameter characteristic of the nature of the solvents and the type of hydrocarbon.

Correlations for calculating ψ_{12} are given in Table 13.

Table 15. Correlations for Calculating Induction Parameter.

Type of hydrocarbon	ψ_{12}
a saturated hydrocarbon	$0.399(\tau_1 - \tau_2)^2$
an olefin	$0.388(\tau_1 - \tau_2)^2$
an aromatic	$0.447(\tau_1 - \tau_2)^2$

The nonpolar solubility parameter of a polar solvent is obtained from its homomorph:

$$\lambda^2 = \Delta U^v/V \qquad (10)$$

Table 16 lists the expressions needed for calculating the nonpolar solubility parameter.

Table 16. Correlations for Calculating the Nonpolar Solubility Parameter.

Solvent Homomorph	λ^2
n-paraffin	$77\ V^{-0.127} e^{-0.00161V} / T_r^{(0.2566\ln(V)-0.3553)}$
cycloparaffin	$225.3V^{-0.35} / T_r^{0.7}$
aromatic	$1616V^{(0.0017V - 0.73)} e^{(-0.00872V)} / T_r^{(0.003V + 0.4)}$

where ΔU^v is the energy of vaporization (kcal/mol), V is the molar volume (cm^3/mol), and T_r is the reduced temperature.

The polar solubility parameters are then obtained by difference:

$$\tau^2 = \delta^2 - \lambda^2 \qquad (11)$$

where δ is the total cohesive energy density,

$$\delta^2 = (\Delta H - RT)/V \qquad (12)$$

where ΔH is the enthalpy of vaporization (kcal/mol).

For hydrocarbon and solvent solutions, an approximate expression can be used to measure solubility roughly for high γ^∞[98]:

$$\text{solvency} = 1/\gamma^\infty \qquad (13)$$

It should be noted that this expression is approximatly used only for hydrocarbons with high polar solvents. It cannot be extended to other mixtures. If solvency is too small, then the solvent will form two phases with solutes. This is not expected for extractive distillation. When a solvent satisfies the following criterion, then the solvent will be kept for the further consideration:

$$\text{solvency} > 0.02 \qquad (14)$$

After this criterion, the expert system will show the number of the selected solvents and the name of each selected solvent.

Phase 3. We use selectivity criterion to select solvents, selectivity is defined as[49]:

$$S^{\infty}_{12} = \gamma_1^{\infty}/\gamma_2^{\infty} \tag{15}$$

If selectivity of a solvent satisfies the following criterion:

$$\text{selectivity} > 1.5 \tag{16}$$

then the solvent is recommended for the further verification either by the economic analysis or by experimentation. The list of solvents recommended will show on the screen along with their selectivities. It should be noted that the value of 1.5 is a default which can be changed by the end-user.

Aqueous System Branch

If extractive distillation is specified and the mixture to be separated is aqueous, then the end-user selects a solvent from each chemical family with high polarity, at the same time, the solvent selected should satisfy Berg's boiling point criterion. Then ACID for each component in the mixture with each selected solvent are calculated by using the external UNIFAC program (see Appendix for the detailed UNIFAC equations). These ACID values are then entered into the database.

In the present version of SSS, the ACID database is for methanol-water and ethanol-water systems with 12 different solvents.

Phase 1. When the end-user enters into the aqueous system branch using extractive distillation as a separation method, the expert system prompts the user to enter the ratio of solvent to mixture, actual composition of the mixture as the feed stream, and ACID for each component in the mixture. Then the expert system prompts the user to enter the name and number of the chemical groups of each component by using a table equipped with the different main group parameters for the UNIQUAC model.

With ACID data available, the expert system selects solvents by applying the selectivity criterion (selectivity > 1.5). With the UNIQUAC thermodynamic model, we can calculate activity coefficients at the specified composition for different ratios of the solvent to mixture (see Appendix D for the detailed description of the required equations).

Phase 2. The solvents which pass the selectivity criterion are examined by the following relative volatility criterion:

$$\text{relative volatility} > 1.5 \tag{17}$$

Relative volatility is defined as:

$$\alpha_{12} = \gamma_1 P^{\circ}_1 / \gamma_2 P^{\circ}_2 \tag{18}$$

where $P^{\circ}_{1,2}$ are the saturation pressures of the components.

The expert system then displays its recommendations for the promising solvents.

Nonaqueous Nonhydrocarbon Branch

If the end-user enters the nonaqueous nonhydrocarbon branch, the expert system will check if the components in the mixture exist in the database for hydrocarbon branch and in the database for nonaqueous nonhydrocarbon. If the components do exist in the database, the user does not need to enter the physico-chemical properties for the expert system. If the components do not exist in the database, the following physico-chemical properties (defined below) need to be entered:

1. class name
2. molecular formula
3. molar volume at 25°C (cm^3/mol)
4. solubility parameters ($MPa^{1/2}$)
    a. dispersion parameter
    b. polarity parameter
    c. hydrogen bonding parameter
5. Kamlet basicity parameter

Where class name is defined in the same way as in Appendix A. Solubility parameters, as used here, are Hansen's extended solubility parameters[83]. Kamlet, Taft and others [99] have developed scales of hydrogen bond acidity/basicity and dipolarity/polarizability, based upon extensive spectroscopic measurements used to determine solvatochromic parameters (π^*, α_{KT}, and β_{KT}). The molecular interactions for compounds in solutions are characterized by the three scales: the π^* scale for dipolarity/polarizability, the α_{KT} scale for hydrogen bond donor (HBD) strength, and the β_{KT} scale for hydrogen bond acceptor (HBA) strength. Each of the scales is based upon spectroscopic measurements coupled with a linear free energy relationship approach to separate the effects of various interactions in solution. The hydrogen bond acidity/basicity parameters are used to evaluate basic and acidic solubility parameters for Karger-Snyder-Eon equation. Some values of β_{KT} are taken from the literature[99]. If they are not available, we use rules provided in the literature[104] to estimate them.

Then the expert system enters into the nonaqueous nonhydrocarbon branch.

Phase 1. In this branch, Berg's classification for solvents is used as a guide to make a preliminary selection of solvents (see Appendix D for the detailed classification of solvents). Classes I, II, and III from the five Berg's classes are selected on this level. Also, Sheibel's rule is used for solvent selection in this phase[20]:

Any member of the homologous series of either component of the mixture can be used as an agent to separate the azeotropic mixture by extractive distillation.

At this point, the screen will display the list of solvents based on the above heuristics.

Phase 2. The expert system uses the same boiling point rule as described above (20°C higher) to make a more critical selection. After this rule is applied, the expert system will display the number of selected solvents and their names.

Phase 3. Karger-Snyder-Eon equation is used to calculate ACID[55]:

$$\ln \gamma_1^{\infty} = V/RT[(\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 +$$

$$(\delta_{1a} - \delta_{2a})(\delta_{1b} - \delta_{2b})] + \ln(V_1/V_2) + 1 - (V_1/V_2) \quad (19)$$

where δ_d, δ_p, δ_a, δ_b are the dispersion solubility parameter, polar solubility parameter, basic solubility parameter, and acidic solubility parameter, respectively. V is molar volume. δ_d and δ_p are adopted from Hansen's dispersion parameter and polar parameter. In this study, it was found that a linear relationship exists between the δ_b-value of Karger et al.[55] and the β_{KT}-value of Kamlet et al.[99]:

$$V^{1/2}\delta_b = 60.1\beta_{KT} + 2.45 \quad (20)$$

As for acidic solubility parameter, δ_a, the α-values given by Kamlet et al. are less accurate than β_{KT}-values. δ_a can be obtained using the following equation:

$$2\delta_a\delta_b = \delta_T^2 - \delta_d^2 - \delta_p^2 = \delta_h^2 \quad (21)$$

Then the selectivity criterion is applied to solvents as follows:

$$\text{selectivity} > 1.5 \quad (22)$$

The definition of selectivity is the same as described before. After the selectivity criterion, the expert system displays the number of the recommended solvents and their names along with their selectivities.

Azeotropic Branch

As for azeotropic distillation, the current database is only for the methanol-acetone system for illustration. In this branch, only Berg's rules[11] have been implemented to date.

If the mixture is a close-boiling one or maximum azeotrope, then select solvents which form a binary minimum azeotrope with one component, or form binary minimum azeotrope with each component but one minimum azeotrope boils at a significantly lower temperature than the other.

If the mixture is a minimum azeotrope, then solvents that form a binary minimum azeotrope with one component that boils at a significantly lower temperature than the original minimum azeotrope can be selected. Here we subjectively assign as a "significantly lower temperature," 15°C.

When the end-user enters this branch, the expert system prompts for the following information to be entered:

Is it a close-boiling mixture or azeotrope?

If it is an azeotrope, is it a minimum or maximum azeotrope?

What is the composition of the azeotrope? What is the boiling point of the azeotrope?

With the information available, the end-user can direct the expert system into the aqueous branch.

If the mixture is a close-boiling or a maximum azeotrope, then select solvents from the azeotropic database for component 1 and from the azeotropic database for component 2. Then if solvents from the two databases are not identical in terms of their common names and CAS names, add them to the recommendation list; otherwise compare the boiling point of azeotrope 1 (component 1 in it) with that of azeotrope 2 (component 2 in it), if the difference between the two boiling points are greater than 15°C, then add the solvent into the recommendation list; otherwise discard the solvent.

If the mixture is a minimum azeotrope, then select solvents from the azeotropic database for component 1 and from the azeotropic database for component 2. If solvents from the two databases are identical, discard them. If solvents from the two databases are not identical, then compare the boiling point of the new azeotrope with that of the original azeotrope. If the difference between the boiling point of the new azeotrope and that of the original one is greater than 15°C, then add the solvent into the recommendation list, if not, discard it.

Appendix D lists all rules and thermodynamic models applied in the systems.

Application Examples

Example 1: Selection of Solvents for Separation of Xylene Isomers

Xylenes are dimethylbenzenes and exist as three distinct isomers, depending upon the relative positions of the methyl groups on the aromatic ring. p-Xylene is an important raw material for manufacture of terephthalic acid and dimethyl terephthalate, both used to manufacture polyester synthetic fibers. o-Xylene is used as a raw material for the manufacture of phthalic anhydride which is used in turn for the manufacture of dioctyl phthalate and other phthalates, which are used as plasticizers for polyvinyl chloride. m-Xylene is almost entirely used for gasoline blending and conversion into the other isomers through isomerization. p-Xylene has the greatest demand in relation to the availability of the various isomers from refinery streams. Various properties of the three xylene isomers are shown in Table 17. From the table, it can be seen that the boiling points are quite close together. From the boiling points and the changes in boiling points with respect to pressure it can be computed that the relative volatility of p-xylene to m-xylene is 1.02[100], which is so slight that separation by conventional distillation is out of the question.

First, we specified as a test a separation problem that a mixture of m-xylene and p-xylene with the feed concentration of 50% m-xylene. The mixture is close-boiling. The boiling points are 139.5°C and 138.7°C, respectively.

Table 17. Physical Properties of Xylene Isomers.

	o-Xylene	m-Xylene	P-Xylene
Boiling point, °C	144.2	139.5	138.7
Freezing point, °C	-25.0	-47.7	13.5
Molecular weight	106.16	106.16	106.16
Heat of Vaporization, KJ/kg	347.00	343.00	340.00
Density at 293 K, Mg/m^3	0.8802	0.8642	0.8610

The first task is to determine which separation process will be used. Since the boiling points of both components are lower than 170°C, and compositions do not fall into a category favoring liquid-liquid extraction, both extractive and azeotropic distillation processes are favored. The end-user can choose any option of extractive distillation or azeotropic distillation. For purposes of this example, extractive distillation is arbitrarily specified at this point.

Both components are hydrocarbons, so the end-user directs the program into the branch in which hydrocarbon mixtures are handled.

Phase 1. In this module, the first screen shows the solvent list obtained by using Berg's boiling point rule and polarity criteria as shown in the form of a WHEN NEEDED METHOD,

```
WHEN NEEDED
  BEGIN
  IF number of components = 2 THEN
     boil_point[3] := 0.0
     boil_point[4] := 0.0
  IF number of components = 3 THEN
     boil_point[4] := 0.0
   i := 0
FIND dB3 SOLV_SUB 1
  WHERE boil_point OF dB3 SOLV_SUB 1 >= 20.0 + MAX
                (boil_point[1], boil_point[2]
                 boil_point[3], boil_point[4])
  AND (classname OF dB3 SOLV_SUB 1 := "monoalcohols"
  OR   classname OF dB3 SOLV_SUB 1 := "polyalcohols"
  OR   classname OF dB3 SOLV_SUB 1 := "acids"
  OR   classname OF dB3 SOLV_SUB 1 := "esters"
  OR   classname OF dB3 SOLV_SUB 1 := "aldehydes"
  OR   classname OF dB3 SOLV_SUB 1 := "amines"
  OR   classname OF dB3 SOLV_SUB 1 := "org_sulfur_comp"
  OR   classname OF dB3 SOLV_SUB 1 := "phenols"
  OR   classname OF dB3 SOLV_SUB 1 := "nitriles"
  OR   classname OF dB3 SOLV_SUB 1 := "nitroparaffins")
 WHEN FOUND
  i := i + 1
  solv coeff.solv name[i] := dB3 SOLV_SUB 1.commonname
  solv coeff.boil point[i] := dB3 SOLV_SUB 1.boil_point
  solv coeff.crit temp[i] := dB3 SOLV_SUB 1.crit_temp
  solv coeff.mol vol[i] := dB3 SOLV_SUB 1.mol_vol
```

```
      solv coeff.heat of vap[i] := dB3 SOLV_SUB 1.heat_vap
      solv coeff.subdiv[i] := dB3 SOLV_SUB 1.subdiv
     MAKE solv attri show
      WITH solv number := i
      WITH solv name := solv coeff.solv name[i]
      WITH boil point := solv coeff.boil point[i]
      WITH crit temp := solv coeff.crit temp[i]
      WITH mol vol := solv coeff.mol vol[i]
      WITH heat vap := solv coeff.heat vap[i]
      WITH subdiv := solv coeff.subdiv[i]
     FIND END
      total number OF solv coeff := i
      record OF dB3 SOLV_SUB 1 := 1
      full screen OF main window := FALSE
      title OF main window := "AUTO Solvent Selection System"
     ASK SolvAttri display
    END
```

the system comes up with 30 potential solvents from the database containing 145 solvents.

Phase 2. The second screen gives the solvent list after considering solvency criterion as shown below,

```
  WHEN NEEDED
   BEGIN
    solvency_solvents.solv number := 0
   FOR idac.gamma12[i] <= 50.0 AND idac.gamma22[i] <= 50.0
    THEN
    BEGIN
    solvency_solvents.solv number := 1 +
                      solvency_solvents.solv number
    solvency_solvents.solv name[solvency_solvents.solv number]
                   := solv coeff.solv name[i]
    solvency_solvents.gamma12[solvency_solvents.solv number]
                   := idac.gamma12[i]
    solvency_solvents.gamma22[solvency_solvents.solv number]
                   := idac.gamma22[i]
    solvency_solvents.selectivity[solvency_solvents.solv
           number] := idac.gamma12[i]/idac.gamma22[i]
    MAKE solv list
     WITH solv number := solvency_solvents.solv number
     WITH solv name := solvency_solvents.solv name
    END
     solvency_solvents.total number :=
                         solvency_solvents.solv number
     END
     ASK solvent list_solvency
   END
```

the program cuts one solvent off from 30 potential solvents on the previous screen and ends up with 29 potential solvents.

Phase 3. The third screen presents the solvent list after considering the selectivity criterion which is also executed by a WHEN NEEDED METHOD as the following,

```
WHEN NEEDED
 BEGIN
 FORGET solv name
 FORGET selectivity
   selectivity_solvents.solv number := 0
  FOR ( i= 1 TO solvency_solvents.total number]
   BEGIN
    IF solvency_solvents.selectivity[i] >= 1.2
     OR 1.0/solvency_solvents.selectivity >= 1.2 THEN
      BEGIN
      selectivity_solvents.solv number := 1 +
                    selectivity_solvents.solv number
      selectivity_solvents.solv name
               [selectivity_solvents.solv number] :=
                       solvency_solvents.solv name[i]
      selectivity_solvents.selectivity
               [selectivity_solvents.solv number] :=
                       solvency_solvents.selectivity[i]
     MAKE solvent list
      WITH solv number := selectivity_solvents.solv number
      WITH solv name := selectivity_solvents.
              solv name[selectivity_solvents.solv number]
      WITH selectivity := selectivity_solvents.
              selectivity[selectivity_solvents.solvnumber]
      END
     selectivity_solvents.total number :=
                   selectivity_solvents.solv number
     END
      ASK solvent list_selectivity
   END
```

the total number of potential solvents shown on the screen is 0, that is, all of the 145 solvents in the current database have been excluded as potential candidates for this very difficult separation, based upon four rules. Figure 36 shows the selection procedure and the number of solvents at each

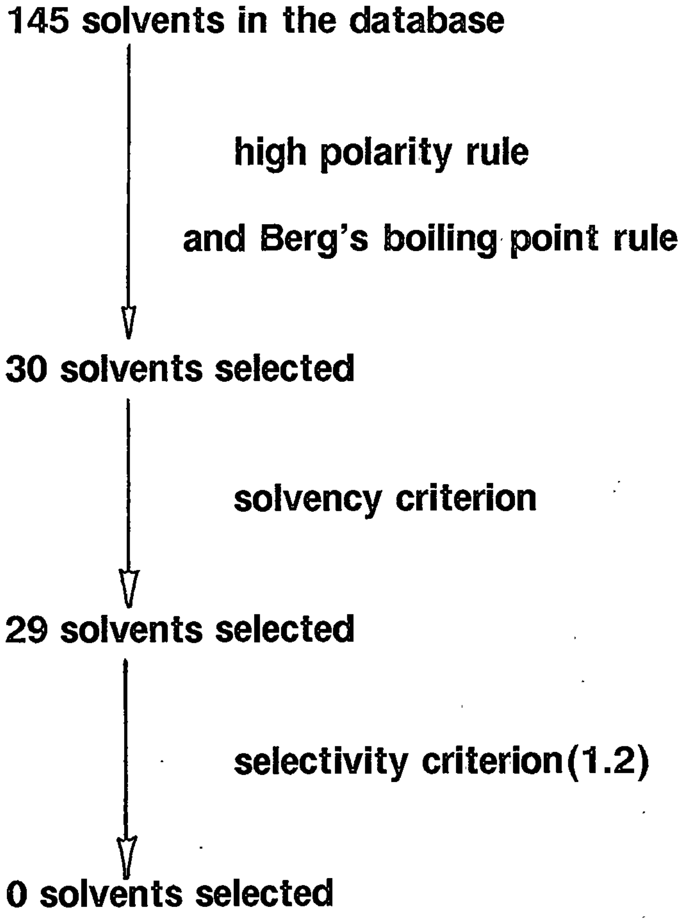


Figure 36 Selection procedure and results for p-xylene and m-xylene

selection stage for the p-xylene and m-xylene system. This negative result in fact agrees with experimental results to date. Dr. Lloyd Berg has run about 5,000 experiments but ended up with no promising solvents for the separation of p-xylene and m-xylene.

We also tested m-xylene and o-xylene system.

Phase 1. After the primary selection based on polarity criterion and Berg's boiling point rule, the expert system comes up with 35 potential solvents from 145 solvents in the database.

Phase 2. After the solvency criterion is applied, 32 potential solvents are displayed on the screen.

Phase 3. The final recommended solvents after considering the selectivity criterion are 16, which are given along with their selectivities in Table 18. Table 18 also shows relative volatilities for several solvents obtained from experiments by Dr. Lloyd Berg[101][102]. As we can see, Dimethyl sulfoxide, Dimethyl acetamide, and 1-Octanol show some promise by both the expert system and experiments. 1,4-Butanediol and propylene glycol were proposed as a co-solvent with Dimethyl sulfoxide in the literature[102]. Other solvents listed in Table 18 should be verified further by experiments. Figure 37 shows the selection procedure and the number of solvents at each stage.

Table 18. The Selected Solvents by SSS with Their Selectivities.

Solvent	Computed Selectivity	Experimental Relative Volatility
cyclohexanol	1.28	--
sec-heptyl alcohol	1.45	--
1-octanol	1.38	1.38 [101]
ethyl hexyl alcohol	1.42	--
propylene glycol	1.31	--
1,3-butanediol	1.34	--
1,4-butanediol	1.26	--
dibutylamine	1.52	--
dimethyl acetamide	1.35	1.33 [102]
dimethyl sulfoxide	1.24	1.30 [102]
butyric acid	1.36	--
valeric acid	1.35	--
isovaleric acid	1.37	--
hexanoic acid	1.33	--
octanoic acid	1.33	--
propionic anhydride	1.44	--

Example 2. Selection of Solvents for Separation of Water from Ethanol

Water and ethanol form a minimum azeotrope which contains 89 mol% ethanol and 11 mol% water. The azeotrope cannot be separated by conventional rectification regardless of the number of theoretical plates used. Table 19 shows the boiling points of ethanol, water, and the minimum-boiling azeotrope at one atmosphere.

In order to produce ethanol free of water, either azeotropic distillation or extractive distillation can be applied. For the design of these processes, a suitable solvent should be determined first.

We use this example to illustrate the use of the expert system to screen solvents for the separation of an aqueous

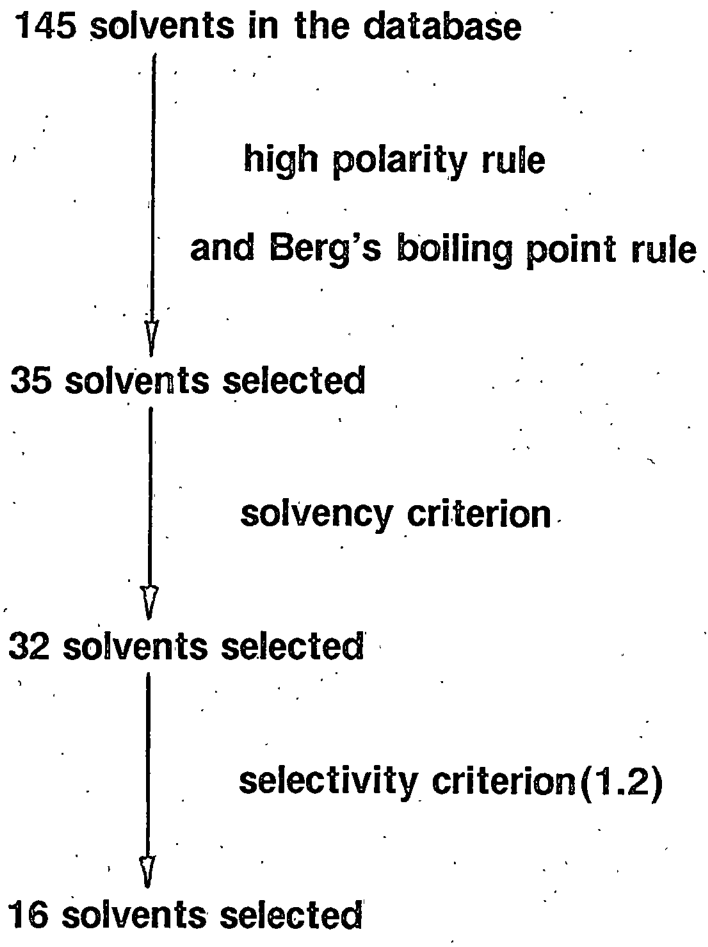


Figure 37 Selection procedure and results for o-xylene and m-xylene

Table 19. Properties of Components and Azeotrope at 1 Atm for Ethanol and Water.

	n.b.p., °C	Azeotrope composition
Ethanol	78.3	
Water	100.0	
Ethanol-Water azeotrope	78.15	89 mol% ethanol

mixture by extractive distillation.

At the beginning, the expert system asks for information about the mixture. The number of the components is specified as <u>two</u>, and then the names of both components in the mixture are entered by the end user as <u>water</u> and <u>ethanol</u>. After that, the components are checked against the database, the result of the checking step shows that both components exist in the database, therefore the end user does not need to type in the physical properties of the components in the mixture. Then, we specify the separation method as extractive distillation. At this point, the system asks the end user whether the mixture is <u>aqueous nonhydrocarbons</u>, <u>nonaqueous nonhydrocarbs</u>, or <u>hydrocarbons</u>. Obviously, this mixture is <u>aqueous nonhydrocarbons</u>. The expert system then chains to the branch dealing with aqueous nonhydrocarbon mixtures. This branch requires more information about the mixture. The mole fractions of the azeotrope are entered as 0.11 and 0.89 for water and ethanol, respectively. Activity coefficients at infinite dilution for water as solute and ethanol as solvent and for ethanol as solute and water as solvent are 2.35 and

5.42[65], respectively. The ratio of any solvent to the mixture is entered as one.

The database in the expert system contains several solvents for different mixtures. Each solvent is a representative of a different chemical group. In this prototype system, activity coefficients at infinite dilution for some mixtures with different solvents are calculated by an external program written in QBasic. Table 20 shows activity coefficients at infinite dilution for water-ethanol with different solvents.

Table 20. Activity Coefficients at Infinite Dilution for Water-Ethanol with Different Solvents

Solvent	Solute	γ^{∞}_{1}	γ^{∞}_{2}
ethylene glycol	water	0.836	0.732
	ethanol	1.3601	1.4114
acrylonitrile	water	23.128	49.317
	ethanol	3.6965	2.8836
dimethyl sulfoxide	water	0.229	0.047
	ethanol	0.5912	0.3022
dimethyl formamide	water	0.75	0.501
	ethanol	1.5473	1.8599
furfural	water	11.2	88.834
	ethanol	5.5041	4.5449
2-nitropropane	water	24.434	391.07
	ethanol	6.8454	5.6948

The expert system uses infinite dilution activity coefficients to calculate selectivity by Equation (6), then the selectivity criterion is applied in the form of a WHEN CHANGED METHOD:

```
BEGIN
  solvent number OF control := 0
 FIND solv selectivity
  WHERE solv selectivity.selectivity >= 1.5
```

```
    OR ( 1/solv selectivity.selectivity ) >= 1.5
    WHEN FOUND
     control.solvent number := control.solvent number + 1
    MAKE pri solvent
         WITH number := control.solvent number
         WITH name := solv selectivity.solvent name
         WITH selectivity := solv selectivity.selectivity
   FIND END
         ASK first level solv display
  END.
```

Then the solvents along with their selectivities are displayed on the screen, as illustrated in Table 21.

Table 21. Solvents for Water-Ethanol Based upon Selectivity.

Solvents	Selectivity
ethylene glycol	0.6146
acrylonitrile	6.2567
dimethyl sulfoxide	0.3873
dimethyl formamide	0.4847
furfural	2.0348
2-nitropropane	3.5694

With the selectivity of different solvents for the mixture, the expert system uses UNIQUAC model to calculate the relative volatility for each solvent. After the relative volatility criterion, which is very similar in form to the selectivity criterion, is applied, the expert system comes up with the proposed solvent list as shown in Table 22.

Ethylene glycol is already used in industry. Dimethyl formamide has been suggested in the literature on the basis of experimental vapor-liquid equilibrium data[103]. Furfural and 2-nitropropane need to be further verified by experiment.

Table 22. Solvents Selected for Separation of Water-Ethanol Based upon Relative Volatility.

Solvent	Boiling Point, °C	Relative volatility
ethylene glycol	197.3	2.327
dimethyl formamide	153.0	1.940
furfural	161.8	5.521
2-nitropropane	120.25	5.885

Example 3. Selection of Solvents for Separation of Methyl acetate from Methanol

Methyl acetate and methanol form a minimum-boiling azeotrope which contains 18.7 wt.% methanol and 81.3 wt.% methyl acetate. The azeotrope cannot be separated by conventional rectification regardless of the number of theoretical plates used. Table 23 shows the boiling points of methanol, methyl acetate and the minimum boiling azeotrope at one atmosphere.

In order to produce pure methanol from the 50 wt.% methanol and methyl acetate solution, either azeotropic distillation or extractive distillation can be used. We use extractive distillation to accomplish the separation task. The

Table 23. Properties of Components and Azeotrope at 1 Atm for Methanol and Methyl acetate.

	n.b.p., °C	Azeotrope composition
Methanol	64.3	
Methyl acetate	56.3	
Methanol-Methyl acetate azeotrope	54	18.7 wt.% methanol

expert system will be directed to the nonaqueous nonhydrocarbon branch. The selection process comprises three selection stages: primary selection, critical selection, and reselection. At the primary selection stage, the expert system selects solvents of several chemical classes with high or moderate hydrogen bonding ability or polarity and the homologies of the same chemical classes as those for the components in the mixture to be separated. At the critical selection stage, the solvent selection is carried out according to Berg's boiling point rule. Finally, at the reselection stage, the selectivity criterion is applied to select solvents. We call this stage "reselection" because calculation of selectivity involves using a thermodynamic model which is a time-consuming procedure. This stage uses deep knowledge as a refining selection step. Figure 38 shows the selection procedure and the number of solvents at each selection stage for the methanol and methyl acetate system. Table 24 lists part of the solvents recommended by the expert system. From

Table 24. Partial Solvent List Selected for Separating Methanol from Methyl Acetate.

Solvent	Selectivity (Methanol/MA)
Ethylene glycol	143.6
Propylene glycol	1424.0
Glycerol	7875.2
Ethyl formate	47.2
n-Propyl acetate	33.7
Ethyl butyrate	29.8

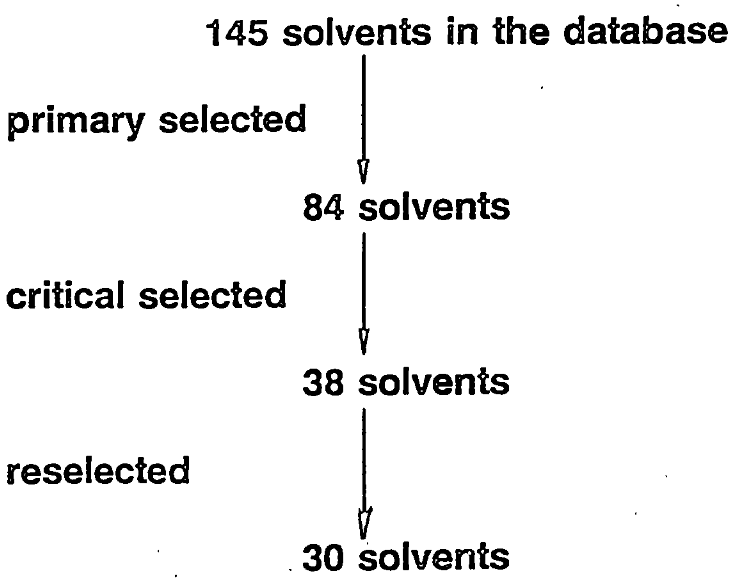


Figure 38 Selection procedure and results for methanol and methyl acetate

the table, we can see that the selectivity values are not reliable. This is due to inaccurate estimation of solubility parameters and inadequacies in the current thermodynamic model. The current thermodynamic model is based upon the solubility approach in which interactions between solvent and/or molecules is divided into three parts: dispersion interaction, dipole interaction, and hydrogen bonding. The total interaction is the summation of the three interactions which are expressed by three solubility parameters: dispersion parameter, polarity parameter, and hydrogen parameter. Some of these available parameters are not accurate and the current estimation procedure is not reliable.

Much attention and many research efforts have been given to modifying the thermodynamic models based upon the solubility approach, and more advanced and more accurate models are continuing to appear in the literature. The selectivity calculation might be reasonably reliable and acceptable if these more advanced thermodynamic models are incorporated into the expert system.

Another way to overcome the inadequacy is to use the Wilson or NRTL equations to calculate the selectivity. But this approach suffers the disadvantages that for many solvent-solute systems there are not empirical interaction parameters available since they are estimated based on the experimental vapor-liquid equilibrium data.

CHAPTER 7

SUMMARY

Conclusions

1. A knowledge-based system (expert system) utilizing both qualitative and quantitative approaches has been developed in this work and applied to helping the solvent selection for separation of xylene isomers by extractive distillation. The expert system comes up with no promising solvents for separating p-xylene from m-xylene. This result agrees with experimental results to date. For separating o-xylene from m-xylene, the expert system proposes several solvents which have appeared in the patent literature. Other solvents proposed by the expert system need to be verified by experiment.

2. For the ethanol-water mixture to be separated by extractive distillation, the expert system confirms some solvents suggested in the literature and proposes additional solvents for further experimental verification.

3. For the methyl acetate-methanol system, the expert system can make selection of solvents for extractive distillation but the expert system gives unreliable selectivity results due to inadequacies in the current thermodynamic model.

Recommendation for the Future Development

Admittedly, the prototype expert system presented here is not complete and far from perfect. First of all, there were numerous subjective decisions which went into the assignment of values within the system. For instance, the selectivity (or relative volatility) attribute was assigned a clear-cut value of 1.5 as a criterion; while in practice, a range of selectivities is usually considered. Therefore, fuzzy logic or even confidence factors might be introduced into the system to take these uncertainties into account for the solvent recommendation.

Second, at present, the theory that can predict activity coefficients for aqueous systems is still under development and far from accurate, with the exception of the UNIFAC method, which is moderately accurate for the prediction. In our system, UNIFAC is used to estimate infinitely dilute activity coefficients and UNIQUAC to calculate selectivity and relative volatility at finite concentrations and different temperatures. One of the disadvantages of the current prototype system is that the calculation of infinitely dilute activity coefficients and selectivity at finite concentrations is separated from the expert system and the subroutine program is written in the QBasic language. This calculation routine should be converted into a WINDOWS-compatible external program which can communicate directly with the LEVEL 5 OBJECT programs.

Third, the solvent database for azeotropic distillation is quite primitive, and even the solvent databases for extractive distillation are not large, so the choices of promising solvents are very limited. The more knowledge the expert system possesses, the more difficult problems it can tackle. Great effort should be made to expand these databases.

Fourth, some solvatochromic parameters that are not available have been estimated manually based on rules of thumb published in the literature references [103]. The expert system might be more efficient and more powerful if the estimate is made automatically, as a part of the expert system. The solvatochromic parameter approach has been successfully applied in the prediction of solute-solvent interaction. This direction of development is worth consideration.

Fifth, the selection of solvents for liquid-liquid extraction differs in significant ways from the process required for extractive and azeotropic distillation, but, to some extent, they are similar. The expert system presented here can be extended to solve the solvent selection problems for liquid-liquid extraction because, by using a modular development approach, a new module for the selection of solvents for liquid-liquid extraction can be attached easily into the system.

NOMENCLATURE

NOMENCLATURE

A, B, C = Antoine's vapor pressure correlation constants
c = constant
H = enthalpy of mixing (Kcal/mol)
N_{min} = minimum number of theoretical plates
P = system pressure (Atm)
P^{o}_{i} = saturated vapor pressure of component i (Atm)
R = gas constant ($m^3Pa/mol/K$)
S = selectivity
T = absolute temperature (K)
T_b = boiling point (°C)
T_c = critical temperature (°C)
T_r = reduced temperature
U = internal energy (Kcal/mol)
V = molar volume (cm^3/mol)
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

α_{KT} = acidity scale
α_F = relative volatility at feed
α_{ij} = relative volatility
α^{s}_{ij} = separation factor

β_{KT} = basicity scale

γ = activity coefficient

Δ = incremental change

λ = nonpolar solubility parameter $(cal/cm^3)^{1/2}$

π^* = dipolarity scale

τ = polar solubility parameter $(cal/cm^3)^{1/2}$

ψ = polar-polar and polar-nonpolar induction energy $(cal/cm^3)^{1/2}$

Subscripts

c = critical conditions

i,j = component i, component j

1,2 = component number

Superscripts

∞ = infinite dilution

v = vaporization

ABBREVIATIONS

ABBREVIATIONS

AI	artificial intelligence
ACID	activity coefficients at infinite dilution
DMSO	dimethyl sulfoxide
ED	extractive distillation
ES	expert system
MEK	methyl ethyl ketone
NTP	number of theoretical plates
RV	relative volatility
SE	solvent extraction
SSS	solvent selection system
Temp.	temperature

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LITERATURE CITED

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APPENDICES

APPENDIX A

INDUSTRIAL SOLVENTS FOR THE EXPERT SYSTEM DATABASE

Appendix A. Industrial Solvents for the Expert System Database

Class	CAS name	Common name	Mol. formula
Water	water	water	H2O
Monoalcohols	methanol	methanol	C1H4O
	ethyl alcohol	ethanol	C2H6O
	1-propanol	n-propanol	C3H8O
	2-propanol	isopropanol	C3H8O
	1-butanol	n-butanol	C4H10O
	2-butanol	sec-butanol	C4H10O
	2-methyl-1-propanol	isobutanol	C4H10O
	2-methyl-2-propanol	tert-butanol	C4H10O
	1-pentanol	n-amyl alcohol	C5H12O
	2-pentanol	sec-amyl alcohol	C5H12O
	3-pentanol	3-pentanol	C5H12O
	3-methyl-1-butanol	isobutylcarbinol	C5H12O
	2-methyl-2-butanol	dimethylethylcarbinol	C5H12O
	cyclohexanol	hexahydrophenol	C6H12O
	1-hexanol	n-hexyl alcohol	C6H14O
	2-heptanol	methylamylcarbinol	C7H16O
	1-octanol	heptylcarbinol	C8H18O
	2-ethyl-1-hexanol	2-ethylhexyl alcohol	C8H18O
	benzyl alcohol	benzyl alcohol	C7H8O
	2-propen-1-ol	allyl alcohol	C3H6O
Polyalcohols	1,2-ethanediol	ethylene glycol	C2H6O2
	1,2-propanediol	propylene glycol	C3H8O2
	1,3-propanediol	isopropylene glycol	C3H8O2
	1,3-butanediol	1,3-butylene glycol	C4H10O2
	1,4-butanediol	1,4-butylene glycol	C4H10O2
	1,2,3-propanetriol	glycerol	C3H8O3
Ketones	methyl ketone	acetone	C3H6O
	2-butanone	methyl ethyl ketone	C4H8O
	3-pentanone	diethyl ketone	C5H10O
	2-hexanone	methyl n-butyl ketone	C6H12O
	3-hexanone	ethyl propyl ketone	C6H12O
	2-heptanone	methyl n-amyl ketone	C7H14O
	4-methyl-3-penten-2-one	mesityl oxide	C6H10O
	4-methyl-2-pentanone	methyl isobutyl ketone	C6H12O
	methylphenyl ketone	acetophenone	C8H8O
	3-methyl-2-butanone	methyl isopropyl ketone	C5H10O
	2,6-dimethyl-4-heptanone	diisobutyl ketone	C9H18O
	3,5,5-trimethyl-2-cyclohexene-1-one	isophorone	C9H14O

Appendix A. Industrial Solvents for the Expert System Database -- Continued

Class	CAS name	Common name	Mol. formula
Ketones	cyclohexyl ketone	cyclohexanone	C6H10O
	4-hydroxy-4-methyl-2-pentanone	diacetone alcohol	C6H12O2
Amines	1-aminopropane	propylamine	C3H9N
	2-aminopropane	isopropylamine	C3H9N
	1-aminobutane	butylamine	C4H11N
	1-amino-2-methylpropane	isobutylamine	C4H11N
	2-aminobutane	sec-butylamine	C4H11N
	diethylamine	diethylamine	C4H11N
	triethylamine	triethylamine	C6H15N
	di-n-propylamine	dipropylamine	C6H15N
	2,4-dimethyl-3-azapentane	diisopropylamine	C6H15N
	di-n-butylamine	dibutylamine	C8H19N
	aminocyclohexane	cyclohexylamine	C6H13N
	1,2-ethanediamine	ethylenediamine	C2H8N2
	2-aminoethanol	monoethanolamine	C2H7ON
	phenylamine	aniline	C6H7N
	n,n-dimethylformamide	dimethylformamide	C3H7ON
	n,n-dimethylacetamide	dimethylacetamide	C4H9ON
	azole	pyrrole	C4H5N
	pyrrolidone	2-pyrrolidinone	C4H7ON
	1-methyl-2-pyrrolidone	n-methylpyrrolidone	C5H9ON
	azine	pyridine	C5H5N
	diethylene oximide	morpholine	C4H9ON
Hydrocarbons	cyclopentane	cyclopentane	C5H10
	n-pentane	pentane	C5H12
	cyclohexane	cyclohexane	C6H12
	n-hexane	hexane	C6H14
	n-heptane	heptane	C7H16
	n-octane	octane	C8H18
	n-nonane	nonane	C9H20
	n-decane	decane	C10H22
	n-dodecane	dodecane	C12H26
	benzene	benzene	C6H6
	methylbenzene	toluene	C7H8
	1,2-dimethylbezene	m-xylene	C8H10
	1,3-dimethylbenzene	o-xylene	C8H10
	1,4-dimethylbenzene	p-xylene	C8H10
	1-hexene	1-hexene	C6H12
	1-heptene	1-heptene	C7H14
	1-octene	1-octene	C8H16
	1-nonene	1-nonene	C9H18

Appendix A. Industrial Solvents for the Expert System Database -- Continued

Class	CAS name	Common name	Mol. formula
Hydrocarbons	1-decene	1-decene	C10H20
	cyclohexene	cyclohexene	C6H10
	styrene	styrene	C8H8
Acids	methanoic acid	formic acid	C1H2O2
	ethanoic acid	acetic acid	C2H4O2
	methylacetic acid	propionic acid	C3H6O2
	butanoic acid	butyric acid	C4H8O2
	2-methylpropionic acid	isobutyric acid	C4H8O2
	pentanoic acid	valeric acid	C5H10O2
	3-methylbutanoic acid	isovaleric acid	C5H10O2
	caproic acid	hexanoic acid	C6H12O2
	caprylic acid	octanoic acid	C8H16O2
	propenoic acid	acrylic acid	C3H4O2
	ethanoic anhydride	acetic anhydride	C4H6O3
	propanoic anhydride	propionic anhydride	C6H10O3
Esters	methyl methanoate	methyl formate	C2H4O2
	ethyl methanoate	ethyl formate	C3H6O2
	propyl methanoate	propyl formate	C4H8O2
	butyl methanoate	butyl formate	C5H10O2
	2-methyl-1-propyl methanoate	isobutyl formate	C5H10O2
	methyl ethanoate	methyl acetate	C4H6O2
	ethenyl ethanoate	vinyl acetate	C4H8O2
	acetic ester	ethyl acetate	C4H8O2
	propyl acetate	n-propyl acetate	C5H10O2
	2-propyl ethanoate	isopropyl acetate	C6H12O2
	butyl acetic ether	butyl acetate	C6H12O2
	2-methyl-1-propyl ethanoate	isobutyl acetate	C6H12O2
	pentyl acetate	amyl acetate	C7H14O2
	isopentyl acetate	isoamyl acetate	C7H14O2
	2-methyl-1-propyl-2-methylpropanoate	isobutyl isobutyrate	C8H16O2
	benzyl ethanoate	benzyl acetate	C9H10O2
	ethyl propanoate	ethyl propionate	C5H10O2
	ethyl butanoate	ethyl butyrate	C6H12O2
	methyl benzenecarboxylate	methyl benzoate	C8H8O2
	ethyl benzenecarboxylate	ethyl benzoate	C9H10O2
	propyl benzenecarboxylate	propyl benzoate	C10H12O2
	benzyl benzenecarboxylate	benzyl benzoate	C14H12O2
Halohydrocarbons	dichloromethane	methylene chloride	C1H2Cl2
	methylene trichloride	chloroform	C1H1Cl3
	carbon tetrachloride	tetrachloromethane	C1Cl4
	1,1-dichloroethane	ethylidene chloride	C2H4Cl2

Appendix A. Industrial Solvents for the Expert System Database -- Continued

Class	CAS name	Common name	Mol. formula
Halohydrocarbons	1,2-dichloroethane	ethylene chloride	C2H4Cl2
	1,1,1-trichloroethane	methlychloroform	C2H3Cl3
	1,1,2,2-tetrachloroethane	tetrachloroethane	C2H2Cl4
	1,1,1,2,2-pentachloroethane	pentachloroethane	C2H1Cl5
	o-dichlorobenzene	1,2-dichlorobenzene	C6H4Cl2
Nitriles	ethyl nitrile	acetonitrile	C2H3N
	ethyl cyanide	propionitrile	C3H5N
	n-propyl cyanide	butyronitrile	C4H7N
	phenyl cyanide	benzonitrile	C7H5N
	vinyl cyanide	acrylonitrile	C3H3N
Organic sulfur compounds	methylsulfinylmethane	dimethyl sulfoxide	C2H6OS
	tetramethylene sulfone	sulfolane	C4H8O2S
Aldehydes	2-furancarboxaldehyde	furfural	C5H4O2
	acetaldehyde	ethanal	C2H4O
	propionaldehyde	propanal	C3H6O
	butyraldehyde	butanal	C4H8O
	2-methylpropanal	isobutyraldehyde	C4H8O
	pentanal	n-valeraldehyde	C5H10O
Nitroparaffins	nitrocarbol	nitrocarbol	C1H3O2N
	nitroethane	nitroethane	C2H5O2N
	1-nitropropane	1-nitropropane	C3H7O2N
	2-nitropropane	2-nitropropane	C3H7O2N
	nitrobenzol	nitrobenzene	C6H5O2N
Phenols	carbolic acid	phenol	C6H6O
	1-methyl-2-methylbenzene	o-cresol	C7H8O
	1-methyl-3-methylbenzene	m-cesol	C7H8O
	1-methyl-4-methylbenzene	p-cresol	C7H8O

APPENDIX B

SOLVENTS RECOMMENDED BY DR. LLOYD BERG

Appendix B. Solvent Recommended by Dr. Lloyd Berg for the Expert System Database

CAS name	Common name	Mol. formula
1,4-dicyanobutane	adiponitrile	C6H8N2
2,3-dimethyl phenol	2,3-dimethyl phenol	C8H10O
2,4-dimethyl phenol	2,4-dimethyl phenol	C8H10O
3,4-dimethyl phenol	3,4-dimethyl phenol	C8H10O
3,5-dimethyl phenol	3,5-dimethyl phenol	C8H10O
2-nitrotoluene	2-nitrotoluene	C7H7NO2
4-nitrotoluene	4-nitrotoluene	C7H7NO2
2-hydroxybiphenyl	2-phenyl phenol	C12H10O
4-hydroxybiphenyl	4-phenyl phenol	C12H10O
2-nitrophenol	2-nitrophenol	C6H5O3N
4-nitrophenol	4-nitrophenol	C6H5O3N
2-butyl acetate	sec-butyl acetate	C6H12O2
2-methoxyethanol	ethylene glycol methyl ether	C3H8O2
2-ethoxyethanol	ethylene glycol ethyl ether	C4H10O2
2-butoxyethanol	ethylene glycol butyl ether	C6H14O2
diethylene glycol methyl ether	diethylene glycol methyl ether	C5H12O3
diethylene glycol ethyl ether	diethylene glycol ethyl ether	C6H14O3
1,3-dioxolane-2-one	ethylene carbonate	C3H4O3
1,2-propanediol cyclic carbonate	propylene carbonate	C4H6O3
dimethyl carbonate	dimethyl carbonate	C3H6O3
diethyl carbonate	diethyl carbonate	C5H10O3
1,4-dioxane	p-dioxane	C4H6O3
methyl o-hydroxybenzoate	methyl salicylate	C8H8O3
ethyl o-hydroxybenzoate	ethyl salicylate	C9H10O3
cyclododecanol	cyclododecanol	C12H24O
heptanoic acid	heptanoic acid	C7H14O2
nonanoic acid	pelargonic acid	C9H18O2
decanoic acid	capric acid	C10H20O2

APPENDIX C

QBASIC PROGRAM FOR CALCULATING ACID FOR THE EXPERT SYSTEM

Appendix C. QBasic Program for Calculating ACID for the Expert System.

```
1 REM  This is an external program to calculate activity
       coefficient at infinite dilution
       for the expert system
2 REM  The example system is ethanol-water-ethylene glycol
6 REM  enter volume and area data into lines 10-40
7 REM  enter interaction parameters into 50-100
8 REM  the temp. is set
9 REM  ethanol is component 1; water is component 2; ETHYLENE
       GLYCOL is component 3
10 DATA 1, 1, 1, 0.6325, 1.0608:
        'CH3=1,CMP=1:ethanol,NU(1)=1,R(1),Q(1)
11 DATA 2, 1, 1, 0.6325, 0.7081:
        'CH2=2,CMP=1:ETHANOL,NU(2)=1,R(2),Q(2)
12 DATA 3, 1, 1, 1.0630, 0.8663:
        'OH=3,CMP=1:ETHANOL,NU(3)=1,R(3),Q(3)
16 DATA 4, 2, 1, 1.7334, 2.4561:
        'water=4,CMP=2:WATER,NU(4)=1,R(4),Q(4)
18 DATA 5, 3, 1, 2.0880, 2.4000: 'DOH=5,CMP=3:ETHYLENE
        GLYCOL,NU(5)=1,R(5),Q(5)
20 DATA  -1, 0, 0, 0,  0 : 'The condition to terminate input
         UNIFAC parameters
49 REM The following is the data array for interaction
       parameters
50 DATA  0,0,0, 0,0,0, 2777.0,-4.6740,0.1551e-2,
         1391.3,-3.6156,0.1144e-2, 897.70,0,0
52 DATA  0,0,0, 0,0,0, 2777.0,-4.6740,0.1551e-2,
         1391.3,-3.6156,0.1144e-2, 897.70,0,0
56 DATA  1606.0,-4.746,0.9181e-3, 1606.0,-4.746,0.9181e-3,
         0,0,0, -801.9, 3.824, -.007514, 499.8,-2.4100,0
58 DATA  -17.253,0.8389,0.9021e-3, -17.253,0.8389,0.9021e-3,
         1460,-8.6730,0.1641e-1, 0,0,0, 372.50,-0.9091,0
60 DATA  28.170,0,0, 28.170,0,0, -468.8,2.421,0,
         -368.80,0.7775,0, 0,0,0
70 REM INPUT COMPOSITIONS
86 DATA 1e-40,1, 1,1e-40
89 DATA -1
98  temp = 323
100 DIM NGP(50), CMP(50), NU(50), R(50), Q(50)
105 DIM psi(30, 30), AA(30, 30), BB(30, 30), CC(30, 30)
110 DIM RR(50), QQ(50), PHP(50), PH(50), TH(50), LNGC(50),
        x(50), LNGR(50)
120 DIM g(50), CAPX(50), CAPT(50), LNCAPG(50), SSUB(50, 50)
130 N = 0: ENT = 0
140 FOR I = 1 TO 100
150 READ NGP(I), CMP(I), NU(I), R(I), Q(I)
155 REM VOL-AREA IS READ
160 IF NGP(I) = -1 THEN 220
```

```
162 REM occurs when entry of Table is complete
170 ENT = ENT + 1: 'no. of entries in vol-area Table
180 CMP = CMP(I)
190 IF NGP(I) < N THEN 210
200 N = NGP(I)
210 NEXT I
220 PRINT N
230 REM read interaction parameters
240 FOR j = 1 TO N
250 FOR k = 1 TO N
260 READ AA(j, k), BB(j, k), CC(j, k)
270 psi(j, k) = EXP(-(AA(j, k) + BB(j, k) * temp + CC(j, k) *
                 temp ^ 2) / temp)
280 NEXT k
290 NEXT j
300 FOR j = 1 TO CMP
305 RR(j) = 0
310 QQ(j) = 0
320 L(j) = 0
330 FOR k = 1 TO ENT
340 IF j <> CMP(k) THEN 370
350 RR(j) = RR(j) + R(k) * NU(k)
360 QQ(j) = QQ(j) + Q(k) * NU(k)
362 REM RR(J) and QQ(J) are volume & area parameters for pure
    components
370 NEXT k
380 L(j) = 4 * RR(j) - 5 * QQ(j) + 1
390 NEXT j
400 FOR L = 1 TO CMP
410 FOR j = 1 TO CMP
420 x(j) = 0
430 NEXT j
440 x(L) = 1
450 GOSUB 1000: 'pure component group activity coefficient are
    calculated
460 NEXT L
470 PRINT "TEMP        CONC(X)         ACT. COEFF."
480 PRINT
490 FOR SET = 1 TO 100
500 FOR I = 1 TO CMP
510 READ x(I)
520 IF x(I) = -1 THEN 810
522 REM this condition occurs when all data have been
    processed
530 NEXT I
540 GOSUB 1000: 'Group activity coefficients are calculated in
    the mixture
550 SUM1 = 0
560 SUM2 = 0
570 sum3 = 0
580 FOR j = 1 TO CMP
590 SUM1 = SUM1 + x(j) * RR(j) ^ (3 / 4)
```

```
600 SUM2 = SUM2 + x(j) * RR(j)
610 sum3 = sum3 + x(j) * QQ(j)
620 NEXT j
630 FOR k = 1 TO CMP
635 PHP(k) = RR(k) ^ (3 / 4) / SUM1
640 PH(k) = RR(k) / SUM2
650 TH(k) = QQ(k) / sum3
660 LNGC(k) = 1! - PHP(k) + LOG(PHP(k)) - 5! * QQ(k) * (1! -
              PH(k) / TH(k) + LOG(PH(k) / TH(k)))
670 NEXT k
680 FOR I = 1 TO CMP
690 LNGR(I) = 0
700 FOR j = 1 TO ENT
710 IF I <> CMP(j) THEN 730
720 LNGR(I) = LNGR(I) + NU(j) * (LNCAPG(NGP(j)) - SSUB(I,
              NGP(j)))
730 NEXT j
740 NEXT I
743 sumc = x(1) + x(2)
745 x(1) = x(1) / sumc
746 x(2) = 1 - x(1)
747 x(3) = x(3) / sumc
750 FOR I = 1 TO CMP
760 g(I) = EXP(LNGR(I) + LNGC(I))
770 PRINT temp, x(I), g(I)
780 NEXT I
790 PRINT
800 NEXT SET
810 END

1000 FOR I = 1 TO ENT
1010 SUMM = SUMM + (x(CMP(I))) * NU(I)
1020 NEXT I
1030 FOR j = 1 TO ENT
1040 CAPX(j) = 0: 'CAP X(J) IS THE GP. MOLE FRACTION
1050 FOR k = 1 TO ENT
1060 IF j <> NGP(k) THEN 1080
1070 CAPX(j) = CAPX(j) + NU(k) * x(CMP(k))
1080 NEXT k
1090 CAPX(j) = CAPX(j) / SUMM
1100 NEXT j
1110 SUMM = 0
1120 A = 1
1130 FOR I = 1 TO ENT
1140 IF NGP(I) < A THEN 1170
1150 A = NGP(I)
1160 SUMM = SUMM + Q(I) * CAPX(A)
1170 NEXT I
1180 A = 1
1190 FOR j = 1 TO ENT
1200 IF NGP(j) < A THEN 1230
1210 A = NGP(j)
```

```
1220 CAPT(A) = Q(j) * CAPX(A) / SUMM
1230 NEXT j
1240 A = 1
1250 FOR I = 1 TO ENT
1260 IF NGP(I) < A THEN 1440
1270 A = NGP(I)
1280 SUM1 = 0
1290 FOR j = 1 TO N
1300 SUM1 = SUM1 + CAPT(j) * psi(j, A)
1310 NEXT j
1320 SUM4 = 0
1330 FOR j = 1 TO N
1340 sum3 = 0
1350 FOR k = 1 TO N
1360 sum3 = sum3 + CAPT(k) * psi(k, j)
1370 NEXT k
1380 SUM4 = SUM4 + CAPT(j) * psi(A, j) / sum3
1390 NEXT j
1400 LNCAPG(A) = Q(I) * (1 - LOG(SUM1) - SUM4)
1405 REM LNCAPG is the gp. activity coeff.
1410 FOR M = 1 TO CMP
1420 IF x(M) = 1 THEN SSUB(M, A) = LNCAPG(A)
1430 NEXT M
1440 NEXT I
1450 SUMM = 0
1460 RETURN
```

APPENDIX D

RULES AND THERMODYNAMIC MODELS FOR THE EXPERT SYSTEM

Appendix D. Rules and Thermodynamic Models for the Expert System

I. Rules for the Method Selection:

The separation method is determined based on the given information by using the following heuristic[11]:

If the boiling point of one of the components in the mixture is higher than 170 °C, then prefer azeotropic distillation; if the boiling points of all components in the mixture are lower than 170 °C, then ask an end-user to specify whether extractive distillation or azeotropic distillation is used to separate the mixture.

II. Rules and Thermodynamic Models for the Selection of Solvents for Extractive Distillation

A. Hydrocarbon system:

Berg's rule[11]

Boiling point of a solvent for extractive distillation should be greater than the highest boiling point of components in the mixture to be separated.

Tasso's rule[22]

If the mixture is composed of hydrocarbons, choose a solvent with high polarity.

Infinite Dilute Activity Coefficients[50]

$$\ln\gamma_1^{\infty} = v_1[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\psi_{12}]/RT + \ln(v_1/v_2) + 1 - v_1/v_2 \qquad (1)$$

$$\psi_{12} = c(\tau_1 - \tau_2)^2 \tag{2}$$

$\lambda_{1,2}$: The nonpolar solubility parameters of the solute and solvent;

$\tau_{1,2}$: The polar solubility parameters of the solute and solvent;

$v_{1,2}$: The molar volume of the solute and solvent;

$\psi 12$: Induction parameter characteristic of the nature of the solvents and the type of hydrocarbon

If it is a saturated hydrocarbon, then

$$\psi_{12} = 0.399(\tau_1 - \tau_2)^2 \tag{3}$$

If it is an olefin, then

$$\psi_{12} = 0.388(\tau_1 - \tau_2)^2 \tag{4}$$

If it is an aromatic, then

$$\psi_{12} = 0.447(\tau_1 - \tau_2)^2 \tag{5}$$

The nonpolar solubility parameter of a polar solvent is obtained from its homomorph

$$\lambda^2 = \Delta U^v/V \tag{6}$$

If it is a n-paraffin, then

$$\Delta U^v/V = 77\ V^{-0.127} e^{-0.00161V}/T_r^{(0.2566\ln(V)-0.3553)} \tag{7}$$

If it is a cycloparaffin, then

$$\Delta U^v/V = 225.3V^{-0.35}/T_r^{0.7} \tag{8}$$

If it is an aromatic, then

$$\Delta U^v/V = 1616V^{(0.0017V - 0.73)} e^{(-0.00872V)}/T_r^{(0.003V + 0.4)} \tag{9}$$

where ΔU^v is the energy of vaporization, V is the molar volume, and T_r is the reduced temperature.

The polar solubility parameters then being obtained by difference:

$$\tau^2 = \delta^2 - \lambda^2 \tag{10}$$

where δ is the total cohesive energy density,

$$\delta^2 = (\Delta H - RT)/V \tag{11}$$

where ΔH is the enthalpy of vaporization.

Solvency

$$\text{solvency} = 1/\gamma^\infty \tag{12}$$

Solvency > 0.02

If solvency is too small, then the solvent will form two phases with solutes.

Selectivity[49]

$$S^\infty_{12} = \gamma_1^\infty/\gamma_2^\infty \tag{13}$$

Check Selectivity > 1.5

The value of 1.5 should be changeable. If an end user would like to narrow the range to solvents with higher selectivity, he can change 1.5 to a larger value. At infinitely dilute concentration, selectivity tends to be maximum.

B. Aqueous System

Chemical Family Rule

Select one to two solvents from different chemical families with high polarity.

Infinite dilute activity coefficients

Use the UNIFAC thermodynamic model to calculate infinite dilution activity coefficients for the solvents selected above. In the modified UNIFAC model, the activity coefficient is the sum of a combinatorial and a residual part:[63]

$$\ln \gamma_i = \ln\gamma_i^{C} + \ln\gamma_i^{R} \tag{14}$$

The combinatorial part can deal with compounds very different in size:

$$\ln \gamma^{C}_i = 1 - V'_i + \ln V'_i - 5q_i(1 - V'_i/F_i + \ln(V_i/F_i)) \tag{15}$$

The parameter V'_i can be calculated by using the relative van der Waals volumes, R_k, of the different groups.

$$V_i = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}} \tag{16}$$

$$V_i = \frac{r_i}{\sum_j x_j r_j} \tag{17}$$

$$r_i = \sum_k \nu_k^{(i)} R_k \tag{18}$$

$$F_i = \frac{q_i}{\sum_j x_j q_j} \tag{19}$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \tag{20}$$

The residual part can be obtained by using the following relations:

$$\ln\gamma_i^{R} = \sum_k \nu_k^{(i)} (\ln\Gamma_k - \ln\Gamma_k^{(i)}) \tag{21}$$

$$\ln\Gamma_k = Q_k(1 - \ln(\sum_m \theta_m \Psi mk) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi nm}) \tag{22}$$

whereby the group area fraction θ_m and group mole fraction X_m are given by the following equations:

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{23}$$

$$X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j \sum_n \nu_n^{(j)} x_j} \tag{24}$$

In the modified UNIFAC model temperature-dependent parameters are introduced to permit a better description of the real Behavior(activity coefficients) as a function of temperature.

$$\Psi_{nm}=\exp\left(-\frac{a_{nm}+b_{nm}T+c_{nm}T^2}{T}\right) \tag{25}$$

Selectivity

The definition is the same as in the hydrocarbon system.

Select UNIQUAC Parameters

Select area and volume parameters for UNIQUAC model from the interface. These values are stored in the database. Use the infinite dilute activity coefficients calculated from UNIFAC to calculate the interaction parameters for UNIQUAC.

At infinite dilution the UNIQUAC expression for a binary system can be written in the following form

$$\ln\gamma_1^\infty=\ln\frac{r_1}{r_2}+q_1\left(5\ln\frac{q_1r_2}{q_2r_1}-\ln\tau_{21}+1-\tau_{12}\right)+l_1-\frac{r_1}{r_2}l_2 \tag{26}$$

$$\ln\gamma_2^\infty=\ln\frac{r_2}{r_1}+q_2\left(5\ln\frac{q_2r_1}{q_1r_2}-\ln\tau_{12}+1-\tau_{21}\right)+l_2-\frac{r_2}{r_1}l_1 \tag{27}$$

After rearrangement we get

$$\ln\tau_{21}+\tau_{12}=A_1-\ln\frac{\gamma_1^\infty}{q_1} \tag{28}$$

$$\ln\tau_{12}+\tau_{21}=A_2-\ln\frac{\gamma_2^\infty}{q_2} \tag{29}$$

So that we are able to calculate the UNIQUAC parameters τ_{12} and τ_{21} from γ_1^∞ and γ_2^∞,

where

$$A_1=\frac{1}{q_1}\left(l_1+\ln\frac{r_1}{r_2}-\frac{r_1}{r_2}l_2\right)+5\ln\frac{q_1r_2}{q_2r_1}+1 \tag{30}$$

A_1 and A_2 contain only the relative van der Waals parameters

$$A_2=\frac{1}{q_2}(l_2+\ln\frac{r_2}{r_1}-\frac{r_2}{r_1}l_1)+5\ln\frac{q_2r_1}{q_1r_2}+1 \qquad (31)$$

r_i and q_i. These parameters can be calculated from the van der Waals group parameters R_k and Q_k that are stored in the database.

The activity coefficients at feasible concentrations are calculated by UNIQUAC model.

Relative volatilities

$$\alpha_{12} = \gamma_1 P^\circ_1/\gamma_2 P^\circ_2 \qquad (32)$$

where $P^\circ_{1,2}$ are the saturation pressures of the components.

Relative volatility > 1.5

This value should be changeable.

C. Nonhydrocarbon, Nonaqueous System

Berg's Classification Rule[11]

Water, glycol, glycerol, amino alcohol, hydroxylamine, hydroxy acids, and amides are class I.

Alcohols, acids, phenols, primary and secondary amines, nitrocompounds with alpha-hydrogen atoms, nitriles with alpha-hydrogen atoms are class II.

Ethers, ketones, aldehydes, esters, tertiary amines (including pyridine type), nitrocompounds and nitriles without alpha-hydrogen atoms are class III.

Class IV consists of liquids composed of molecules containing active hydrogen atoms but no donor atoms. These are molecules having two or three chlorine atoms on the same carbon as a hydrogen atom, or one chlorine on the same carbon atom and one or more chlorine atoms on adjacent carbon atoms.

All other liquids are class V. These are liquids having no hydrogen bond forming capabilities.

Solvents in classes I,II,III are selected because of strong or moderate hydrogen bonding ability.

<u>Scheibal's rule</u>[20]

Any member of the homologous series of either component of the mixture can be used to separate the azeotropic mixture by extractive distillation.

<u>Berg's Boiling Point Rule</u>[11]

The same as for the hydrocarbon branch.

<u>Infinite Dilution Activity Coefficients</u>

Modified Karger-Snyder-Eon equation combined with solvatochromic parameter approach is used to calculate infinitely dilute activity coefficients[55]:

$$\ln \gamma_1^\infty = V/RT[(\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 + 2(\delta_{1a} - \delta_{2a})(\delta_{1b} - \delta_{2b})] \qquad (33)$$

where δ_d, δ_p, δ_a, δ_b are dispersion solubility parameter, polar solubility parameter, basic solubility parameter, and acidic solubility parameter, respectively. If the differences due to molecular volumes are taken into account, then equation 33 becomes

$$\ln \gamma_1^\infty = V/RT[(\delta_{1d} - \delta_{2d})^2 + (\delta_{1p} - \delta_{2p})^2 + (\delta_{1a} - \delta_{2a})(\delta_{1b} - \delta_{2b})] + \ln(V_1/v_2) + 1 - (V_1/V_2) \qquad (34)$$

In this study, the values of the dispersion solubility parameters and polar solubility parameters are adopted from Hansen's solubility parameter values. As for basic solubility parameter, δ_b, Kamlet et al. [96] used spectrometric methods to obtain two solvatochromic parameters, α and β. The α-scale of the solvent provided a measure of proton-donor capacity, and the β-values quantified the ability of the solvent to accept a proton. Kamlet et al.[99] have prepared an extensive table of β values for solvents, and Hickey et al.[100] documented rules of thumb for estimations of α-scale and β-scale. Karger et al. provided a limited number of δ_a and δ_b values for solvents. One shortcoming is that they assumed equal values of δ_a and δ_b for alcohols, while most alcohols do not behave this way. In this study, it was found that a linear relationship exists between the δ_b-value of Karger et al. and the β-value of Kamlet et al.:

$$V^{1/2}\delta_b=60.1\beta+2.45 \tag{35}$$

As for acidic solubility parameter, δ_a, the α-values given by Kamlet et al. are less accurate than β-values. δ_a can be obtained using the following equation:

$$2\delta_a\delta_b=\delta_T^2-\delta_d^2-\delta_p^2=\delta_h^2 \tag{36}$$

Selectivity

The definition is the same as in the hydrocarbon system.

Selectivity > 1.5

The reason that selectivity is greater than 1.5 is the same as for the hydrocarbon branch.

III. Rules for the Solvent Selection for Azeotropic Distillation

As for azeotropic distillation, the current database is only for methanol-acetone system for illustration. In this branch, Berg's rules[11] are used for the time being:

If the mixture is a close-boiling one or maximum azeotrope, then select solvents which form a binary minimum azeotrope with one component, or form binary minimum azeotrope with each component but one minimum azeotrope boils at a significantly lower temperature than the other.

If the mixture is a minimum azeotrope, then select solvents that form a binary minimum azeotrope with one component that boils at a significantly lower temperature than the original minimum azeotrope.

Here we subjectively assign a significantly lower temperature as 15 °C.

When the end-user enters this branch, the expert system prompts the following information to be entered:

Is it a close-boiling mixture or azeotrope?

If it is an azeotrope, is it a minimum or maximum azeotrope?

What is the composition of the azeotrope? What is the boiling point of the azeotrope?

If the mixture is a close-boiling or a maximum azeotrope, then select solvents from the azeotropic database for component 1 and from the azeotropic database for component 2.

Then if solvents from the two databases are not identical in terms of their common names and CAS names, add them to the recommendation list; otherwise compare the boiling point of azeotrope 1 (component 1 in it) with that of azeotrope 2 (component 2 in it), if the difference between the two boiling points are greater than 15°C, then add the solvent into the recommendation list; otherwise discard the solvent.

If the mixture is a minimum azeotrope, then select solvents from the azeotropic database for component 1 and from the azeotropic database for component 2. If solvents from the two databases are identical, discard them. If solvents from the two databases are not identical, then compare the boiling point of the new azeotrope with that of the original azeotrope. If the difference between the boiling point of the new azeotrope and that of the original one is greater than 15°C, then add the solvent into the recommendation list, if not, discard it.