MONTANA STATE UNIVERSITY

A study of the reversing of relative volatilities by extractive distillation
by An-I Yeh

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering
Montana State University
© Copyright by An-I Yeh (1986)

Abstract:
The separation of the close-boiling mixture, m-xylene-o-xylene; three binary azeotropes: ethanol-water, methyl acetate-methanol, acetone-methanol, and four ternary azeotropes: n-propyl acetate-n-propanol-water, isopropyl acetate-isopropanol-water, n—butyl acetate-n- butanol-water, isobutyl acetate-isobutanol-water has been enhanced by extractive distillation. The azeotropes have been negated and the relative volatilities of key components have been reversed by the agents used.

The plot of polar interaction versus hydrogen bonding, called polarity diagram, was used to compare the affinity of agents for key components. Thus the key component which will be the overhead product can be predicted. The three solubility parameters were used to describe the intermolecular forces occurring between agents and key components in extractive distillation. The MOSCED model was used to calculate the activity coefficients of the key components using the properties of the pure compounds. The calculated values fitted the experimental data well. The advantage of this model was to calculate the. relative volatilities of key components in the presence of the agent using the properties of pure compounds instead of using the properties of mixtures.

Temperature inversion, where the overhead temperature was higher than the stillpot temperature, was observed for the acetone-methanol system when ketones were used as the agents. The data showed that the temperature inversion could be caused by the dissolving of the vapor of key components in the liquid agents.

A STUDY OF THE REVERSING OF RELATIVE VOLATILITIES BY EXTRACTIVE DISTILLATION

by

An-I Yeh

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in
Chemical Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

April 1986

D378
Y347

APPROVAL

of a thesis submitted by

An-I Yeh

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.

April 23, 1986 — Date
Lloyd Berg — Chairperson, Graduate Committee

Approved for the Major Department

April 23, 1986 — Date
John T Sears — Head, Major Department

Approved for the College of Graduate Studies

April 23, 1986 — Date
Henry L Parsons — Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under the rules of the Library. I further agree that copying of this thesis is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this thesis should be referred to University Microfilms International, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted "the exclusive right to reproduce and distribute copies of the dissertation in and from microfilm and the right to reproduce and distribute by abstract in any format"

Signature Am-Y Yeh

Date April 11, 1986

ACKNOWLEDGEMENT

The author wishes to thank the faculty and staff of the Chemical Engineering Department at Montana State University for their encouragement and help. A special thanks goes to Dr. Lloyd Berg, director of this research, for his guidance. Dr. Dan Shaffer and all the thesis committee members are acknowledged for their help. Dr. John Sears, Department Head of Chemical Engineering, is acknowledged for his support of this project.

Appreciation is extended to Lyman Fellows for his fabrication and maintenance of research equipment. A special appreciation goes to my brother, Dr. Angong Yeh, for his encouragement and suggestions. To my parents, their patience is appreciated.

TABLE OF CONTENTS

	Page
APPROVAL	ii
STATEMENT OF PERMISSION TO USE	iii
ACKNOWLEDGEMENT	iv
TABLE OF CONTENTS	v
LIST OF TABLES	viii
LIST OF FIGURES	xi
ABSTRACT	xiv
I. INTRODUCTION	1
Separation Factor	3
Fractional Distillation	5
Extractive and Azeotropic Distillation	8
Behavior of Agents	17
Choice of Agents	19
Research Objective	21
Selection of Mixtures	21
m-Xylene and o-Xylene System	21
Ethanol and Water System	23
Methanol and Methyl Acetate System	25
Acetone and Methanol System	26
Ternary Azeotropes	27
II. THEORETICAL ASPECTS	33
Vapor-Liquid Equilibrium	33
The Fenske Equation	38
Effect of Adding An Agent	40
Factors Affecting Selectivity	47
Temperature	47
Pressure	48
Volume Fraction of Agent	48
Relative Size of Molecule	48
Chemical Effect of Hydrogen Bonding	49
Approaches to the Activity Coefficients	49
Enthalpic Models	50

TABLE OF CONTENTS--Continued

	Page
Entropic Models	56
MOSCED Model	59
Proposed Effect of The Agents	65
III. APPARATUS, CHEMICALS AND PROCEDURES	67
Vapor-Liquid Equilibrium Still	67
Plate Column	69
Packed Column	74
Calibration of the Extractive Distillation Columns	74
Analytical Equipment	81
Gas Chromatograph Calibration	82
Equipment for Agent Recovery	82
Chemicals As The Agents	91
Experimental Procedures	91
Vapor-Liquid Equilibrium	91
Extractive Distillation	98
Liquid-Liquid Equilibria for Ternary Mixtures	99
Agent Recovery	100
IV. RESULTS AND DISCUSSION	103
Vapor-Liquid Equilibria	103
m-Xylene and o-Xylene System	106
Ethanol and Water System	108
Methyl Acetate and Methanol System	111
Acetone and Methanol System	111
Temperature Inversion	117
The Reversing of Relative Volatility	127
Ternary Azeotropes	134
Liquid-Liquid Equilibria	134
Application of The Polarity Diagram	139
Effects of Agents	141
V. SUMMARY	149
Conclusions	149
Recommendation for Further Studies	151
NOMENCLATURE	152
ABBREVIATIONS	156

TABLE OF CONTENTS--Continued

	Page
LITERATURE CITED	158
APPENDICES	168
APPENDIX A. PARAMETER ESTIMATION FOR MOSCED MODEL.	169
APPENDIX B. CALCULATED PARAMETER VALUES FOR MOSCED MODEL.....	172
APPENDIX C. THE PROGRESSION OF THE OVERHEAD AND STILLPOT TEMPERATURES FOR METHANOL-ACETONE SYSTEM.....	176
APPENDIX D. HYPOTHETICAL CALCULATION FOR TEMPERATURE INVERSION.	188

LIST OF TABLES

		Page
I.	Column cost for different relative volatility.....	12
II.	Properties of components and azeotrope at 1 Atm.	26
III.	The uses of some alcohols and acetates	28
IV.	The normal boiling points of pure components and azeotropes.	29
V.	Azeotropic compositions of binary and ternary azeotropes.	31
VI.	Solubilities of acetates and alcohols in water	32
VII.	Previous formulations of activity coefficients using solubility parameter.	63
VIII.	The calculated relative volatilities of methanol to acetone.	76
IX.	The comparison of experimental bottoms composition from with pseudo McCabe-Thiele method.....	80
X.	Molecular structures and physical properties of glycols..	92
XI.	Molecular structures and physical properties of nitrocompounds.....	93
XII.	Molecular structures and physical properties of ketones..	94
XIII.	Molecular structures and physical properties of benzoates	96
XIV.	Molecular structures and physical properties of miscellaneous agents.....	97
XV.	The initial compositions and temperatures of agents for separating binary mixtures.....	100
XVI.	The performance of plate and packed columns.	107
XVII.	The results of separating m-xylene from o-xylene.	107
XVIII.	The effect of initial composition on relative volatility of water to ethanol.	109

LIST OF TABLES--Continued

		Page
XIX.	The initial evaluation of the nitrocompounds for the methyl acetate-methanol system	112
XX.	The relative volatility of methanol to methyl acetate examined by extractive distillation	112
XXI.	Initial evaluation of the agents which cause acetone to be more volatile.	113
XXII.	Initial Evaluation of Ketones.	115
XXIII.	The effects of ketones used as the agents in extractive distillation	116
XXIV.	Results from different initial compositions using methyl ethyl ketone as the agent.	116
XXV.	The overhead and bottoms compositions for pure methanol and pure acetone systems with MEK	123
XXVI.	The compositions for acetone-methanol system using MEK as the agent	124
XXVII.	Solubility parameters and specific volumes of key components	128
XXVIII.	The comparison of the relative volatility for methanol(1)-acetone(2) system	133
XXIX.	The comparison of the relative volatility for methanol(1)-methyl acetone(2) system	133
XXX.	Solubility parameters and specific volumes of the key components	140
XXXI.	Solubility parameters and specific volumes of the agents	140
XXXII.	Initial evaluation of the agents for the acetate-alcohol-water systems	143
XXXIII.	The effectiveness of the agents shown in the plate extractive distillation	143
XXXIV.	The calculated parameter values for MOSCED model used for the methanol-acetone system	174

LIST OF TABLES--Continued

Page

XXXV. The calculated parameter values for MOSCED model used for the methanol-methyl acetate system..... 175

LIST OF FIGURES

		Page
1.	General separation process	2
2.	Conventional fractionating column	6
3.	Number of theoretical plates as a function of relative volatility	10
4.	Azeotropic distillation scheme for ethanol dehydration with benzene	13
5.	Schematic diagram of an extractive distillation process	14
6.	Phase diagram fro various types of binary systems	34
7.	Physical interactions between molecules	43
8.	Bond energies of different types of bondings	45
9.	Othmer-type vapor-liquid equilibrium still	68
10.	Diagram of the batch-wise extractive distillation column	70
11.	Perforated plate arrangement	71
12.	Perforated plate scheme	72
13.	Berl saddle packing	75
14.	Pseudo McCabe-Thiele method for isopropyl ether-acetone system with DMSO as the agent	77
15.	Pseudo McCabe-Thiele method for methyl acetate-methanol system with DMSO as the agent	78
16.	Pseudo McCabe-Thiele method for acetone-methanol system with methyl ethyl ketone as the agent	79
17.	Calibration curve for the m-xylene-o-xylene mixture	83
18.	Calibration curve for the methanol-acetone mixture	84
19.	Calibration curve for the ethanol-water mixture	85
20.	Calibration curve for the n-propyl acetate-n-propanol mixture	86

LIST OF FIGURES--Continued

Page

21. Calibration curve for the isopropyl acetate-isopropanol mixture..... 87

22. Calibration curve for the n-butyl acetate-n-butanol mixture.. 88

23. Calibration curve for the isobutyl acetate-isobutanol mixture 89

24. Diagram of the simple distillation..... 90

25. The map for constant ratios of one component to another one in a ternary mixture..... 101

26. Vapor-liquid equilibrium curves for the isopropyl ether-acetone system..... 104

27. Vapor-liquid equilibrium curves for methanol-acetone system.. 105

28. The progression of overhead and stillpot temperatures for methanol-acetone system with MEK as the agent..... 118

29. The change of temperature difference with time and normal boiling points of the agents..... 120

30. The progression of the overhead and stillpot temperatures for pure methanol and pure acetone using MEK as the agent.... 122

31. The effect of the agent temperature on temperature inversion. 126

32. Polarity diagram for methanol-acetone system..... 129

33. Polarity diagram for water-ethanol system..... 130

34. Polarity diagram for methanol-methyl acetate system..... 131

35. Liquid-liquid equilibrium diagram for n-propyl acetate-n-propanol-water system..... 135

36. Liquid-liquid equilibrium diagram for isopropyl acetate-isopropanol-water system..... 136

37. Liquid-liquid equilibrium diagram for n-butyl acetate-n-butanol-water system..... 137

38. Liquid-liquid equilibrium diagram for isobutyl acetate-isobutanol-water..... 138

39. Polarity diagram for acetate-alcohol-water systems..... 142

LIST OF FIGURES--Continued

Page

40. Selectivities for the agents with different polarity..... 145

41. Molecular structures of DMSO and DMFA..... 147

42. The progression of the overhead and still pot temperatures for methanol-acetone without agents..... 178

43. The progression of the overhead and still pot temperatures for methanol-acetone with different initial composition and an agent of MEK..... 179

44. The progression of the overhead and still pot temperatures for methanol-acetone with 2-pentanone as the agent..... 180

45. The progression of the overhead and still pot temperatures for methanol-acetone with 3-pentanone as the agent..... 181

46. The progression of the overhead and still pot temperatures for methanol-acetone with methyl isoamyl ketone as the agent. 182

47. The progression of the overhead and still pot temperatures for methanol-acetone with 2,4-pentanedione as the agent..... 183

48. The progression of the overhead and still pot temperatures for methanol-acetone with diisobutyl ketone as the agent..... 184

49. The progression of the overhead and still pot temperatures for methanol-acetone with acetophenone as the agent..... 185

50. The progression of the overhead and still pot temperatures for methanol-acetone with ethyl acetoacetate as the agent.... 186

51. The progression of the overhead and still pot temperatures for methanol-acetone with the mixture of benzil (diphenyl ethanedione) and methyl ethyl ketone as the agent..... 187

ABSTRACT

The separation of the close-boiling mixture, m-xylene-o-xylene; three binary azeotropes: ethanol-water, methyl acetate-methanol, acetone-methanol, and four ternary azeotropes: n-propyl acetate-n-propanol-water, isopropyl acetate-isopropanol-water, n-butyl acetate-n-butanol-water, isobutyl acetate-isobutanol-water has been enhanced by extractive distillation. The azeotropes have been negated and the relative volatilities of key components have been reversed by the agents used.

The plot of polar interaction versus hydrogen bonding, called polarity diagram, was used to compare the affinity of agents for key components. Thus the key component which will be the overhead product can be predicted. The three solubility parameters were used to describe the intermolecular forces occurring between agents and key components in extractive distillation. The MOSCED model was used to calculate the activity coefficients of the key components using the properties of the pure compounds. The calculated values fitted the experimental data well. The advantage of this model was to calculate the relative volatilities of key components in the presence of the agent using the properties of pure compounds instead of using the properties of mixtures.

Temperature inversion, where the overhead temperature was higher than the stillpot temperature, was observed for the acetone-methanol system when ketones were used as the agents. The data showed that the temperature inversion could be caused by the dissolving of the vapor of key components in the liquid agents.

I. INTRODUCTION

Separation processes are those operations which transfer a mixture of substances into two or more products which differ from each other in composition. Often separation itself can be the main function of an entire process. The need for separation processes can account for most of the cost of a pure substance. A simple schematic of a separation process is shown in Figure 1. The feed may consist of one or of several streams of matter. There must be at least two product streams which differ in composition from each other. This follows from the fundamental nature of a separation. The separation is caused by the addition of a separating agent, which takes the form of another stream of matter or/and energy. Usually the energy input required for the separation is supplied by the separating agent, and the separating agent could cause the formation of a second phase of matter.

We can categorize separation processes in several ways: (i) mechanical vs. diffusional processes, (ii) equilibration processes vs. rate-governed processes, (iii) energy-separating-agent vs. mass-separating-agent process. A separation device which receives a heterogeneous feed consisting of more than one phase of matter and singly serves to separate the phases from each other is called a mechanical separation process. Mechanical processes are important industrially but are not a primary concern of this study. Diffusional separation processes receive a homogeneous feed and involve a

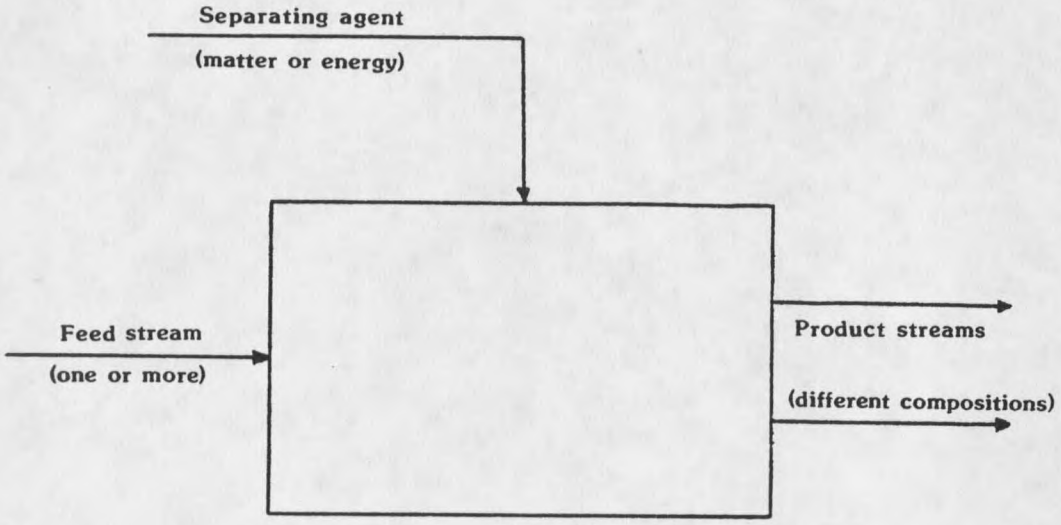


Figure 1. General separation process.

diffusional transfer of matter from the feed stream to one of the product streams. Most diffusional separation processes operate through equilibration of two immiscible phases which have different compositions at equilibrium. They are the principal subject matter of this study. On the other hand, some separation processes work by virtue of difference in transport rate through some medium under the impetus of an imposed force, resulting from a gradient in pressure, temperature, composition, electric potential, or the like. These are the rate-governed processes. Energy-separating-agent processes use energy as the separating agent such as distillation. In mass-separating-agent processes, matter is used as the separating agent such as liquid-liquid extraction.

Separation Factor

The degree of separation which can be obtained with any particular separation process is indicated by the separation factor. Since the object of a separation device is to produce products of differing compositions, it is logical to define the separation factor in terms of product compositions.

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

The separation factor α^{s}_{ij} between components i and j is the ratio of the mole fractions of those two components in product 1 divided by the ratio in product 2. The separation factor will remain unchanged if all

the mole fractions are replaced by weight fractions, by molar flow rates of the individual components, or by mass flow rates of the individual components.

An effective separation is accomplished to the extent that the separation factor is significantly different from unity. If $\alpha_{ij}^{s} = 1$, no separation of components i and j has been accomplished. If $\alpha_{ij}^{s} > 1$, 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 $\alpha_{ij}^{s} < 1$, component j tends to concentrate preferentially in product 1. By convention, components i and j are generally selected so that α_{ij}^{s}, defined by Equation 1, is greater than unity.

The separation factor reflects the differences in equilibrium compositions and transport rates due to the fundamental physical phenomena underlying the separation. It can also reflect the construction and flow configuration of the separation device. For this reason it is convenient to define an inherent separation factor, which we shall denote by α_{ij}. This inherent separation factor is the separation factor which would be obtained under idealized conditions, as follows:

1. For equilibration separation processes, the inherent separation factor corresponds to those product compositions which will be obtained when simple equilibrium is attained between the product phases.
2. For rate-governed separation processes, the inherent separation factor corresponds to those product compositions which will occur in the presence of the underlying physical transport mechanism alone, with no

complication from competing transport phenomena, flow configurations, or other extraneous effects.

Both the inherent separation factor α_{ij} and the actual separation factor α_{ij}^{s}, based on the actual product compositions through Equation 1, can be used for the analysis of separation processes. When α_{ij} can be derived relatively easily, the most common approach is to analyze a separation process on the basis of the inherent separation factor α_{ij} and allow for deviations from ideality through efficiencies. This procedure is advantageous since α_{ij} is frequently insensitive to changes in mixture composition, temperature, and pressure.

Fractional Distillation

The ultimate application of distillation is for the purpose of separating two or more components occurring in a mixture to produce products which meet certain specifications. These specifications may be sales specifications which require certain purity or characteristics based on boiling range, or process specifications which require purity or concentration with respect to one or more components for use in subsequent processes. The economic consideration of yield of material of specified characteristics has resulted in the development of the fractional distillation which may be of the stage type or differential type.

A conventional fractionating column is shown in Figure 2. From a simplified point of view, multi-stage fractional distillation may be considered to be a process in which a series of flash vaporization

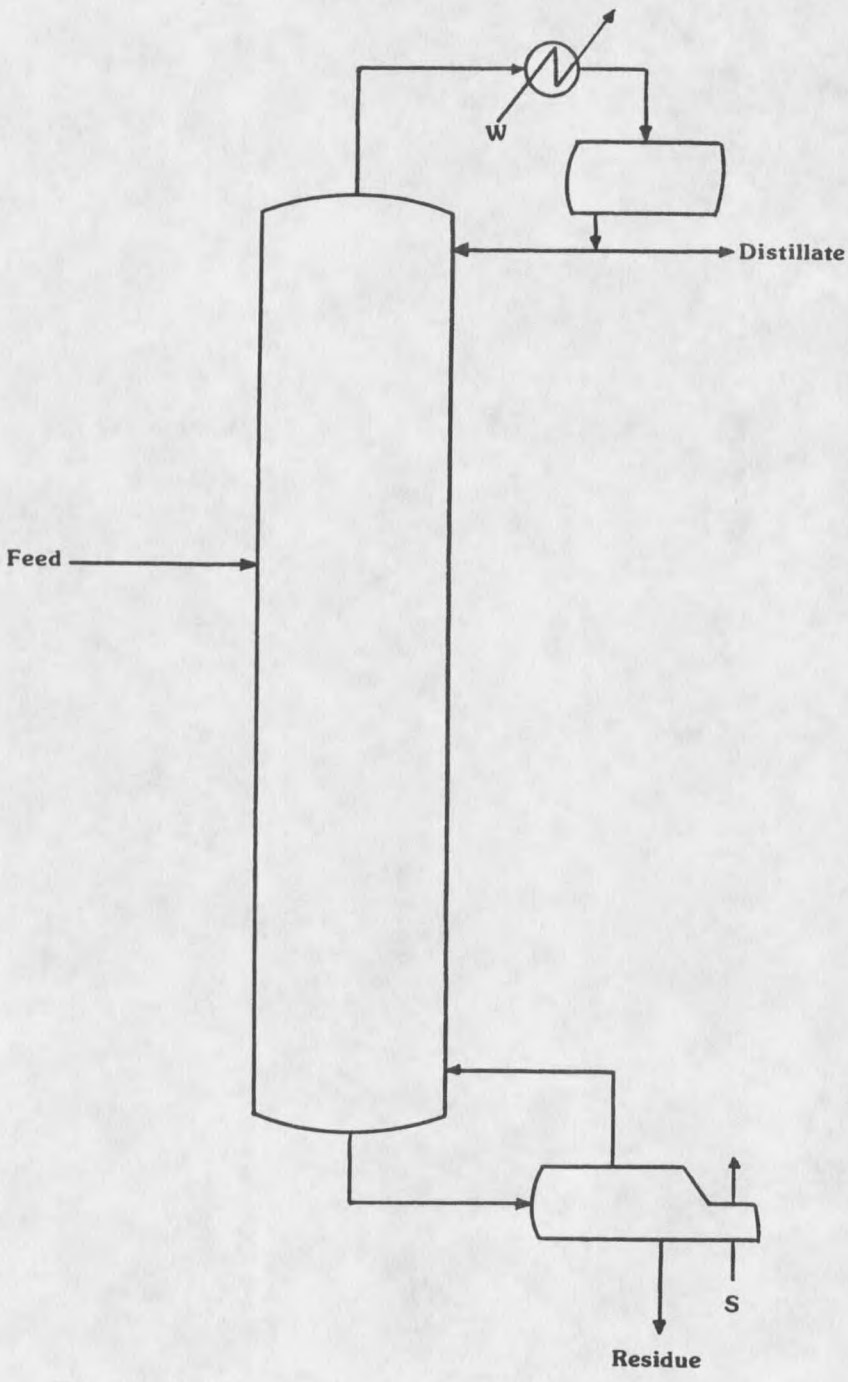


Figure 2. Conventional fractionating column.

stages are arranged in series in such a manner that the products from each stage are fed to adjacent stages. The vapor produced in one stage is conducted to the stage above and the liquid to the stage below. In turn, this stage receives the liquid from the stage above and the vapor from the stage below as its feed material. In this arrangement the concentration of the lower boiling component(s) is being increased in the vapor from each stage in the direction of vapor flow and decreased in the liquid in the direction of the liquid flow. Because the lower boiling constituents are concentrating in the vapor from each successive stage, the temperature decreases from stage to stage and reaches the minimum as the final vapor is produced from the process. Similarly, the temperature increases along with the direction of flow of the liquid, and the maximum temperature is reached at the point where the liquid product is withdrawn from the process. Since temperature is a measure of the level of heat energy, it is obvious that heat energy is necessary to the distillation process. In addition to the heat energy involved in maintaining a temperature differential, an amount of heat energy roughly equivalent to the latent heat of the vapor evolved from the last stage (with respect to vapor flow) must be supplied. This heat energy may be supplied in the feed, in the last stage from which the liquid product is withdrawn, or in both places.

In general, fractional distillation can apply when:

1. The components have appreciable differences in volatility or the relative volatility of the components to be separated is 1.05 or greater.
2. There is no azeotrope formation.

3. There is no chemical reaction between components.

4. There is no decomposition or polymerization of one or more of the components.

5. The components are capable of vaporization at practical temperature and pressure.

However, in some cases, distillation techniques other than fractional distillation have to be used for a specific separation. Those cases are (a) two or more of the components to be separated have but slight difference in volatility (relative volatility approximately equal to unity) and their vapor pressure curves are essentially of the same shape; (b) two or more of the components form a homogeneous minimum azeotrope which is not pressure sensitive or which is pressure sensitive but will not provide sufficient relative volatility change near $x_i = 1$ or $x_i = 0$; (c) one or more of the compounds will decompose or change chemically at temperature and pressure within economic distillation ranges.

Extractive and Azeotropic Distillation

Azeotrope is a synonym for constant-boiling mixture, a specific mixture of two or more components, which cannot be readily separated by ordinary distillation. Also, it is very difficult to separate mixtures whose components boil very close together. These are the cases a and b for which fractional distillation is not applicable. The separation can be sometimes greatly facilitated by adding a third component, called herein an "agent". In these cases two methods , namely azeotropic and

extractive distillation, have been developed commercially. Azeotropic and extractive distillation are old processes which have become widely used since about 1930. In 1908 Guillaume [1] patented an extractive distillation process for the removal of fusel oil from fermentation alcohol. Extractive and azeotropic distillation have the property in common that a substance not normally present in the mixture to be separated is added to increase the difference in volatility of the most difficultly separable components. Benedict and Rubin [2] have defined extractive and azeotropic distillation. Extractive distillation is distillation in the presence of a substance which is relatively non-volatile compared to the components to be separated and which, therefore, is charged continuously near the top of the distilling column so that an appreciable concentration is maintained on all the plates of the column. Azeotropic distillation is the process in which the substance added forms an azeotrope with one or more of the components and by virtue of this fact is present on most of the plates of the column in appreciable concentration. Applications of azeotropic and extractive distillation have continued to expand because many very close boiling mixtures may be separated economically by use of those techniques. The separation of such mixtures by conventional distillation methods is usually uneconomical because of the large number of plates which would be required to affect such separation. For a separation of a binary mixture, both overhead and bottoms products are specified to have 99% purity. Figure 3 shows the number of theoretical plates as a function of relative volatility. It can be seen that the theoretical plates number approaches infinite as the relative volatility

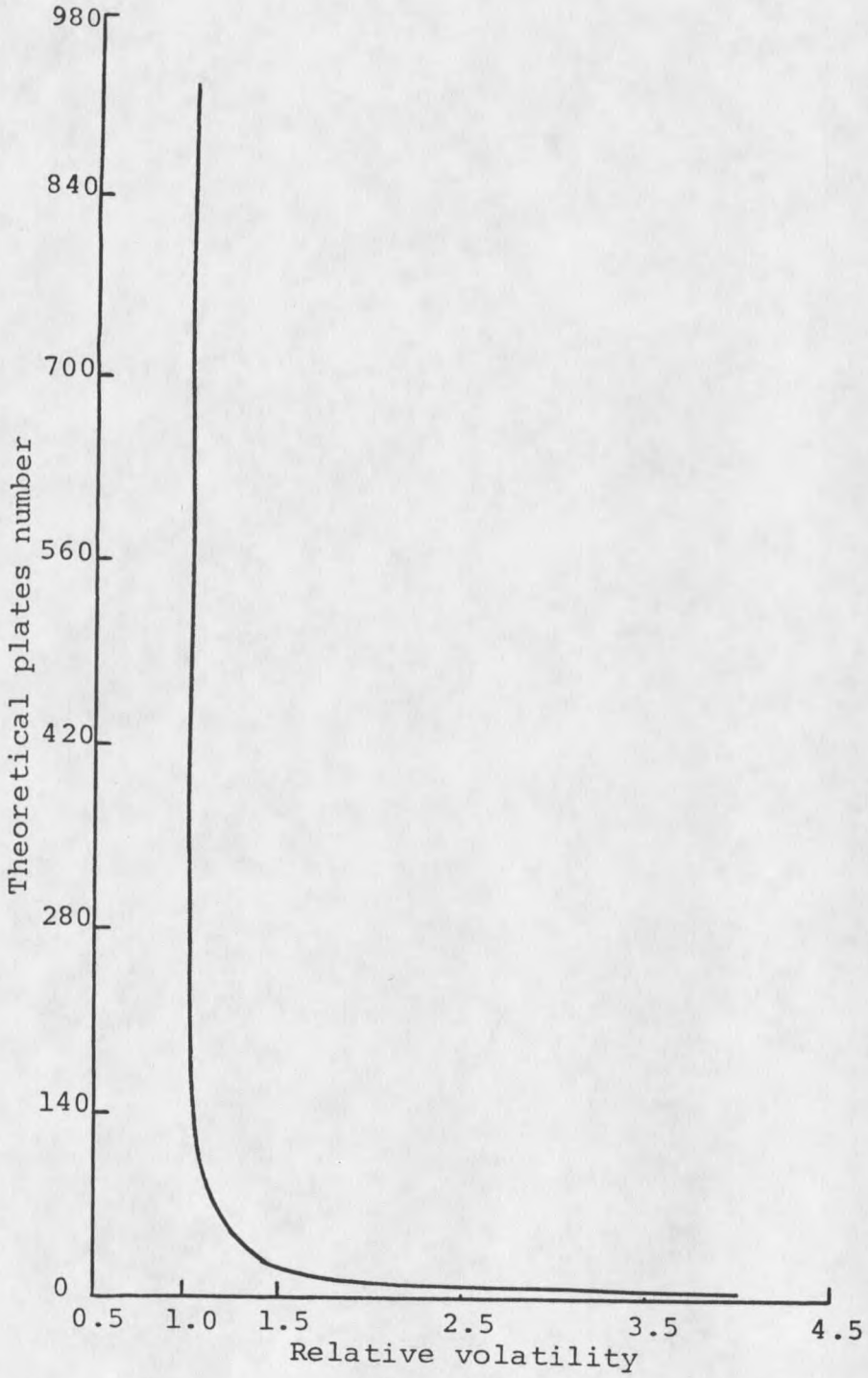


Figure 3. Number of theoretical plates as a function of the relative volatility. In a separation of a binary mixture, the overhead and bottoms products are specified to have 99% purity.

becomes closer to unity. That is the situation for the presence of a minimum-boiling azeotrope. The theoretical plates number drops rapidly when the relative volatility increases to about 1.25. If the plate efficiency is 75% and the column cost is linearly proportional to the plate number, the comparison of the column cost for different relative volatilities is shown in Table I. The column cost is a relative value which is based on a value of relative volatility of 1.05. The linear proportionality of column cost to plate number occurs up to some point. Beyond that point, the column will become more expensive than the linearly proportional price. In addition, higher pressure drop accompanys more plates. This causes more heat requirement to evaporate the liquid mixture and operational difficulties. Therefore, it is very advantageous to increase the relative volatility.

In azeotropic distillation the agent has about the same vapor pressure as the feed components and is removed with the overhead product with which it forms a minimum-boiling azeotrope. Figure 4 shows the schematic of dehydration of ethanol with benzene by azeotropic distillation. In column I the minimum ternary azeotrope, ethanol-water-benzene, comes out as the overhead product. Ethanol is obtained from the bottoms. Benzene is recovered from column II and then recycled. Water is removed from column III. In extractive distillation the agent has a low vapor pressure, so the agent is added near the top of the column and removed with the bottom product. The agent flows down the column, washing the ascending vapors and absorbing one of the components preferentially. A typical scheme for separating a binary mixture, components A and B, by extractive distillation is shown in Figure 5. In

Table I. Column cost for different relative volatility.

Relative volatility	Plate number	Column cost
1.01	1231.5	490.25
1.02	618.8	246.34
1.03	414.5	165.01
1.04	312.4	124.36
1.05	188.4	100.00
1.06	210.3	83.72
1.08	159.2	63.38
1.10	128.5	51.15
1.12	108.1	43.03
1.15	87.7	34.91
1.17	78.0	31.05
1.20	67.2	26.75
1.30	46.7	18.59
1.40	36.4	14.49
1.80	20.8	8.28
2.00	17.7	7.05
2.40	14.0	5.57
2.80	11.9	4.74
3.00	11.2	4.46
3.50	9.7	3.86
4.00	8.8	3.50

The column cost is a relative value based on a value of relative relative volatility of 1.05.

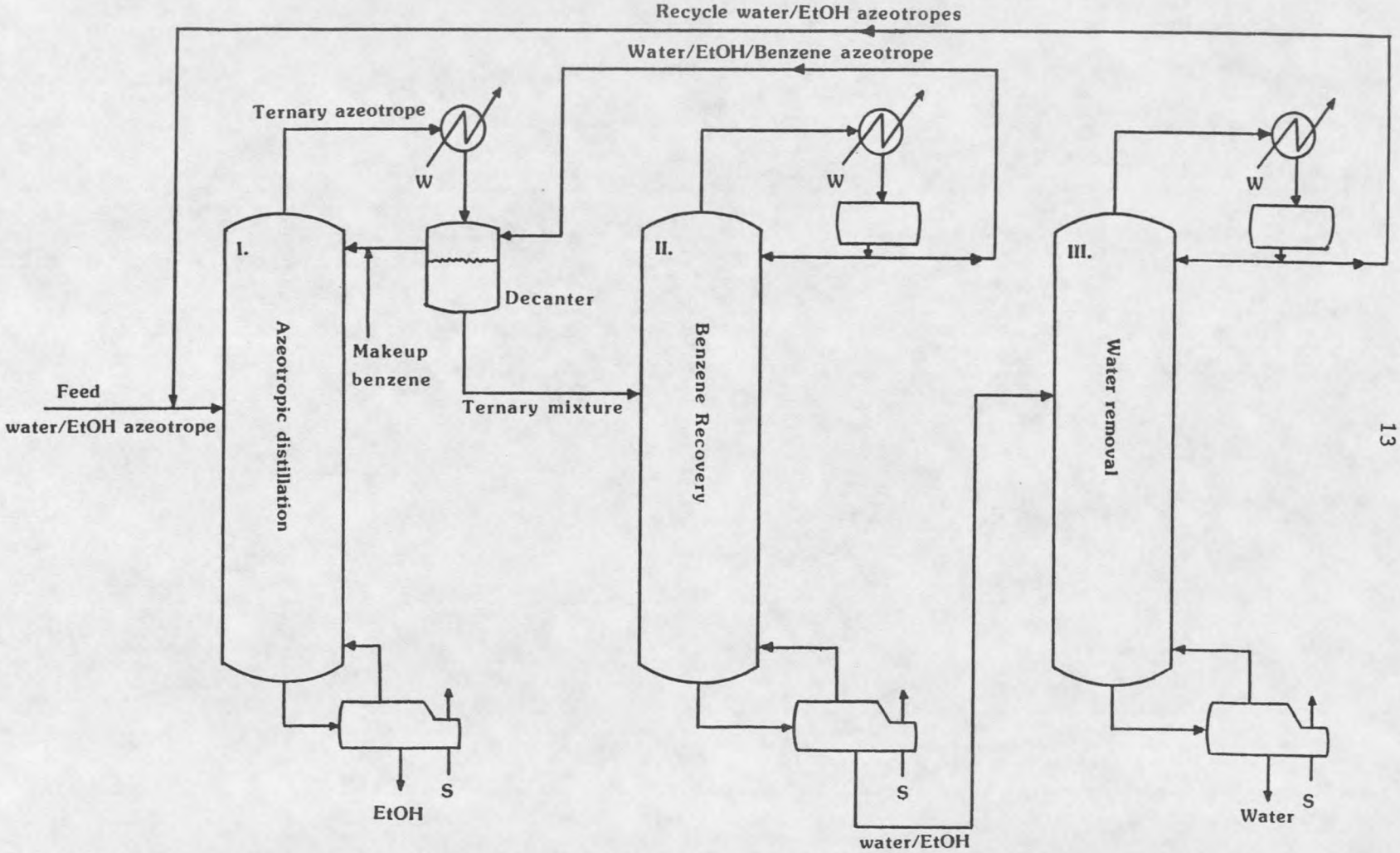


Figure 4. Azeotropic distillation scheme for ethanol dehydration with benzene.

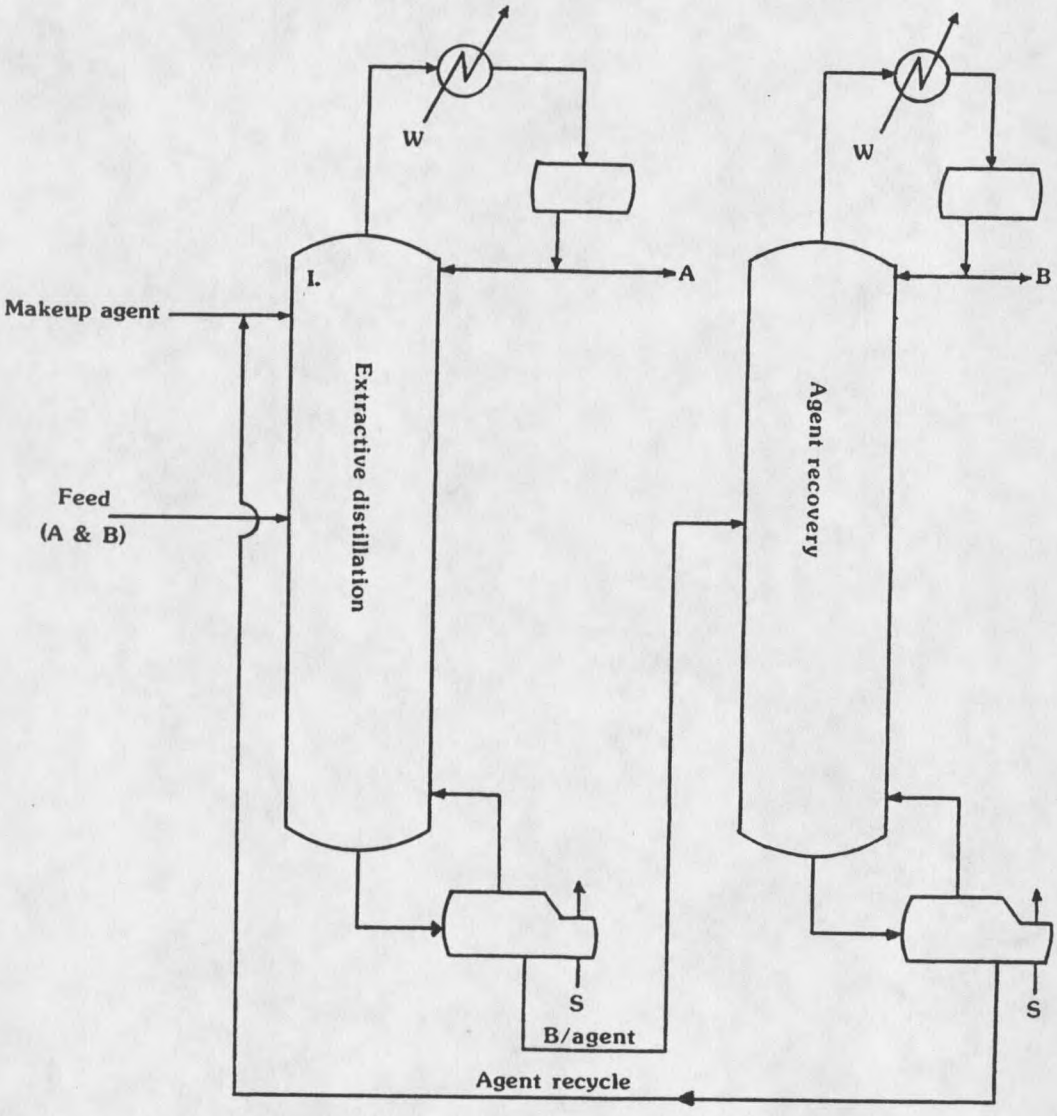


Figure 5. Schematic diagram of an extractive distillation process.

column I, component A is obtained as overhead product. The bottom product, mixture of component B and the agent, is fed to the second column and B is obtained as overhead product. The agent is recovered and recycled.

Obviously, for azeotropic or extractive distillation to be economically attractive, the improvement in relative volatility, and resulting saving in column height and steam and water costs, should more than offset the added costs of recirculating the agent, recovering it from the products, and providing make up agent because of losses in recirculation. In azeotropic distillation an agent immiscible with the overhead product can be separated by decantation, and with a hydrocarbon overhead product a water-soluble agent can used and then recovered by washing the overhead product with water. As shown in Figure 4, three columns are needed to complete the separation of water and ethanol, agent recovery, and water removal. In extractive distillation, agent recovery from the bottoms product is easily affected in a separate stripping column because of the agent's low vapor pressure. As shown in Figure 5, only two columns are required to complete the separation of a binary mixture and agent recovery. Comparing Figures 4 and 5 shows that the capital cost for extractive distillation could be lower than that for azeotropic distillation.

The principal difference between the processes of azeotropic and extractive distillation is that the agent is almost entirely recovered in the distillate in azeotropic distillation, and in extractive distillation the agent is recovered in the residue or bottoms. Also, the optimum point of adding of the agent to the column is different for

the two types of processes. Gerster [3] illustrated the difference between these two methods by the various special-agent distillations required at Celanese's Bishop, Texas plant. If the feed is a close-boiling hydrocarbon pair, the differences in the nature of the feed components are usually comparatively small, so that the 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 and is discharged at the bottom of the column. Azeotropic distillation is particularly useful where the feed component selected to come overhead as an azeotrope with the agent is present in the feed in small amount. In such an instance the amount of agent needed to be circulated is small, resulting in only small additional steam costs because of the presence of the agent and in a low-agent recovery cost.

In many industrial mixtures the key components under consideration can be separated either by extractive or azeotropic distillation by the selection of the proper agent, and the economic comparison of the processes will usually indicate the one more suitable for the purpose. Another important consideration in the selection of a process is the thermal stability of the components, particularly that of the heavy key and heavier key components. 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 bottoms at its lowest point. A heavy agent would increase the bubble point above this temperature and could have a deleterious effect on the components in the residue.

Treybal [4] has pointed out that extractive distillation is generally considered to be more desirable than azeotropic distillation since (i) there is a greater choice of agents because the process does not depend upon the accident of azeotrope formation and (ii) generally smaller quantities of agent must be vaporized. Due to the increase in energy costs, extractive distillation is worth considering even when the conventional approach is feasible. Sucksmith [5] has shown that 42 million Btu/hour are required to separate the mixture of n-heptane and toluene by conventional distillation; only 18 million Btu/hour are required for the same separation by extractive distillation. If an agent provides approximately 40% greater relative volatility, Bojnowski and Hanks [6] suggested that the extractive distillation could be considered instead of conventional fractional distillation.

Behavior of Agents

An effective agent for an extractive distillation is one which is attractive to one or more of the components. This attraction of the agent for these components reduces the volatility of the agent as well as the volatility of the components to which it is attracted. It is desirable that the attraction occur in the natural direction, that is, that the agent be attracted to the relatively heavy components. However, this is not a necessary condition for the behavior of the agent. Many separations are carried out in which one of the relatively light components is attracted by the agent and removed in the bottoms product with the agent. In this case, the energy consumption for

recovering the agent in a stripping column can be reduced due to lower bubble point of the mixture of the agent and the relatively light component.

A variety of theories has been advanced for the roles of the agent in azeotropic and extractive distillation. In the case of extractive distillation, attraction of the agent for certain components of the mixture is commonly attributed to one or more or a combination of the following phenomena: (1) hydrogen bonding, (2) polar characteristics of the agent and components of the mixture, (3) the formation of weak unstable chemical complexes, and (4) chemical reactions between the agent and one or more of the components of the mixture.

In the case of azeotropic distillation, the agent should have the capacity to reduce the tendency of attraction between molecules. For example, a nonpolar agent may be added to a mixture of polar molecules in order to increase the volatilities of the more polar compounds relative to the less polar compounds.

Although any one theory does not sufficiently explain all applications of azeotropic and extractive distillation, the theories do provide qualitative values for the selection of agents. The role of polarity has been elucidated by Hopkins and Fritsch [7] who described the use of products obtained by oxidation of selected hydrocarbons. Because of the dissimilarities in molecular structure, the oxidation products can be arranged in the order of increasing polarity [8], namely, esters, oxides, aldehydes, ketones, acetals, and alcohols. In any class of compounds, the polarity is inversely proportional to the molecular weight, the polarity of straight-chain molecules is greater

than that of branched-chain structures, and olefinic compounds are more polar than their corresponding paraffin derivatives.

Choice of Agents

Among the desirable features for an agent are the following:

1. It should have a high capacity for the species being separated by it. The higher the agent capacity, the lower the agent circulation rate required.
2. It should be selective, having a wider range of temperature and concentration of miscibility with one or more of the components being separated while having a small range of the miscibility with other components.
3. It must have a low molar latent heat since it is to be vaporized.
4. It should be chemically stable, i.e., it should not undergo irreversible reactions with components of the feed stream or during recovery.
5. It should be easily separable from the components with which it associates. Thus it can be reused again and again.
6. It should be nontoxic and noncorrosive and should not be a serious contaminant to the process stream being handled.
7. It should be inexpensive to keep the cost of maintaining agent inventory and of replacing lost agent low.
8. It should have a low enough viscosity to be pumped and flow by gravity easily.
9. It should have a density different enough from that of the feed

stream for the phases to counterflow and separate readily.

10. It should not form so stable an emulsion that the phases cannot be separated adequately.

11. It should be completely soluble with the components in the distilling system at the temperature and concentrations in the column.

The selection of the agent can be based upon its ability to modify the relative volatility of the system. However, its final selection must be determined through economic evaluation wherein all variables and criteria are considered in conjuction with selectivity to determine the minimum operating and investment cost for the process. Colburn and Schoenborn [9] and others have analyzed the selection of agents on the cost basis.

In some cases an agent mixture may be used to derive properties that cannot be achieved with pure agents. Gerster [10] discussed agent selection in more detail. Obviously no agent will be best from all of these viewpoints, and the selection of a desirable agent involves compromises between these various factors, e.g., between capacity and selectivity.

It is necessary to emphasize that the whole process must be considered in the selection of an effective agent, and the recovery process must be included in the evaluation. An agent must have the best selectivity of all of those of an entire group considered, but it might be more difficult to be separated from the components with which it associates than an agent having low selectivity, and economic considerations might prove the use of the latter to be more feasible.

Research Objective

Close-boiling compounds and azeotropic mixtures are difficult or impossible to separate by ordinary distillation. The objective of the research is to study the solution behavior of agents in terms of molecular interactions. To accomplish this, some agents, which (i) would negate the azeotropes or alter the relative volatility of the close-boiling compounds and (ii) are easy to recover from the bottoms product, have been examined to enhance the separation by extractive distillation. The agent could be a pure compound or a mixture of compounds.

Selection of Mixtures

Four binary mixtures which included one close-boiling pair of compounds and three binary azeotropes and four acetate-alcohol-water ternary azeotropes were studied. These systems are described following.

m-Xylene and o-Xylene System

Xylenes are major precursors to many processes for making plastics and dyes. In these uses it is essential that the xylenes be very pure. It is the presence of impurities that make them poor polymerization agents as a plastic or render them inconsistent as dye intermediates. The xylenes of commerce originate either from coal tar or from petroleum, usually via the hydroforming of the corresponding naphthenes and thus are always found as mixtures of isomers. m-Xylene boils at

139.2°C and o-xylene boils at 144.5°C at one atmosphere. Berg [11] has reported that the relative volatility of m-xylene to o-xylene is 1.12. Extractive distillation would be an attractive method if agents can be found to increase the apparent relative volatility of m-xylene to o-xylene to a value higher than 1.3.

The operation to prepare benzene from close boiling non-aromatic hydrocarbons has been well described by Butler [12]. He suggested a large number of pure compounds including alcohols, glycol ethers and sulfolanes to separate both benzene and toluene. No information was given on the relative volatility and thus relative performance of these compounds as extractive distillation agents. Atlani et al. [13] described the use of several cyanamide derivatives as agents for separating aromatics including benzene from naphthenes and dienes. Cooper [14] employed molten phthalic anhydride as the agent to separate aromatics including benzene from non-aromatic hydrocarbons. Mikitinko, Cohen, and Asselinieau [15] used these same reagents with water added to bring the non-aromatic hydrocarbons off overhead as a two-phase azeotrope and thus lower the boiling point. Eisenlohr and Mueller [16] reported an improved equipment arrangement to separate both benzene and toluene from non-aromatic hydrocarbons by extractive distillation. Preusser et al. [17] described the use of morpholine and some of its derivatives for this separation. Improved equipment for this separation was presented by Mueller and John [18]. Berg [19] described the use of chloro compounds and oxygenated compounds to separate ethylbenzene from p-xylene and m-xylene. Although the separation of hydrocarbons has been

studied, the separation by extractive distillation of one xylene from another xylene has not been studied.

Berg et al. [20] have shown that packed columns can also be used in extractive distillation. In this study, both the perforated plate and packed columns were used to examine the effects of agents.

Ethanol and Water System

The separation of water (normal b.p.=100°C) from ethanol (normal b.p.=78.5°C) is one of the world's oldest technical problems. Two principal methods of producing ethanol are by the fermentation of carbohydrates and the hydration of ethylene. Both methods are in aqueous solutions and so the separation of ethanol from the reaction mixture in either case involves the formation of the ethanol-water azeotrope. The fermentation of carbohydrates to ethanol typically produces a product, wine, with 14 wt.% ethanol. At that level, the bacteria die and the fermentation ceases. Distillation of the wine will increase the ethanol content. The minimum azeotrope of water and ethanol contains 95.5 wt.% ethanol, 4.5 wt.% water and limits the upper concentration of ethanol that can be obtained by rectification regardless of the number of theoretical plates employed. This is the case shown in Figure 3. The theoretical plates number approaches infinite when the relative volatility is unity.

In order to produce ethanol free of water, absolute alcohol, three general methods can be employed. Distillation with a third component which forms a minimum azeotrope that boils lower than 78.15°C, the boiling point of the ethanol-water azeotrope, such as water-ethyl ether,

reported by Othmer and Wentworth [21], or a ternary azeotrope such as benzene-water-ethanol, well described in Kirk and Othmer [22]. While the benzene-water-ethanol ternary is probably the most widely used method of dehydrating ethanol, these methods require a great deal of boiling and consequently a large heat requirement. Figure 4 shows that three columns are needed to carry out the separation.

Removal of water with a solid dehydrating agent is well known. Fresh quicklime, anhydrous calcium chloride, anhydrous calcium sulfate, fused anhydrous potassium acetate and sodium acetate, barium oxide and silica gel have been widely used. Barium oxide used to react with water to form barium hydroxide gets the last traces of water from ethanol. Silica gel is probably currently the most widely used. All of these reagents have the disadvantage in that they must be extensively treated to remove water before they can be reused.

Extractive distillation is a third general method. The earliest application of extractive distillation to the dehydration of ethanol is probably Schneible [23] who used glycerine as the extractive agent. Smith and Carlson [24] employed ethoxyethanol and butoxyethanol as the extractive agents and Catterall [25] reported gasoline as being effective. Drout and Dowling [26] used glycols, glycol ethers or glycol esters as the agents and Washall [27] dehydrated the higher alcohols using ethylene glycol as the extractive distillation agent. All of these extractive distillation processes have one thing in common; they took out ethanol as the overhead product and water and the agent came out the bottom of the column. Only two columns are required for this process.

Water has a higher latent heat, 970 btu/lb at its normal boiling point, than ethanol, 367.5 btu/lb at its normal boiling point. In the previous studies, water was taken out as bottoms product, i.e., water was heated twice in the whole separation process. In the first step water was heated in the extractive distillation column and taken out as the bottoms product with the agent. As a component of the bottoms product, water gives up its latent heat in the first column and becomes liquid. In the agent recovery column, water was heated again. Energy consumption can be reduced if water is vaporized only once instead of twice. In the second method, water is the overhead product of the extractive distillation column. It was attempted to screen out some agents which can reverse the volatility of ethanol and water.

Methanol and Methyl Acetate System

Methyl acetate can be used as a solvent for nitrocellulose, acetylcellulose, many resins and oils, and in the manufacture of artificial leather. Also it has a new use in the manufacture of artificial leather. One of the commercially important ways to manufacture methyl acetate is by the catalytic esterification of methanol with acetic acid. Methyl acetate (normal b.p. of 56.3°C) and methanol (normal b.p. of 64.5°C) form a binary azeotrope boiling at 54°C and containing 81.3 wt.% methyl acetate, 18.7 wt.% methanol. Methyl acetate also forms a binary azeotrope with water which boils at 56.1°C and contains 95 wt.% methyl acetate. Methyl acetate, methanol, and water do not form a ternary azeotrope. Thus in rectification of methanol with acetic acid to form methyl acetate and water, the

rectification of this mixture yields the lowest boiling constituent, namely the methyl acetate-methanol azeotrope.

Berg and Yeh [28] have applied some agents, such as DMSO and ethylene glycol, to separate methyl acetate from methanol by extractive distillation. They obtained methyl acetate as the overhead product, a normal result, the lower boiling component coming out overhead. However, Yeh [29] reported that nitrobenzene could cause methanol to be more volatile than methyl acetate.

Acetone and Methanol System

Acetone and methanol are two of the most widely used solvents, and mixtures of these two occur with great frequency. The usual method of recovering volatile solvents is by rectification in a multiplate column. However, in this case, complete recovery by rectification is practically impossible due to the formation of the minimum azeotrope between these two compounds. Table II [30] shows the boiling points of acetone, methanol, and the minimum-boiling azeotrope at one atmosphere. The normal boiling point of acetone is 8.65°C lower than that of methanol. The effect of pressure change on the vapor liquid equilibrium of acetone

Table II. Properties of components and azeotrope at 1 Atm.

	n.b.p., °C	Azeotrope composition
Acetone	56.15	
Methanol	64.7	
Acetone - Methanol azeotrope	55.0	86 wt.% acetone

and methanol has been reported by Britton et al. [31]. However, a minimum-boiling azeotrope with about 25 wt.% methanol exists at 200 mm Hg. It would be very costly to separate this binary mixture by vacuum distillation. Extractive distillation would be an attractive method to separate this mixture.

Ternary Azeotropes

One of the commercially important ways to manufacture acetates, such as n-propyl acetate, is by the catalytic esterification of the corresponding alcohol, such as n-propanol, with acetic acid. The reaction can be generalized as

$$\underset{\text{(Alcohol)}}{R\text{-}OH} + \underset{\text{(Acetic acid)}}{CH_3COOH} \rightleftharpoons \underset{\text{(Acetate)}}{ROCOCH_3} + \underset{\text{(Water)}}{H_2O} \qquad (2)$$

Water is always a by-product of this synthesis. Many of the lower molecular weight acetates form minimum ternary azeotropes with alcohol and water and therefore recovery by distillation brings most of the acetate out overhead as the ternary azeotrope. Table III [32] lists the uses of some alcohols and acetates.

Four systems, n-propyl acetate(nPAc)-n-propanol(nPOH)-water, isopropyl acetate(IPAc)-isopropanol(IPOH)-water, n-butyl acetate(nBAc)-n-butanol(nBOH)-water, and isobutyl acetate(IBAc)-isobutanol(IBOH)-water were studied. However, there are three minimum binary azeotropes and one minimum ternary azeotrope in each of these systems. Table IV [30] lists the normal boiling points of the key components and azeotropes.

Table III. The uses of some alcohols and acetates.

Compound	Uses
n-Propanol	A solvent for resins and cellulose esters, etc.
n-Propyl acetate	Manufacturing flavors, perfumes. solvent for resins, cellulose derivatives, plastics.
Isopropanol	In antifreeze compositions, as solvent for gums, shellac, essential oils; in the extraction of alkaloids, in quick-drying oil, in quick-drying inks; in denaturing ethanol, in body rubs,hand lotions, after-shave lotions, and similar cosmetics. solvent for cresol, resins and gums.
Isopropyl acetate	Solvent for cellulose derivatives, plastics, oils and fats, in perfumery.
n-Butanol	Solvent for fats, waxes, resins, shellac, varnish, gums, manufacture lacquers, rayon, detergents, other butyl compounds, in microscopy for preparing paraffin imbedding materials.
n-Butyl acetate	Manufacture lacquers, artificial leather, photographic films, plastics, safety glass.
Isobutanol	Manufacturing esters for fruit flavoring essences, solvent in paint, varnish removers.
Isobutyl acetate	Flavoring and solvent.

Table IV. The normal boiling points of pure components and azeotropes.

Compounds	Normal boiling point, °C
H_2O	100.0
n-Propanol	97.2
n-Propyl acetate	101.6
n-Propanol, H_2O	81.7[a]
n-Propyl acetate, H_2O	82.4[b]
n-Propyl acetate, n-propanol	94.7
n-Propyl acetate, n-propanol, H_2O	82.5
Isopropanol	82.5
Isopropyl acetate	91.0
Isopropanol, H_2O	80.1
Isopropyl acetate, H_2O	76.6
Isopropyl acetate, isopropanol	80.1
Isopropyl acetate, isopropanol, H_2O	75.5
n-Butanol	117.8
n-Butyl acetate	125.5
n-Butanol, H_2O	92.4
n-Butyl acetate, H_2O	90.2
n-Butyl acetate, n-butanol	116.2
n-Butyl acetate, n-butanol, H_2O	90.7
Isobutanol	108.0
Isobutyl acetate	117.2
Isobutanol, H_2O	89.8
Isobutyl acetate, H_2O	87.4
Isobutyl acetate, isobutanol	107.4
Isobutyl acetate, isobutanol, H_2O	86.8

a: at 600 mm Hg; b: at 700 mm Hg.

In these four systems, the acetate, except isopropyl acetate (n.b.p. 91°C), is the highest boiling individual component in each ternary mixture. Table V [30] lists the azeotropic compositions for binary and ternary azeotropes. The solubility of acetates in water is very low. Only n-propanol and isopropanol are miscible with water at any compositions. Table VI [33] shows the solubility of acetates and alcohols in water.

Table V. Azeotropic compositions of binary and ternary azeotropes.

Azeotrope	Composition, wt.%
nPAc, nPOH	51.1% nPAc+48.9% nPOH
nPAc, H_2O	86% nPAc+14% H_2O
nPOH, H_2O	71.5% nPOH+28.5% H_2O
nPAc, nPOH, H_2O	73% nPAc+10% nPOH+ 17% H_2O
IPAc, IPOH	47.7% IPAc+52.3% IPOH
IPAc, H_2O	89.6% IPAc+10.4% H_2O
IPOH, H_2O	88% IPOH+12% H_2O
IPAc, IPOH, H_2O	76% IPAc+13% IPOH+11%H_2O
nBAc, nBOH	36.7% nBAc+63.3% nBOH
nBAc, H_2O	71.3% nBAc+28.7% H_2O
nBOH, H_2O	57.2% nBOH+42.8% H_2O
nBAc, nBOH, H_2O	63% nBAc+8% nBOH+ 29% H_2O
IBAc, IBOH	45% IBAc+55% IBOH
IBAc, H_2O	83.5 IBAc+16.5% H_2O
IBOH, H_2O	67% IBOH+33% H_2O
IBAc, IBOH, H_2O	46.5% IBAc+23.1% IBOH+30.4% H_2O

Table VI. Solubilities of acetates and alcohols in water.

Compound	Solubility, g./100 g. water
n-Propyl acetate	1.6^{16}
Isopropyl acetate	3.0^{20}
n-Butyl acetate	0.7
Isobutyl acetate	0.6^{25}
n-Propanol	Miscible
Isopropanol	Miscible
n-Butanol	9.0^{15}
Isobutanol	10.0^{15}

The numbers of the superscript are the degrees in C.

II. THEORECTICAL ASPECTS

Vapor-Liquid Equilibrium

Distillation is a method of separating the components of a liquid mixture. It depends upon the distribution of the substances between a gas and a liquid phase applied to cases where all components are present in both phases at the pressure and temperature of the system. Instead of introducing a new substance into the mixture in order to provide the second phase, as is done in gas absorption or desorption, the new phase is created from the original solution by vaporization or condensation. This process is concerned with the separation of a solution where all the components are appreciably volatile. When the two (or more) phases are in a state of physical equilibrium, the maximum relative difference in concentration of the materials in the phases occurs. Therefore, attainment of an equilibrium condition is desirable in the distillation process. The application of distillation methods depends greatly upon an understanding of the equilibria existing between the vapor and liquid phases of the mixture encountered.

Vapor-liquid equilibrium data, except in the special situations of ideal and regular solutions, must be determined experimentally. Phase diagrams are used to describe two-component systems by plotting two of the three independent variables, composition, temperature, and pressure, at a constant value of the remaining one. In Figure 6, the a, e, i diagrams are typical of regular or normal systems. The b, f, j diagrams

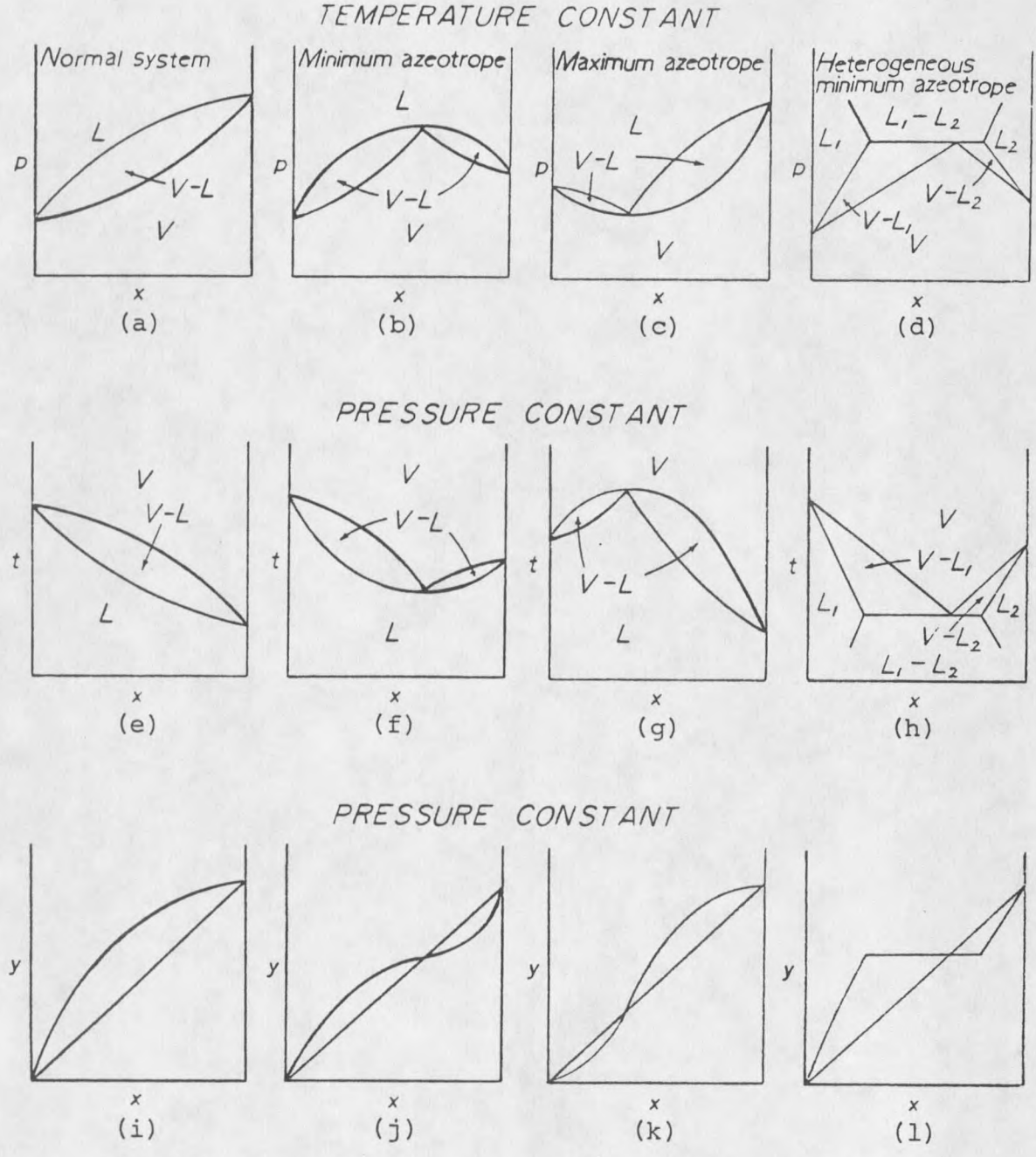


Figure 6. Phase diagrams for various types of binary systems.

are typical of minimum-boiling homogeneous azeotropes, the c, g, k diagrams of maximum-boiling homogeneous azeotropes, and the d, h, l diagrams of minimum-boiling heterogeneous azeotropes. In the first three systems only one liquid phase exists; whereas in the fourth, two liquid phases can exist at and below the azeotrope temperature.

For an ideal solution, the equilibrium partial pressure p_i° of a constituent at a fixed temperature equals the product of its vapor pressure, p_i, when pure at this temperature times its mole fraction, x_i, in the liquid phase. This is Raoult's law

$$p_i^{\circ} = p_i x_i \tag{3}$$

In a nonideal solution, the extent of deviation from nonideality of components in liquid mixtures is measured by the activity coefficient, γ. When the observed activity coefficients are greater than unity, the solution is said to exhibit positive deviation from Raoult's law. This is the usual case, and all solutions where dispersion or van der Waals forces dominate exhibit positive deviations from Raoult's law. Strong positive deviations are also typical of solutions that are termed associated. An associated solution is one in which one (or more) of the components undergoes exceptionally strong self-interactions, but which exhibits only normal intermolecular potentials with the other components. For example, in the solutions of alcohols in hydrocarbons, the alcohols hydrogen-bond strongly with themselves, but not with hydrocarbons. As a result, dilution of the alcohol by the hydrocarbon

causes disruption of hydrogen bonding, and this increases the volatility, or fugacity, of the alcohol to well above the ideal case.

On the other hand, negative deviations from Raoult's law are defined by activity coefficients of less than unity. Frequently, but not always, strong negative deviations from Raoult's law are attributable to the phenomenon known as solvation. Solvated solutions occur when the unlike-pair intermolecular forces are markedly stronger than the like-pair interactions, thus reducing the fugacities of the components in the mixture. An example of such behavior is the solution of chloroform with ether. The proton in chloroform can form a hydrogen bond with the ether oxygen, but neither pure species can hydrogen-bond itself.

Strong deviations from Raoult's law may often result in the phenomenon known as azeotropy. Very strong positive deviations lead to liquid-liquid immiscibility. For example, the strongly associated solution of ethanol-benzene shows a maximum in the isothermal vapor-pressure curve, and the solvated solution of acetone-chloroform shows a minimum in this type of plot. The extremum in the ethanol-benzene solution is called a minimum-boiling azeotrope. The extremum in the acetone-chloroform solution is called a maximum-boiling azeotrope.

Applying this correction factor to Raoult's law results in

$$p_i^{o} = \gamma_i x_i p_i \qquad (4)$$

Here we assumed that the standard state fugacity, f_i^{o}, can be approximated by the pure-component vapor pressure, p_i, at low-to-

moderate pressures and temperature. At equilibrium, the fugacities of any component i in the vapor and liquid phases must be equal. This can be expressed as:

$$\phi_i \, y_i \, P = \gamma_i \, x_i \, p_i \tag{5}$$

where ϕ_i is the fugacity coefficient of component,

P is the total pressure of the system, and

y_i is the mole fraction of i in vapor phase.

The greater the distance between equilibrium curves and diagonals of Figure 6 i, j, k, l, the difference in vapor and liquid compositions is greater and the easier the separation by distillation. One numerical measure of this is called the separation factor, or, particularly in the case of distillation, the relative volatility, α_{ij}. This is the ratio of the concentration ratio of i and j in one phase to that in the other phase and is a measure of the separability.

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} = \frac{\gamma_i p_i \phi_j}{\gamma_j p_j \phi_i} \tag{6}$$

The value of α_{ij} will ordinarily change as x varies from 0 to 1.0. If $y_i = x_i$ (except at x = 0 or 1.0), $\alpha = 1.0$ and no separation is possible by conventional rectification. The larger the value of a above unity, the greater the degree of separability.

Britton et al. [31] have reported that pressure has a marked effect on the azeotropic composition and vapor liquid equilibrium diagrams of alcohol-ketone systems. If the system is insensitive to pressure, the

addition of an agent is another method to change the equilibrium curve. The addition of an agent was believed to alter the relative volatility of two key components being separated. An effective agent should alter the relative volatility in the direction of making the separation easier, i.e., the relative volatility is increased. However, some agents may reverse the relative volatility of two compounds. In other words, the less volatile compound would become more volatile.

The Fenske Equation

In an ideal case the ratio of vapor pressures of the key components is very close to a constant, i.e., the relative volatility is constant. If this case can be assumed without introducing excessive error in a distillation process, the number of theoretical plates required at total reflux may be calculated by the Fenske equation [34]

$$\alpha_{av}^{N} = \left(\frac{y_i}{y_j}\right)_O \left(\frac{x_j}{x_i}\right)_B \tag{7}$$

where N is the minimum theoretical plates at total reflux and subscripts O and B denote the overhead and bottoms products.

α_{av} may be evaluated as the arithmetic average between the overhead and bottoms temperature.

$$\alpha_{av} = (\alpha_O + \alpha_B)/2 \tag{8}$$

where α_O is the relative volatility at the overhead temperature and composition, and

α_B is the relative volatility at the bottoms temperature and composition.

However, α_{av} may be also be evaluated as the geometric average of the values of the overhead and bottoms products [4].

The weight percent can be expressed in terms of molecular weight and mole fraction as follows:

vapor phase:

$$W_{yi} = \frac{W_{io}}{W_{TO}} = \frac{m_i y_i}{m_i y_i + m_j y_j} \tag{9}$$

where W_{io} is the weight of component i in the vapor phase,

W_{TO} is the total weight in the vapor phase, and

m_i is the molecular weight of component i;

liquid phase:

$$W_{xi} = \frac{W_{iB}}{W_{TB}} = \frac{m_i x_i}{m_i x_i + m_j x_j} \tag{10}$$

where W_{iB} is the weight of component i in the liquid phase and W_{TB} is the total weight in the liquid phase.

Substituting Equation 9 and 10 into Equation 7 yields

$$\alpha_{av}{}^N = \left(\frac{W_{yi}}{W_{yj}}\right)_O \left(\frac{W_{xj}}{W_{xi}}\right)_B \tag{11}$$

The basic assumption for the Fenske equation is constant relative volatility. In the other words, the validity of the Fenske equation is

restricted to ideal solutions. In extractive distillation the solution behavior is very non-ideal. Thus the use of the Fenske equation in this study is only an approximate approach and thus the comparison can be made on the same basis. Equation 11 was used to calibrate the rectification column and calculate the relative volatilities in this investigation. Thus everything was done on a consistently comparable basis.

Effect of Adding An Agent

Examination of Equation 6 indicates that the relative volatility may be changed by three ways:

1. Alter the ratio of pure-component vapor pressures. This ratio increases slightly as temperature is reduced, but not usually enough to enhance separation to a significant degree.
2. Alter the ratio of vapor-phase fugacity coefficients. These are measures of the nonideality of the vapor-phase mixture. At moderate pressures, these coefficients are usually close to one and do not provide a practical means of changing relative volatility.
3. Alter the ratio of liquid-phase activity coefficients. Many liquid mixtures are highly nonideal, and therefore these coefficients can be much greater than one. The ratio of the two coefficients can be changed substantially by adding an agent that is chemically more similar to one component than to the other. This approach is the basis of extractive distillation.

Scheibel [35] has pointed out three main ideas on selecting a proper agent: (i) the agent must not form an azeotrope with any components in the mixture to be separated, (ii) it must be less volatile than any components, (iii) the agent must have a different effect on the partial pressure of each of the components in the mixture. Berg [11] suggested that the boiling point difference between the compounds being separated and the agent should be twenty degrees Celsius or more. As the previous discussion on the deviation from Raoult's law shows that an agent can best enhance the separation if the agent forms a positive deviation with one key component and a negative deviation with another key component. The ratio of the activity coefficients will be changed considerably.

Besides the relative volatility, selectivity can be used to indicate the effect of an agent on separation. Quantitatively, selectivity is defined as the ratio of the relative volatility of the key components in the mixture which are to be separated in the presence of the separating agent to their relative volatility before the addition of the agent. One expression used to define selectivity [36] is

$$S_{ij} = \frac{[\alpha_{ij}]_P}{[\alpha_{ij}]_A} = \frac{[(y_i/x_i)/(y_j/x_j)]_P}{[(y_i/x_i)/(y_j/x_j)]_A} = \frac{[\gamma_i p_i \phi_j / \gamma_j p_j \phi_i]_P}{[\gamma_i p_i \phi_j / \gamma_j p_j \phi_i]_A} \qquad (12)$$

where the subscript P indicates the presence of agent and the subscript A indicates the absence of agent.

To obtain the selectivity on a strictly comparable basis, it should be evaluated for the same relative liquid composition of the key

components; and, if the temperature is widely different, the activity coefficients and vapor pressures of the components should be corrected to the same basis. If the agent used in extractive distillation is added at the bubble point of the agent-free mixture, and if the temperature is far below the boiling point of the agent (i.e., its vapor pressure is low), the correction is small and negligible.

Selectivity or the ability of a compound to affect the behavior of other compounds in solution to the extent that their relative volatilities are changed is the result of molecular interaction. The work of Hildebrand [37], van Arkel [38], London [39] and others have resulted in the recognition of two broad forms of molecular interaction, namely physical and chemical forces. Figure 7 illustrates the physical interactions in a solution containing one polar and one nonpolar or one polar component.

The physical forces causing molecular interactions in which energy effects are thermodynamically positive in sign (endothermic) are classified by Hildebrand [37] as:

1. Dispersion forces which tend to cause a perturbation in the electronic motion of one molecule as the result of its being within the field of influence of another. This is considered a nonpolar effect.
2. Induction forces which are exerted by one molecule on another, the first having a permanent dipole moment which makes it capable of inducing a polarization or induced dipole in the other. This is an attractive force.
3. Orientation forces which are exerted by the action of one permanent

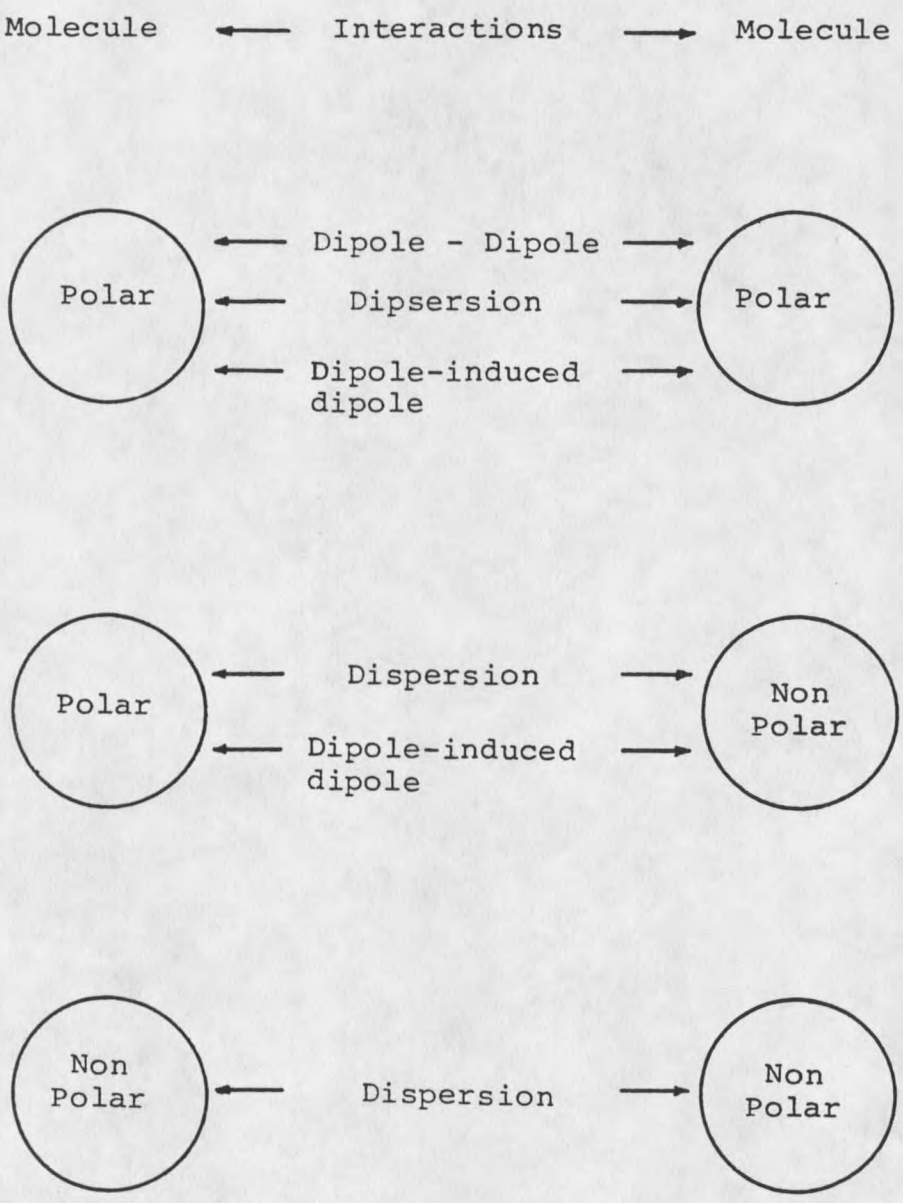


Figure 7. Physical interactions between molecules.

dipole on another permanent dipole causing molecules to orient with respect to one another.

It has been shown [37, 38, 39] that molecules which are nonpolar in makeup or electroneutral - such as the saturated hydrocarbons - when forming a nonideal solution with other nonpolar molecules, only dispersion forces are involved. Where nonideal mixtures of nonpolar and polar molecules are formed, both dispersion and induction forces are involved with the mixture formation accompanied by an endothermic heat of mixing. When polar-polar mixtures are formed, all three physical effects of dispersion, induction, and orientation are in evidence to contribute to a positive endothermic heat of mixing.

The chemical forces are usually attributed to hydrogen bonding or complexing of the molecules in a solution. These forces cause molecular interactions in which the energy effects are thermodynamically negative in sign or exothermic. Effective chemical-complexing agents and key components tend to give reaction bond energies falling in a certain critical range. Figure 8 shows this range and gives four examples of classes of chemical interactions with bond energies within that range. It is believed that van der Waals forces, acid-base interactions and hydrogen bonding occur mostly in this range for extractive distillation.

Ewell et al. [40] concluded that hydrogen can coordinate between two molecules of O_2, N_2 and/or F, and can coordinate between O_2, N_2, F and C if a number of negative atoms are attached to the carbon atom. They suggested the following classification of hydrogen bonds as "strong" or "weak".

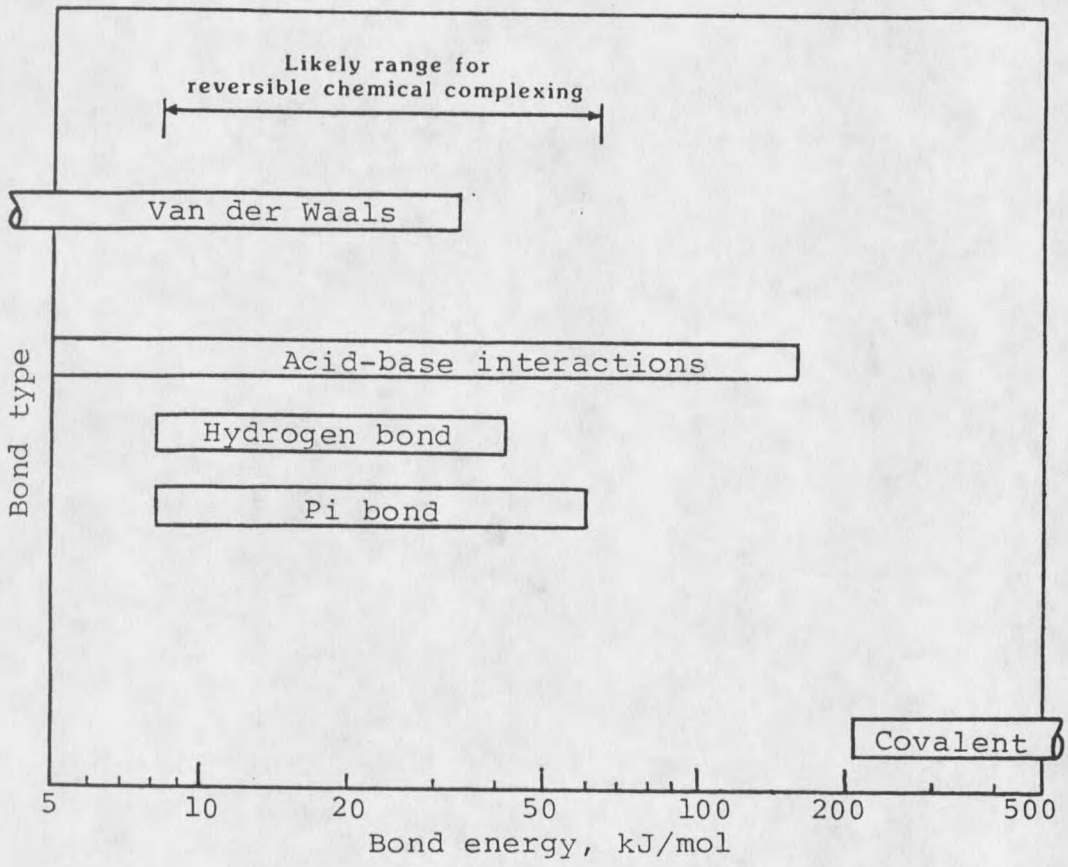
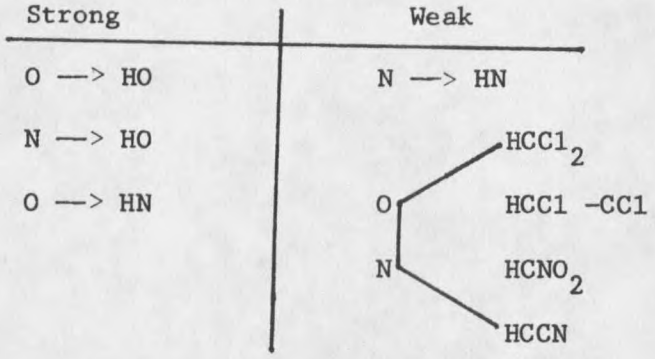


Figure 8. Bond energies of different types of bondings.



They also classified the liquid materials into five groups based on the potential for forming hydrogen bonds as follows:

Class I. Liquids capable of forming three-dimensional networks of strong hydrogen bonds, e.g., water, glycol, glycerol, amino alcohols, hydroxylamine, hydroxy acids, polyphenols, amides, etc. Compounds such as nitromethane and acetonitrile also form three-dimensional networks of hydrogen bonds but the bonds are much weaker than those involving OH and NH groups. Therefore, these types of compounds are placed in class II.

Class II. Other liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen, and fluorine), e.g., alcohols, acids, phenols, primary and secondary amines, oximes, nitro compounds with α-hydrogen atoms, nitriles with α-hydrogen atoms, hydrazine, hydrogen fluoride, hydrogen cyanide, etc.

Class III. Liquids composed of molecules containing donor atoms but no active hydrogen atoms, e.g., ethers, ketones, aldehydes, esters, tertiary amines (including pyridine type), nitrocompounds and nitriles without α-hydrogen atoms, etc.

Class IV. 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, e.g., $CHCl_3$, CH_2Cl_2, CH_3CHCl_2, CH_2Cl-CH_2Cl, $CH_2Cl-CHCl-CH_2Cl$, $CH_2Cl-CHCl_2$, etc.

Class V. All other liquids, i.e., liquids having no hydrogen-bond-forming capabilities, e.g., hydrocarbons, carbon disulfide, sulfides, mercaptans, halohydrocarbons not in class IV, nonmetallic elements such as iodine, phosphorus, sulfur, etc.

Factors Affecting Selectivity

The variables affecting selectivity of one compound for another are numerous, and the quantitative extent, and in some instances even the qualitative extent, and direction of the effects are little understood. Experimental study of the effects of some of the variables has given some insight to the problem for some systems, but in the study of some systems the experimental results are not readily explained by accepted theory.

Temperature

Temperature is believed to affect selectivity in that an increase in temperature tends to increase mutual solubility of compounds in a liquid mixture and thus decrease the selectivity of one component for another. This may be referred to as a physical effect as contrasted to

a chemical effect. In addition to the physical effect of solubility, the chemical effect of complexing is generally considered to be affected by temperature. Prausnitz [41] and others observed that the complex stability decreased with an increase in temperature and, therefore, the selectivity attributed to complexing was decreased by an increase in temperature. This is consistent with the generalization that exothermic reactions are favored by lower temperature level.

Pressure

In general, the specific effect of pressure on activity coefficient is negligible, and therefore pressure can be said to have no effect on selectivity at low-to-moderate ranges.

Volume Fraction of Agent

The quantity of agent relative to the quantity of original mixture (as volume fraction, mole fraction, or weight fraction) can exert a strong effect on the selectivity. It is possible for the dilution effect of further additions of agent to break complexes formed in the solutions with less content of the agent, to reduce the absolute values of $(y_i/x_i)(y_j/x_j)$ to insignificance, and to reduce the solubility of the less soluble component to the point of immiscibility.

Relative Size of Molecule

Anderson et al. [42] pointed out that the logarithm of the activity coefficient for individual paraffin hydrocarbons mixed with a polar agent increased approximately linearly with the number of carbon atoms

in the paraffin molecule where there is no hydrogen bonding or chemical effect. In addition, the larger molecule will have the greater activity coefficient of that of two differently sized paraffin molecules in the same agent.

Chemical Effect of Hydrogen Bonding

The hydrogen-bonding theory accounts for molecular association between like and also unlike molecules, usually designated as the chemical effect in nonideal behavior of liquids. H-bond energies vary from 2 to 8 Kcal/mole compared to a regular bond strength of 87 Kcal/mole for C-H bonds and 84 Kcal/mole for N-H bonds. This accounts for easy breaking of H bonds.

Approaches to the Activity Coefficients

Partial molar excess Gibbs energy, which yields an activity coefficient is given by

$$\ln \gamma_i = [\partial(n_T G^E/RT)/\partial n_i]_{T,P,n_j} \qquad (13)$$

Thus the excess Gibbs energy represents a solution to the Gibbs-Duhem differential equation, and from it, expressions for γ may be evaluated.

Innumerable solutions have been proposed for the Gibbs-Duhem equation, ranging from the empirical to the highly theoretical. In general, these take the form of models of excess Gibbs energy, and as

long as they satisfy proper boundary conditions, all of them give values of activity coefficients from Equation 13.

Basically, there are two major types of solutions - enthalpic and entropic. The former, including the Margules, van Laar, and regular solution treatment, accounts for energetic difference between solutions and pure components. The entropic treatments, on the other hand, tend to emphasize differences in structure or arrangement in solutions, ordering or disordering, the mixing of large and small molecules, or local ordering. Typical of such treatments are Flory-Huggins and Wilson equations.

Enthalpic Models

Perhaps the simplest conceptual model of the liquid state is the lattice liquid, or the strictly regular solution theory of Guggemheim [43]. The liquid is pictured as a pseudocrystal in this treatment, in which molecules of the same size and shape are interchangeable on the lattice sites. It is assumed further that the excess entropy and excess volume of mixing are both zero, and finally that one has a knowledge of the potential energies for all pairwise interactions, and these are given as

1-1 interaction, potential energy = ω_{11}/s,

2-2 interaction, potential energy = ω_{22}/s,

1-2 interaction, potential energy = ω_{12}/s,

where s is the assumed coordination number for the quasilattice. The internal energy of the mixture is then taken as the sum of all pairwise interactions, so that a quadratic expression in composition results.

$$\Delta\mu^E = 1/2\{(x_1^2\omega_{11}+2x_1x_2\omega_{12}+x_2^2\omega_{22})-x_1\omega_{11}-x_2\omega_{22}\} \quad (14)$$

where the factor of 1/2 prevents double counting. Thus excess Gibbs energy is

$$\Delta G^E = x_1x_2\omega \quad (15)$$

Then from Equation 14 the activity coefficients are

$$\ln \gamma_1 = x_2^2\omega \quad (16)$$

$$\ln \gamma_2 = x_1^2\omega \quad (17)$$

where the interchange energy represents physically the difference between like-pair and unlike-pair interactions.

If the interchange energy is taken not as a quantity determined from intermolecular forces, but merely as an empirical measure of two-body interactions, strictly regular solution provides the leading term in a series expansion, several of which are commonly used. The Redlich-Kister [44] series is given as

$$\Delta G = x_1x_2[A+B(x_1-x_2)+C(x_1-x_2)+....] \quad (18)$$

from which one obtains the activity coefficients,

$$RT \ln \gamma_1 = x_2^2[A-B(4x_2-3)+C(2x_2-1)(6x_2-5)-.....] \quad (19)$$

$$RT \ln \gamma_2 = x_1^2[A+B(4x_1-3)+C(2x_1-1)(6x_1-5)+.....] \quad (20)$$

In this type of expression, the first term is similar to the pair

interchange energy, and in a loose sense, higher-order terms tend to correspond to higher-order interactions. In any event, one often uses either this series form or the similar one of Margules [45], which gives a series expansion of γ. For two constants and a binary solution, the Margules series are

$$\ln \gamma_1 = x_2^2[A+2(B-A)x_1] \tag{21}$$

$$\ln \gamma_2 = x_1^2[B+2(A-B)x_2] \tag{22}$$

Van Laar [46, 47] began by assuming that both the excess entropy and volume are zero and that van der Waals equations apply to fluid and fluid mixtures. He then calculated the internal energy of mixing pure liquids into liquid mixture as the sum of three parts:

$$\Delta U^M = \Delta U_I + \Delta U_{II} + \Delta U_{III} \tag{23}$$

where ΔU_I = energy to evaporate pure liquid to ideal gases,

ΔU_{II} = energy to mix ideal gases,

ΔU_{III} = energy to condense ideal-gas mixture to liquid mixture.

Of course, $\Delta U_{II} = 0$, and ΔU_I and ΔU_{III} may be found if the functional dependence of molecular volume, ν, on the internal energy, U, is known:

$$(\partial U/\partial \nu)_T = T(\partial P/\partial T)_\nu - P = a/\nu^2 \tag{24}$$

Equation 24 was applied to both pure components and to the mixture, using the empirical mixing rules for the usual van der Waals constants a and b,

$$\sqrt{a_{mix}} = x_1\sqrt{a_1} + x_2\sqrt{a_2} \tag{25}$$

$$b_{mix} = x_1 b_1 + x_2 b_2 \tag{26}$$

and the result for the excess Gibbs energy is given as

$$\Delta G^E = \Delta U^M = x_1 x_2 b_1 b_2 (\sqrt{a_1}/b_1 - \sqrt{a_2}/b_2)^2/(x_1 b_1 + x_2 b_2) \tag{27}$$

Equation 27 thus gives a relationship for calculating activities in solution from pure component properties only - the van der Waals constants. The constants are defined as

$$A = b_1/b_2 \tag{28}$$

$$B = b_1(\sqrt{a_1}/b_1 + \sqrt{a_2}/b_2)^2/R \tag{29}$$

Then

$$\Delta G^E/RT = x_1 B/T(Ax_1/x_2 + 1) \tag{30}$$

and the activity coefficients in a binary mixture are given in the familiar van Laar form as

$$\ln\gamma_1 = B/T(1 + Ax_1/x_2)^2 \tag{31}$$

$$\ln\gamma_2 = AB/T(A + x_2/x_1)^2 \tag{32}$$

Not only did van Laar's method provide a good empirical equation, but it also formed a basis for the development of the Scatchard-Hildebrand regular solution theory [48, 49, 50], which is probably the

most generally applicable method now available for the prediction of mixture properties from pure component properties.

The development of Hildebrand was quite similar to that of van Laar; he assumed zero excess volume and zero excess entropy, but he did not use the van der Waals equation. Rather he observed that in Equation 24 the term $T(\partial P/\partial T)$ was far larger than P, and may be expressed in terms of the isothermal compressibility, β, and the coefficient of thermal expansion, α, which have been measured experimentally for many common nonpolar liquids:

$$T(\partial P/\partial T) = -T(\partial P/\partial v)_T/(\partial T/\partial v)_P = T\alpha/\beta \qquad (33)$$

Empirically, he found that to a good approximation $(\partial U/\partial v)_T$ was given by the configurational energy (very close to the internal energy of vaporization) per unit volume, where the energy (intrinsically negative) is proportional to the volume,

$$-U = cv \qquad (34)$$

and the constant of proportionality is the cohesive energy density. Then the energy of a binary mixture is given as

$$-U(mix.)=(c_{11}v_1^2x_1^2+2c_{12}v_1v_2x_1x_2+c_{22}v_2^2x_2^2)/(x_1v_1+x_2v_2) \qquad (35)$$

This can be expressed in terms of volume fraction Φ

$$\Phi_1 = x_1v_1/(x_1v_1+x_2v_2) \qquad (36)$$

and the following relationship results when the pure-component properties are subtracted:

$$\Delta U^E = (c_{11}+c_{22}-2c_{12})\Phi_1\Phi_2(x_1\nu_1+x_2\nu_2) \tag{37}$$

If the substances 1 and 2 are nonpolar or only slightly polar, the London theory suggests the mixing rule for unlike-pair interactions

$$c_{12} = \sqrt{c_{11}c_{22}} \tag{38}$$

Using this result, and defining the solubility parameter δ as the square root of c, we obtain from Equation 37

$$\Delta G^E = (x_1\nu_1+x_2\nu_2)\Phi_1\Phi_2(\delta_1-\delta_2)^2 \tag{39}$$

Note that the right-hand side of Equation 39 contains only pure-component properties, as the solubility parameter may be estimated from the heat of vaporization (available in turn from the vapor-pressure curve and the Clausius-Clapeyron equation):

$$\delta \simeq (\Delta U_{vap}/\nu)^{1/2} = [(\Delta h_{vap} - RT)/\nu]^{1/2} \tag{40}$$

The resulting expressions for the activity coefficients in the mixture are then

$$RT \ln\gamma_1 = \nu_1\Phi_2^2(\delta_1-\delta_2)^2 \tag{41}$$

$$RT \ln\gamma_2 = \nu_2\Phi_1^2(\delta_1-\delta_2)^2 \tag{42}$$

Entropic Model

The first of the entropic expressions was that developed by Flory [51, 52, 53] and Huggins [54, 55] for athermal solutions. It applies rigorously to solutions with no differences in intermolecular forces, but only in molecular size, such as, the solution of a poly ethylene polymer in a hydrocarbon solvent. The excess Gibbs energy for a general N-component mixture is given by

$$\Delta G^E/RT = \Sigma\, x_i \ln(\Phi_i/x_i) \qquad (43)$$

where Φ is the volume fraction as described by Equation 36.

Although the major entropic concept embodied in the Flory-Huggins treatment is the effect of size differences, entropic contribution due to nonrandom mixing can also be shown to have large effects. In addition, effects occur in many associated solutions that can not be rationalized by any of the common enthalpic expressions.

The Wilson equation [56] uses an entropic approach based on the concept of "local volume fraction", which has been successfully applied to the representation of both binary and multicomponent data [57, 58, 59]. Wilson assumed that in a binary solution of types 1 and 2, a central molecule of type 1 would have a fraction x_{12} of type-2 neighbors and a fraction of x_{11} of type-1 neighbors:

$$x_{12}/x_{11} = x_2 \exp(-\omega_{12}/RT)/x_1 \exp(-\omega_{11}/RT) \qquad (44)$$

where the probabilities are weighted by Boltzman factors and ω_{ij} are

pair potential energies between molecules i and j. This lead to a local volume fraction ζ_1 of type-1 neighbors about a type-1 central molecule as:

$$\zeta_1 = x_1\nu_1\exp(-\omega_{11}/RT)/[x_1\nu_1\exp(-\omega_{11}/RT)+x_2\nu_2\exp(-\omega_{12}/RT)] \qquad (45)$$

A similar expression is derived for ζ_2 (note that ζ_1 and ζ_2 are independent, $\zeta_1+\zeta_2\neq 1$). When these local volume fractions are substituted into the Flory-Huggins expressions, the result is

$$\ln\gamma_1 = -\ln(x_1+x_2\Lambda_{12})+x_2[\Lambda_{12}/(x_1+x_2\Lambda_{12})-\Lambda_{21}/(x_2+x_1\Lambda_{21})] \qquad (46)$$

$$\ln\gamma_2 = -\ln(x_2+x_1\Lambda_{21})-x_1[\Lambda_{12}/(x_1+x_2\Lambda_{12})-\Lambda_{21}/(x_2+x_1\Lambda_{21})] \qquad (47)$$

where $\Lambda_{ij} = \nu_j\exp[(\omega_{ij}-\omega_{ii})/RT]/\nu_i$. When $x_1=0$, $\ln\gamma_1^{\infty}=-\ln\Lambda_{12}+1-\Lambda_{21}$; when $x_2=0$, $\ln\gamma_2^{\infty}=-\ln\Lambda_{21}+1-\Lambda_{12}$.

For practical purposes only the terms $\omega_{ij}-\omega_{ii}$ are empirically determined, and they represent energy terms related to the difference in cohesive energy between an i-j pair of molecules and an i-i pair. To a good first approximation this energy difference is relatively temperature independent over a modest range.

Wilson's equation has a number of distinct advantages, but also certain limitations. It requires only two parameters per binary mixture, and it does have a "built-in" temperature dependence. It gives excellent results for some highly nonideal systems - such as dilute alcohols in hydrocarbons. The parameters are relatively easy to obtain, and they have more physical significance. The great advantage is the

unambiguous extension to multicomponent systems. The two greatest limitations of Wilson's equation are its incapacity to predict either partial immiscibility or a maximum in the activity coefficient.

A number of other very useful entropic expressions have been developed. For example, the NRTL equation of Renon and Prausnitz [60] provides a good entropic expression for use with partially miscible system, though it is probably not as good for vapor-liquid equilibrium in fully miscible mixtures.

Quite recently a much more general expression was developed by Hsieh and Eckert [61] on the basis of the concept of "free coordinates". They have shown that in real liquid mixtures the number of independently determinable neighbors for a given molecules lies closer to unity than the actual coordination number, depending on structure. From the application of statistical mechanics to such as approach, the Zeta equation, is derived as

$$G^E/RT = \varepsilon(x_1\nu_1+x_2\nu_2)[\Phi_1 \ln(\Phi_1+\psi_{12}\Phi_2)+\Phi_2 \ln(\Phi_2+\psi_{21}\Phi_1)]+ x_1 \ln(\Phi_1/x_1)+x_2\Phi_2/x_2 \quad (48)$$

where the Φ's are volume fractions, ε is the constant proportional to the number of "free coordinates", and the parameters, ψ, are given in terms of the cohesive energy density c as

$$\psi_{12} = \exp[-(c_{11}-c_{12})/\varepsilon RT] \quad (49)$$

$$\psi_{21} = \exp[-(c_{22}-c_{12})/\varepsilon RT] \quad (50)$$

This Zeta equation has a number of very interesting and useful properties. First of all, for certain values of the parameters it degenerates in limiting cases to the Scatchard-Hildebrand regular solution theory, to the Wilson equation, or to the NRTL equation. It is capable of great precision in representing binary vapor-liquid equilibria, and this representation is quite insensitive to the value of ε used. Conversely, it is not possible to determine ε by fitting such data.

However, heats of mixing, partial miscibilities, and infinite dilution activity coefficients are all quite sensitive to the value of ε, and may be used to determine it. The Zeta equation is found to represent successfully not only vapor-liquid equilibria, but also liquid-liquid equilibria and enthalpy data. Moreover, it is particularly well suited for use with limited data, such as infinite activity coefficients measured by chromatographic techniques. Thus this very general type of semiempirical equation, including all of the common forms as special cases, shows great promise for future application.

MOSCED Model

Van Arkel [38], Small [62] and Prausnitz and co-workers [41, 48, 63, 64, 65, 66, 67] divided up the total cohesive parameter into two main components, defining a nonpolar cohesion parameter (δ_τ) and a polar parameter (δ_λ). Although this tends to neglect induction interactions, these may be taken care of by an additional parameter. These parameters are related to the Hildebrand parameter by

$$\delta^2 = \delta_\lambda^2 + \delta_\tau^2 \tag{51}$$

The assumption for evaluating δ_λ and δ_τ is that the polar energy of vaporization is the difference between the experimentally determined total energy of vaporization and the energy of vaporization of a nonpolar liquid having molecules very nearly the same size and shape as those of the polar liquid.

If it is assumed that the cohesive energy is made up of a linear combination of contributions from nonpolar or dispersion interactions, $(-U_d)$, polar interactions, $(-U_p)$, and hydrogen bonding or similar specific association interactions, $(-U_h)$, then it is given by

$$-U = -U_d - U_p - U_h \tag{52}$$

It follows that the corresponding cohesive pressure and cohesion parameter can be defined so that

$$-U/\nu = -U_d/\nu - U_p/\nu - U_h/\nu \tag{53}$$

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{54}$$

This method was developed by Hansen et al. [68 - 83] on an empirical basis and by means of semiempirical equations [83, 84, 85], but it may also be used for theoretical subdivisions of the Hildebrand parameter. With the aid of relationships of the physical forces causing molecular interactions, the Hansen parameters can be described in terms of molecular parameters related to intermolecular forces and molecular size

[86]. With the comparison of Equations 51 and 54, the relationship between the parameters are

$$\delta_\lambda = \delta_d \tag{55}$$

$$\delta_\tau^2 = \delta_p^2 + \delta_h^2 \tag{56}$$

δ_τ or the square root of $(\delta_p^2+\delta_h^2)$ is considered as the polarity of the molecule [67].

While the regular solution equation gives a good semiquantitative representation of the excess Gibbs energy of nonpolar or moderately polar solutions, it is not applicable to mixtures containing highly polar or protic components. To extend the usefulness of Equations 41 and 42, later researchers (Arkel and Vlex [86]; Arkel [38]; Blanks and Prausnitz [64]; Weimer and Prausnitz [66]; Gordon [87]; Hansen [69]; Helpinstill and van Winkle [88]; Nelson et al. [89]; Keller et al. [90]; Hsieh [91]; Barton [92]; Koenhen and Smolders [93]; Karger et al. [94]; Tijssen et al. [95]; Karger and Snyder [96]) assumed that the forces contributing to c act independently and are additive. Most such extensions yield forms for the cohesive energy density similar to

$$c_{11} = \lambda_1^2 + \tau_1^2 + \sigma_1\tau_1 + \alpha_1\beta_1 \tag{57}$$

$$c_{22} = \lambda_2^2 + \tau_2^2 + \sigma_2\tau_2 + \alpha_2\beta_2 \tag{58}$$

$$c_{12} = \lambda_1\lambda_2 + \tau_1\tau_2 + 0.5(\sigma_1\tau_2 + \sigma_2\tau_1 + \alpha_1\beta_2 + \alpha_2\beta_1) \tag{59}$$

where the $\lambda_i\lambda_j$, $\tau_i\tau_j$, $\sigma_i\tau_j$, and $\alpha_i\beta_j$ terms represent the dispersion,

orientation, induction, and hydrogen bonding forces, respectively. Here λ is a measure of a molecule's polarizability, τ represents its polarity, σ reflects the ability of the nonpolar part of molecule to interact with a dipole, and α and β are acidity and basicity parameters, respectively. Using the above expression for the cohesive energy densities, the activity coefficient for component 1 infinitely dilute in solvent 2 becomes

$$\ln \gamma_1^{\infty} = \nu_1[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+(\sigma_1-\sigma_2)(\tau_1-\tau_2)+(\alpha_1-\alpha_2)(\beta_1-\beta_2)]/RT \quad (60)$$

To account for differences in molecular size, a Flory-Huggins [51, 52, 54] term d_{12} was added where

$$d_{12} = \ln(\nu_1/\nu_2) + 1 - (\nu_1/\nu_2) \quad (61)$$

The final expression then becomes

$$\ln \gamma_1^{\infty} = \nu_1[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+(\sigma_1-\sigma_2)(\tau_1-\tau_2)+ (\alpha_1-\alpha_2)(\beta_1-\beta_2)]/RT + \ln(\nu_1/\nu_2)+1-(\nu_1/\nu_2) \quad (62)$$

Table VII is a summary of some previous attempts at a model of this type. To simplify Equation 62, it is rewritten in a form analogous to Weimer and Prausnitz [66]

$$\ln \gamma_1^{\infty} = \nu_1[(\lambda_1-\lambda_2)^2+q_1^2q_2^2(\tau_1-\tau_2)^2+(\alpha_1-\alpha_2)(\beta_1-\beta_2)]/RT+ \ln(\nu_1/\nu_2)+1-(\nu_1/\nu_2) \quad (63)$$

Table VII. Previous formulations of activity coefficients using solubility parameter.

Expressions	Investigator
$\ln\gamma_1^{\infty}=\nu_1(\delta_1-\delta_2)^2\Phi_2^2/RT$	Hildebrand & Scott [37].
$\ln\gamma_1^{\infty}=\nu_1[(\delta_{n1}-\delta_{n2})+\delta_{p2}^2]+2\nu_2\xi_{12}/RT$	Prausnitz and Anderson [41].
$\ln\gamma_1^{\infty}=\nu_1[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2-2\psi_{12}]/RT+\ln(\nu_1/\nu_2)$ $+1-\nu_1/\nu_2$; $\psi_{12}=c(\tau_1-\tau_2)^2$	Weimer and Prausnitz [66]
$\ln\gamma_1^{\infty}=\nu_1[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+(\sigma_1-\sigma_2)(\tau_1-\tau_2)]/RT$ $+\ln(\nu_1/\nu_2)+1-\nu_1/\nu_2$	Hsieh [91] & Newman [97].
$\ln\gamma_1^{\infty}=\nu_1[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+(\alpha_1\beta_1-\alpha_2\beta_2)^2]/RT+$ $\ln(\nu_1/\nu_2)+1-\nu_1/\nu_2$	Hansen [69].
$\ln\gamma_1^{\infty}=\nu_1[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+2(\alpha_1-\alpha_2)(\beta_1-\beta_2)]/RT$ $+\ln(\nu_1/\nu_2)+1-\nu_1/\nu_2$	Tijssen et al. [95].
$\ln\gamma_1^{\infty}=\nu_1[(\lambda_1-\lambda_2)^2+(\tau_1-\tau_2)^2+2(\alpha_1-\alpha_2)(\beta_1-\beta_2)$ $+2(\alpha_1-\alpha_2)(\tau_1-\tau_2)]/RT$	Karger et al. [94].

Weimer [66] assumed that q is a function only of the class of compound of the solute, i.e., paraffin, olefin, or aromatic, where q is a measure of the dipole-induced dipole energy. However, the greater the differences in polarity or degree of hydrogen bonding, the more the symmetry in volume fraction assumption appears to fail. Thomas and Eckert [98] modified Equation 63 to include a term ψ and a term ξ to account for this asymmetry effect. Their model is called a modified separation of cohesive energy density model (MOSCED). The equation is

$$\ln \gamma_1^{\infty}=\nu_1[(\lambda_1-\lambda_2)^2+q_1^2q_2^2(\tau_1-\tau_2)^2/\psi_2+(\alpha_1-\alpha_2)(\beta_1-\beta_2)/\xi_2]/RT+ \ln(\nu_1/\nu_2)+1-(\nu_1/\nu_2) \quad (64)$$

Thomas and Eckert has reported that MOSCED model yielded better results than UNIFAC which applies the group contribution method. However, some limitations restrict the applicability of this model. The prediction were poorest for systems where steric considerations predominate. Another limitation is the model's inapplicability to aqueous system. They also described the parameter estimation and temperature dependence. These are summarized in Appendix A.

The parameter q reflects the ability of the nonpolar part of a molecule to interact with a polar part. Equation 64 can be modified to be

$$\ln \gamma_1^{\infty}=\nu_1\{(\lambda_1-\lambda_2)^2+q_1^2q_2^2[(\tau_1-\tau_2)^2/\psi_2+(\alpha_1-\alpha_2)(\beta_1-\beta_2)/\xi_2]\}/RT +\ln(\nu_1/\nu_2)+1-(\nu_1/\nu_2) \quad (65)$$

When studying solution behavior in the past, scientists and engineers frequently embraced solubility parameter approaches because of their simplicity and intuitive appeal, but they often shunned them because of their qualitative predictive ability. This work attempted to apply solubility parameters to study the molecular interactions between organic molecules in extractive distillation.

Proposed Effect of The Agents

The net energy of interaction or internal energy, U, of nonbonded atoms or molecules is the result of both attractive and repulsive effects. There is one major repulsive interaction, the tendency of two molecules to avoid occupying the same space, this energy term rising very steeply to high positive values when the intermolecular separation falls below a certain distance but otherwise having little effect on the internal energy. There are several possible attractive interactions, collectively called van der Waal's forces, and all of these have weaker dependence on intermolecular separation than the repulsive interactions, and therefore dominate at larger distances. Consequently,

1. The equilibrium intermolecular separation is largely determined by the repulsive interactions.
2. The net energy of interaction at equilibrium is mainly a function of the attractive interaction.

It is assumed that the repulsive interactions are negligible. Therefore, the attractive interactions will dominate the effect of an agent in extractive distillation. As shown in Figure 7, there are three

kinds of physical interactions occurring between two polar molecules. Thus in a mixture two key components and an agent, there are three pairs of molecular interactions, i.e., (i) key component 1 - key component 2, (ii) key component 1 - agent, (iii) key component 2 - agent. If the first pair of molecular interactions is negligible, only two pairs of attractive interactions need to be considered. In this case, the selectivity of the agent is dependent upon which pair has greater attractive interaction. If the second pair, key component 1 - agent, has greater interaction, the key component 1 will be brought by the agent to the bottom of the column and the key component 2 will be the overhead product, and vice versa.

The comparison of the attractive interactions is the major problem on selecting agents. The solubility parameter is proposed to be the measure of the attractive interactions. It is assumed that the three solubility parameters can describe the attractive interactions in terms of dispersion force, δ_d, polar interaction, δ_p, and hydrogen bonding, δ_h. In this study, the three solubility parameters were used to compare the attractive interactions between the agent and key components. Therefore, the solubility parameter can be used for initial evaluation of agents.

III. APPARATUS AND CHEMICALS

Vapor-Liquid Equilibrium Still

An Othmer type equilibrium still was used to conduct the experiments for vapor-liquid equilibrium. Figure 9 shows the setup of the equipment. The still is constructed of Pyrex glass and wrapped with insulation to prevent heat loss from the still. Heat is supplied by a heating coil around the still. There are two condensers. The main condenser is to condense the vapor coming from the still. The secondary condenser around the vent tube is to condense any vapor going out the vent and preventing a loss of vapor. Thus the quantity of the compounds being tested remains constant. The vent keeps the still at atmospheric pressure and is a safety measure. The condensate will accumulate in the sampling tube and then flow back to the still. The liquid level in the still must be lower than point B and higher than point A to assure good operation. Due to the negligible heat loss from the still, vapor does not condense on the inside wall of the still. In several hours running, the vapor and liquid phase will reach equilibrium. Thus this setup comprises one theoretical stage. The samples can be taken from the sampling tube of the condenser and still. A gas chromatograph was used to analyze the samples. They represent the vapor and liquid composition at equilibrium. A mercury thermometer was used to measure the vapor temperature. A K-type thermocouple was used to detect the temperature

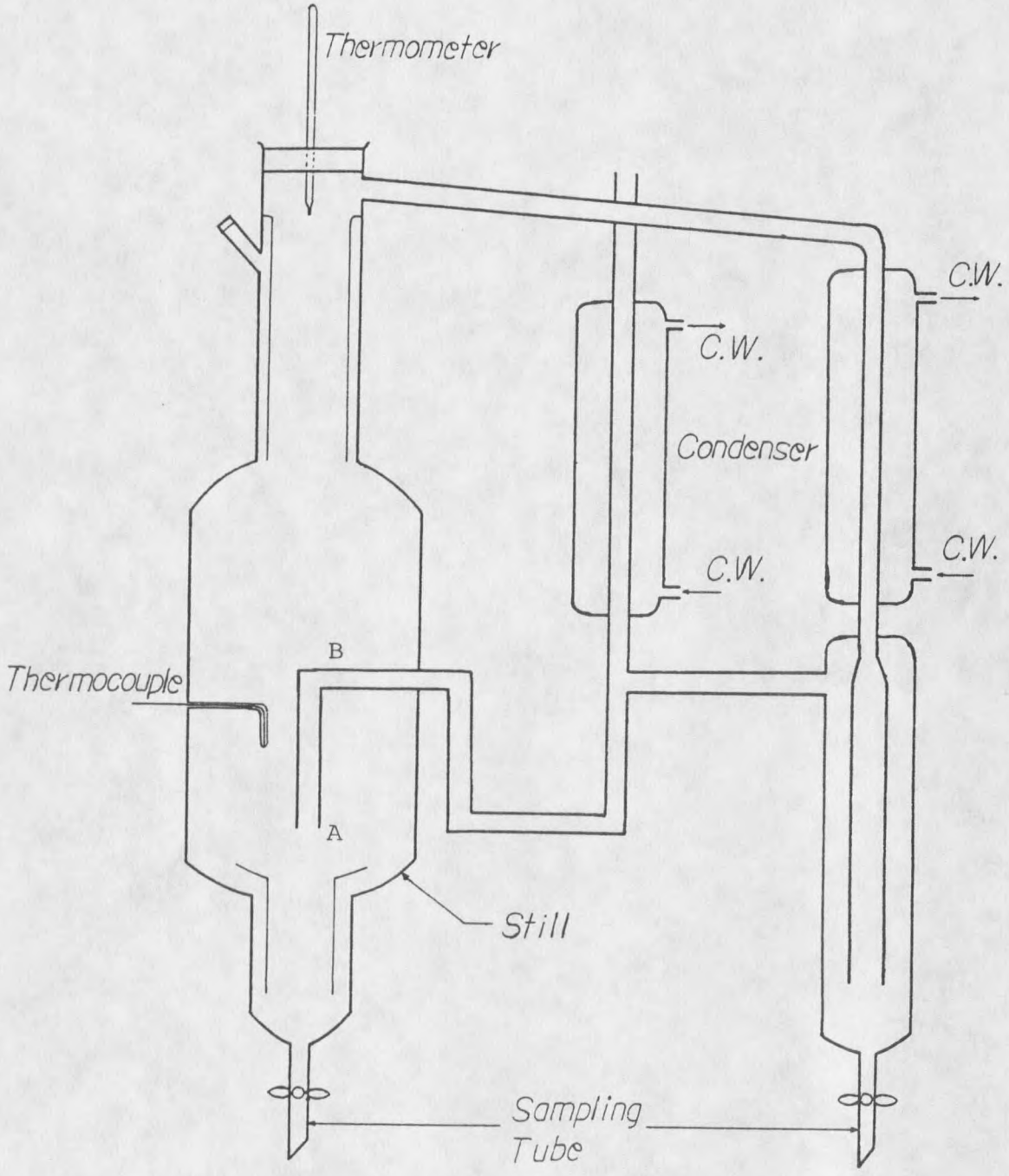


Figure 9. Othmer-type vapor-liquid equilibrium still.

of the liquid phase. A temperature indicator, OMEGA 2176A, was connected to the thermocouple to read the temperature.

Plate Column

In order to carry out the necessary operations for batch extractive distillation, a setup was designed incorporating a condenser, a vapor-liquid extractive distillation contacting section, a heat source for introducing vapor to the bottom of the contacting section, and a means of feeding the agent to the top of the extractive distillation section. The general assembly of the equipment is shown in Figure 10. It consisted of eight parts as described below.

(1) A Corad condensing head, A, condensed the vapor to the liquid phase. The vapor that condensed on the inside surface of the inner tube and was divided by means of vertical strips into six different sized parallel parts. The condensate from any one part could be taken off as product while the remainder was returned as reflux to the column. A sidearm sampling port was suspended from the Corad condensing head. The Corad head was considered a total condenser.

(2) A contacting section which was 20 inch long and 1.5 inch in diameter, B, contained five Oldershaw perforated plates. It was made of Pyrex glass. The arrangement of the glass perforated plate is shown in Figure 11. The tray spacing was 1.8 inch and the weir was 3/8 inch high. Figure 12 illustrates the direction of liquid flow on the plate. The column was equipped with a silvered vacuum jacket with a thickness of 3/4 in. The silvered vacuum jacket effectively reduced heat loss

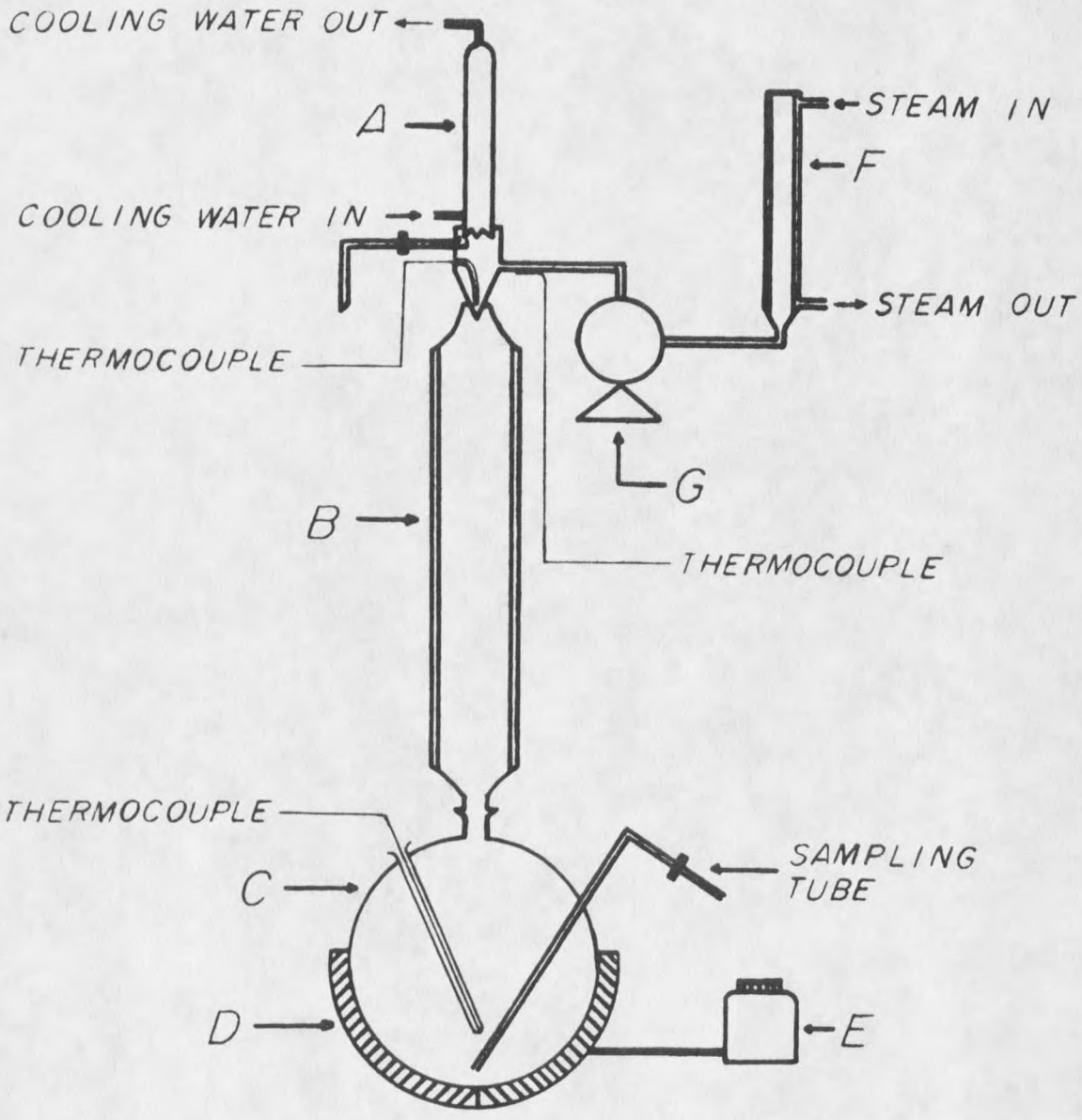


Figure 10. Diagram of the batch-wise extractive distillation column.

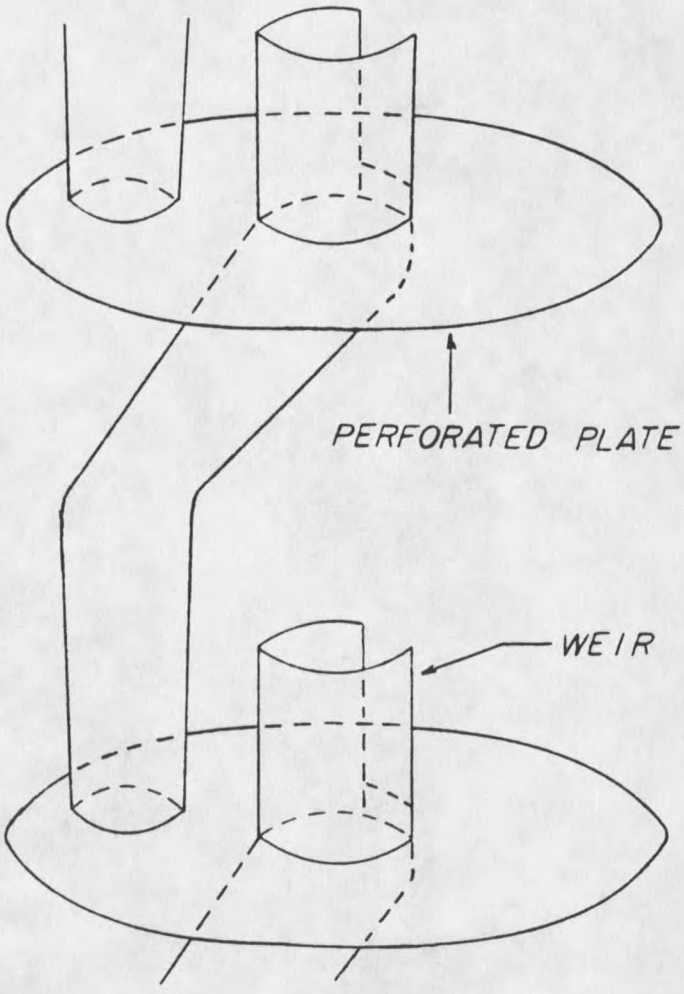


Figure 11. Perforated plate arrangement.

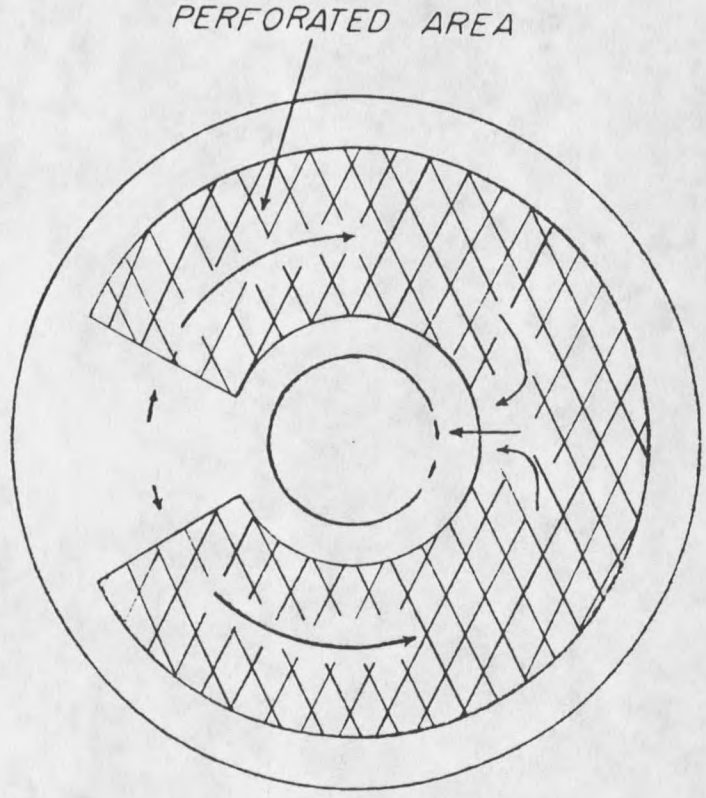


Figure 12. Perforated-plate scheme. Arrows show the direction of liquid flow.

from the column to a negligibly small amount.

(3) A 5-liter round-bottom Pyrex glass flask served as a reboiler or stillpot, C. It was fitted with a thermocouple well and sampling tube.

(4) Column heat was supplied electrically by means of a Glas-Col mantle, D, which was further lagged to reduce the heat loss from the stillpot. The maximum allowable temperature was 450°C.

(5) A Variac, E, adjusted the heat input into the stillpot and controlled the boil-up rate. The input side was for 115 volts, 50/60 Hz, single phase; and the output was 0 to 140 volts, and a maximum rating of 1.4 KVA.

(6) Agent was stored in a cylindrical, F, steam-jacketed separatory funnel. It was made of Pyrex glass and had a capacity of 200 ml. The steam jacket was used to control the temperature of the agent entering the column.

(7) A fluid metering pump, G, adjusted the addition rate of agents. The pump was a micro-bellows metering pump made by Research Appliance Company. It was a standard model, 0.5 inch I.D., 316-stainless bellows.

(8) Five K-type thermocouples were used to measure the temperature at the overhead, stillpot, vapor and liquid of the top plate, and the agent entering the column. The thermocouples for vapor and liquid phases of the top plate are not shown in the drawing.

Auxiliaries not shown on the drawing included a nichrome heating wire wrapped on the pump line, a Glas-Col mantle connected to the heating wire, a digital temperature indicator, OMEGA 2176A, connected to the K-type thermocouples, and two ball-and-socket joints. The first two were used to control the temperature of the agent entering the column.

The temperature indicator was used to read the temperature at the overhead, stillpot, top plate, and pump line. A 65/40 female ball-and-socket joint and 65/40 male ball-and-socket joint connected the column with the Corad condensing head and stillpot, respectively.

Packed Column

Berg et al. [20] have reported that packed columns can also be used for extractive distillation. The assembly of the equipment was similar to that of the plate column except the type of the column. Berl saddle packing used is shown in Figure 13. The packings were made of ceramics and packed randomly in the column. The packed column had a diameter of 1.25 inches and contains 90 gm. of the packing. The size of the Berl saddle was 3/4 inch from one end to the other end and with the width of 3/8 inch. The depth of the packing was 5 inches. The column was wrapped with insulation to reduce the heat loss from the column.

Calibration of the Extractive Distillation Columns

The glass perforated plate rectification column with the stillpot was calibrated with a ethylbenzene and p-xylene which possesses an average relative volatility of 1.06. The setup was found to have 4.5 theoretical plates [99]. This number was tested against the vapor-liquid equilibria data reported by Harper et al. [100] using the methanol-acetone mixture. The experimental data was obtained from ordinary distillation. The relative volatilities calculated from the

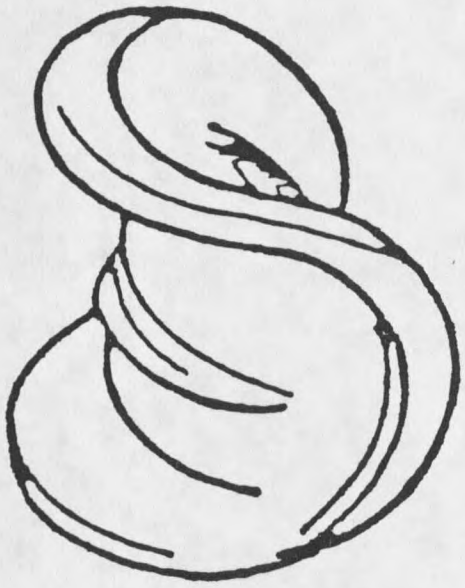


Figure 13. Berl saddle packing.

Table VIII. The calculated relative volatilities of methanol to acetone.

wt.% of methanol	Corresponding VLE data from Harper et al.[79]	Relative volatility
10.5 in vapor	9.6 in liquid	1.105
7.1 in liquid	7.8 in vapor	1.107

literature data are shown in Table VIII. The average relative volatility of 1.106 can be calculated by Equation 8. If the overhead product contains 10.5 wt.% methanol and the bottoms contains 7.1 wt.% methanol, a relative volatility of 1.10 can be obtained by using the Fenske equation with 4.5 theoretical plates. This is the experimental result. This comparison fits well that the column has 4.5 theoretical plates.

However, it is necessary to check the theoretical plates of the setup under the operation of extractive distillation. The equilibrium data in the presence of agents was gathered from the Othmer-type vapor-liquid equilibrium still at atmospheric pressure. Isopropyl ether-acetone and methyl acetate-methanol systems were used with dimethyl sulfoxide (DMSO) as the agent. The acetone-methanol system was investigated with methyl ethyl ketone (MEK) as the agent. The methanol-acetone system with MEK as the agent was conducted in the extractive distillation column. The overhead and bottoms compositions were obtained. Yeh [29] has reported the data for the other two systems. Figures 14, 15 [101] and 16 show the equilibrium curves with the compositions based on agent free and the pseudo McCabe-Thiele method,

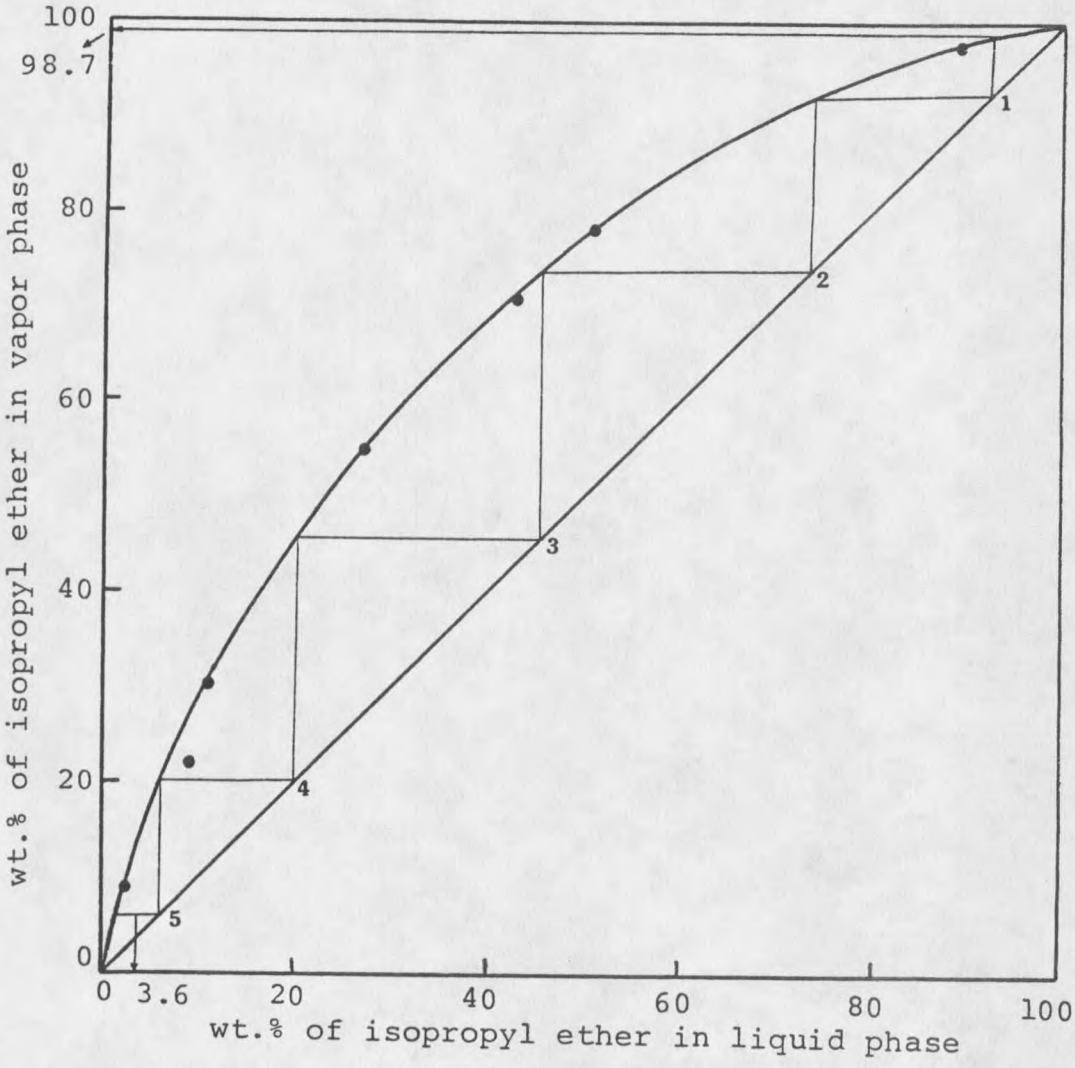


Figure 14. Pseudo McCabe-Thiele method for isopropyl ether-acetone system with DMSO as the agent.

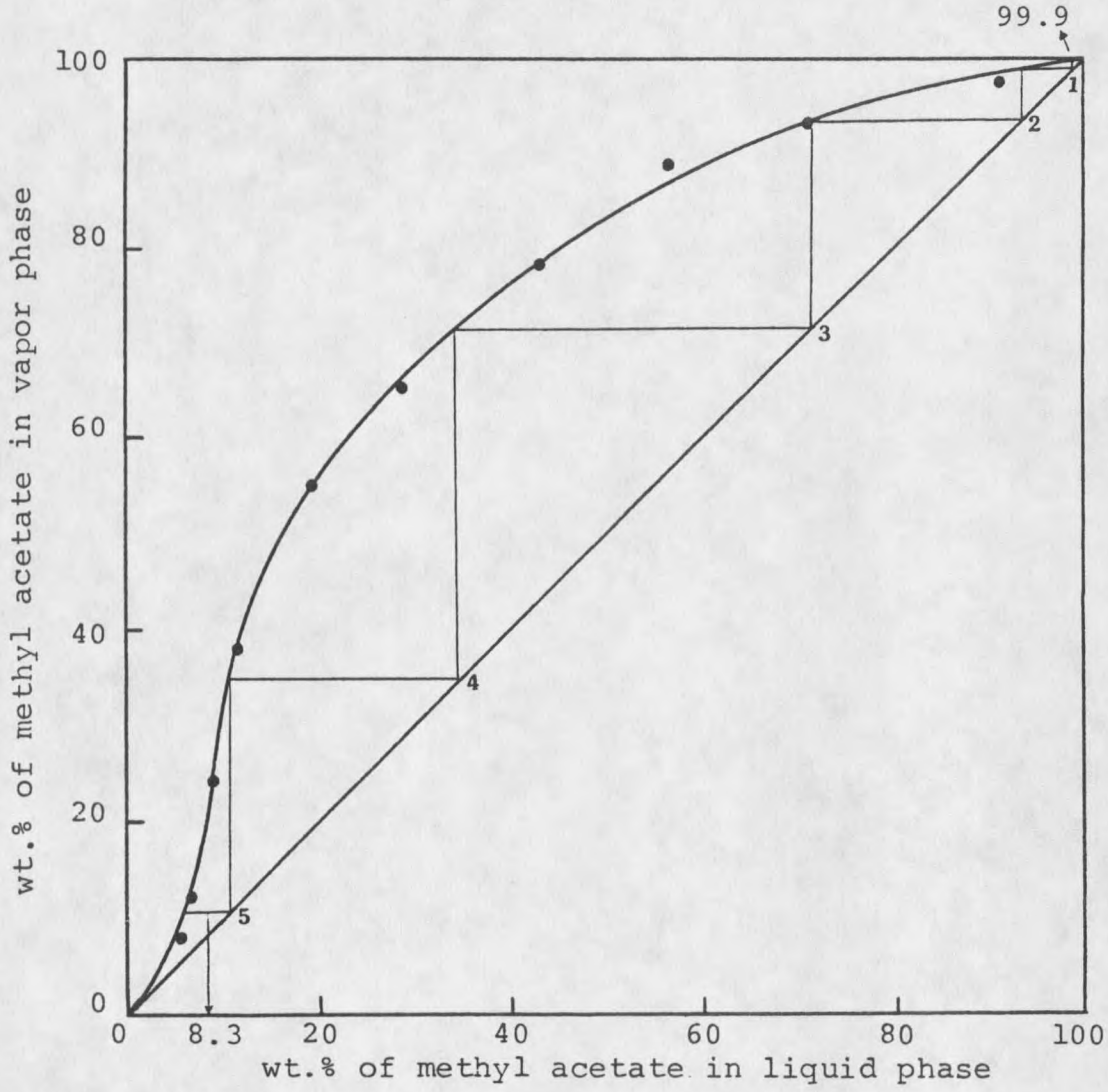


Figure 15. Pseudo McCabe-Thiele method for methyl acetate-methanol system with DMSO as the agent.

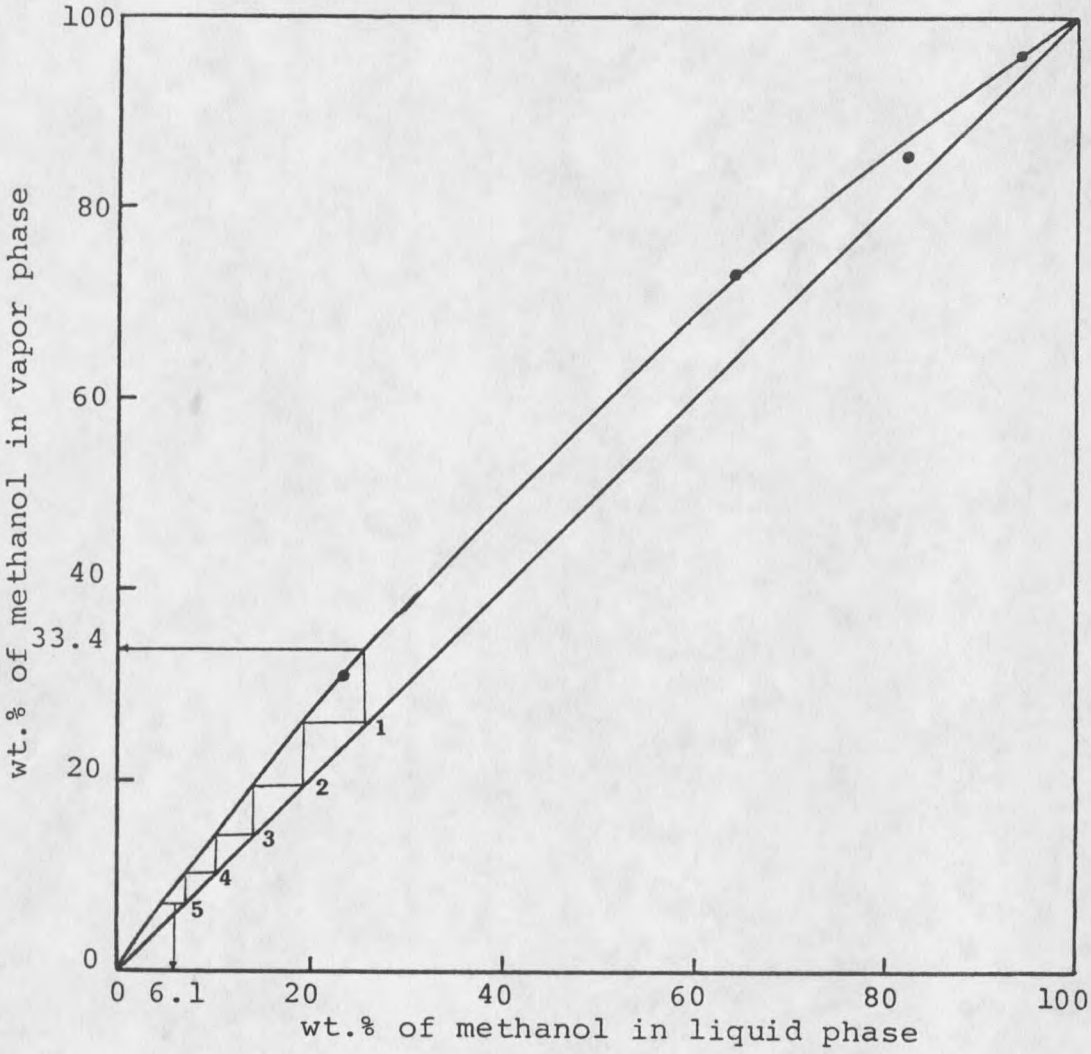


Figure 16. Pseudo McCabe-Thiele method for acetone-methanol system with MEK as the agent.

using the step-by-step procedure. During the operations, the temperature of the outlet cooling water was in the range of 5 to 10°C. It is reasonable to say that the Corad head is a total condenser. Thus the condensates have the same compositions as the vapor coming out from the top plate. Thus the overhead composition is considered a vapor composition on the top plate. Due to the total reflux operation, the 45° diagonal was the operating line. The step-by-step procedure started at the overhead composition and tried to reach the experimental bottoms composition. The corresponding compositions were called "predicted bottoms compositions". Table IX lists the experimental and predicted bottoms compositions.

Table IX. The comparison of bottoms composition from experiments experiments with pseudo McCabe-Thiele method.

Run	Overhead composition, wt.%	Bottoms composition, wt% Experimental	Predicted
1.	98.7 Isopropyl ether	3.0 IPE	3.6 IPE
2.	33.4 Methanol	6.4 MeOH	6.1 MeOH
3.	99.9 MeAc	9.2 MeAc	8.3 MeAc

From the figures, it appeared that the setup has 5.5 theoretical plates. The addition of the agent into the column would increase the efficiency of the plates. If the setup has 5.5 theoretical plates, the column has an average plate efficiency of 90%. It is far from the average plate efficiency of 40 - 60% which has been reported. It is more reasonable to say that the setup has 4.5 theoretical plates, i.e.,

the average plate efficiency is 70%. To compare the effect of agents on the same basis, 4.5 theoretical plates and Fenske were used to calculate the relative volatilities of key components. The packed column was calibrated with a ethylbenzene and p-xylene mixture which possesses an average relative volatility of 1.06. The packed column was found to have 1.5 theoretical plates. This number was used without further checking. The data obtained from the VLE still is just one point in a phase diagram and the data obtained from the extractive distillation columns is an average value. Therefore, the data obtained from the columns are considered more reliable than that obtained from the VLE still.

Analytical Equipment

A gas chromatograph was used to analyze the samples. The actual apparatus included an Aerograph 1800 ionization gas chromatograph hooked to a Sargent recorder, Model SR. The column in the chromatograph was 15 feet long and 1/8 inch in outside diameter. The column packing was made up as follows: 0.5 g. each of Bentone 34 (an organo clay complex, National Lead Bariod Division) and diisodecyl phthalate were deposited on 9.0 g. of chromosorb P using the conventional vaporization and slurry techniques. The detector was of the four-filament type, tungsten-rhenium WX, hot wire which had a temperature limit of 400°C. The operating conditions used were: column temperature, 75°C; injection port temperature, 200°; detector temperature, 140°C; helium flow rate, 20-30

ml. per minute; hydrogen flow rate, 20-30 ml. per minute; air flow rate, 250-400 ml. per minute.

Gas Chromatograph Calibration

A series of known composition mixtures were made up and analyzed on the gas chromatograph. The peak height percents of the chromatograph tracing of the components in the mixtures were correlated to the actual weight percents of the components in the mixtures. The calibrations are shown in Figures 17 through 23. The calibration curve for methyl acetate-methanol mixture has been reported by Yeh [29]. The shape of the calibration curve varies from system to system. Thus it is necessary to calibrate the gas chromatograph for a particular system. From these calibration curves, the weight percents of the components in the samples were obtained. In this study, all the analyses were on an agent-free basis.

Equipment for Agent Recovery

The agents were reclaimed by simple distillation. Figure 24 illustrates the assembly of the apparatus. A 2-liter distilling flask served as a stillpot. A mercury thermometer was used to indicate the temperature of vapor in the distilling flask. After every run made in extractive distillation column, the agent was recovered by distilling off everything below the boiling point of the mixture being studied. The operation was typically carried out in one hour for each batch. The

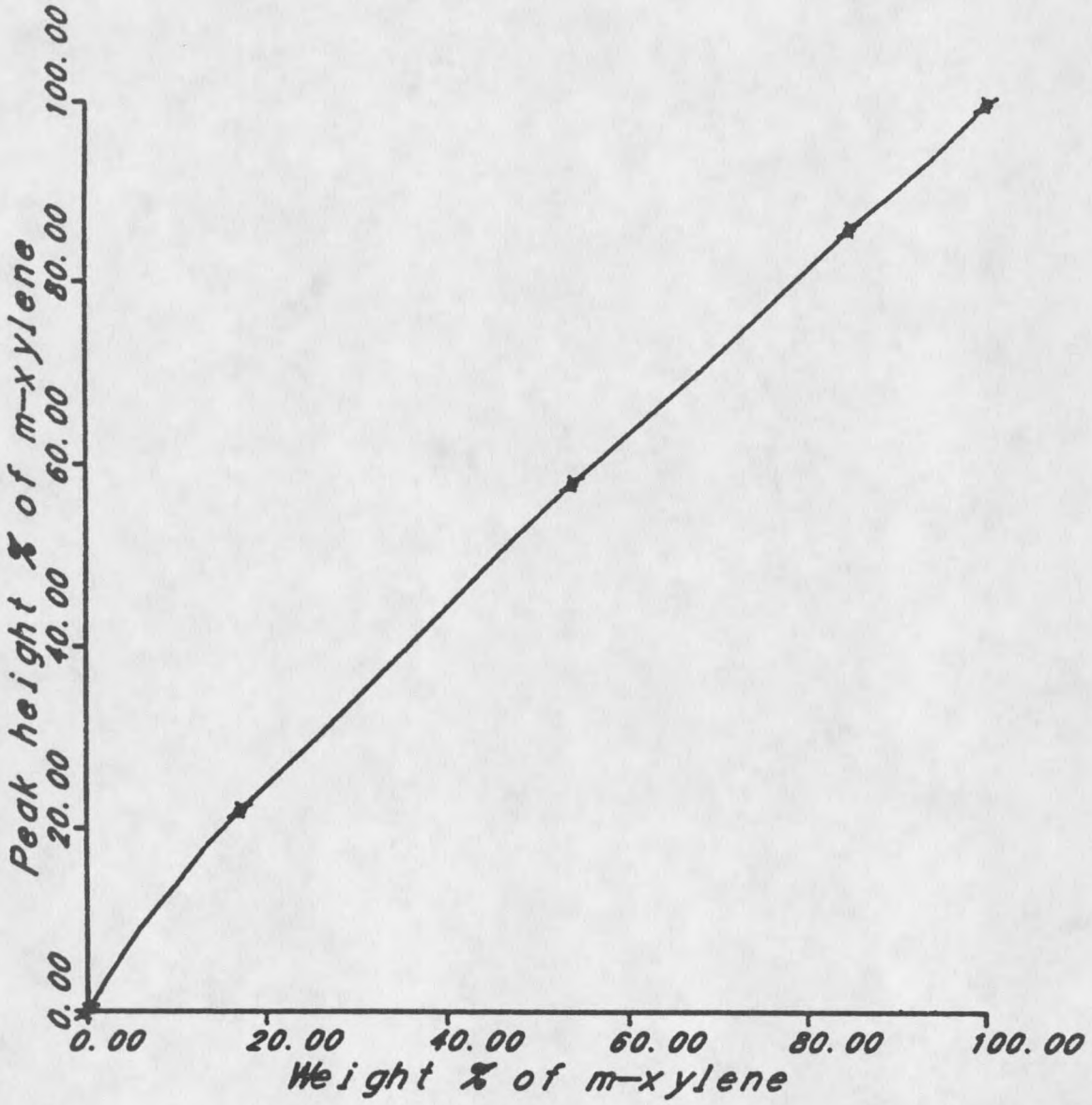


Figure 17. Calibration curve for the m-xylene-o-xylene mixture.

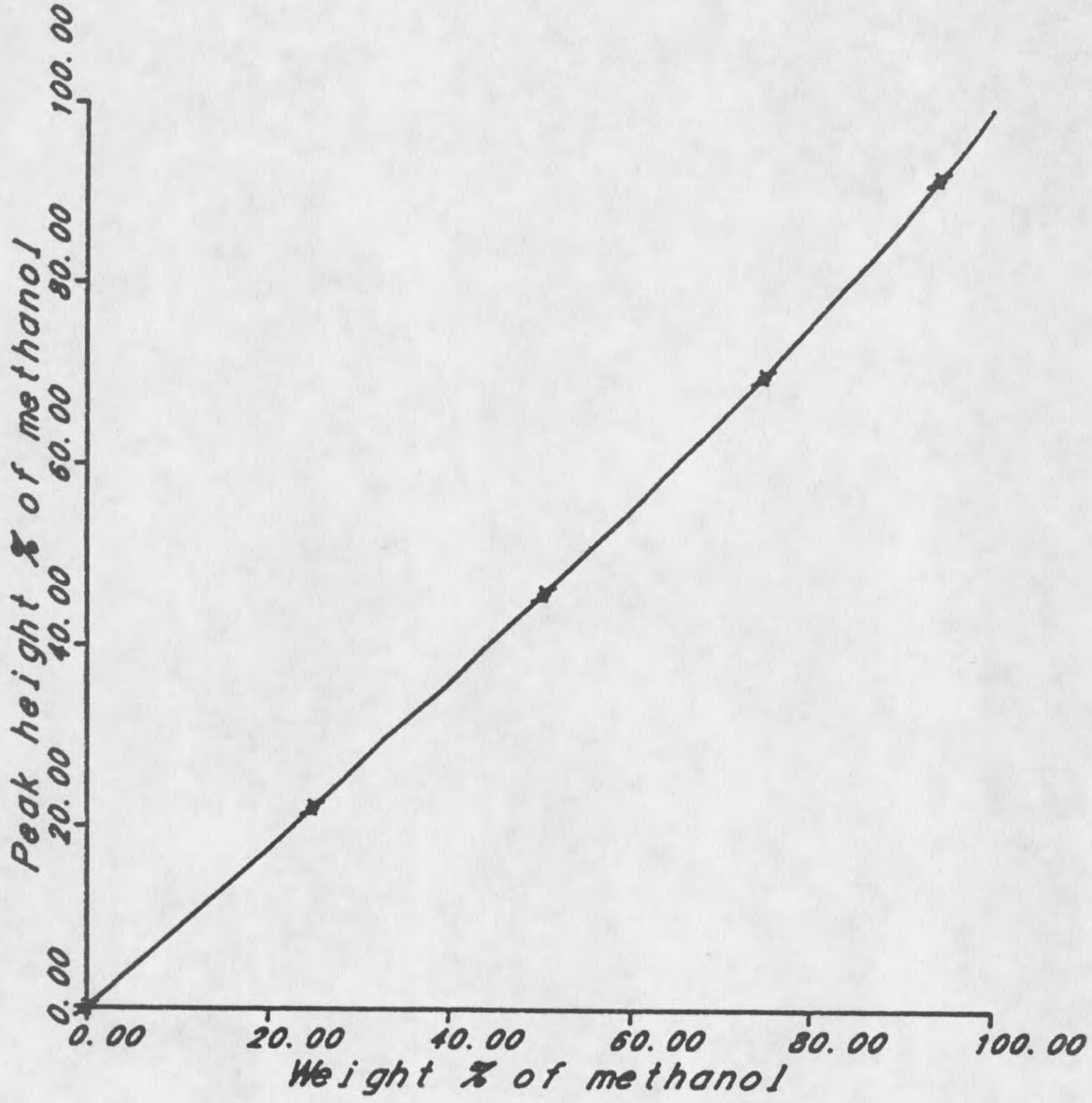


Figure 18. Calibration curve for the methanol-acetone mixture.

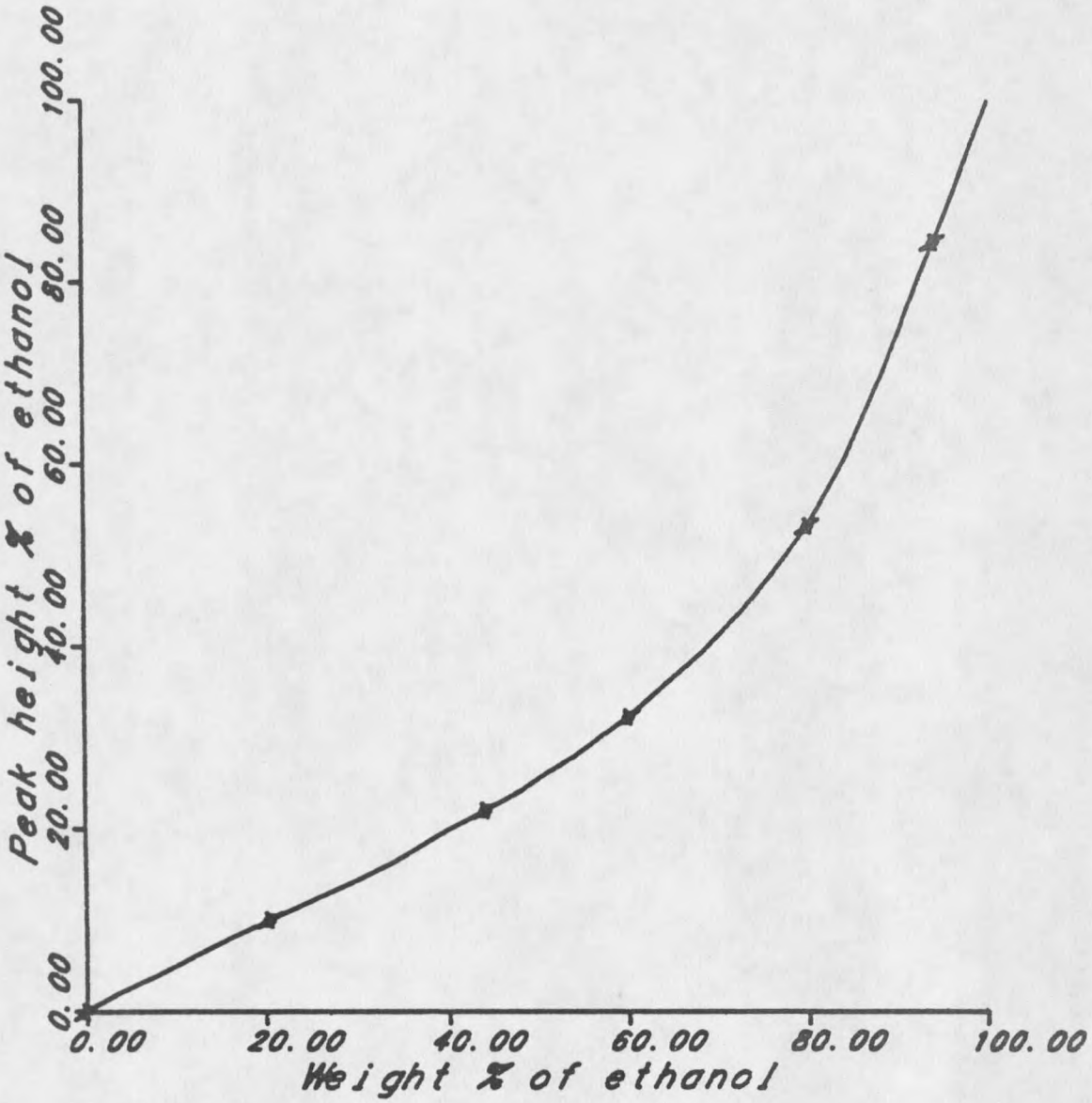


Figure 19. Calibration curve for the ethanol-water mixture.

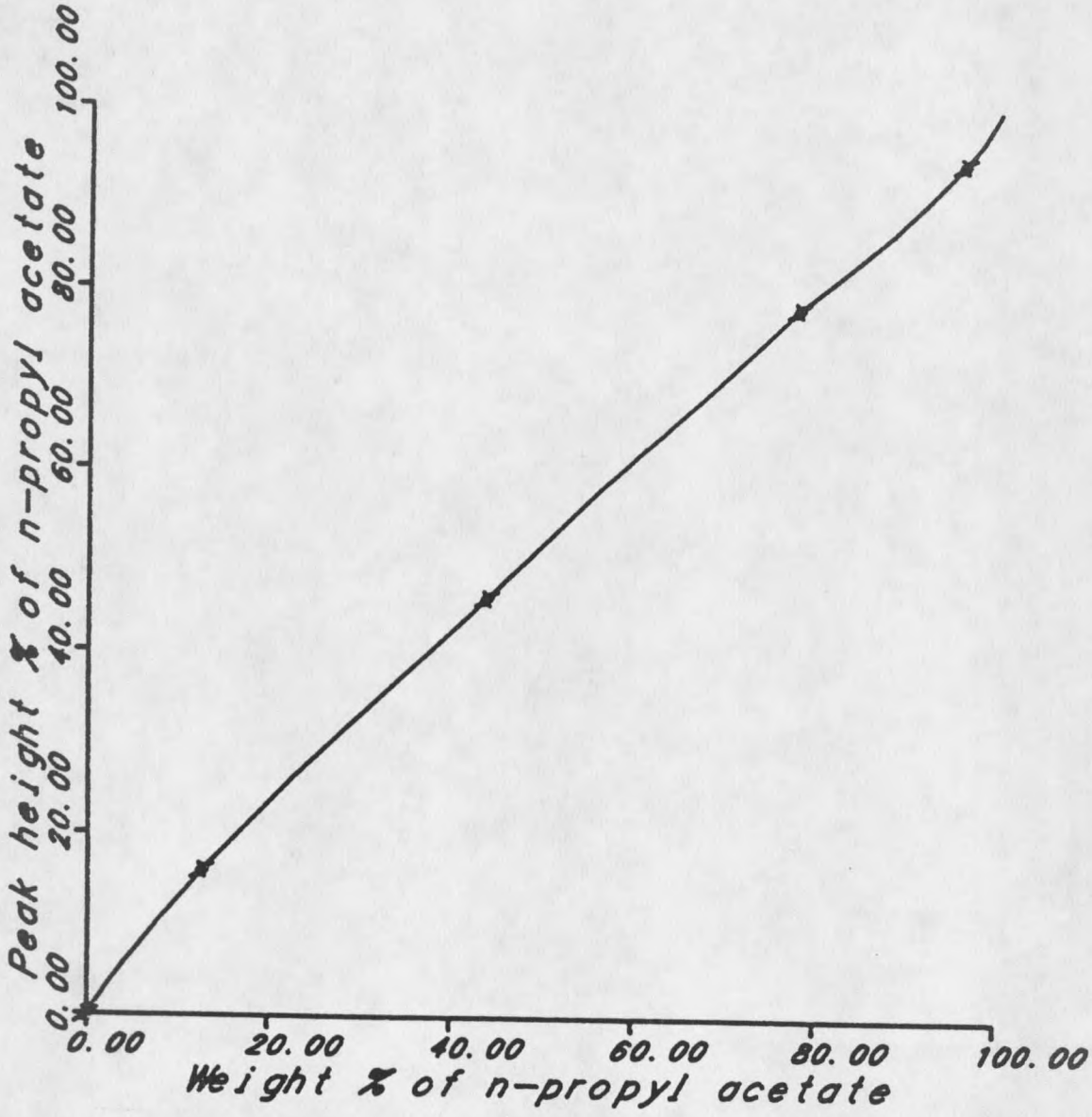


Figure 20. Calibration curve for the n-propyl acetate-n-propanol mixture.

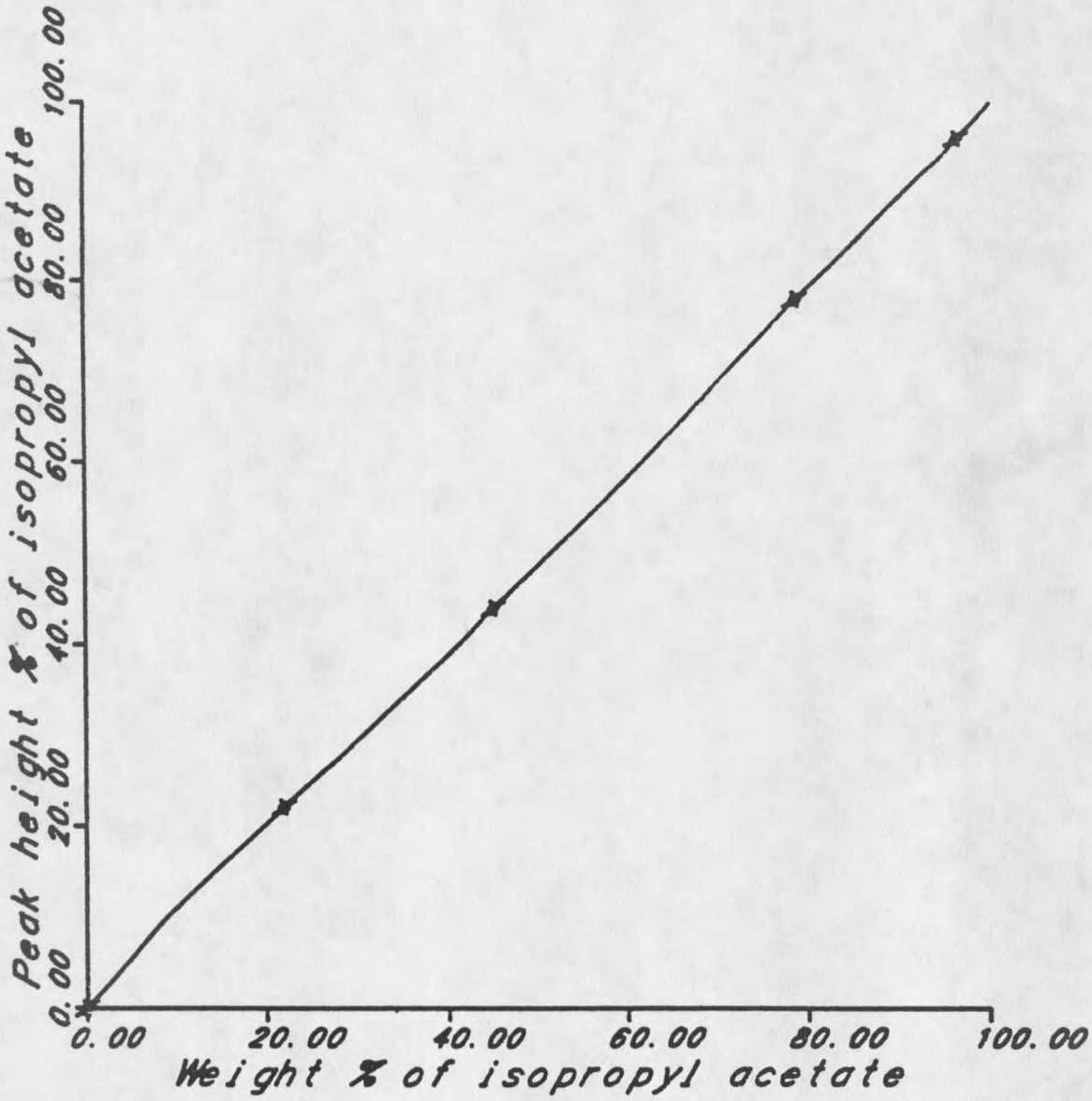


Figure 21. Calibration curve for the isopropyl acetate-isopropanol mixture.

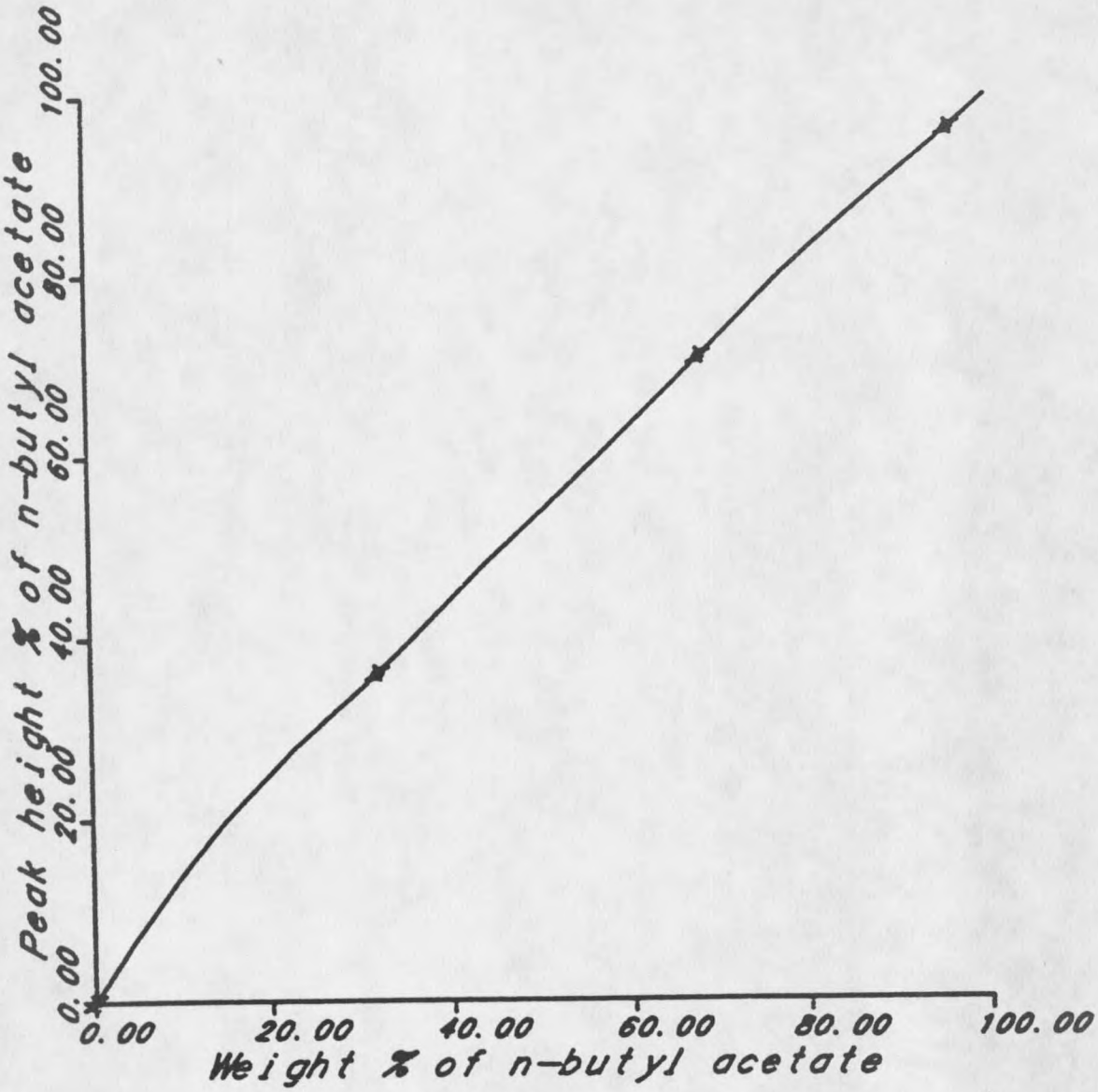


Figure 22. Calibration curve for the n-butyl acetate-n-butanol mixture.

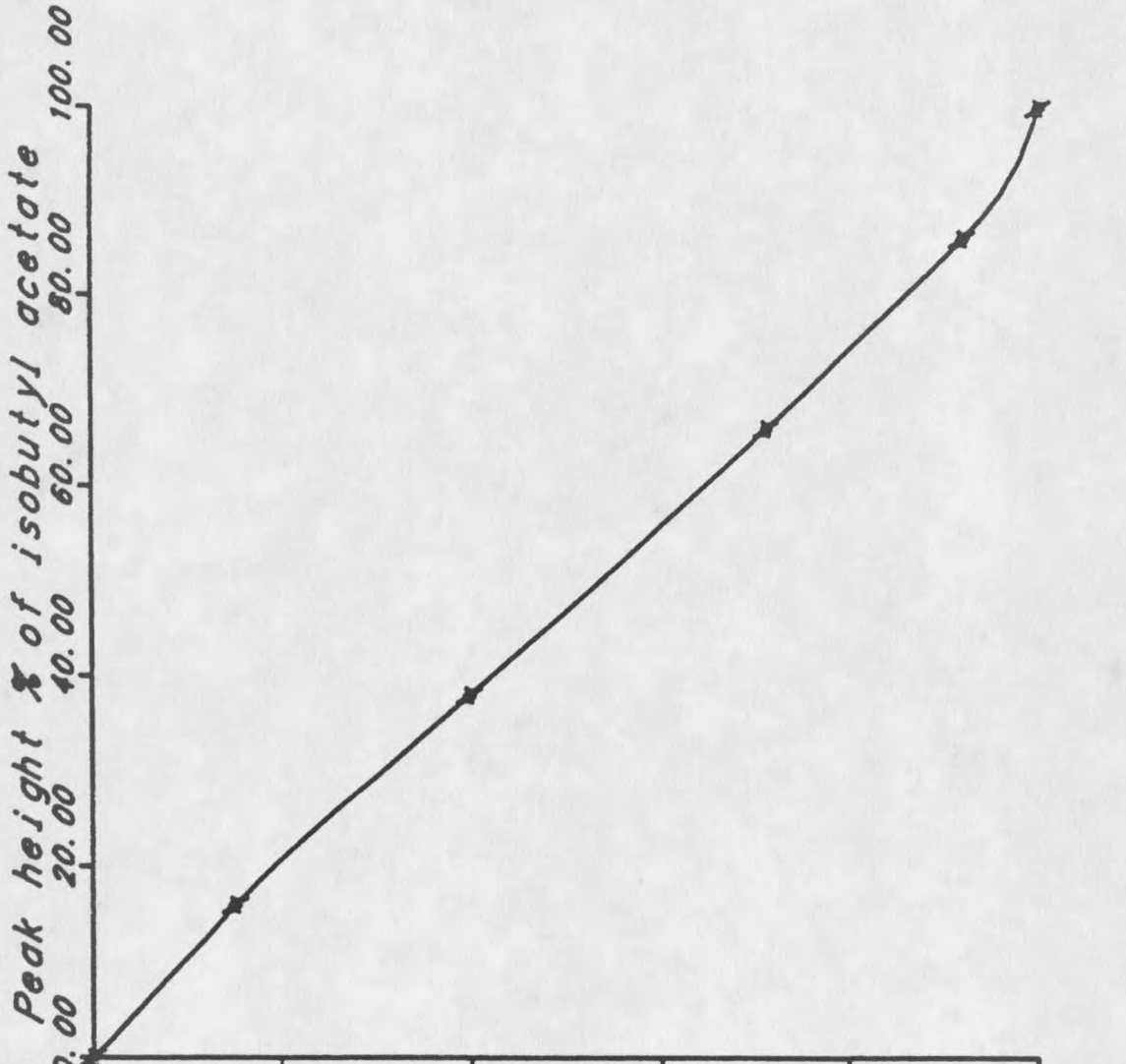


Figure 23. Calibration curve for the isobutyl acetate-isobutanol mixture.

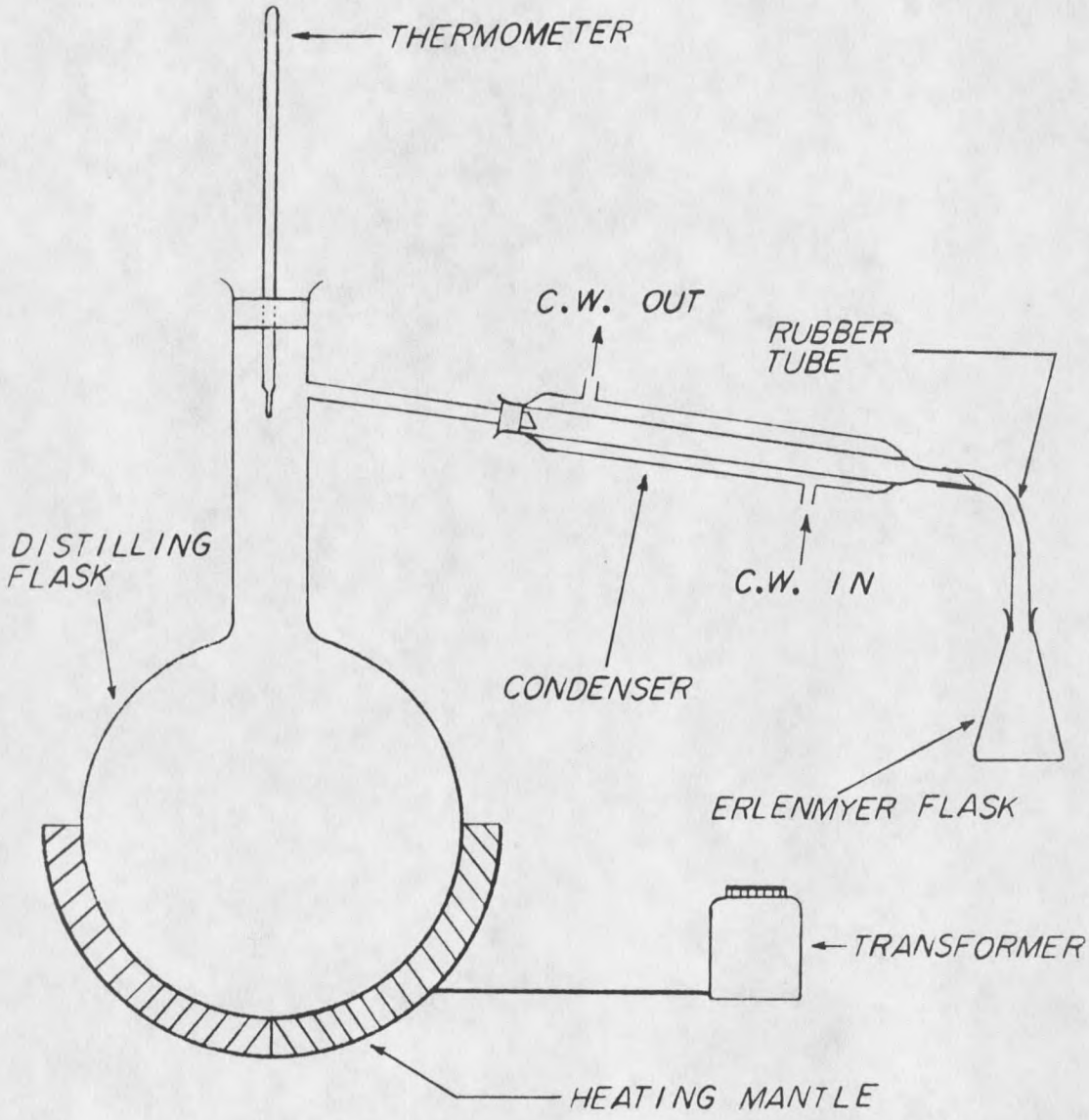


Figure 24. Diagram of the simple distillation.

purpose of reclaiming the agents is to check the stability of the agents. To reuse the agent, the stability is a requirement for industrial application.

Chemicals As The Agents

The chemicals used as the agents can be categorized into five groups: glycols, nitrocompounds, ketones, benzoates, and miscellaneous. Tables X through XIV [32, 102, 103] list the molecular formulas, boiling points, melting points and vapor pressure of the agents. The glycols were donated by Dow Chemical Co. Nitrocompounds were supplied by W. R. Grace & Co. Methyl ethyl ketone was obtained from Columbia Paint Company Manufacturers. Other ketones were obtained from Aldrich Chemical Co., Inc. Benzoates except dipropylene glycol dibenzoate (DGDB) were produced by Hercofina Co. DGDB was manufactured by Kalama Chemical Inc. Dimethyl sulfoxide (DMSO) was from Crown Zellerbach. Adiponitrile and dimethyl formamide (DMFA) were from E. I. du Pont Co. 1-Pentanol was supplied by Aldrich Chemical Co., Inc. The acetates and alcohols were supplied by Union Carbide Company.

Experimental Procedures

Vapor-Liquid Equilibrium

The Othmer-type equilibrium still was used to conduct the experiments. For the systems without any agents added, 100 grams binary mixture of a specific composition was charged into the still and then

Table X. Molecular structures and physical properties of glycols.

Compound	Molecular structure	B.P. °C	M.P. °C	Vapor pressure (mm Hg)
Ethylene glycol	$CH_2(OH)-CH_2(OH)$	197.6	-13	3 @ 70°C
Propylene glycol	$CH_3CH(OH)-CH_2(OH)$	188	-60	1 @ 45°C
1,3-Butanediol	$CH_2(OH)CH_2CH(OH)CH_3$	207.5	below 50	0.06 @ 20°C
1,4-Butanediol	$CH_2(OH)CH_2CH_2CH_2(OH)$	230	19	10 @ 120°C
1,5-Pentanediol	$CH_2(OH)CH_2CH_2CH_2CH_2(OH)$	239	-18	3 @ 12°C
Diethylene glycol	$O(CH_2CH_2OH)_2$	244.8	-6.5	< 0.01 @ 20°C
Triethylene glycol	$CH_2(OCH_2CH_2OH)_2$	290	-5	14 @ 165°C
Dipropylene glycol	$O(CH_2CHOHCH_3)_2$	231.8	-	0.03 @ 20°C
1,6-Hexanediol	$CH_2(CH_2CH_2CH_2OH)_2$	208	42.8	10 @ 134°C

Table XI. Molecular structures and physical properties of nitrocompounds.

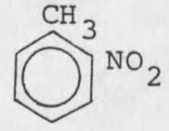
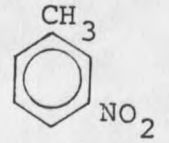
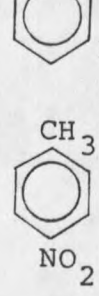
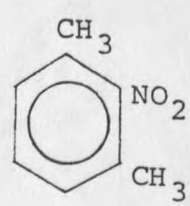
Compound	Molecular structure	B.P. °C	M.P. °C	Vapor pressure mm Hg
Nitromethane	CH_3NO_2	101.2	-29	40 @ 27°C 100 @ 47°C
Nitroethane	$CH_3CH_2NO_2$	114	-50	16 @ 20°C
1-Nitropropane	$CH_3CH_2CH_2NO_2$	131.6	-108	7.5 @ 20°C 94 @ 70°C
2-Nitropropane	$CH_3CH(NO_2)CH_3$	120.3	-93	7 @ 10°C 95 @ 60°C
Nitrobenzene		210.9	5.7	2.2 @ 50°C
o-Nitrotoluene		222	-10	10 @ 94°C
m-Nitrotoluene		231.9	15.5	1 @ 50°C 5 @ 81°C
p-Nitrotoluene		238	53	10 @ 100°C
2-Nitro-m-xylene		246	2	-

Table XII. Molecular structures and physical properties of ketones.

Compound	Molecular structure	B.P. °C	M.P. °C	Vapor pressure mm Hg
Methyl ethyl ketone	$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$	79.6	-86	100 @ 25°C
1-Choloro-2-Propanone	$ClCH_2\overset{\overset{O}{\|}}{C}CH_3$	119.7	-44.5	12 @ 20°C
2-Pentanone	$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$	102	-78	10 @ 18°C
3-Pentanone	$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$	101.5	-42	100 @ 56°C
Methyl isobutyl ketone	$CH_3\overset{\overset{O}{\|}}{C}CH_2CH\begin{matrix}CH_3\\ \diagdown\\ \diagup\\ CH_3\end{matrix}$	117	-84.7	15.7 @ 20°C
5-Hexen-2-one	$CH_2CHCH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$	127	-	-
2-Heptanone	$\begin{matrix}CH_2CH_2CH_2CH_3\\ \vert\\ CH_2\overset{\overset{O}{\|}}{C}CH_3\end{matrix}$	151.5	-35	21 @ 111°C
3-Heptanone	$\begin{matrix}CH_2CH_2CH_2CH_3\\ \vert\\ \overset{\overset{O}{\|}}{C}CH_2CH_3\end{matrix}$	148	-39	10 @ 55°C
Methyl isoamyl ketone	$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH\begin{matrix}CH_3\\ \diagdown\\ \diagup\\ CH_3\end{matrix}$	144	-73.9	-
2-Octanone	$\begin{matrix}CH_2CH_2CH_2CH_3\\ \vert\\ CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3\end{matrix}$	172	-16	10 @ 60.9°C
Diisobutyl ketone	$\begin{matrix}CH_2CH\begin{matrix}CH_3\\ \diagdown\\ \diagup\\ CH_3\end{matrix}\\ \diagup\\ O{=}C\\ \diagdown\\ CH_2CH\begin{matrix}CH_3\\ \diagdown\\ \diagup\\ CH_3\end{matrix}\end{matrix}$	168.1	-41.5	1.7 @ 20°C

Table XII. Molecular structures and physical properties of ketones. (continued)

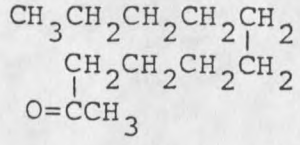
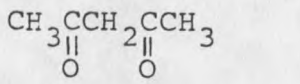
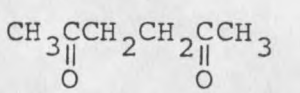
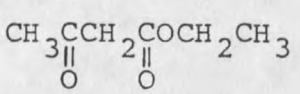
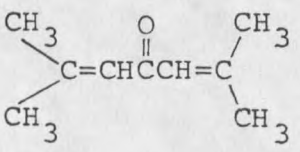
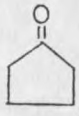
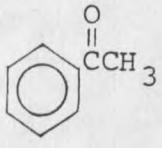
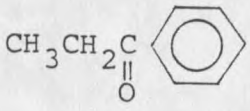
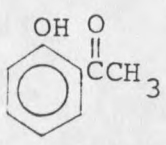
Compound	Molecular structure	B.P. °C	M.P. °C	Vapor pressure mm Hg
2-Undecanone		231	15	10 @ 109°C
2,4-Pentanedione		140.5	-23	-
2,5-Hexanedione		188	-9	0.43 @ 20°C
Ethyl acetoacetate		180.8	-45	5 @ 54°C
Phorone		198	28	17 @ 88°C
Cyclopentanone		130.6	-58.2	10 @ 23°C
Cyclohexanone		155.6	-32.1	60 @ 78°C
Acetophenone		202	20.5	10 @ 78°C
Phenyl ethyl ketone		218	21	10 @ 92°C
o-Hydroxy acetophenone		213	-	-

Table XIII. Molecular structures and physical properties of benzoates.

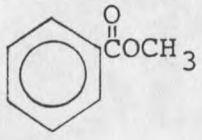
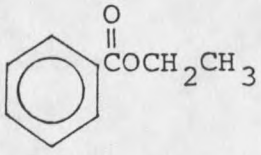
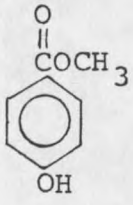
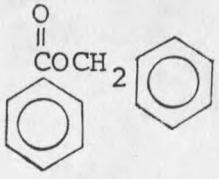
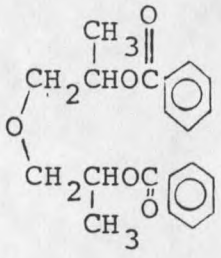
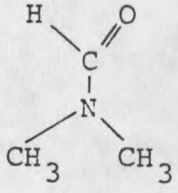
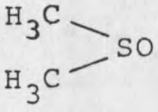
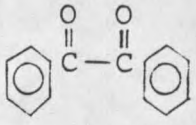
Compound	Molecular structure	B.P. °C	M.P. °C	Vapor pressure mm Hg
Methyl benzoate		198	-15	10 @ 77°C
Ethyl Benzoate		211	-34	10 @ 86°C
Methyl p-hydroxybenzoate		270	131	-
Benzyl benzoate		323	21	4.5 @ 156°C
Dipropylene glycol dibenzoate		250 @ 10 mm Hg	-	-

Table XIV. Molecular structures and physical properties of miscellaneous agents.

Compound	Molecular structure	B.P. °C	M.P. °C	Vapor pressure mm Hg
1-Pentanol	$CH_2CH_2CH_2CH_2CH_3$ (OH)	137.5	-79	10 @ 45°C 40 @ 68°C
N,N-Dimethylformamide (DMFA)		153	-61	4 @ 25°C 39 @ 76°C
Dimethyl sulfoxide (DMSO)		189	18.5	5 @ 57°C
Glycerine	$CH_2CH_2CH_2$ (OH OH OH)	290	17.9	1 @ 125°C
Adiponitrile	$CH_2CH_2CH_2CH_2$ (CN, CN)	308	1.0	10 @ 154°C
Benzil		346	95	12 @ 188°C

refluxed for 6 hours. For the systems with an agent added, 50 grams agent and 50 grams binary mixture with different compositions were charged into the still and then refluxed for 6 hours too. All the samples were analyzed by a gas chromatograph and on an agent-free basis.

Extractive Distillation

The operational procedures for the semi-batch extractive distillation are described as follows:

(1) The stillpot was filled with 400 grams of the mixture to be studied and then heated.

(2) When the condensate refluxed and the system was stable, the agent was added at a rate of 20 ml/min. and the temperature desired. The time for initial addition of the agent was recorded as the time zero.

(3) The total reflux rate was controlled by adjusting the Variac for varying the heat input to the stillpot. If reflux rate is too high, the effect of the agent will be reduced, sometimes even causing flooding. If the reflux rate is too low, the operation becomes more and more difficult.

(4) The temperatures of the agent, overhead, stillpot, vapor and liquid phases on the top plate were recorded every ten minutes from time zero.

(5) The system was operated at total reflux. Therefore, no products were taken out except the samples. By allowing the system to reach equilibrium, the highest relative volatility could be obtained.

(6) Three sets of samples were taken from overhead and stillpot at one hour, one and half hours and two hours operation. The samples were analyzed by gas chromatography and the weight percents were obtained

from the calibration curves. The average of three sets of data was reported.

(7) During the operation, the agent was pumped continuously into the system and accumulated in the stillpot during the operation.

(8) After the system was shut down, the mixture of the agents and components being studied was poured into the distilling flask for agent recovery. The reclaimed agent was reused in order to check its stability.

The same procedures were used for both the plate and packed columns. Here, one can define a term "blank run". It was defined as the system operating without adding any agents. Therefore, the steps (2), (7), and (8) were omitted.

The operation time for the methanol-acetone system was 30 minutes longer than for the other systems. The addition of agents was conducted for 120 minutes and then stopped. After stopping the agents, the system was operated 30 minutes more and shut down. The initial compositions and temperatures of the agents for separating binary mixtures are listed in Table XV. For the ternary mixtures, the initial compositions were the azeotropic compositions listed in Table V. The agents were added at temperatures of 60°C and the total reflux rate was controlled at 10 -16 ml/min.

Liquid-Liquid Equilibrium for Ternary Mixtures

The experiments were conducted by adding the third component(water) into the binary mixture with a specific ratio of two components(acetate

Table XV. The initial compositions and temperatures of agents for separating binary mixtures.

Mixture	Initial composition wt.%	Temperature of agents, °C	Total reflux
m-Xylene & o-xylene	30% m-xylene and 70% o-xylene	65	5-10
Ethanol & water	five different compositions, see Table XII.	67	10-16
Methanol & methyl acetate	15% methanol and 85% methyl acetate	48	10-15
Methanol & acetone	7% methanol and 93% acetone	25	15-20

Total reflux is in the units of ml/min.

and alcohol) until two phases appeared. This was repeated for several different ratios of acetate to alcohol.

For a ternary mixture, the analysis becomes more complicated than that for a binary mixture. Figure 25 shows that the constant ratio of component B to component C is on a straight line with varied content of component A. Therefore, the ratio of acetate to alcohol can be an indication of the composition except water content. So the relative volatility of acetate to alcohol was used to evaluate the effectiveness of agents.

Agent Recovery

After every run made in extractive distillation columns, the agent was recovered by distilling off everything boiling 20°C higher than the boiling points of the key components in the simple distillation system.

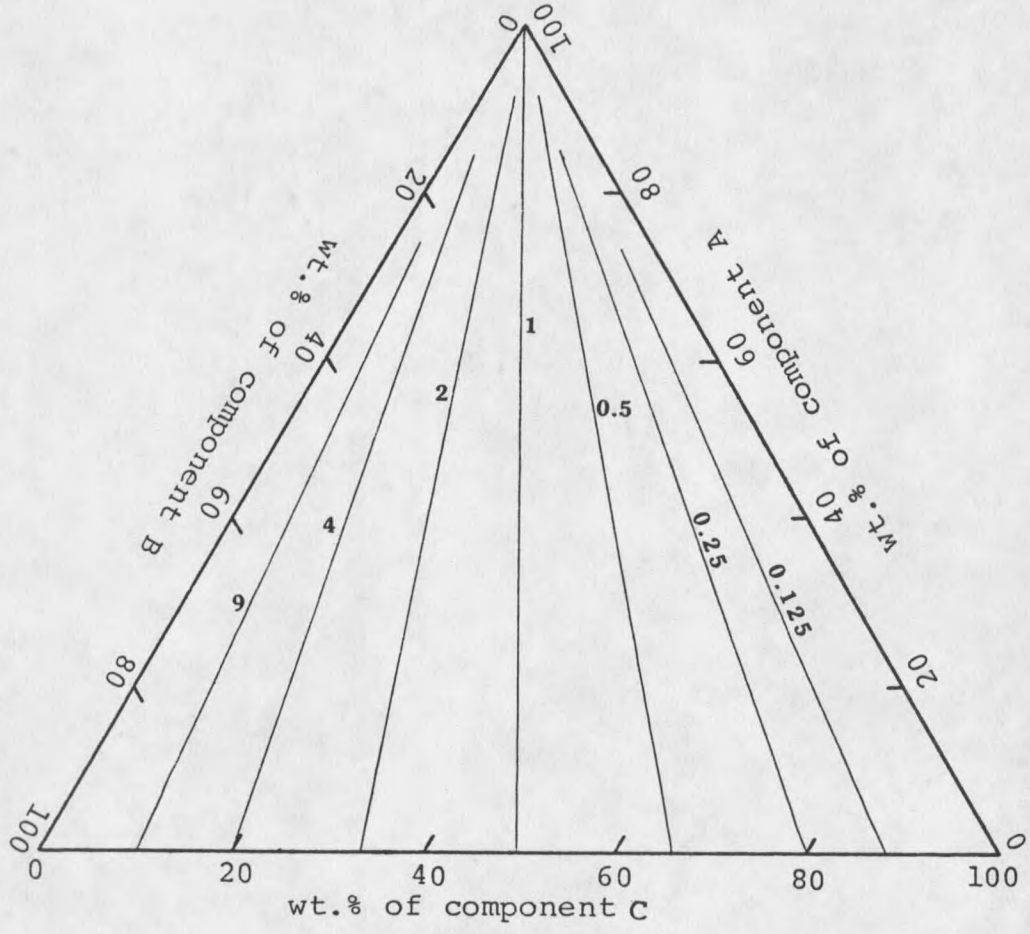


Figure 25. The map for constant ratios of one component to another one in a ternary mixture.

The operation was typically carried out in one hour for each batch. The reclaimed agent was reused without checking the purity.

IV. RESULTS AND DISCUSSION

Vapor-Liquid Equilibria

Figure 26 shows the vapor-liquid equilibria of isopropyl ether and acetone. It is a comparison between the systems with and without an agent. The agent used was DMSO. The experiments were conducted by using the Othmer-type equilibrium still. Due to the limitation of the equipment, the pressure of the system could not be controlled and could only be the same pressure as the barometric pressure. However, the barometric pressure only varied from 630 to 645 mm Hg during the experiments. The variation was small and ignored.

In the system without the agent, isopropyl ether (n.b.p. 68.5°C) was less volatile than acetone (n.b.p. 56.5°C) when the content of isopropyl ether was higher than 42 wt.%, and the minimum-boiling azeotrope existed at a composition of 42 wt.% isopropyl ether. However, not only the azeotrope was negated but also the relative volatility of isopropyl ether to acetone was increased by adding DMSO as the agent. Berg and Yeh [104] have reported this phenomenon from the results of extractive distillation.

The vapor-liquid equilibrium data for the acetone-methanol mixture is shown in Figure 27. There were two agents, DMSO and methyl ethyl ketone, used. When no agents were added, the minimum azeotrope with a composition of 86.1 wt.% acetone existed in the system. The azeotrope was negated by adding DMSO and MEK. However, the relative volatility of

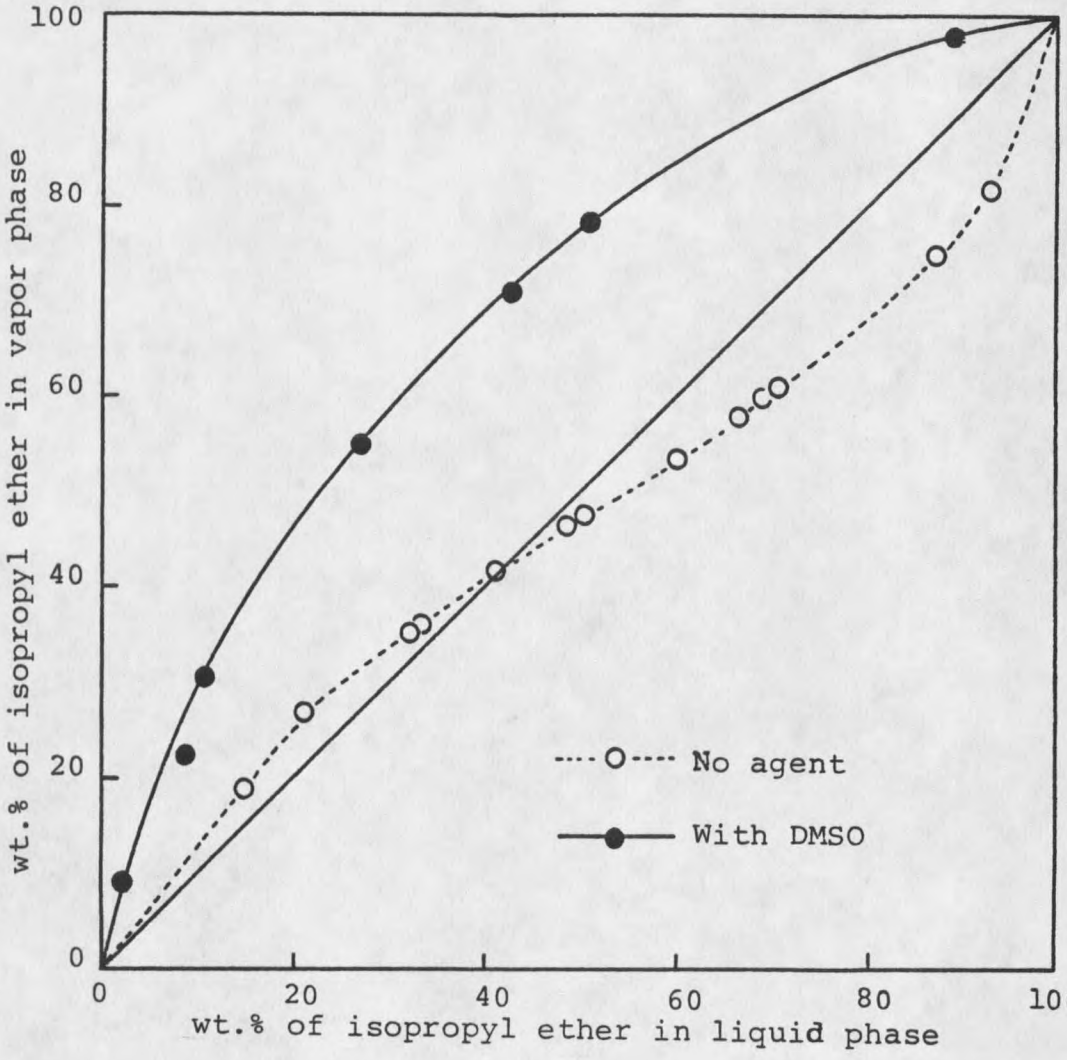


Figure 26. Vapor-liquid equilibrium curves for the isopropyl ether-acetone system.

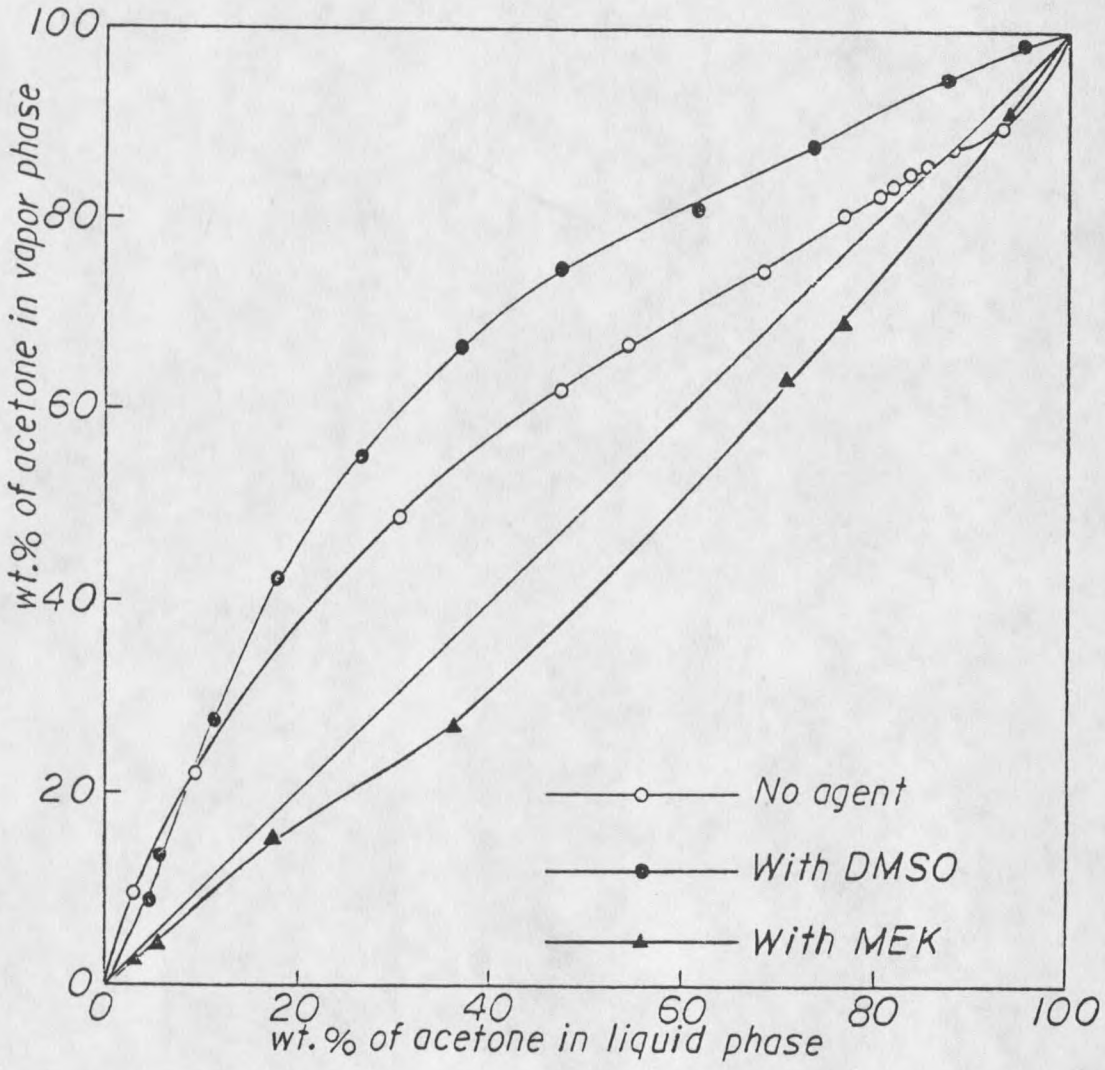


Figure 27. Vapor-liquid equilibrium curves for the methanol-acetone system.

acetone to methanol was increased by DMSO and reversed by MEK. Thus methanol became more volatile than acetone when MEK was used as the agent.

Assuming that the gas phase is ideal gas, Equation 5 can be simplified to be

$$y_i P = \gamma_i x_i p_i \tag{66}$$

Under the barometric pressure, with the same value of x_i, y_i can be changed only by altering the values of γ_i and p_i. Even with 20°C variation, p_i will not have a significant effect of increasing or decreasing y_i. The results show that y_i's have been altered quite a bit by adding the agent. This shows that the main effect of adding an agent is to alter the activity coefficients.

m-Xylene and o-Xylene System

The comparison of the two kinds of columns is shown in Table XVI. The results show that both plate and packed columns are suitable for extractive distillation. The relative volatilities obtained in the packed column were a little bit higher than those obtained in the plate column. This could be due to slight foaming in the plate column. When foam is formed, the packed column is better than the plate column.

Pure compounds, methyl benzoate and ethyl benzoate, did not increase the relative volatility to be higher than 1.3. The performance of the plate and packed columns is similar. Thus the choice of the

Table XVI. The performance of plate and packed columns.

Agent	Column type	wt.% of m-xylene Overhead	Bottoms	Relative volatility
Methyl-	(1) Plate	51.2	31.1	1.21
Benzoate	(2) Packed	40.7	28.4	1.26
Ethyl-	(1) Plate	50.0	30.6	1.20
Benzoate	(2) Packed	41.6	26.1	1.29

Relative volatility is of m-xylene relative to o-xylene.

Table XVII. The results of separating m-xylene from o-xylene.

Agent	Column type	wt.% of m-xylene Overhead	Bottoms	Relative volatility
Benzyl Benzoate	Plate	50.7	27.8	1.24
DGD+DMSO	Plate	54.3	24.9	1.33
Adiponitrile	Packed	40.6	31.0	1.19
Methyl-2-hydroxy benzoate+ DMSO	Packed	40.8	29.7	1.23

Relative volatility is of m-xylene relative to o-xylene.

column was dependent upon whether foaming was present or not. If foaming existed, the packed column was chosen. Table XVII lists the effectiveness of some agents in plate or packed columns. Only the mixture of dipropylene glycol dibenzoate (DGDB) and DMSO ensured a value of relative volatility higher than 1.3. The weight ratio of DGDB to DMSO was one. From Table I, the column cost for α=1.3 is less than half of that for α=1.12. Not only is the column cost lower, but also the ease of operation and heat required are more advantageous. Thus extractive distillation is a valuable method for separating m-xylene from o-xylene. Both plate and packed columns can be used in extractive distillation.

Ethanol and Water System

The initial evaluation of the agents has been reported elsewhere [105]. One pure agent, 1-pentanol, and one mixed agent, 1-pentanol and dipropylene glycol dibenzoate, were used as the agents for extractive distillation. There were five different initial compositions tested for each agent. This was to study the effect of water content on the separation. Table XVIII shows the relative volatilities of water to ethanol with and without agents.

The relative volatility of water to ethanol decreased with an increase of water content in the initial mixture for blank runs. The water composition of the overhead product varied from 6.2% to 6.9% when the initial water content varied from 29.94% to 80.05%. It appeared to have an upper limit for water content in the overhead product. This

Table XVIII. The effect of initial composition on relative volatilities of water to ethanol.

Agent: None

Initial composition wt.% of water	wt.% of water Overhead	Bottoms	Relative volatility
5.0	4.0	5.6	0.92
19.25	5.9	17.5	0.76
29.94	6.2	25.7	0.69
40.63	6.3	35.0	0.63
80.05	6.9	84.2	0.39

Agent: 1-Pentanol

Initial composition wt.% of water	wt.% of water Overhead	Bottoms	Relative volatility
5.0	22.1	3.8	1.55
19.25	31.9	14.3	1.26
29.94	30.3	21.8	1.10
40.63	33.5	33.5	1.00
80.05	40.7	70.3	0.75

Agent: 1-Pentanol + Dipropylene glycol dibenzoate

Initial composition wt.% of water	wt.% of water Overhead	Bottoms	Relative volatility
5.0	18.4	3.2	1.53
19.25	20.8	14.9	1.09
29.94	28.6	21.6	1.09
40.63	25.1	32.9	0.92
80.05	31.4	83.8	0.58

could be due to the strong hydrogen bonding between water molecules. More water molecules yield stronger hydrogen bonds and thus less volatile. This could be the characteristics of water. 1-Pentanol caused water to be more volatile than ethanol when the initial binary mixture contained less than 40 wt.% water. The mixture of 1-pentanol and dipropylene glycol dibenzoate caused water to be more volatile than ethanol when the initial binary mixture contained less than about 35 wt.% water. Dipropylene glycol dibenzoate reduced slightly the effect of 1-pentanol. When water is more volatile, higher relative volatility was obtained if 1-pentanol was used as the agent. However, when water is less volatile than ethanol, the mixed agent yielded a higher relative volatility.

The affinity between homologous compounds usually is higher than that between nonhomologous compounds. 1-Pentanol is a homologous compound of ethanol. The other reason could be the molecular sizes of water and ethanol. Ethanol is about three times the size of water (see Table XXVII). The agent would collide more frequently with the molecule with the larger size. So the larger molecules would be brought down to the stillpot by the agent. In this case, it was ethanol. These two reasons could be why 1-pentanol brought water down to the stillpot. However water molecules have very strong hydrogen bonding. This could offset the effects mentioned above. Therefore which key component would be brought by down to the stillpot by 1-pentanol would depend upon the strength of the hydrogen bonding of water molecules. When water content is small, less water and less hydrogen bonding capacity existed. Thus 1-pentanol brought its homologous compound, ethanol, down to the

stillpot. Once water has enough hydrogen bonding capacity to compete with the molecular interaction between two homologous compounds, water would interact more strongly with 1-pentanol than ethanol and ethanol was obtained as overhead product. So in the presence of 1-pentanol, water was more volatile than ethanol only at low water content. This result shows that water behaves differently in solution due to strong hydrogen bonding.

Methyl Acetate and Methanol System

Some of the initial evaluation are listed in Table XIX. The detailed results are reported elsewhere [106]. The effect of some agents were illustrated by using the extractive distillation column. The results are shown in Table XX. In Table XX, the relative volatility increases with the increase of carbon number of nitrocompound which is a nitro paraffin. However, nitrobenzene has a lower relative volatility. That could be due to the characteristics of the benzene ring which withdraws electrons from nitro functional groups and decreases its potential of attractive intermolecular forces with methyl acetate.

Acetone and Methanol System

The initial evaluation of the agents was done using the Othmer type still. Table XXI lists the results for some agents which increased the relative volatility of acetone to methanol. The details of the results are reported elsewhere [107]. The glycols with two to five carbons

Table XIX. The initial evaluation of the nitrocompounds for the methyl acetate-methanol system.

Agent	wt.% of methanol Vapor	Liquid	Relative volatility
Nitromethane	20.3	10.9	1.98
Nitrobenzene	23.3	12.1	2.21
2-Nitrotoluene	18.2	10.1	1.98
3-Nitrotoluene	18.0	9.6	2.07
4-Nitrotoluene	19.8	10.5	2.10
2-Nitro-m-xylene	19.0	13.4	1.52

The relative volatility is of methanol to methyl acetate.

Table XX. The relative volatility of methanol to methyl acetate examined by extractive distillation.

Agents	Temp., °C Overhead	wt.% of methanol Overhead	Bottoms	α_{ij}
Nitromethane	62.2	75.3	10.6	2.06
Nitroethane	61.8	77.9	6.4	2.40
1-Nitropropane	60.8	74.0	3.4	2.65
2-Nitropropane	61.8	78.9	3.7	2.77
Nitrobenzene	60.6	76.5	11.0	2.08

α_{ij} is the relative volatility of methanol to methyl acetate.

Table XXI. Initial evaluation of the agents which cause acetone to be more volatile.

Agent[a]	wt.% of acetone		Relative Volatility*
	Vapor	Liquid	
Glycerine	89.8	72.7	3.3
DMSO	88.5	70.1	3.3
Ethylene Glycol	90.2	77.0	2.7
Propylene Glycol	88.7	76.7	2.4
1,3-Butanediol	88.5	77.9	2.2
1,4-Butanediol	90.0	78.2	2.5
1,5-Pentanediol	88.8	77.7	2.3
DMSO, 3-Pentanone	93.0	88.5	1.7
DMSO, Isophorone	93.5	13.5	2.2

a: The weight ratio of agents in mixtures is one.

*: The relative volatility is expressed in terms of acetone relative to methanol.

are reported elsewhere [107]. The glycols with two to five carbons yielded almost the same values of the relative volatility. The glycols were chosen due to their hydrogen bonding capability. However, 3-pentanone and isophorone reduced significantly the effect of DMSO. DMSO and glycerine were two effective agents. Ketones could attract more strongly with acetone than with methanol due to higher affinity. If so, methanol should be the overhead product when ketones were used as the agents. Figure 27 has shown this effect with MEK as the agent. Table XXII lists the results of the initial evaluation for ketones. All ketones caused methanol to be more volatile. The most effective one was 3-hexen-2-one which yielded a relative volatility (methanol relative to acetone) of 3.2.

Warren [108] demonstrated the effect of some agents listed in Table XXI using an extractive distillation column. His results confirmed that DMSO was a very effective agent. Acetone was the overhead product when DMSO and glycols were the agents. Several runs with the ketone agents were demonstrated in the plate extractive distillation column. The relative volatilities of methanol to acetone are listed in Table XXIII. The results are very close to those listed in Table XXII. This confirmed that methanol was brought out overhead in extractive distillation when ketones were used as the agents. This phenomenon could be altered by changing the composition of the initial mixture similar to that of the ethanol-water system. Table XXIV shows that the negation of the azeotrope by methyl ethyl ketone (MEK) is independent of the initial mixture composition. The methanol content in the initial binary mixture was varied from 7 to 80 wt.%. Methanol was

Table XXII. Initial Evaluation of Ketones.

Agent	wt.% of methanol Vapor	Liquid	Relative Volatility*
Methyl ethyl ketone	15.5	12.7	1.3
3-Pentanone	19.7	14.9	1.4
2-Pentanone	19.4	15.3	1.3
3-Heptanone	18.7	10.8	1.9
Methyl isobutyl ketone	19.4	14.0	1.5
Methyl isoamyl ketone	20.0	15.3	1.4
Acetophenone	19.2	9.1	2.4
2,4-Pentanone	19.6	11.1	2.0
Acetonylacetone	18.4	11.9	1.7
Ethylacetoacetate	10.8	5.2	2.2
2-Heptanone	19.2	14.3	1.4
2-Octanone	18.8	11.1	1.9
Cyclopentanone	19.7	14.9	1.4
Cyclohexanone	18.7	15.3	1.3
2-Undecanone	19.2	13.8	1.5
Chloro-2-propanone	19.2	12.6	1.6
Diisobutyl ketone	17.9	13.8	1.4
Phenyl ethyl ketone	18.8	13.5	1.5
Ethyl butyl ketone	19.7	12.0	1.8
Phorone	19.5	14.3	1.5
3-Hexen-2-one	19.4	7.0	3.2
o-Hydroxyacetophenone	20.4	11.9	1.9

*: The relative volatility is expressed in terms of methanol relative to acetone.

Table XXIII. The effects of ketones used as the agents in extractive distillation.

Agent[a]	wt.% of methanol Overhead	Bottoms	Relative Volatility*
Blank	10.5	7.1	1.10
Methyl ethyl ketone	33.4	6.4	1.56
2-Pentanone	46.1	7.8	1.67
3-Pentanone	46.4	6.7	1.74
Methyl isobutyl ketone	24.8	7.5	1.37
Methyl isoamyl ketone	30.5	5.1	1.59
2,4-Pentanedione	52.9	6.1	1.88
Diisobutyl ketone	32.1	5.3	1.61
Acetophenone	38.4	5.5	1.69
Ethyl acetoacetate	33.7	4.3	1.71
Methyl ethyl ketone, Benzil	39.4	6.4	1.65

a: The weight ratio of the agent in mixtures is one.
*: The relative volatility is expressed in terms of methanol relative to acetone, also in Table XXIV.

Table XXIV. Results from different initial compositions using methyl ethyl ketone as the agent.

Feed composition wt.% of methanol	wt.% of methanol Overhead	Bottoms	Relative Volatility*
7.0	31.1	6.2	1.53
25.0	72.4	29.2	1.51
55.0	84.5	64.7	1.27
80.0	97.6	94.4	1.21

found to be more volatile than acetone in the entire range. The relative volatility of methanol to acetone changed slightly from 1.53 to 1.21. High purity methanol was obtained when the initial mixture contained 80wt.% of methanol. In terms of the three solubility parameters, methanol has a hydrogen bonding of 24 $(J/cm^3)^{1/2}$ and water has a hydrogen bonding of 40.4 $(J/cm^3)^{1/2}$. Thus methanol molecules do not have so strong hydrogen bonding as water molecules. This could be the reason why the methanol content does not change the reversal of the relative volatility of methanol to acetone.

Temperature Inversion

When the ketones were used as the agents, not only did methanol become more volatile but also "temperature inversion" was observed. The temperature inversion was that the overhead temperature was higher than the stillpot temperature. The thermocouples and temperature indicator were recalibrated against a mercury thermometer. The readings were correct. The measurement was checked by measuring the boiling point of methanol. At an atmospheric pressure of 643.5 mmHg, the boiling point of methanol was measured as 60.4°C using the same apparatus. Interpolating from the data reported by Smith [109] yielded a boiling point of 60.6°C. A value of 60.5°C was calculated from the Antoine equation provided by Reid et al. [110]. The measurement was assured.

Figure 28 shows a typical example of the progress of the overhead and stillpot temperature. The initial binary mixture contained 15 wt.% methanol and 85 wt.% acetone. Before the addition of the agent, MEK, the overhead temperature is lower than that of the stillpot. After the

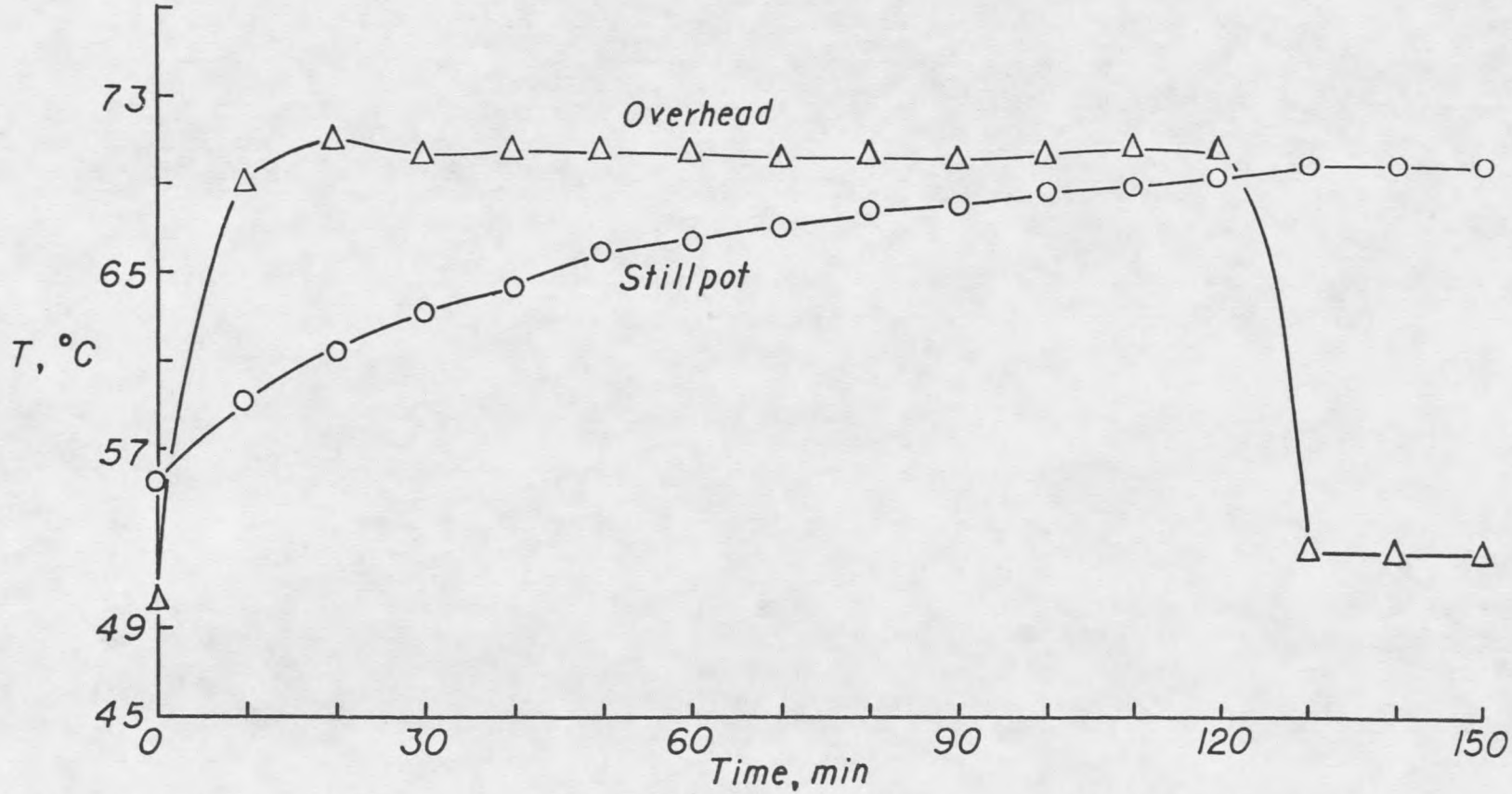


Figure 28. The progression of the overhead and stillpot temperatures for the methanol-acetone system with MEK as the agent.

addition of MEK, the overhead temperature rose rapidly to 69°C in about ten minutes and then stayed at about 70.0 - 70.8°C during the rest of the operation. The stillpot temperature rose gradually due to the addition of agent, MEK. After two hours running time, the addition of MEK was stopped. The stillpot temperature did not change but the overhead temperature dropped rapidly to about the temperature at time zero. This result implies that the separating effect of the agent occurs principally in the column. Similar progression of the overhead and stillpot temperatures with other ketones as agents was observed and shown in Appendix C. The difference of the temperature of overhead and bottoms, $\Delta T=T_o-T_s$, is an indication of the reversed temperature. Temperature inversion exists when ΔT is positive. Figure 29 shows that ΔT changes with time and the normal boiling points of ketones. The numbers on the curves are the minutes during which the operation proceeded. At time zero, the dashed line, ΔT was negative and almost the same for all agents. The overhead temperature was lower than the stillpot temperature. The same ΔT's at time zero was due to the same initial binary mixture. Once the agent was added, the ΔT rose in all the cases studied. Then ΔT decreased gradually due to the gradual rise of the stillpot temperature. This figure shows that the agent with lowest normal boiling point gives the greatest ΔT. As the normal boiling point of the agents increases, ΔT becomes smaller and the time of positive ΔT becomes shorter. The value of normal boiling point is an indication of the volatility of the compound. MEK has the lowest boiling point among the ketones used.

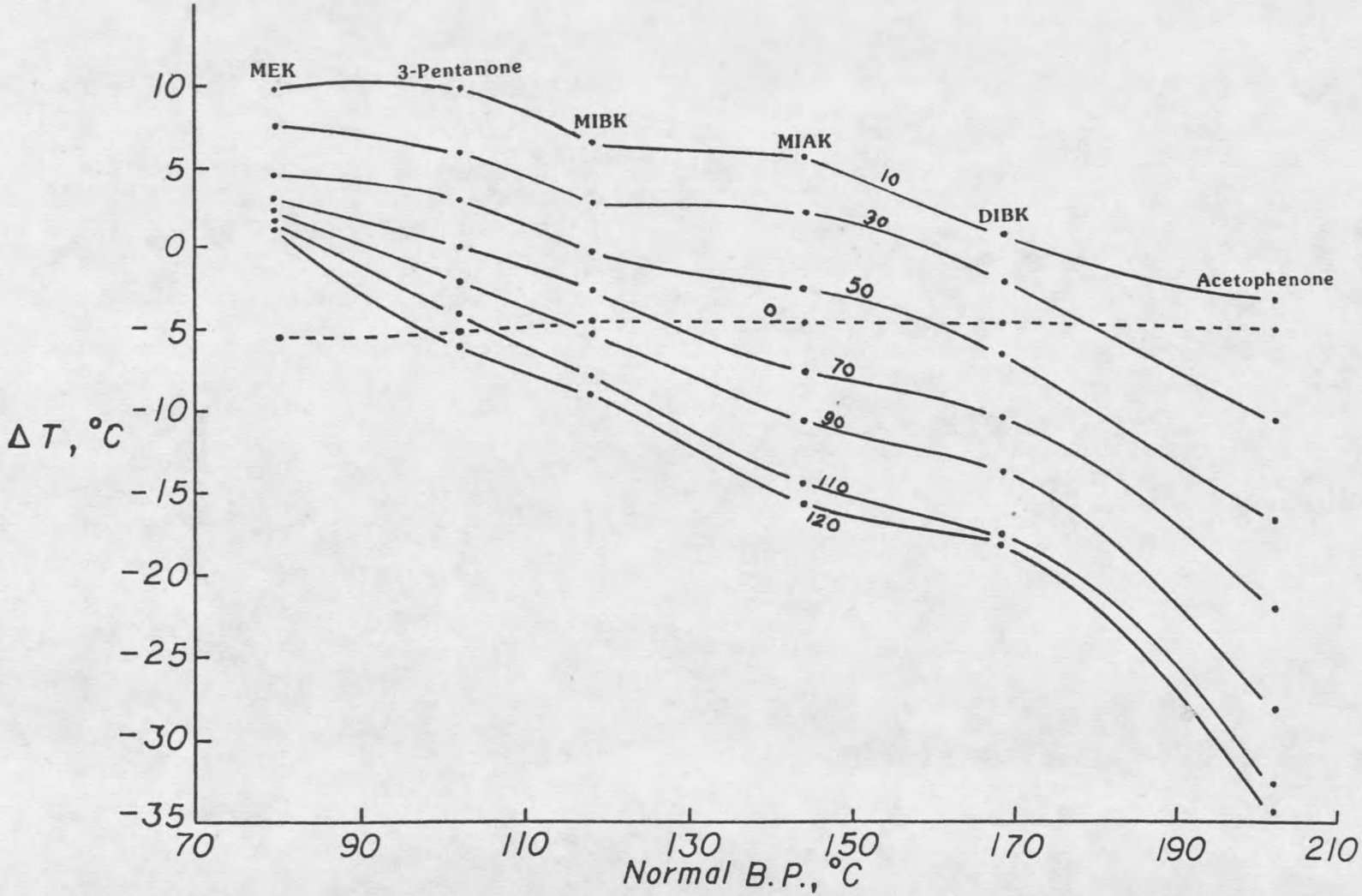


Figure 29. The change of temperature difference with time and normal boiling points of the agents.

Heat of mixing was the first reason suggested. However, no significant temperature rise was observed when MEK was mixed with the acetone-methanol mixture. It has been reported by Christensen et al. [111] that the heats of mixing between methanol acetone, methanol and MEK and acetone and MEK are positive values. Thus no exothermic heat of mixing occurs. MEK can hardly react with acetone or methanol under the operating conditions. To study if the phenomenon was related to azeotropy, pure acetone and pure methanol were used instead of the binary mixture.

The material fed into the stillpot initially was pure acetone (or methanol). The experiments were operated by the procedures described previously except the agent, MEK, was stopped at 50 minutes operation and re-added at 90 minutes operation. Total operation time was 140 minutes. In Figure 30, the overhead temperature dropped when MEK was stopped in both cases. Temperature inversion existed in the two systems when MEK was added into the extractive distillation column. From the analysis, it was found that the overhead contained more MEK than the key component. Table XXV lists the MEK content in the overhead and bottoms products for the pure methanol and pure acetone systems. In the pure methanol system, MEK content was much higher than methanol in the overhead which had higher wt.% of MEK than the bottoms at 50 minutes operation. At 90 minutes operation, MEK had been stopped for 40 minutes, wt.% of MEK dropped from 79.5 to 26.4 which was lower than 66.6, the wt.% of MEK in the bottoms. MEK content in overhead was higher again at 140 minutes operation, as MEK had been re-added for 50 minutes. Similar temperature progression was observed for pure acetone.

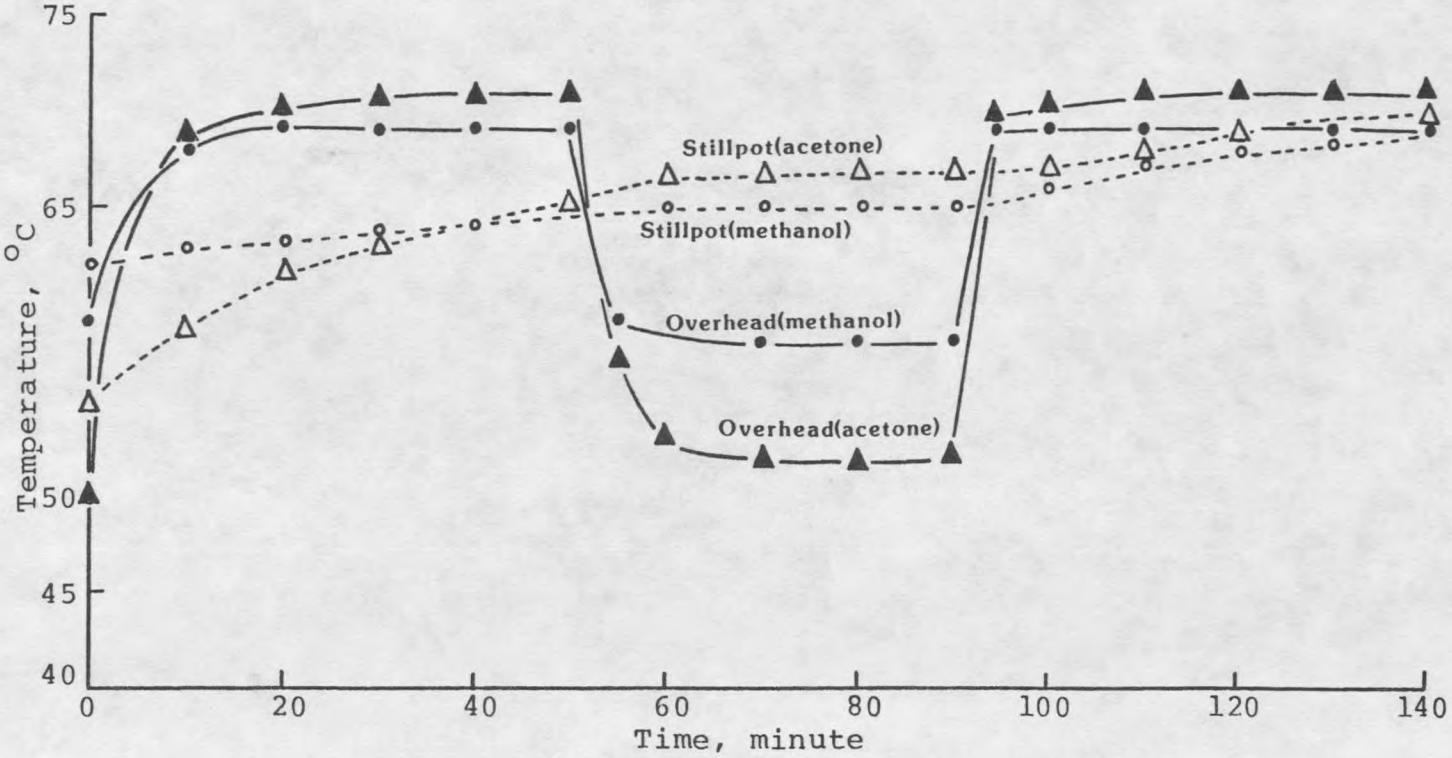


Figure 30. The progression of the overhead and stillpot temperatures for pure methanol and pure acetone using MEK as the agent.

Table XXV. The overhead and bottoms compositions for pure methanol methanol and pure acetone systems with MEK.

	wt.% of MEK		
	50 min.	90 min.	140 min.
Pure methanol			
Overhead	79.5	26.4	76.3
Bottoms	63.9	66.6	80.0
Pure acetone			
Overhead	85.1	6.4	80.7
Bottoms	56.8	58.6	71.8

However, the MEK content at 90 minutes for pure acetone (6.4 wt.%) was lower than that for pure methanol (26.4 wt.%). That was why the overhead temperature for the pure acetone system was lower than that for the pure methanol system during the operation period from 50 to 90 minutes. The boiling point of a solution is a function of the composition. Due to higher content of MEK in the overhead, the boiling point of the overhead is higher than that of the bottoms solution. Therefore, the overhead temperature was higher than the bottoms temperature. The change of the compositions in the pure acetone system behaved similarly. However, the MEK content was 8.9 wt.% higher than that in the bottoms at 140 minutes operation. Thus the overhead temperature was higher than the stillpot temperature. This demonstrated that the temperature inversion was not related to the azeotropy but to the solution composition.

The agent was added near the top of the column. At the beginning of adding an agent, the composition of the agent at the overhead was higher than that in the bottoms. If the agent is much less volatile, the vapor will be condensed and no vapor exists until the stillpot reaches a temperature high enough. If the agent is comparatively volatile, the agent will be vaporized by the vapor. Due to the continuous addition of the agent, the agent content would decrease from the top to bottom of the column. This could cause the temperature inversion. Table XXVI shows higher MEK content in the overhead unless MEK was stopped. To maintain the boiling on each plate, more vapor is required. Thus vapor coming into a plate will partially condense and partially go through the plate. From the idea discussed, one could expect the effect of the agent temperature. Usually, the latent heat of a compound decreases as the temperature increases. If the temperature

Table XXVI. The compositions for acetone-methanol system using MEK as the agent.

		Composition in wt.%			
		1 hr.	1.5 hrs.	2 hrs.	no agent.
Overhead:	acetone	10.1	9.3	6.3	79.2
	methanol	4.6	3.8	3.2	15.2
	MEK	85.3	86.9	90.5	5.6
Bottoms:	acetone	41.8	33.8	26.7	25.1
	methanol	2.7	1.7	1.8	1.4
	MEK	55.5	64.5	71.5	73.5

of the agent is raised and the operational conditions are the same, there would be more agent vaporized due to lower latent heat of the agent at a higher temperature. However, this effect would not be very significant. Thus the overhead temperature would be increased a little bit. Figure 31 shows the comparison of the temperature of the agent, MIBK, at 25°C and 50°C. The stillpot temperature behaved very similarly. The overhead temperature with MIBK at 50°C was slightly higher than that at 25°C. This indicated that the temperature inversion could be caused by the dissolving of the vapor into the liquid phase. The key components coming up the column as a vapor dissolve into the liquid phase on the plate and give up their latent heats. The latent heats given up by the vapor would partially evaporate the liquid and partially increase the temperature of the liquid. To test this idea, the solubility of the vapor of key components in the agents is needed for theoretical calculation. The solubility of the vapor of methanol in liquid methyl ethyl ketone has not been found. However, Copley et al. [112] have reported that the mole fraction solubilities of methanol in amines are in the range of 0.4 to 0.6. To do a hypothetical calculation, the mole fraction solubility of methanol and acetone is assumed being 0.15. The detailed calculation is shown in Appendix D. The calculated results show that it is quite reality possible to heat up the liquid MEK from 45 to 70°C by the latent heats given up by the vapor of methanol and acetone according to the listed vapor solubilities. However, more studies are needed to verify this hypothesis.

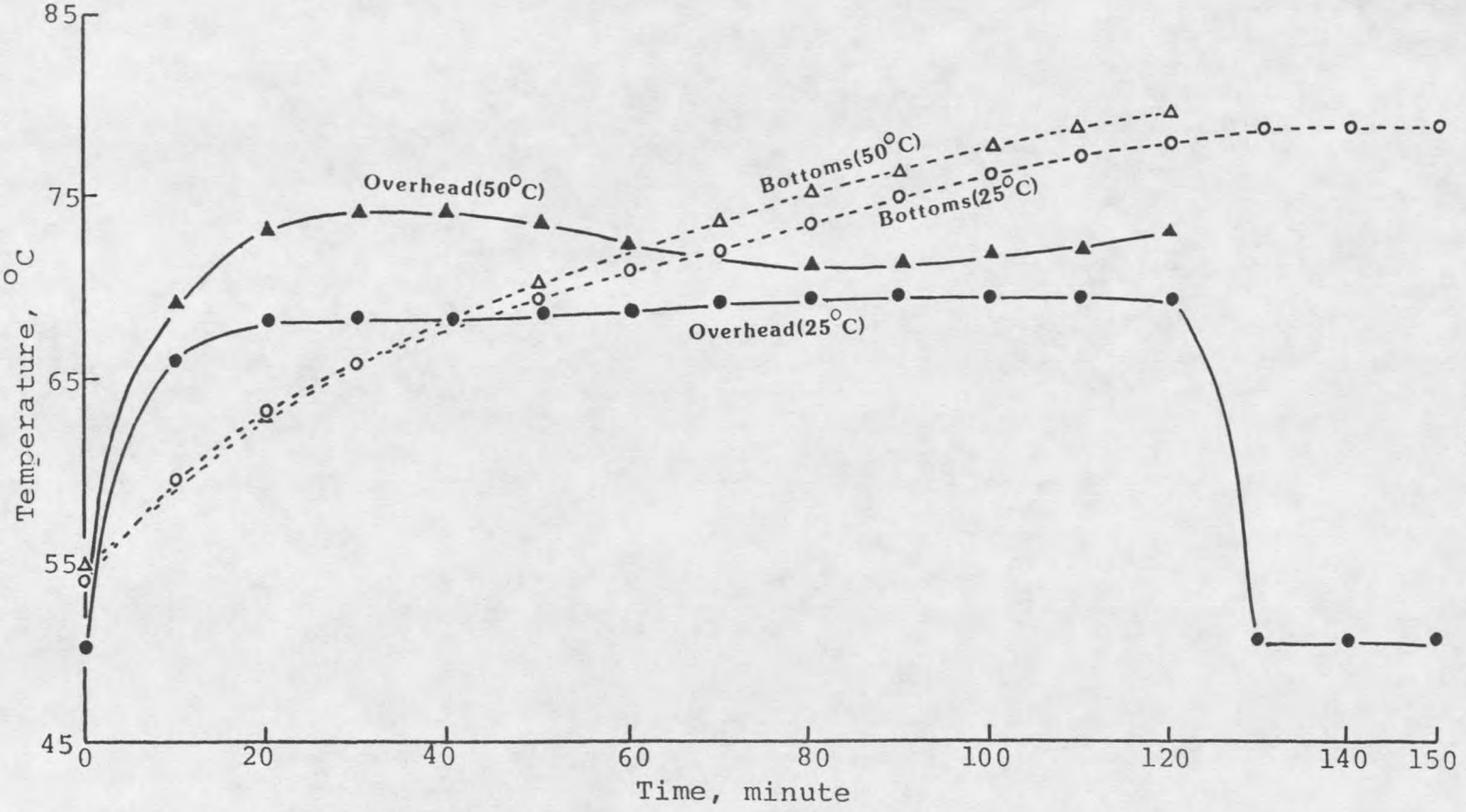


Figure 31. The effect of the agent temperature on temperature inversion. The agent was MIBK at 25°C and 50°C.

The Reversing of Relative Volatilities

The reversal of the relative volatility was first reported in 1947 by Buell and Boatright [113] and more recently in 1983 by Yeh [29]. However, this phenomenon has not been explained satisfactorily. The understanding of the effects of the extractive agents would be improved by studying the reversal of relative volatilities.

The potential of the key component to interact with the agent can be an indication of the effect of the agent. Solubility parameter which includes dispersion force, polar interaction and hydrogen bonding can be used to study the physical forces occurring between molecules. However, the physical forces should be attractive. This indicates that the molecules must have some similar characteristics. This work attempted to categorize the molecules and find a way to select an effective agent by using solubility parameter. Table XXVII [114] lists the three solubility parameters and specific volumes of the key components studied.

The differences between key components in solubility parameters in each system are mainly polar interaction, δ_p, and hydrogen bonding, δ_h. For the acetone-methanol system, the difference in dispersion force between acetone and methanol is only 1.4 $(J/cm^3)^{1/2}$, which is a very small value compared with the differences in polar interaction, 3.2 $(J/cm^3)^{1/2}$, and the difference in hydrogen bonding, 13.0 $(J/cm^3)^{1/2}$. Also the difference in specific volume, 34 cm^3/mol, is appreciable.

Table XXVII. Solubility parameters and specific volumes of key components.

Compounds	ν (cm^3/mol)	δ_d $(J/cm^3)^{1/2}$	δ_p $(J/cm^3)^{1/2}$	δ_h $(J/cm^3)^{1/2}$
Acetone	74.0	13.0	9.8	11.0
Methanol	40.7	11.6	13.0	24.0
Ethanol	58.7	12.6	11.2	20.2
Water	18.1	12.2	22.8	40.4
Methyl acetate	79.9	13.3	9.5	10.4

This discussion can be applied to the ethanol-water and methanol-methyl acetate systems as well and it can be concluded that that the dispersion force can be ignored when discussing the molecular interaction in this study. Figures 32, 33, and 34 show the plots of δ_p versus δ_h, herein called polarity diagram, for the systems of acetone-methanol, ethanol-water, and methanol-methyl acetate respectively. In Figure 32, the location of methanol is referred to as the point A and the location of acetone is referred to as the point B. We can draw a segment AB to connect these two points. There is one point C which makes the ratio of AC to CB equal the ratio of the specific volume of acetone to that of methanol. Drawing a line perpendicular to AB through the point C divides the polarity diagram into two parts. One is the methanol side and another is the acetone side. Agents, such as glycerine and ethylene glycol, on the methanol side have greater affinity for methanol than for acetone. Those agents would bring methanol down to the stillpot and acetone would be the overhead product.

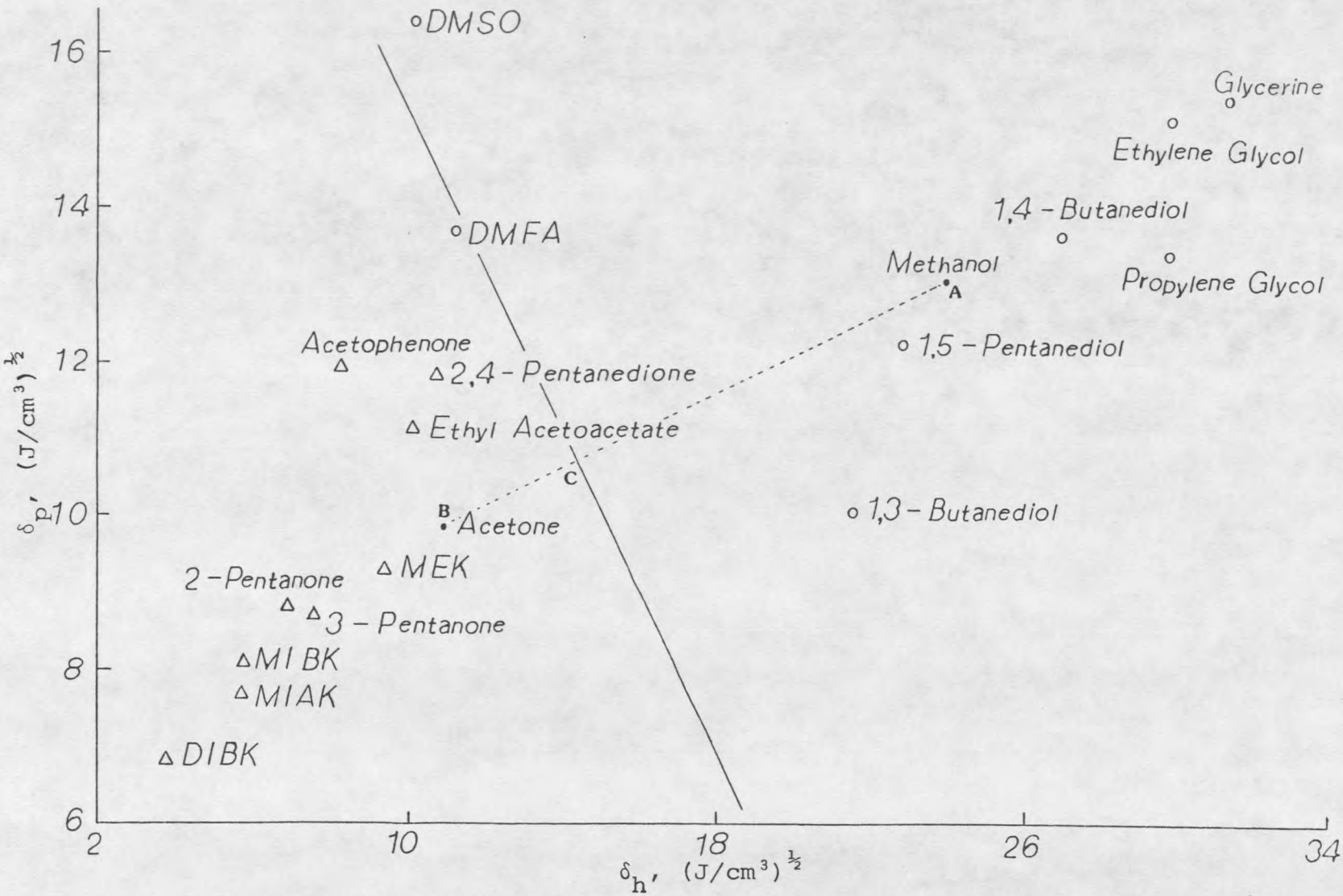


Figure 32. Polarity diagram for the methanol-acetone system.

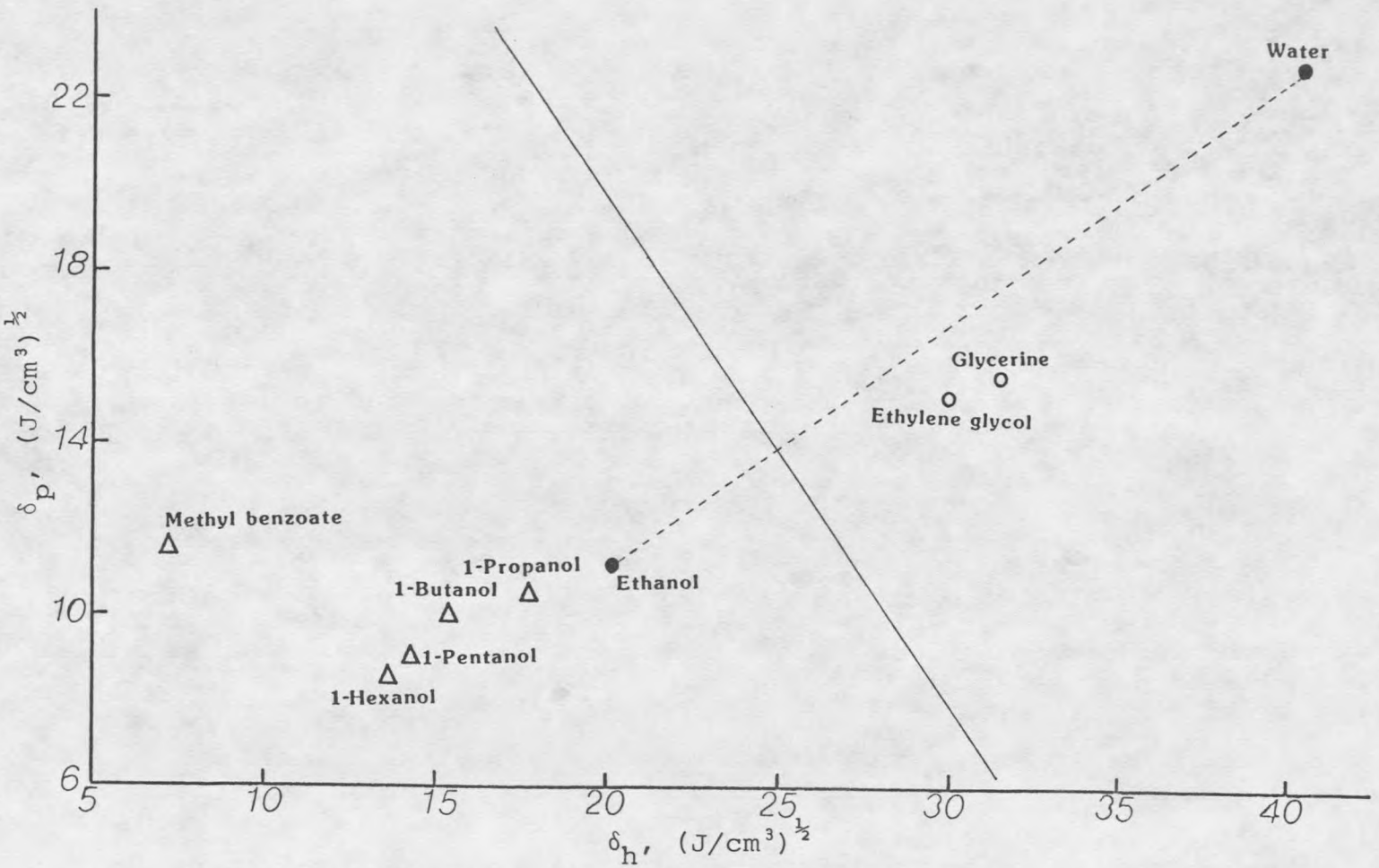


Figure 33. Polarity diagram for the water-ethanol system.

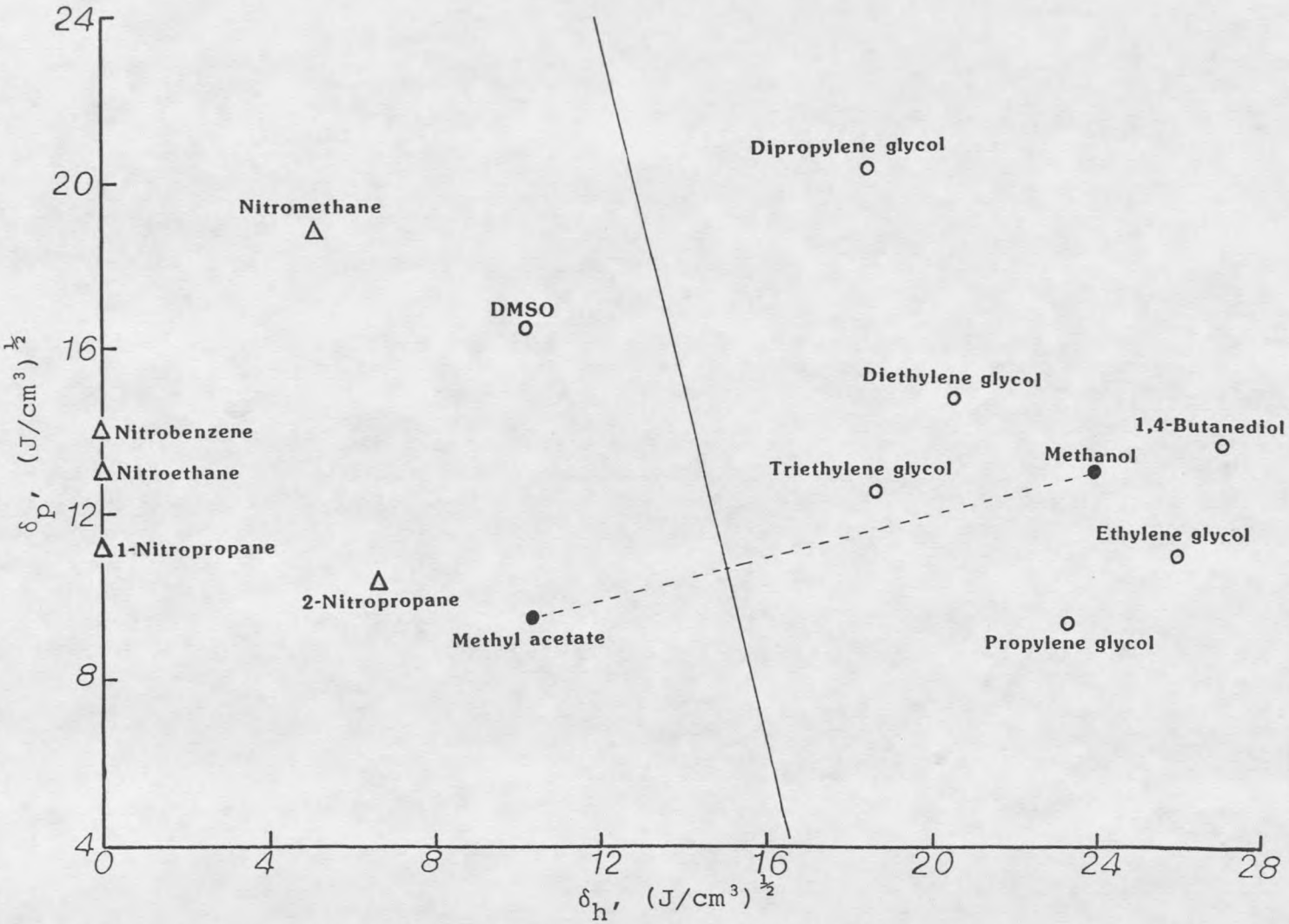


Figure 34. Polarity diagram for the methanol-methyl acetate system.

This concept was confirmed by the data reported in Table XXI. The agents, such as methyl ethyl ketone and acetophenone, on acetone side have greater affinity for acetone than for methanol. Therefore acetone would be the bottoms product. The results presented in Tables XXII and XXIII, with the exception of DMFA, are in accord with this theory. DMFA is on the acetone side but brings methanol down to the stillpot. This indicates that there is a greater molecular interaction between DMFA and methanol. Ritchie [115] has shown that DMSO and DMFA can induce the acidity of alcohols. DMSO and DMFA behaved as the bases. Thus there existed strong molecular interaction between these agents and methanol and thus acetone was obtained as the overhead product. As shown in Figure 8, the acid-base interactions could cause the presence of a chemical complex.

Applying the same technique in Figures 33 and 34 shows the same result as the previous observation. The values of solubility parameters for a number of compounds have been edited by Barton [114]. Thus the method presented previously might be considered the simplest way to predict which key component would be the overhead product.

The method presented above can be an initial estimation of the performance of an agent. However, a more accurate predication of the performance of an agent might be dependent upon the expression of the activity coefficient. Equation 65 was used to calculate the activity coefficients of the key components in the agents. Substituting these values in Equation 6 and assuming that ϕ's are unity yield the values of the relative volatilities. p_i's were calculated from Antoine equations with the parameter values provided by Reid et al. [110]. Tables XXVIII

Table XXVIII. The comparison of the relative volatility for methanol(1)-acetone(2) system.

Agent	Experimental α_{12}	Calculated α_{12}
MEK	1.53	1.46
2-Pentanone	1.66	1.60
3-Pentanone	1.76	1.60
Methyl iso-butyl ketone	1.48	1.69
Diisobutyl ketone	1.64	1.65
Acetophenone	1.71	1.33

Table XXIX. The comparison of the relative volatility for methanol(1)-methyl acetate(2) system.

Agent	Experimental α_{12}	Calculated α_{12}
Nitromethane	2.06	1.72
Nitroethane	2.40	2.41
1-Nitropropane	2.65	2.91
2-Nitropropane	2.77	2.96
Nitrobenzene	2.04	2.83

Experimental α_{12} are the values obtained by using the plate extractive distillation column.

and XXIX show the calculated results compared with the experimental data. In these two tables, the "Experimental" indicates that the relative volatilities were obtained by using the plate extractive distillation column.

In Table XXVIII, the average error is 9.1% with a maximum error of 22.2%. The minimum error is 0.7%. In Table XXIX, the average error is 14.5% with a maximum error of 38.7% and a minimum error of 0.4%. The average error for two tables is 11.5%. The calculated α_{12}'s fit the experimental α_{12}'s fairly well except for the aromatic compounds, nitrobenzene and acetophenone. This could be due to the electron withdrawal of the functional group on the benzene ring in addition to other characteristics of the molecule. The advantage of this model is that only the properties of pure components need be known to calculate the relative volatility of the key components. Unfortunately the model is inapplicable to aqueous systems.

Ternary Azeotropes

Liquid-Liquid Equilibrium

Figures 35, 36, 37, and 38 show the one phase region for each ternary mixture. For the n-butyl and isobutyl systems, a small one phase region in high concentration of water exists. This is due to the solubility of alcohols and acetates in water. If mixtures are in the two phase region, they can be separated first by phase separation and then by distillation. However, if a ternary minimum azeotrope exists, the separation of a one phase mixture can not be done by conventional

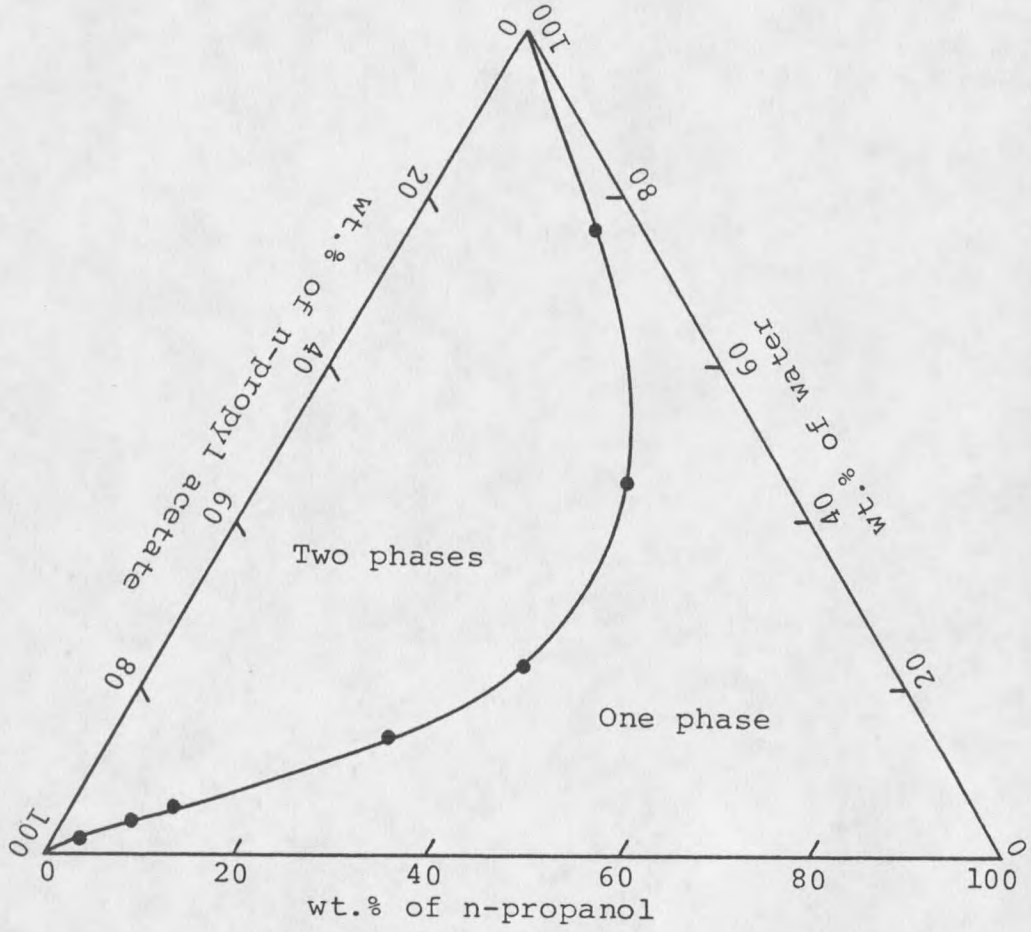


Figure 35. Liquid-liquid equilibrium diagram for the n-propyl acetate-n-propanol-water system.

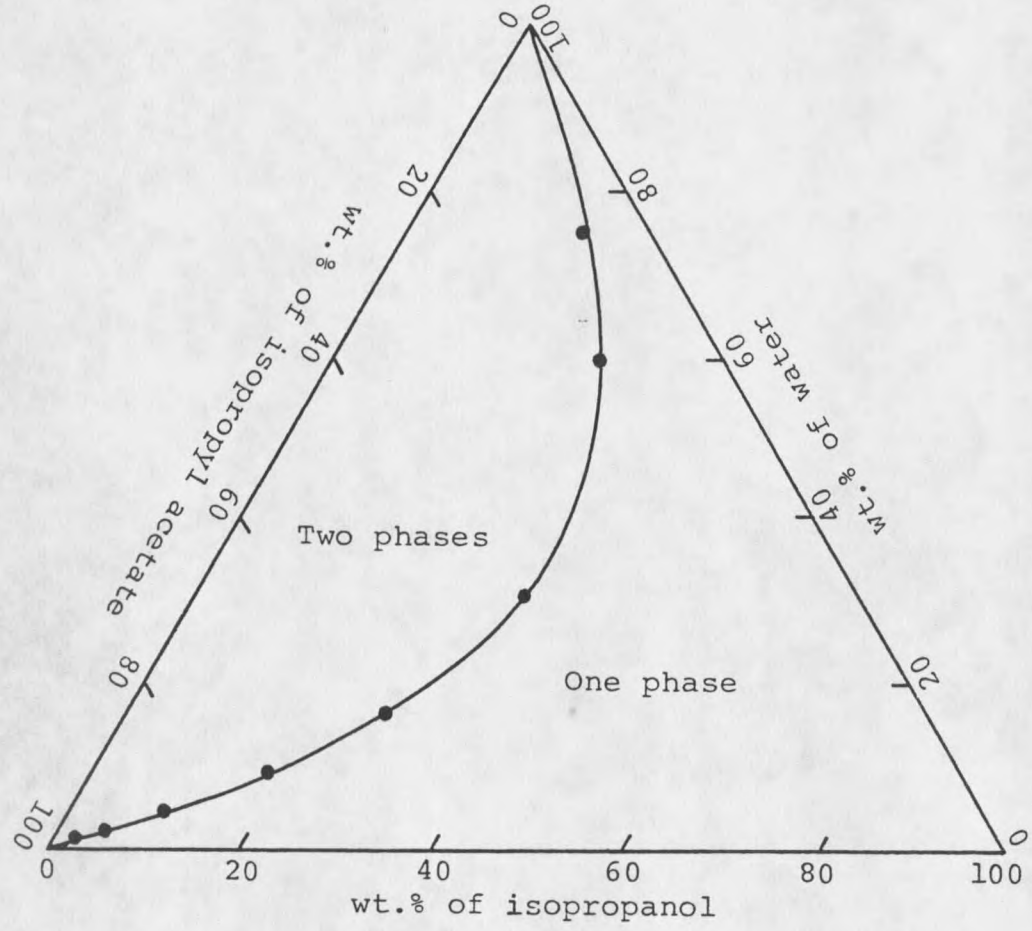


Figure 36. Liquid-liquid equilibrium diagram for the isopropyl acetate-isopropanol-water system.

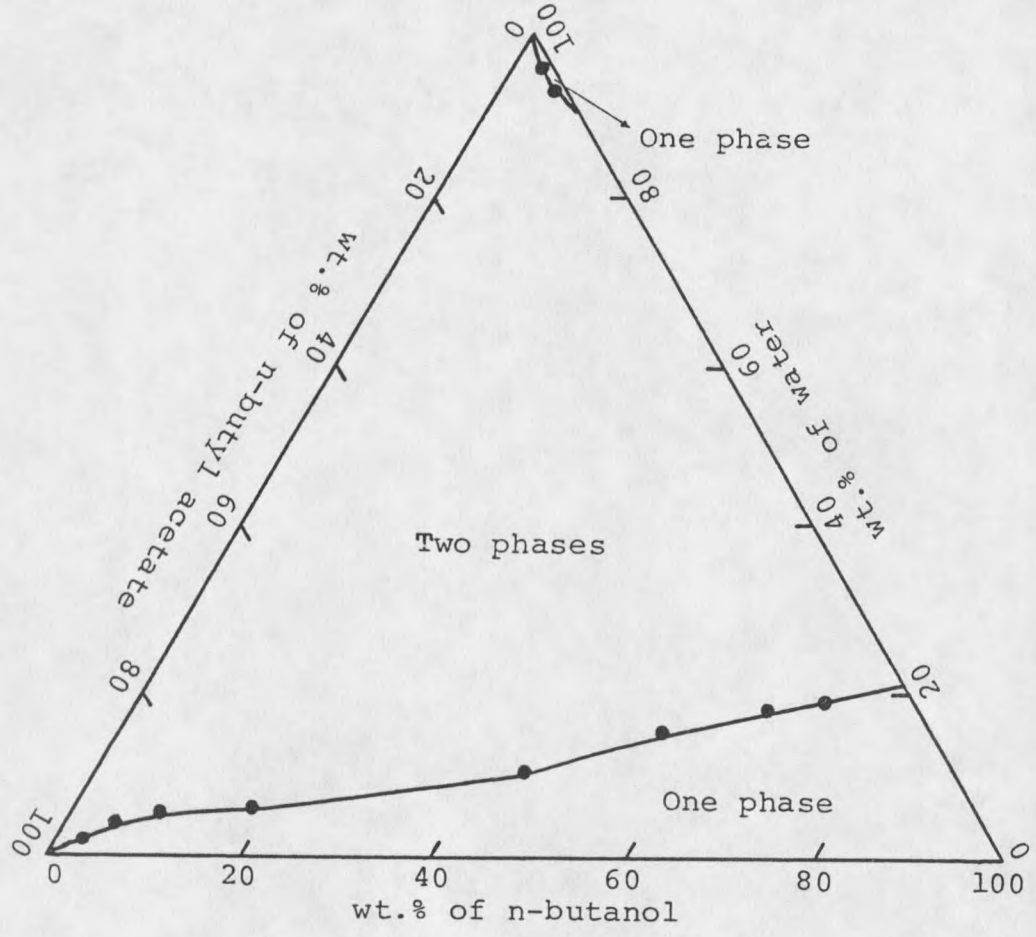


Figure 37. Liquid-liquid equilibrium diagram for the n-butyl acetate-n-butanol-water system.

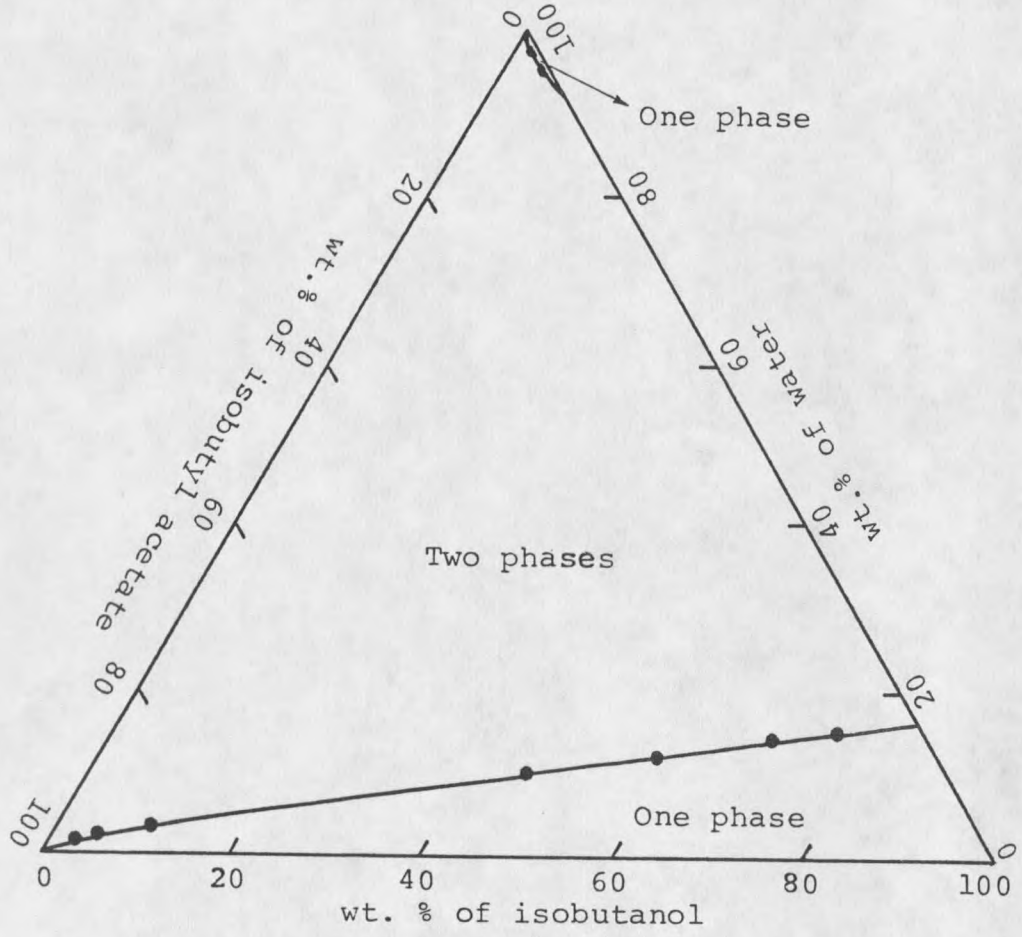


Figure 38. Liquid-liquid equilibrium diagram for the isobutyl acetate-isobutanol-water system.

distillation. If alcohol can be separated from the mixture, the further separation between acetate and water can be done by decantation due to low miscibility of acetate in water.

Application of The Polarity Diagram

This work attempted to apply the polarity diagram to ternary mixtures. To simplified the situation, the acetate and alcohol were considered as the key components in each system. Table XXX [114] lists the three solubility parameters for the key components and water. The main differences between acetates and the corresponding alcohols is the size of the molecule, δ_p, and δ_h. The key components have almost the same values of δ_d. The difference of the molecular size between acetates and the corresponding alcohols is about 41 cm^3/mol. This is an appreciable amount and believed to affect significantly the selectivity of the agent. Alcohols have greater hydrogen bonding and slightly higher polar interaction forces than the corresponding acetates. This implies that an agent with high hydrogen bonding and polar interaction forces would attract more strongly with alcohol than acetate. The polarity of the agent was the main concern in selecting agents. Table XXXI [114] lists the three solubility parameters and the specific volumes of the agents used. The glycols have greater hydrogen bonding. Among the glycols, ethylene glycol has the highest polarity and smallest molecular size. DMSO and DMFA have moderate hydrogen bonding but comparatively great polar interaction forces and moderate specific volumes.

Table XXX. Solubility parameters and specific volumes of the key components.

Component	ν $cm^3/mole$	δ_d $(J/cm^3)^{1/2}$	δ_p $(J/cm^3)^{1/2}$	δ_h $(J/cm^3)^{1/2}$
n-Propyl acetate	115.9	14.1	8.1	7.8
n-Propanol	75.2	14.1	10.5	17.7
Isopropyl acetate	117.9	14.3	8.4	5.7
Isopropanol	77.0	14.0	9.8	16.0
n-Butyl acetate	132.6	14.5	7.8	6.8
n-Butanol	91.9	15.0	10.0	15.4
Isobutyl acetate	134.2	14.5	7.8	5.1
Isobutanol	92.9	14.4	9.8	15.0

Table XXXI. Solubility parameters and specific volumes of the agents.

Agent	ν	δ_d	δ_p	δ_h
DMSO	71.3	18.4	16.4	10.2
DMFA	77.0	17.4	13.7	11.3
Ethylene glycol	55.9	10.1	15.1	29.8
1,4-Butanediol	88.9	15.0	13.6	27.0
Propylene glycol	73.7	11.8	13.3	25.0
Diethylene glycol	95.3	12.4	12.3	23.3
Triethylene glycol	120.3	15.0	12.2	21.8
Dipropylene glycol	132.1	12.2	10.3	17.4

Note: ν, δ_d, δ_p, and δ_h have the same units as which in Table XXX.

Figure 39 shows the location of those compounds in a polarity diagram. The location is an indication of the polarity of the component. We can see that the polarity increases from acetates, alcohols, agents and then water. DMSO and DMFA are two exceptions to this tendency. Applying the same technique as for Figure 32, all the agents are on the alcohol side. Thus those agents would have greater affinity for alcohols than for acetates. It was expected that the alcohols were carried down by the agents to the stillpot and the acetates were forced into the overhead. Thus the effect of the agents can be explained by the attraction of intermolecular forces. Among the glycols, ethylene glycol has the highest values of δ_p and δ_h. This indicated that ethylene glycol has a greater capability for hydrogen bonding and polar interaction than the other glycols. Thus ethylene glycol would have the highest effect on enhancing the separation. Dipropylene glycol, which has the smallest values of δ_p and δ_h, would yield the poorest performance.

Effects of Agents

Two series of experiments were used to study the effects of the agents. First, the agents were evaluated by using the Othmer type VLE still. After the initial evaluation, the effect of the agents were demonstrated by using the plate extractive distillation column.

Some of the results for initial evaluation of the agents are listed in Tables XXXII. The details of the results have been reported elsewhere [116, 117, 118, 119]. DMSO had the highest relative volatilities except for n-butyl acetate-n-butanol-water system. In both

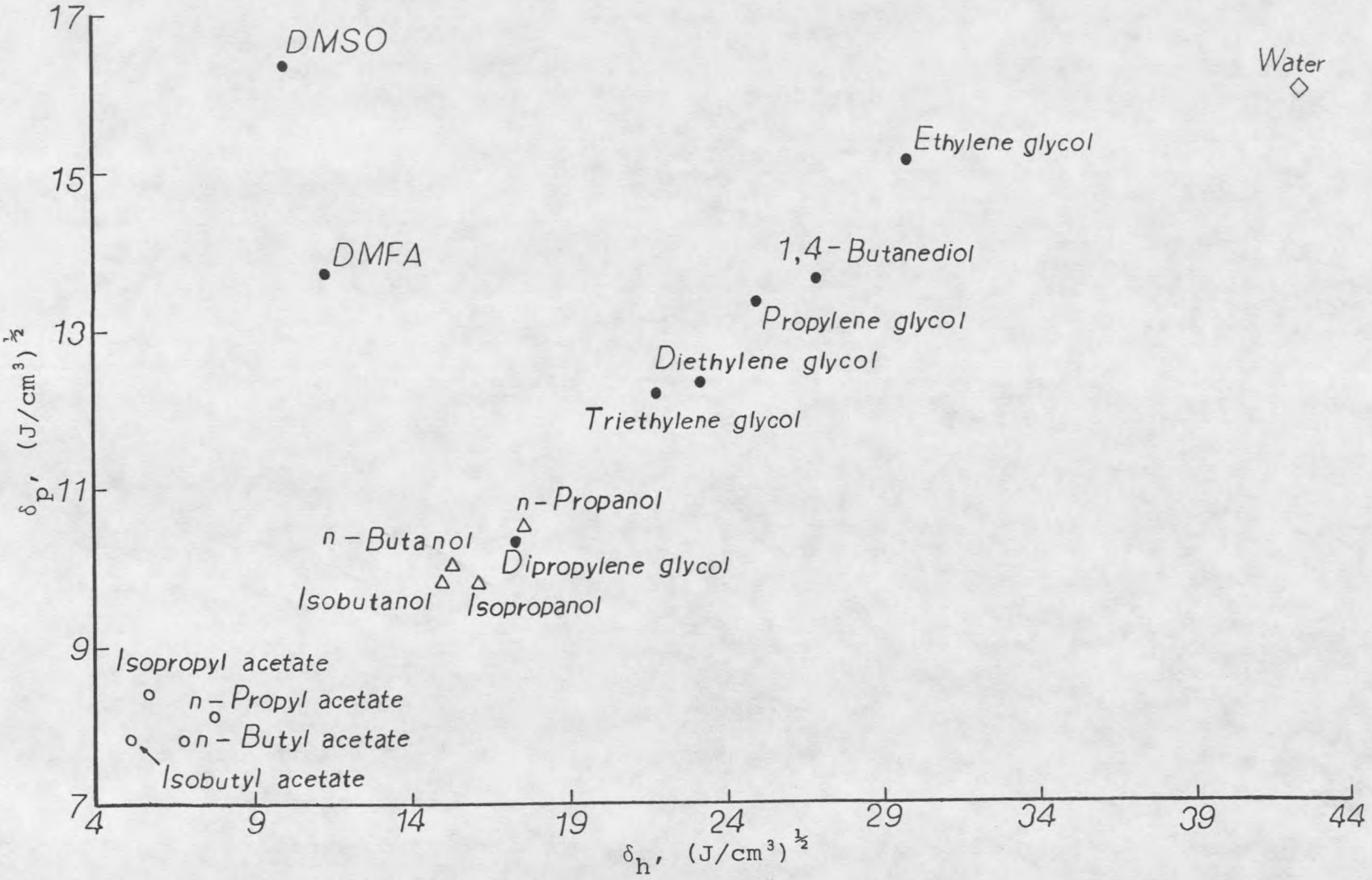


Figure 39. Polarity diagram for the acetate-alcohol water systems.

Table XXXII. Initial evaluation of the agents for the acetate-alcohol-water systems.

Agent	Relative volatility of acetate to alcohol nPAc-nPOH	IPAc-IPOH	nBAc-nBOH	IBAc-IBOH
DMSO	2.73	2.08	1.67	2.55
Ethylene glycol	-	-	1.99	2.18
Propylene glycol	-	1.68	1.31	1.67
1,4-Butanediol	1.70	1.82	1.18	1.84
Diethylene glycol	-	2.12	-	1.64
1,5-Pentanediol	1.58	1.81	-	1.66
Triethylene glycol	-	1.98	-	1.53
Dipropylene glycol	1.05	1.74	-	1.15
1,6-Hexanediol	1.30	1.67	-	1.31

Table XXXIII. The effectiveness of the agents shown in the plate extractive distillation column.

Agent	Relative volatility of acetate to alcohol nPAc-nPOH	IPAc-IPOH	nBAc-nBOH	IBAc-IBOH
Blank	1.25	1.03	0.82	1.12
DMSO	2.77	2.19	2.11	3.05
DMFA	1.85	1.40	1.76	2.65
Ethylene glycol	2.21	1.96	1.86	2.90
1,4-Butanediol	2.00	1.88	1.67	2.48
Propylene glycol	1.74	1.59	1.46	2.55
Diethylene glycol	1.89	1.75	1.61	1.70
Triethylene glycol	1.81	1.49	1.39	1.58
Dipropylene glycol	1.53	1.15	1.37	1.55

n-butyl acetate-n-butanol-water and isobutyl acetate-isobutanol-water, ethylene glycol was the most effective glycol agent. The effects of the agents demonstrated in the plate extractive distillation column are listed in Table XXXIII Again, DMSO yielded the highest relative volatilities for four systems and ethylene glycol was the most effective agent of glycols. Most of the agents had poorest performance in n-butyl acetate-n-butanol-water system with the exception of DMFA and dipropylene glycol. Both of them had the least effect on the isopropyl acetate-isopropanol-water system. In all cases, the acetate and water were obtained in the overhead product which condensed into two layers. The discussion will be based on the results from the extractive distillation column rather than those from the equilibrium still because the column has more theoretical plates and yields more reliable results.

Figure 40 shows the selectivity of the agent varying with polarity. The selectivities were calculated using Equation 12. In Figure 40, the six different values of polarity correspond to the six agents used. In the order of the increase of the polarity, they are dipropylene glycol, triethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, and then ethylene glycol. The selectivities of ethylene glycol, 1,4-butanediol and propylene glycol increase in the order of n-propyl acetate, isopropyl acetate, n-butyl acetate, and isobutyl acetate. However, the selectivities of diethylene glycol, triethylene glycol and dipropylene glycol do not follow this order. Diethylene glycol and triethylene glycol have about the same selectivity on n-propyl acetate and isobutyl acetate and the highest selectivity on n-butyl acetate. Dipropylene glycol has the highest selectivity on n-butyl acetate.

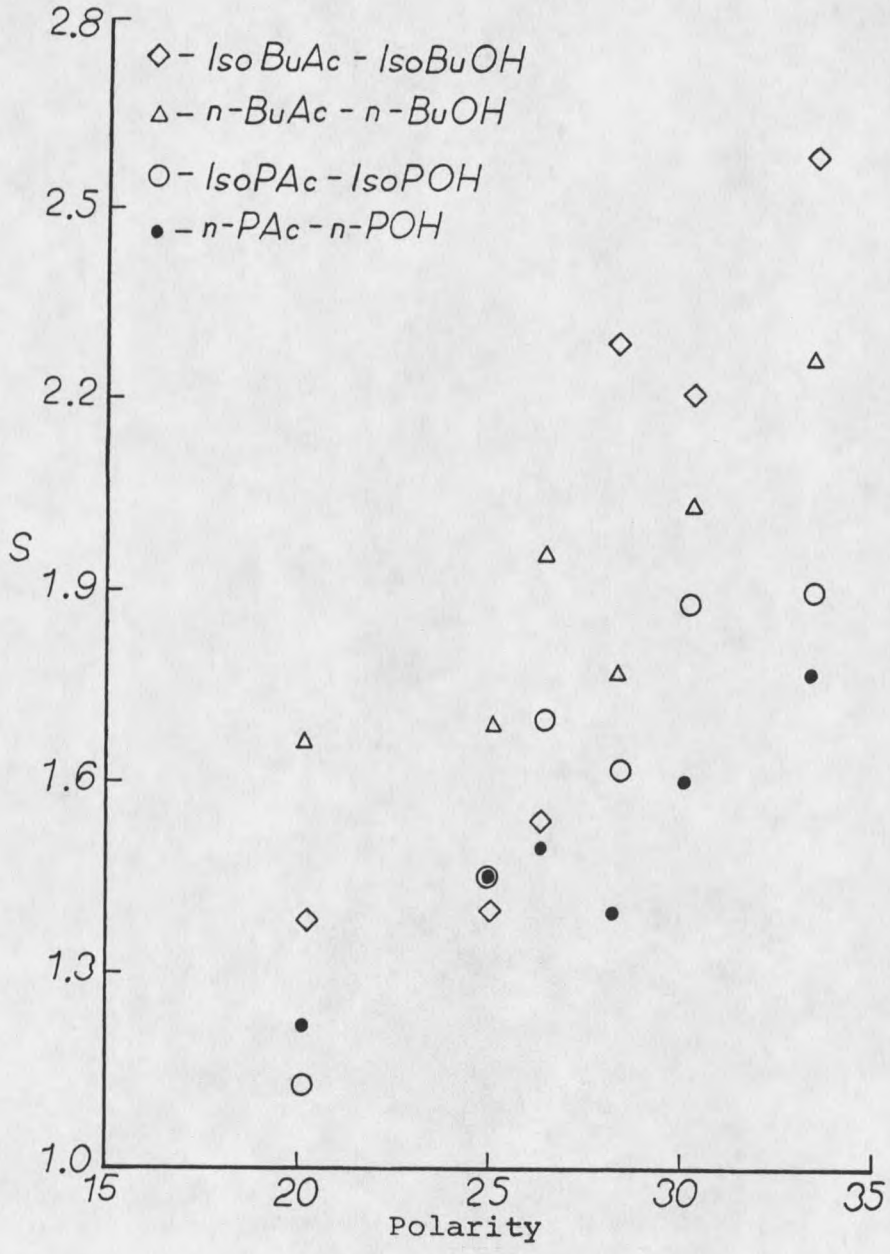
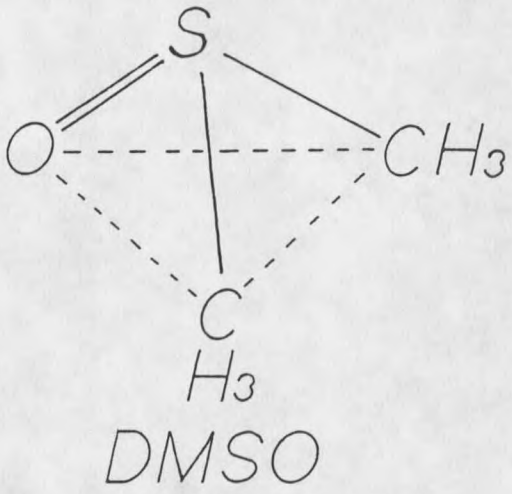


Figure 40. Selectivities of the agents with different polarity. S is the selectivity.

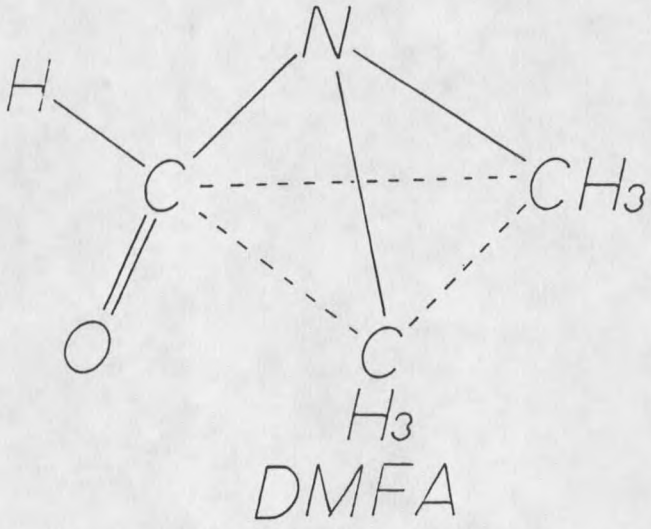
The specific volume of acetates (Table XXX) are in the increasing order of n-propyl acetate (115.9 cm^3/mole), isopropyl acetate, n-butyl acetate, and isobutyl acetate (134.2 cm^3/mole). The specific volumes of alcohols are in the same order but have smaller values. This indicates that the agent would have higher selectivity when the key components have larger specific volumes. This is due to more frequent collisions between the agent and larger molecule. However, if the agents, such as diethylene glycol, triethylene glycol, and dipropylene glycol, have comparatively large specific volume, the selectivity would not be expected in this order and was lower than that yielded by small molecules. This could be because the chance of collision between the agent and two key components was about the same probability and in a random manner.

DMSO and DMFA are aprotic agents and have similar molecular structures as presented in Figure 41. Ritchie [115] has shown that DMSO and DMFA increase the acidities of some alcohols. The increase of acidities of alcohols due to the presence of DMSO and DMFA could occur in this study. DMSO and DMFA would thus become bases. Thus a chemical complex, e.g., a Lewis acid-base complex, could form when these two agents were added. Thus DMSO and DMFA had higher selectivities.

Rouw and Somsen [120] have shown that the negative enthalpy of transfer from DMFA to water of isopropanol is higher than that of n-propanol. The difference between n-butanol and isobutanol is negligible. This could be the reason why DMFA had a higher selectivity for n-propyl acetate-n-propanol-H_2O mixture than for isopropyl acetate-isopropanol-H_2O mixture. In the mixture of n-propyl acetate-n-propanol-



DMSO



DMFA

Figure 41. Proposed conformational structures for DMSO and DMFA.

H_2O, DMFA had a more basic effect on n-propanol due to lesser intermolecular forces with water and thus has higher selectivity. The difference in selectivity of DMFA on n-butyl acetate and isobutyl acetate could be caused by the comformational structure of the molecules. The DMFA molecule could be more compatible with isobutanol due to its short chain length.

Krishnan and Friedman [121] have reported that the standard enthalpy of solution of isopropanol in DMSO (0.87 kcal/mole) is higher than that of n-propanol in DMSO (0.61 kcal/mole). The enthalpy of solution is contributed by two forces: (i) physical forces which give rise to an endothermic heat of mixing, (ii) chemical force which give rise to an exothermic heat of mixing due to the formation of a chemical complex. Thus, there is more chemical complex formed between n-propanol and DMSO. Thus DMSO has a higher selectivity for n-propyl acetate than for isopropyl acetate. Comparing n-butyl acetate and isobutyl acetate, the same reasoning for DMFA can be applied again.

V. SUMMARY

Conclusions

1. The separation of one close-boiling pair of compounds, m-xylene-o-xylene; three binary azeotropes: methyl acetate-methanol, ethanol-water, acetone-methanol; and four ternary azeotropes: n-propyl acetate-n-propanol-water, isopropyl acetate-isopropanol-water, n-butyl acetate-n-butanol-water, isobutyl acetate-isobutanol-water, can be enhanced by extractive distillation. The azeotropes can be negated and the relative volatilities of key components were reversed.

2. The separation of m-xylene from o-xylene has been enhanced by extractive distillation with a proper selection of agents, such as the mixture of dipropylene glycol dibenzoate and DMSO.

3. The relative volatility of water to ethanol can be reversed up to a limitation of water content by extractive distillation. The agents are alcohols which are water- soluble, for example, 1-pentanol.

4. Nitrogenous compounds can reverse the relative volatility of methanol and methyl acetate and negate the binary azeotrope.

5. Ketones can reverse the relative volatility of methanol to acetone and negate the binary azeotrope.

6. The acetate-alcohol-water ternary azeotropes have been negated by extractive distillation. The relative volatility of acetate to the corresponding alcohol can also be reversed.

7. The major factors which affect the solution behavior in extractive distillation are the molecular interactions between the key components and agent.

8. The polarity diagram can be used to compare the affinity of an agent for key components in binary and ternary mixtures. Thus the key component which will be the overhead product can be predicted.

9. The MOSCED model for activity coefficients can be applied successfully to all the extractive distillation systems except the aqueous systems.

10. The MOSCED model is more accurate than the polarity diagram in predicting extractive distillation behavior. However, a large amount of data is needed to apply this model. Only the three solubility parameters and specific volumes of the compounds are needed to apply the polarity diagram. Therefore, the polarity diagram is much easier than the MOSCED model for initial evaluation of the extractive distillation agents.

Recommendation for Further Studies

1. A continuous extractive distillation column would be helpful to understand the temperature inversion. The compositions and temperatures on the plates must be capable of being measured.

2. Statistical mechanics might be a good tool to investigate the temperature inversion.

3. A study of the formation and stability of chemical complexes should be undertaken to improve the understanding of the role of the chemical complex in extractive distillation.

4. A computer simulation using the model developed here should be conducted to understand the whole process and for the design of a new process.

NOMENCLATURE

NOMENCLATURE

c	cohesive energy density.
Δh	heat of vaporization in J/mol.
G^E	excess Gibbs free energy in J/mol.
m_i	molecular weight of component i, in g/mol.
n_i	mole number of component i.
n_T	total number of moles.
P	system pressure in mmHg.
p_i	saturated vapor pressure of component i, in mmHg.
p_i^o	equilibrium vapor pressure of component i, in mmHg.
q	a measure of the dipole-induced dipole energy.
R	gas constant.
s	interchange number for quasilattice.
T	temperature.
T_o	overhead temperature.
T_s	stillpot temperature.
ΔT	overhead temperature minus stillpot temperature.
U	internal energy.
ΔU^E	excess internal energy.
ΔU_I	energy to evaporate pure liquid to ideal gases.
ΔU_{II}	energy to mix ideal gases.
ΔU_{III}	energy to condense ideal-gas mixture to liquid mixture.
w_{iB}	mass of component i in liquid phase.
w_{io}	mass of component i in vapor phase.

w_{TB} total mass in liquid phase.

w_{TO} total mass in vapor phase.

w_{xi} weight percent of component i in liquid phase.

w_{yi} weight percent of component i in vapor phase.

x_i mole fraction of component i in liquid phase.

x_D distillate composition.

y_i mole fraction of component i in vapor phase.

α_{av} average relative volatility.

α_B relative volatility at the bottoms temperature.

α_{ij} relative volatility of component i to component j.

α_{ij}^s separation factor of component i relative to j.

α acidity.

α_o relative volatility at the overhead temperature.

β basicity.

δ solubility parameter in $(J/cm^3)^{1/2}$.

δ_d dispersion force of solubility parameter.

δ_h hydrogen bonding of solubility parameter.

δ_p polar interaction of solubility parameter.

ε constant proportional to the number of free coordinates.

γ activity coefficient.

γ_i^∞ infinite activity coefficient.

λ molecular polarizability.

ϕ_i fugacity coefficient of component i.

σ reflects the ability of the nonpolar part of molecule to interact with a dipole.

τ polarity of molecule.

ν molar volume in cm^3/mol.

ψ asymmetry factor.

ω_{11} pair interchange energy between 1-1 pair.

ω_{12} pair interchange energy between 1-2 pair.

ω_{22} pair interchange energy between 2-2 pair.

ξ asymmetry factor.

ζ local volume fraction.

Φ volume fraction.

Superscript:

N theoretical plates number.

Subscript:

av average

o overhead

B bottoms

p presence of agent

A absence of agent

ABBREVIATIONS

ABBREVIATIONS

Atm.	atmosphere
b.p.	boiling point
DGDB	dipropylene glycol dibenzoate
DIBK	diisobutyl ketone
DMFA	dimethyl formamide
DMSO	dimethyl sulfoxide
IBAc	isobutyl acetate
IBOH	isobutanol
IPAc	isopropyl acetate
IPE	isopropyl ether
IPOH	isopropanol
MeAc	methyl acetate
MEK	methyl ethyl ketone
MeOH	methanol
MIAK	methyl isoamyl ketone
MIBK	methyl isobutyl ketone
n.b.p.	normal boiling point
nBAc	n-butyl acetate
nBOH	n-butanol
nPAc	n-propyl acetate
nPOH	n-propanol
Temp.	temperature
VLE	vapor liquid equilibrium

LITERATURE CITED

LITERATURE CITED

1. Guillaume, E., U.S. Patent 887,793, "Rectifying of Alcoholic Liquid." May 3, (1908).

2. Benedict, M., and L. C. Rubin, "Extractive and Azeotropic Distillation, I. Theoretical Aspects." Trans. AIChE, 41:353, (1945).

3. Gerster, J. A., "Azeotropic and Extractive Distillation." Chem. Eng. Prog., 65:43, (1969).

4. Treybal, R. E., Mass-Transfer Operations., 3rd ed., New York, McGraw-Hill, Inc., (1980).

5. Sucksmith, I., "Extractive Distillation Saves Energy." Chem. Eng., p. 91, June, (1982).

6. Bojnowski, J. H. and D. L. Hanks, "Low-Energy Separation Processes." Chem. Eng., p. 67, May, (1979).

7. Hopkins, W. C. and J. J. Fritsch, "How Celanese Separates Complex Petrochemical Mixtures." Chem. Eng., 51(8):361, (1955).

8. Carlson, C. S., P. V. Smith, Jr. and C. E. Morrell, "Separation Oxygenated Organic Compounds by Water Extractive Distillation." Ind. Eng. Chem., 46:350, (1954).

9. Coburn, A. P., and E. M. Schoenborn, "The Selection of "Separating Agents" for Azeotropic and Extractive Distillation and for Liquid-Liquid Extraction." Trans. AIChE, 41:421, (1945); Errata: 41:645, (1945).

10. Gerster, J. A., "Extraction Equilibrium." Chem. Eng. Prog., 62(9):62, (1966).

11. Berg, L., "Selecting The Agent for Distillation." Chem. Eng. Prog., 65:52, (1969).

12. Butler, R. M., and J. A. Bichard, U.S. Patent 3,114,783., "Separation of Aromatics from Hydrocarbon Streams." December 17, (1963).

13. Atlani et al., French Patent 2,335,584, "Separation of Dienic, Naphthanic, and Aromatic Hydrocarbons from Cuts Containing Them, Using Cyanamide Solvents." July 15, (1977).

14. Cooper, H. B. H., and E. C. Medcalf, U.S. Patent 2,655,467., "Process for Separating Predominantly Aromatic Hydrocarbons from Predominantly Saturated Hydrocarbons by Extractive Distillation." October 13, (1953).

15. Mikitinko, P., G. Cohen, and L. Asselineau, German Patent 2,313,603. "Purification of Benzene and Toluene by Azeotropic Extractive Distillation." September 27, (1973)

16. Eisenlohr, K. H., and E. Mueller, German Patent 2,263,344., "Obtaining Pure Aromatics from Hydrocarbon Mixtures by Extractive Distillation." December 23, (1972).

17. Preusser, G., M. Schulze, K. Richter and W. Henwels, German Patent 1,960,857. "Extractive Distillation of Hydrocarbons with Morpholine Derivatives." December 4, (1969).

18. Mueller, E. and K. P. John, German Patent 1,808,758., "Separation of Pure Aromatic Hydrocarbons from Hydrocarbon Mixtures by Extractive Distillation." November 14, (1968).

19. Berg, Lloyd, U.S. Patent 4,292,142. "Separation of Ethylbenzene from para- and meta-Xylenes by Extractive Distillation." September 29, (1981).

20. Berg, L., P. Ratanapupech, and An-I Yeh, "The Use of Packed Rectification Column in Extractive Distillation." AIChE J., 30:845, (1984).

21. Othmer and Wentworth, Ind. & Eng. Chem., 32:1588, (1940).

22. Grayeon, M., ed., Kirk-Othmer Encyclopedia of Chemical Technology., 3rd ed., John Wiley & Sons Inc., (1978).

23. Schneible J., U.S. Patent 1,469,447. "Absolute Alcohol." October 2, (1923).

24. Smith, P. V. and C. S. Carlson, U.S. Patent 2,559,519. "Extractive Distillation of Alcohols with Glycol Ethers." assigned to Standard Oil Co., July 3, (1951).

25. Catterall, U.S. Patent 2,591,671. "Dehydration of Alcohols by Extractive Distillation." April 8, (1952).

26. Drout, W. M. and J. W. Dowling, French Patent 1,020,351. February 5, (1953).

27. Washall, T. A., U.S. Patent 3,464,896. "Separation of Water from A Single Alcohol by Extractive Distillation with Ethylene Glycol." September 2, (1969).

28. Berg, L. and An-I Yeh, U.S. Patent 4,543,164. "Separation of Methyl Acetate from Methanol by Extractive Distillation." September 24, (1985).

29. Yeh, An-I, "The Separation of Three Azeotropes by Extractive Distillation." M.S. Thesis, Montana State University, Montana, August, (1983).

30. Horsely, L. H.; Azeotropic Data-III. Advances in Chemistry Series 116, American Chemical Society, (1973).

31. Britton, E. C., H. S. Nutting, and L. H. Horsley, U.S. Patent 2,324,255, "Separation of Ketones and Monohydric Alcohols from Mixtures Thereof." July 13, (1943).

32. Windholz, M., The Merck Index: An Encyclopedia of Chemicals and Drugs, 9th ed., Merck & Co. Inc., N.J., (1976).

33. Dean, J. A. Lange's Handbook of Chemistry, 11th ed., McGraw-Hill Book Co., New York, (1973).

34. Fenske, M. R., "Fractionation of Straight-Run Pennsylvania Gasoline." Ind. Eng. Chem., 24:482, (1932).

35. Scheibel, E. G., "Principles of Extractive Distillation." Chem. Eng. Prog., 44:929, (1948).

36. Van Winkle, M., Distillation., New York: McGraw-Hill Inc., (1967).

37. Hildebrand, J. H., and R. L. Scott, "Solubility of Nonelectrolytes., 3rd ed., Am. Chem. Soc. Monograph Series, New York: Reinhold, (1950).

38. Van Arkel, A. E., "Mutual Solubility of Liquids." Trans. Faraday Soc., 42B:81, (1946).

39. London, F., "The General Theory of Molecular Forces." Trans. Faraday Soc., 33:8, (1937).

40. Ewell, R. H., J. M. Harrison, and L. Berg, "Azeotropic Distillation." Ind. Eng. Chem., 36:871, (1944)

41. Prausnitz, J. M., and R. Anderson, "Thermodynamics of Solvent Selectivity in Extractive Distillation of Hydrocarbons." AIChE J., 7:96, (1961).

42. Anderson, R., R. Cambio, and J. M. Prausnitz, "Physical and Chemical Forces in Solvent Selectivity for Hydrocarbons." AIChE J., 8:66, (1962).

43. Guggenheim, E. A., Mixtures, Oxford U.P., London, (1952).

44. Redlich, O., and A. T. Kister and C. E. Turnquist, "Thermodynamics of Solutions: Analysis of Vapor-Liquid Equilibria." Chem.Progr. Symp. Ser., 48(2):49, (1952).

45. Margules, M., Sitoungsber. Akad. Wiss. Wien, Math. Naturwiss. Klasse, 104:1243, (1895).

46. van Laar, J. J., Z. Phys. Chem., 72:723, (1910).

47. van Laar, J. J., Z. Phys. Chem., 185:35, (1929)

48. Hildebrand, J. H., J. M. Prausnitz, and R. L. Scott, Regular and Related Solutions, Van Nostrand Reinhold, New York, (1970).

49. Hildebrand, J. H., and R. L. Scott, Regular Solutions, Prentice-Hall, Englewood Cliffs, N. J., (1962).

50. Hildebrand, J. H., and R. L. Scott, The Solubility of Nonelectrolytes, 3rd ed., Dover, New York, (1964).

51. Flory, P. J., "Thermodynamics of High Polymer Solutions." J. Chem. Phys., 9:660, (1941).

52. Flory, P. J., "Thermodynamics of HIgh Polymer Solutions." J. Chem. Phys., 10:51, (1942).

53. Flory, P. J., Principles of Polymer Chemistry, Cornell U. P., Ithaca, N. Y., (1953).

54. Huggins, M. L., "Solutions of Long Chain Compounds." J. Chem. Phys., 9:440, (1941).

55. Huggins, M. L., "Thermodynamic Properties of Solutions of Long-Chain Compounds." Ann. N. Y. Acad. Sci., 43:1, (1942).

56. Wilson, G. M., "Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing." J. Am. Chem. Soc., 86:127, (1964).

57. Eckert, C. A., J. M. Prausnitz, K. V. Orye, and J. P. O'Connell, AIChE-Inst. Chem. Eng. Symp., Ser. 1, 75, (1965).

58. Orye, R. V. and J. M. Prausnitz, "Multicomponent Equilibria with the Wilson Equation." Ind. Eng. Chem., 57(5):18, (1965).

59. J. M. Prausnitz, C. A. Eckert, R. V. Orye, and J. P. O'Connell, Computer Calculations for Multicomponent Vapor-Liquid Equilibria., Prentice-Hall Englewood Cliffs, N.J., (1967).

60. Renon, H., and J. M. Prausnitz, "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures." AIChE J., 14:135, (1968).

61. Hsieh, C. K., and C. A. Eckert, "The Zeta-Equation - A New Solution to the Gibbs Duhem Equation." Presented at the 71st National AIChE Meeting, Tulsa, Okla., March 12, (1974).

62. Small, P. A., "Some Factors Affecting the Solubility of Polymers.", J. Appl. Chem., 3:71, (1953).

63. Anderson, R., Ph.D. Thesis, Dept. of Chemical Engineering, U. of California, Berkeley, (1961).

64. Blanks, R. F., and J. M. Prausnitz, "Thermodynamics of Polymer Solubility in Polar and Nonpolar System." Ind. Eng. Chem. Fundam., 3:1, (1964).

65. Kumar, R., and J. M. Prausnitz, "Solvents in Chemical Technology", in Solutions and Solubilities, part I, Dack, M. R. J., Ed., John Wiley & Sons Interscience, New York, (1975), chap. 5.

66. Weimer, R. F., and J. M. Prausnitz, "Screen Extraction Solvent This Way." Hydrocarbon Process Petr. Ref., 44:237, (1965).

67. Hansen, C. M., "Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient. Importance in Surface Coating Formulation." Doctoral Dissertation, Danish Technical Press, Coperhagen, (1967).

68. Hansen, C. M., "The Three Dimensional Solubility Parameter - Key to Paint Component Affinities. I. Solvents, Plasticizers, Polymers, and Resins." J. Paint Technol., 39:104, (1967).

69. Hansen, C. M., "The Three Dimensional Solubility Parameter - Key to Paint Affinities. II. Dyes, Emulsifiers, Mutual Solubility and Compatibility, and Pigments." J. Paint Technol., 39:505, (1967).

70. Hansen, C. M., "On the Application of the Three Dimensional Solubility Parameter Concept to the Prediction of Mutual Solubility and Compatibility." Skand. Tidskr.Faerg. Lack, 13:132, (1967).

71. Hansen, C. M., "The Three Dimensional Solubility Parameter and Its Use. I. Introduction and Non-pigment Systems, Skand. Tidskr. Faerg. Lack, 14:14 and 23, (1968). (English)

72. Hansen, C. M., "The Universality of the Solubility Parameter." Ind. Eng. Chem. Prod. Res. Dev., 8:2, (1969).

73. Hansen, C. M., "Characterization of Surface by Spreading Liquids." J. Paint Technol., 42:660, (1970).

74. Hansen, C. M., "Solubility in Coating Industry." Skand. Tidskr. Faerg. Lack, 17:69, (1971). (English)

75. Hansen, C. M., "Surface Dewetting and Coatings Performance." J. Paint Technol., 44(570):57, (1972).

76. Hansen, C. M., "Solvents for Coating." Chemtech, 2:547, (1972).

77. Hansen, C. M., "Solvent Selection by Computer" in Solvent Theory and Practice, (Adv. Chem. Ser. 124), Tess, R. W., Ed., American Chemical Society, Washington, D.C., (1973), chap. 4

78. Hansen, C. M., "Solvents in Water-Borne Coatings." Ind. Eng. Chem. Prod. Res. Dev., 16:266, (1977).

79. Hansen, C. M., "Advances in the Technology of Solvents in Coatings." FATIPEC (Fed. Assoc. Tech. Ind. Paint. Vernis, Emoux Encres Impr. Eur. Cont.) Congr., 14:97, (1978).

80. Hansen, C. M., and A. Beerbower, "Solubility Parameter" in Kirk-Othmer Encyclopedia of Chemical Technology, Suppl. Vol., 2nd ed., Standen, A., Ed., Interscience, New York, (1971), 889.

81. Hansen, C. M., and P. E. Pierce, "Surface Effects in Coating Processes.", Ind. Eng. Chem. Prod. Res. Dev., 13:218, (1974).

82. Hansen, C. M., and K. Skaarup, "The Three Dimensional Solubility Parameter - Key to Paint Component Affinities. III. Independent Calculations of the Parameter Components." J. Paint Technol., 39:511, (1967).

83. Beerbower, A., "Surface Free Energy: A New Relationship to Bulk Energies." J. Colloid Interface Sci., 35:126, (1971).

84. Boetcher, C. J. F., Theory of Electric Polarisation, Elsevier, New York, (1952).

85. Peiffer, D., "The Molecular Factors Affecting the Solubility Parameters." J. Appl. Polym. Sci., 25:369, (1980).

86. Arkel, V. A. E., and S. E. Vlex, "Loslichkeit von Organischen Verbindunden in Wasser." Recl. Trav. Chem., 55:407, (1936).

87. Gordon, J. L., J. Paint Technol., 38:43, (1966).

88. Helpinstill, J. G., and M. van Winkle, "Prediction of Infinite Dilution Activity Coefficients for Polar-Polar Binary Systems." Ind. Eng. Chem. Process. Des. Dev., 7:213, (1968).

89. Nelson, R. C., R. W. Hemwall, and G. D. Edwards, "Treatment of Hydrogen Bonding in Predicting Miscibility." J. Paint Technol., 42:636, (1970).

90. Keller, R. A., B. L. Karger, and L. R. Snyder, "Use of the Solubility Parameter in Predicting Chromatographic Retention and Eluotropic Strength." Gas Chromatogr. Proc. Int. Symp. (Eur.), 8:125, (1971).

91. Hsieh, C. K. R., "Molecular Thermodynamics and High Pressure Kinetics of Polar Reactions in Solutions." Ph.D. Thesis, University of Illinois, Urbana, Il, (1973).

92. Barton, A. F. M., "Solubility Parameters." Chem. Rev., 75(6):731, (1975).

93. Koenhen, D. M., and C. A. Smolders, The Determination of Solubility Parameters of Solvents and Polymers by Means of Correlations with Other Physical Quantities." J. Appl. Poly. Sci., 19:1163, (1975).

94. Karger, B. L., L. R. Snyder, and C. Eon, "An Expanded Solubility Parameter Treatment for Classification and Use of Chromatographic Solvents and Adsorbents: Parameters for Dispersion, Dipole and Hydrogen Bonding Interactions." J. Chromatogr., 125:71, (1976).

95. Tijssen, R., H. A. H. Billet, and P. Schoenmakers, "Use of The Solubility Parameter for Predicting Selectivity and Retention in Chromatography."J. Chromatogr., 122:185, (1976).

96. Karger, B. L., L. R. Snyder, and C. Eon, "Expanded Solubility Parameter Treatment for Classification and Use of Chromatographic Solvents and Adsorbents." Anal. Chem., 50(14):2126, (1978).

97. Newman, B. A., "Molecular Thermodynamics of Polar Reactions." Ph.D. Thesis, University of Illinois, Urbana, IL., (1977).

98. Thomas. E. R., and C. A. Eckert, "Prediction of Limiting Activity Coefficients by A Modified Separation of Cohesive Energy Model and UNIFAC." Ind. Eng. Chem. Process Des. Dev., 23(2):194, (1984).

99. Ratanapupech, P., "Separation of Ethyl Acetate and Ethanol from Methyl Ethyl Ketone and Water, and Ethyl Acetate from Ethanol and Water by Extractive Distillation." Ph.D. Dissertation, Montana State University, February, (1982).

100. Harper, B. G., and J. C. Moore, "Vapor-Liquid Equilibrium - New Still and Method for Determining Vapor-Liquid Equilibrium." Ind. Eng. Chem., 49:411, (1957).

101. Eggen, A. C., "Vapor-Liquid Equilibria and Computer Curve Fitting of Vapor Liquid Equilibrium Data." Report of Senior Individual Project in Chemical Engineering Department, Montana State University, (1984).

102. Hawley, G. G., The Condensed Chemical Dictionary, 3rd ed., Van Nostrand Reinhold Company Inc., New York, (1981).

103. Weast, R. C., CRC Handbook of Chemistry and Physics, 65th ed., CRC Press, Inc., Boca Raton, FL., (1984).

104. Berg, L., and An-I Yeh, "The Unusual Behavior of Extractive Distillation - Reversing the Volatility of the Acetone-Isopropyl Ether System." AIChE J., 31:504, (1985).

105. Berg, L. and An-I Yeh, U.S. Patent appl. 06/752,784. "Dehydration of Ethanol by Extractive Distillation." July 8, 1985.

106. Berg, L. and An-I Yeh, U.S. Patent 4,549,938. "Separation of Methanol from Methyl Acetate by Extractive Distillation." October 29, (1985).

107. Berg, L. and An-I Yeh, U.S. Patent 4,501,645. "Extractive Distillation of Methanol and Acetone." February 26, (1985).

108. Warren, K J., Personal communications.

109. Smith, J. M., "Thermodynamic Properties of Methyl Alcohol." Chem. Eng. Prog., 44(7):521, (1948).

110. Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, The Properties of Gases and Liquids., 3rd ed., McGraw-Hill Book Company, New York, (1977).

111. Christensen, J. J., Hanks, R. W., and Izatt, R. M., Handbook of Heats of Mixing, John Wiley & Sons, Inc., New York, (1982).

112. Copley, M. J., E. Ginsberg, G. F. Zellhoefer, and C. S. Marvel. "Hydrogen Bonding and the Solubility of Alcohols and Amines in Organic Solutions." J. of American Chemical Society., 63:254, (1941).

113. Buell, C. K., and R. G. Boatright, "Furfural Extractive Distillation for Separating of C_4 Hydrocarbons." Ind. Eng. Chem., 39:695, (1947).

114. Barton, Allan E. M., editor, Handbook of Solubility Parameters and Other Cohesion Parameters., CRC Press, Inc., (1983).

115. Ritchie, C. D., and J. E. Coetzee, Solute-Solvent Interactions, Marcel Dekker Inc., New York, (1969).

116. Berg, L., and An-I Yeh, U.S. Patent 4,507,176. "Separation of n-Butyl Acetate from n-Butanol by Extractive Distillation." March 25, (1985).

117. Berg, L., and An-I Yeh, U.S. Patent 4,525,245. "Separation of n-Butyl Acetate from n-Butanol by Extractive Distillation." June 25, (1985).

118. Berg, L., and An-I Yeh, U.S. Patent appl. 06/624,338. "Separation of n-Propyl Acetate from n-Propanol by Extractive Distillation." June (1984).

119. Berg, L., and An-I Yeh, U.S. Patent appl. 06/709,415. "Separation of Isobutyl Acetate from Isobutanol by Extractive Distillation." March (1985).

120. Rouw, A. C., and G. Somson, "The Solvation of Some Alcohols in Binary Solvents: Enthalpies of Solution and Enthalpies of Transfer." J. Chem. Thermodynamics. 13:67, (1981).

121. Krishnan, C. V. and H. L. Fridman, "Solvation Enthalpies of Various Nonelectrolytes in Water, Propylene Carbonate, and Dimethyl Sulfide." The J. of Phy. Chem., 73(5):1572, (1969).

122. Perry, Robert H., and C. H. Chilton. Chemical Engineers' Handbook., 5th edition, McGraw-Hill Book Co., New York, (1973).

APPENDICES

APPENDIX A

PARAMETER ESTIMATION FOR MOSCED MODEL

APPENDIX A

Parameter Estimation for MOSCED Model

The methods for estimating the parameter values for MOSCED model are presented by Thomas and Eckert [76] and cited as follows:

(1) The liquid molar volume, ν. The liquid molar volume was taken as that at 20°C and was assumed constant at all temperatures.

(2) The dispersion parameter, λ. The equations used for estimating λ are as follows:

$$f(n_D) = (n_D^2 - 1)/(n_D^2 + 2) \quad (1)$$

where n_D is the refractive index at 20°C.

$$\lambda_{NA} = 20.3f(n_D) + 3.02 \quad (2)$$

$$\lambda_{AR} = 19.5f(n_D) + 2.79 \quad (3)$$

where λ_{NA} is for nonaromatic compounds, and

λ_{AR} is for aromatic compounds.

(3) The induction parameter, q. For saturated molecules q was given a value of 1.0. A value of 0.9 was given for aromatics and for unsaturated aliphatics q was found by

$$q = 1.0 - (\text{no. C=C})/(\text{no. C}_{\text{atoms}}) \quad (4)$$

(4) The polar parameter, τ. For most monofunctional and primary alkanes, a group approach was used to calculate τ when possible.

$$\tau = C_\tau 4.5(1+(\text{no. C}-1)/100)/(3.5+\text{no. C}) \quad (5)$$

where C_τ is a constant for a particular group and no. C is the number of skeletal carbon atoms.

Without the groups approach, the equation

$$\tau = 33\mu/v^{3/4} \tag{6}$$

will give reasonable approximations for nonalcohols and nonaromatics.

(5) The acidity and basicity parameters, α and β. No satisfactory method of accurately correlating α and β could be found.

The temperature dependence of the parameters are as follows:

$$\tau_T = \tau_{293}(293/T)^{0.4} \tag{7}$$

$$\alpha_T = \alpha_{293}(293/T)^{0.8} \tag{8}$$

$$\beta_T = \beta_{293}(293/T)^{0.4} \tag{9}$$

(6) The asymmetry factors, ψ and ξ. Both ψ and ξ are the asymmetry factors and considered functions only of τ, q, and the degree of association, $\alpha\times\beta$, of the solvent. Thomas and Eckert [76] proposed the following equations to calculate ψ and ξ.

$$POL = q^4(1.15-1.15\exp(-0.020\tau_T^3))+1 \tag{10}$$

$$t = 293/T \tag{11}$$

$$\psi = POL + 0.011\alpha_T\beta_T \tag{12}$$

$$\xi = 0.68(POL-1) + (3.4-2.4\exp((\alpha_o\beta_o)^{1.5}(-0.023)))^{t^2} \tag{13}$$

In the above expressions, a subscript o refers to 20°C and a subscript T represents the temperature of the system.

(7) The combinatorial term, d_{12}. The combinatorial term, d_{12}, was calculated by the equation as follows.

$$d_{12} = \ln (v_2/v_1)^{aa} + 1 - (v_2/v_1)^{aa} \tag{14}$$

where aa was calculated as

$$aa = 0.953 - 0.00968(\tau_2^2+\alpha_2\beta_2) \qquad (2 = \text{solvent}) \tag{15}$$

APPENDIX B

CALCULATED PARAMETER VALUES FOR MOSCED MODEL

APPENDIX B

Calculated Parameter Values for MOSCED Model

The original data was taken from the data set reported by Thomas and Eckert [76]. The temperature dependence equations were used to calculate the parameter values at the temperature of 321°K. However, it was found that the temperature effect on the relative volatilities was very small at the temperature range from 293 to 343°K. The temperature range was used in this study. The calculated parameter values with the temperature correction are listed in Tables XXXIV and XXXV.

Table XXXIV. The calculated parameter values for MOSCED model used for the methanol-acetone system.

Compound	ν	λ	τ	α	β	ψ	ξ	aa
Methanol	40.5	7.14	2.46	6.93	6.93	1.82	3.26	0.43
Methyl acetate	79.3	7.52	3.20	0.0	3.56	1.55	1.38	0.85
Nitrobenzene	102.3	8.95	3.64	0.59	1.26	4.09	1.35	-
Nitromethane	53.7	7.73	6.02	1.21	2.23	2.48	2.01	-
Nitroethane	72.0	7.85	4.68	0.27	2.05	3.48	1.70	-
1-Nitropropane	89.0	7.96	4.00	0.23	1.75	4.21	1.58	-
2-Nitropropane	90.1	7.88	3.98	0.21	1.72	4.27	1.57	-

Table XXXV. The calculated parameter values for MOSCED model used for the methanol-methyl acetate system.

Compound	ν	λ	τ	α	β	ψ	ξ	aa
Methanol	40.5	7.14	2.46	6.93	6.93	1.82	3.26	0.43
Acetone	74.4	7.49	3.95	0.0	4.53	1.82	1.55	0.79
Methyl ethyl ketone	89.6	7.71	3.13	0.0	3.76	2.68	1.36	-
2-Pentanone	106.5	7.83	2.67	0.0	3.19	3.26	1.25	-
3-Pentanone	105.8	7.86	2.67	0.0	3.19	3.26	1.25	-
MIBK	125.1	7.89	2.33	0.0	2.79	3.76	1.18	-
Diisobutyl ketone	176.6	8.07	1.54	0.0	2.23	4.25	1.06	-
Acetophenone	116.9	8.79	2.91	0.80	2.91	2.44	1.39	-

MIBK: Methyl isobutyl ketone.

APPENDIX C

THE PROGRESSION OF THE OVERHEAD AND STILLPOT TEMPERATURES FOR METHANOL-ACETONE SYSTEM

APPENDIX C

The Progression Of The Overhead And Stillpot Temperatures For Methanol-Acetone System

The overhead and stillpot temperature for the methanol-acetone system with and without agents is shown in Figures 42-51. They were obtained in the same manner as described previously. The initial mixtures contained methanol 7 wt.% and acetone 93 wt.% except the data shown in Figure 43 which had the initial mixture of 25 wt.% methanol and 75 wt.% acetone. The data in Figure 42 was obtained from a blank run.

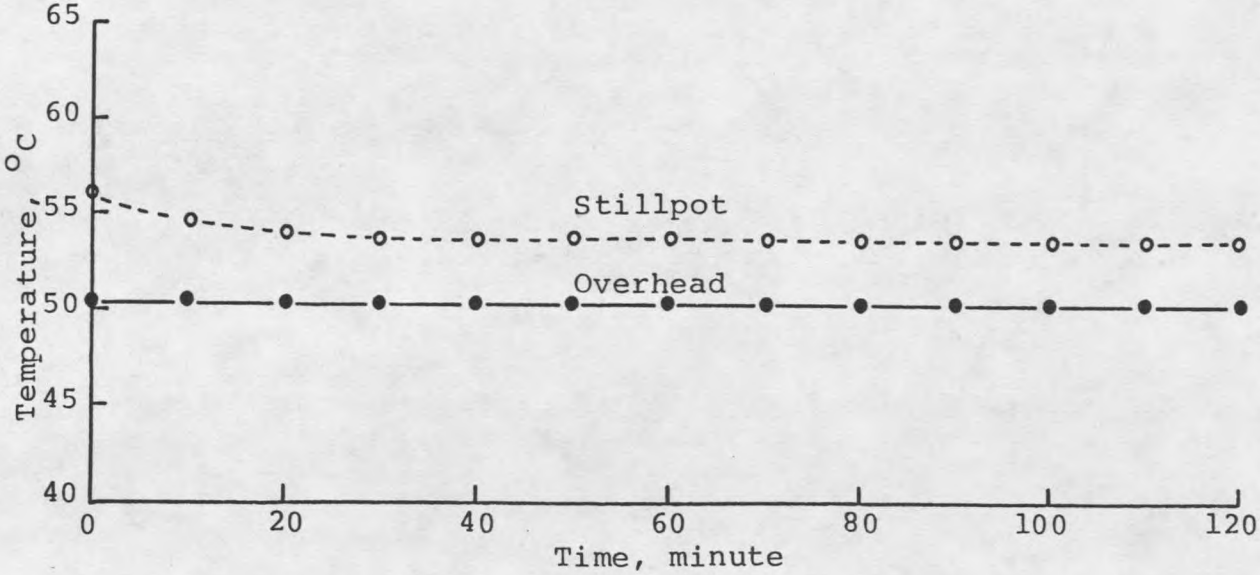


Figure 42. The progression of the overhead and stillpot temperatures for methanol-acetone system without agents.

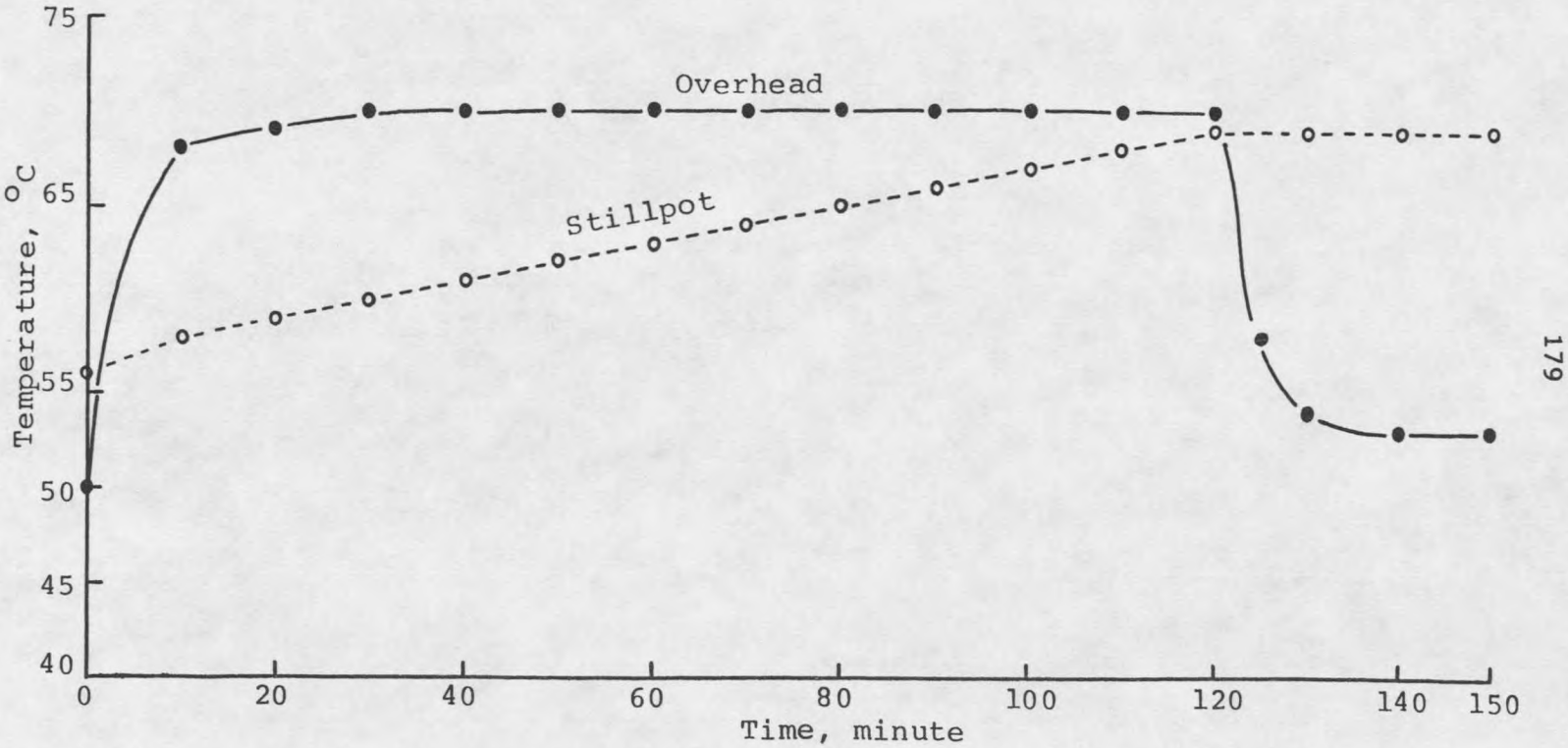


Figure 43. The progression of the overhead and stillpot temperatures for methanol-acetone system with different initial composition and an agent of MEK. The initial mixture contained 25 wt.% methanol and 75 wt.% acetone.

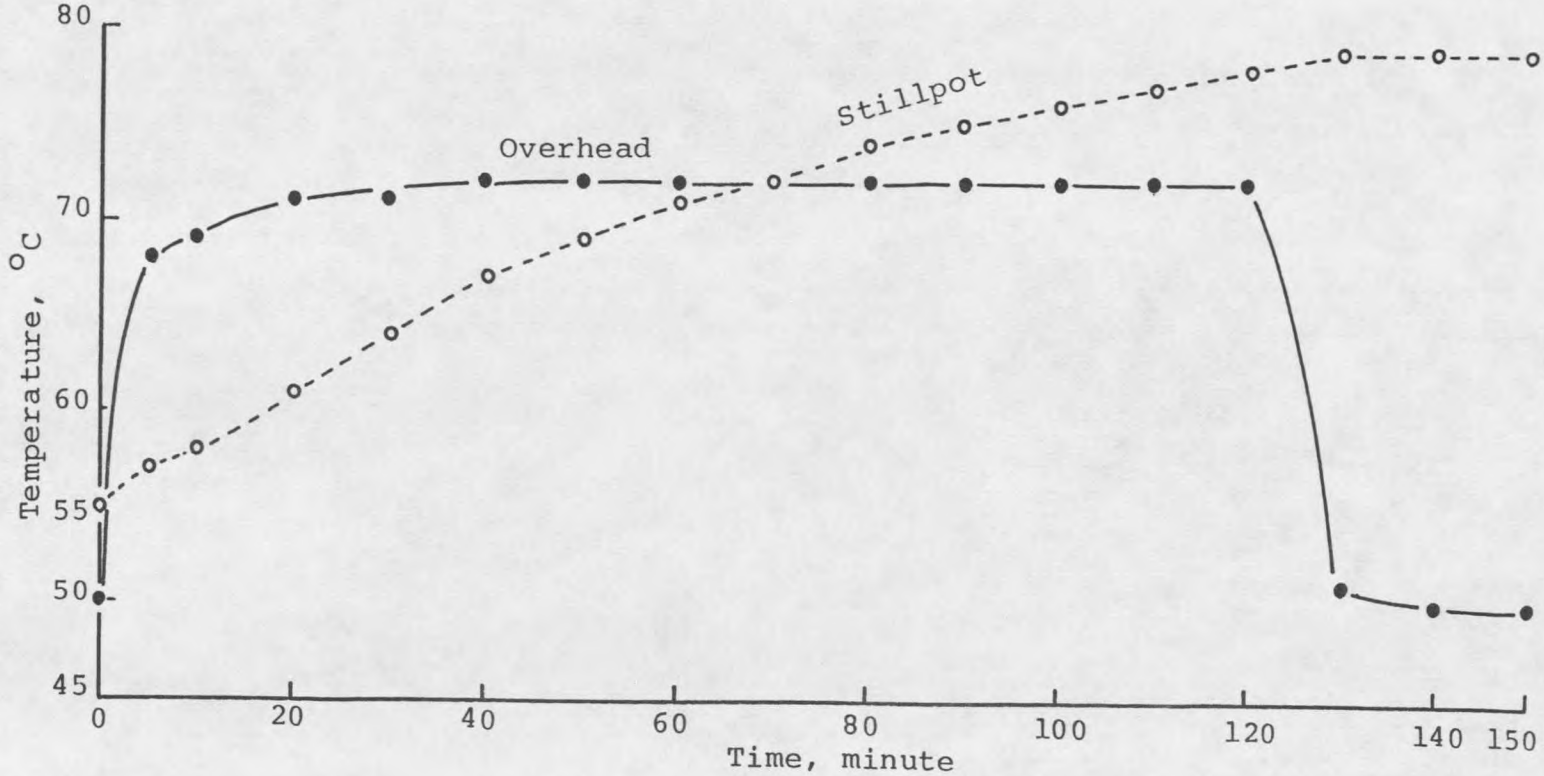


Figure 44. The progression of the overhead and stillpot temperatures for methanol-acetone system with 2-pentanone as the agent.

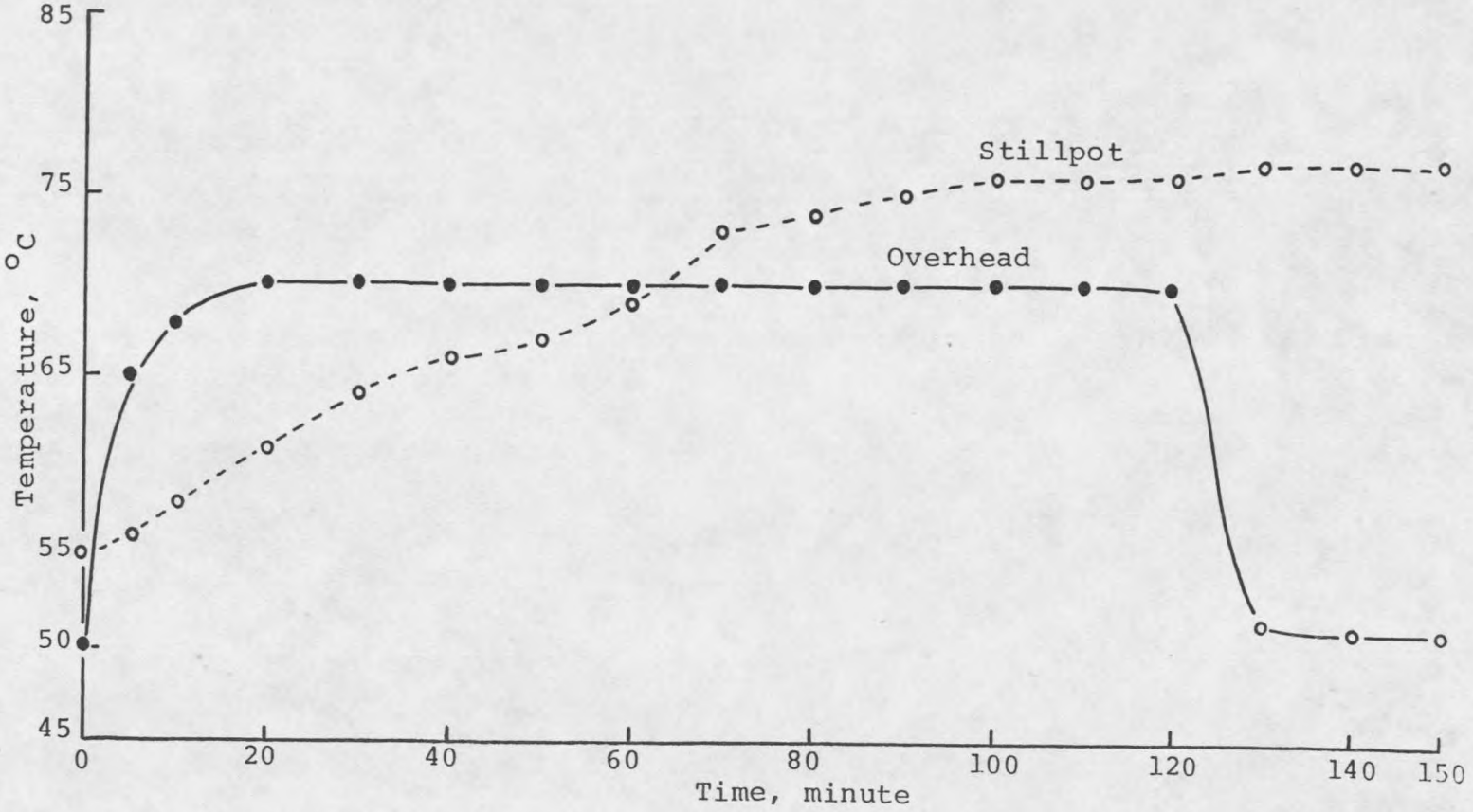


Figure 45. The progression of the overhead and stillpot temperatures for methanol-acetone system with 3-pentanone as the agent.

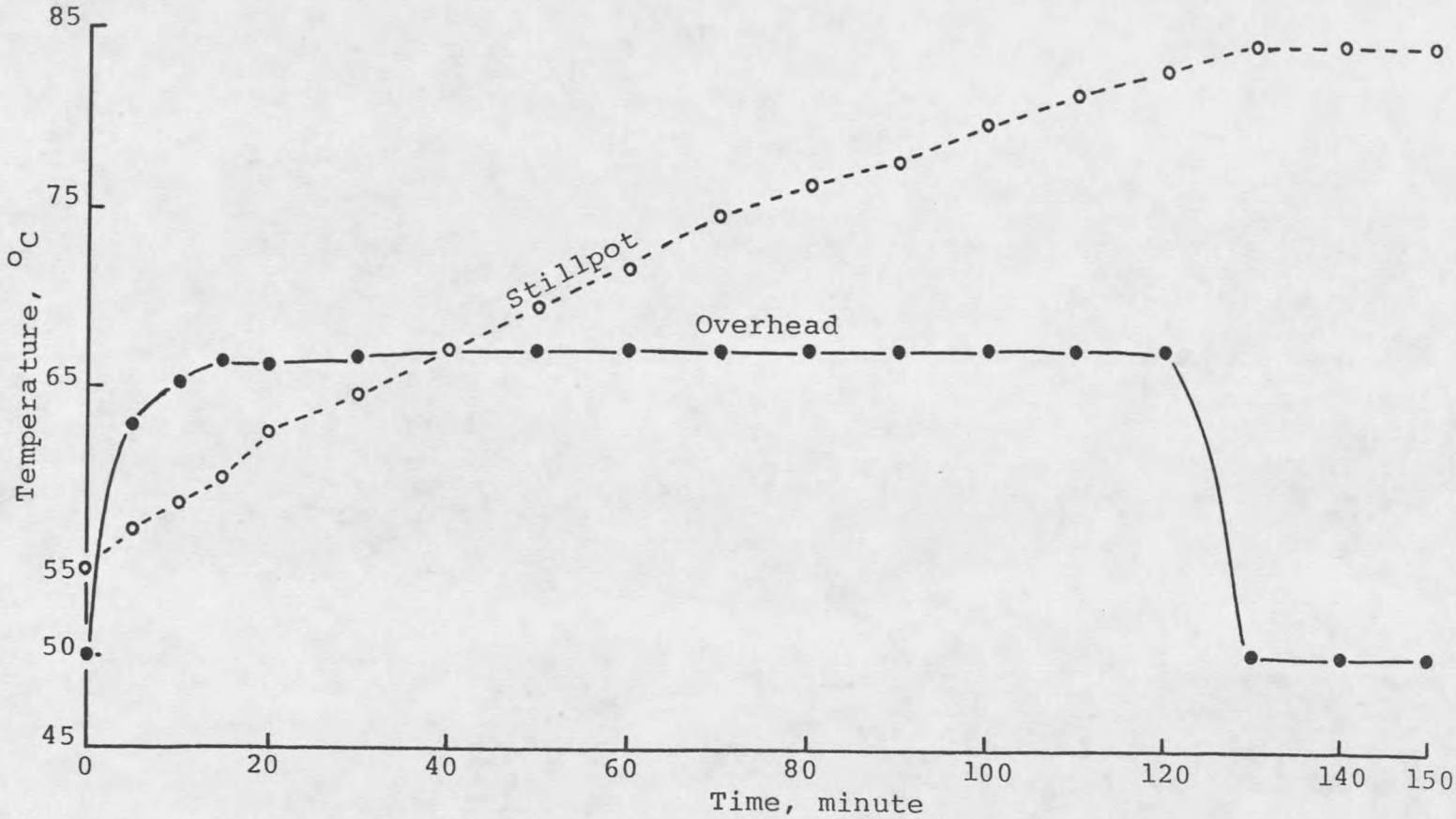


Figure 46. The progression of the overhead and stillpot temperatures for methanol-acetone system with methyl isoamyl ketone as the agent.

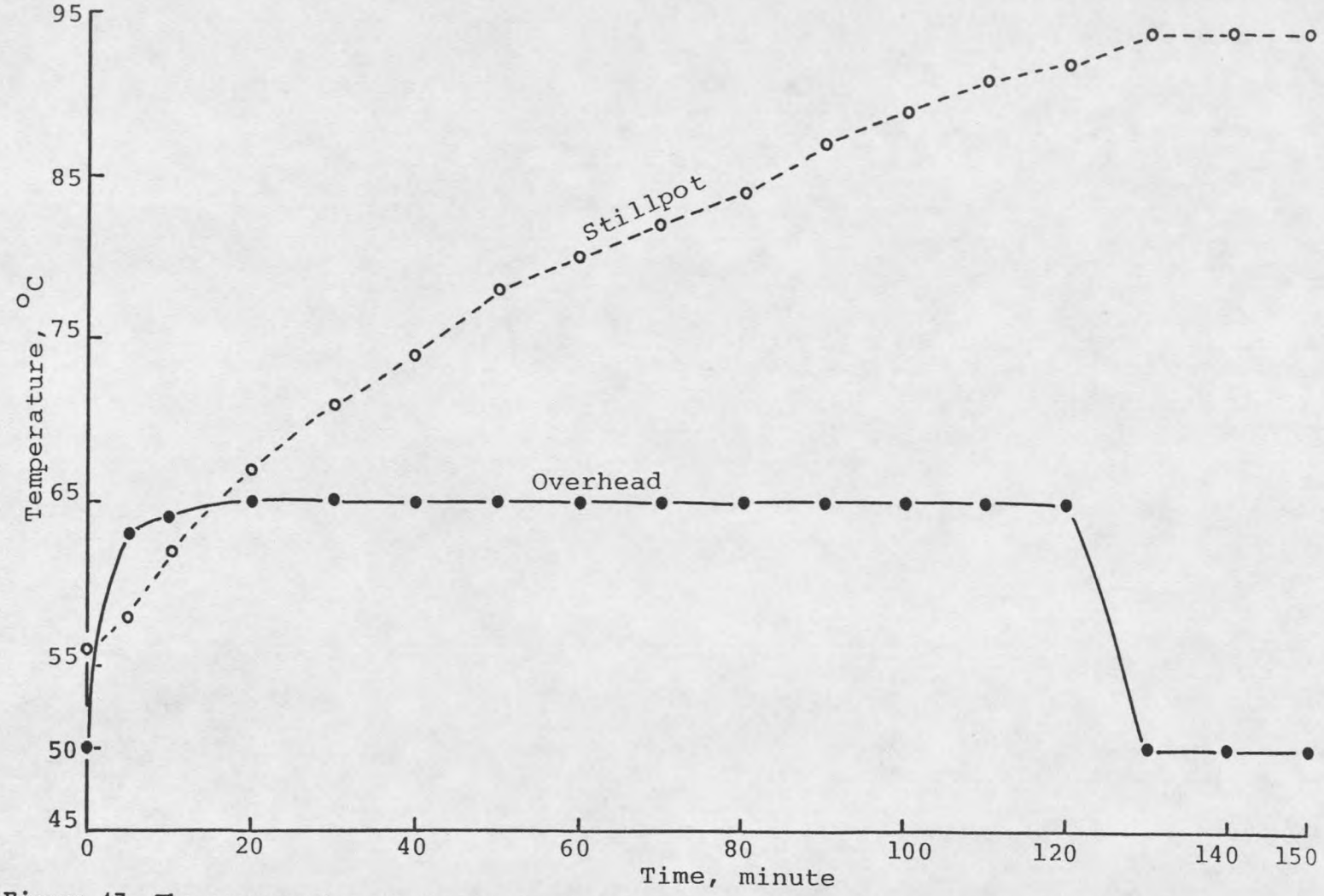


Figure 47. The progression of the overhead and stillpot temperatures for methanol-acetone system with 2,4-pentanedione as the agent.

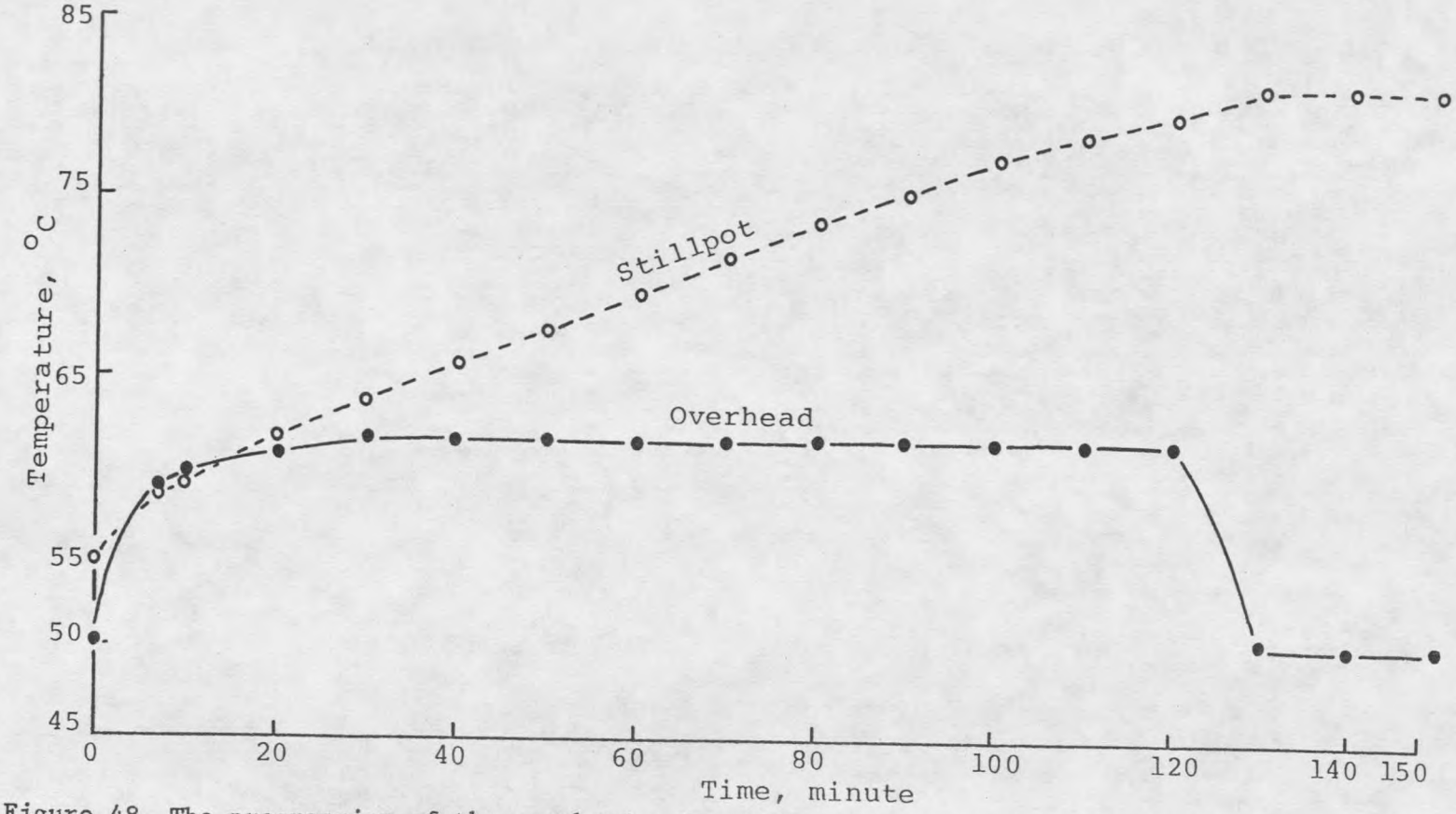


Figure 48. The progression of the overhead and stillpot temperatures for methanol-acetone system with diisobutyl ketone as the agent.

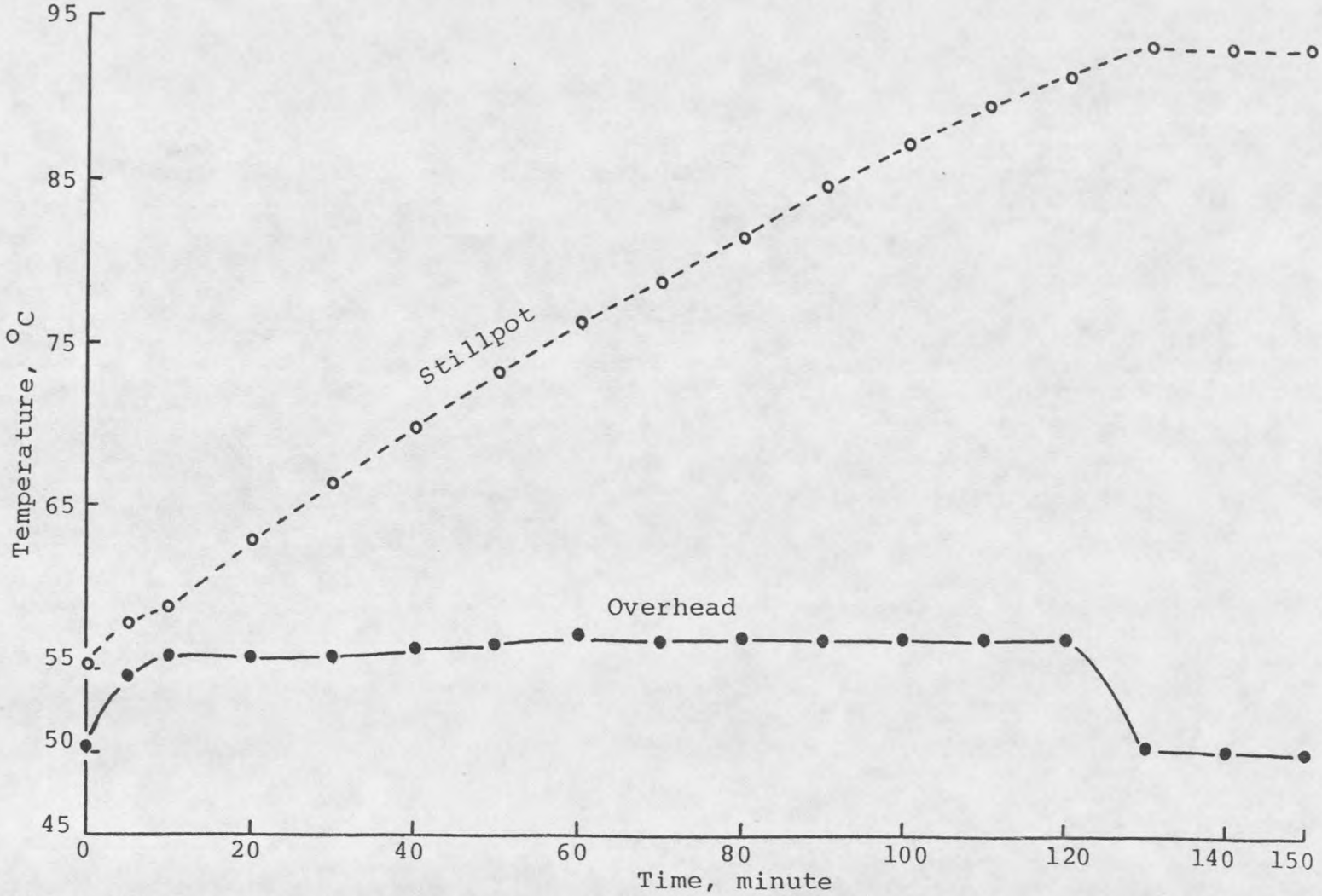


Figure 49. The progression of the overhead and stillpot temperatures for methanol-acetone system with acetophenone as the agent.

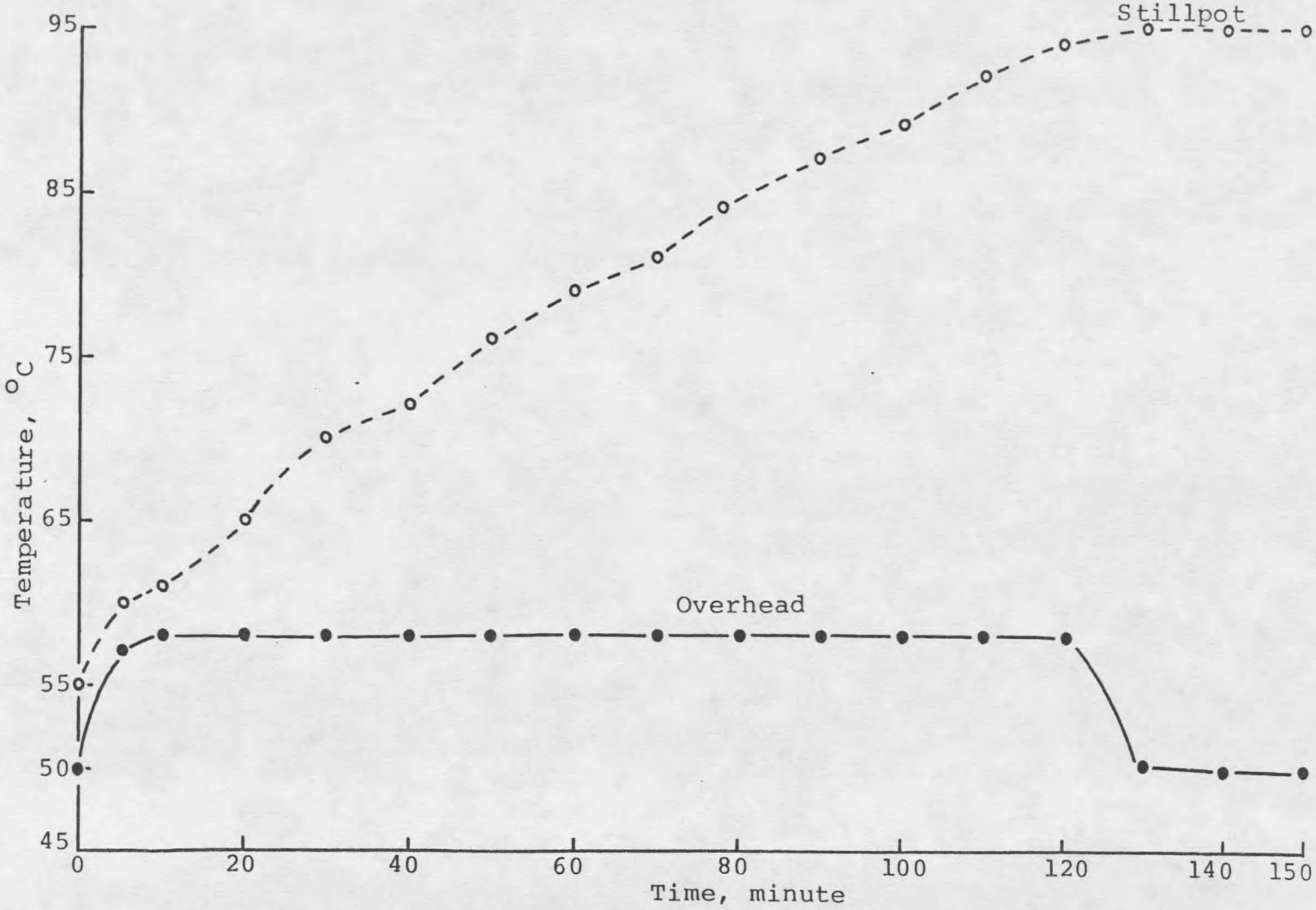


Figure 50. The progression of the overhead and stillpot temperatures for methanol-acetone system with ethyl acetoacetate as the agent.

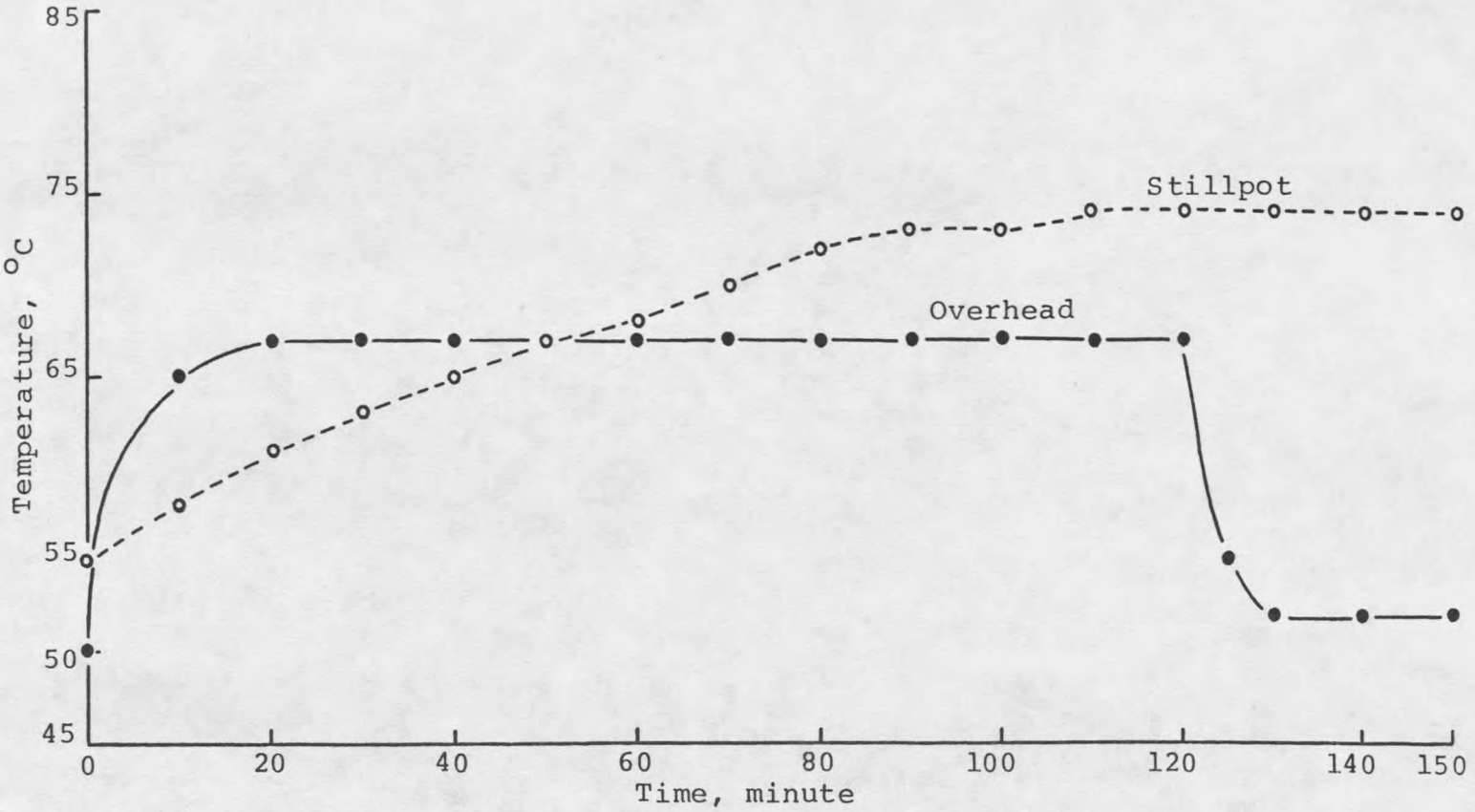


Figure 51. The progression of the overhead and stillpot temperatures for methanol-acetone system with the mixture of benzil and MEK as the agent.

APPENDIX D

HYPOTHETICAL CALCULATION FOR TEMPERATURE INVERSION

APPENDIX D

Hypothetical Calculation for Temperature Inversion

The assumption for this calculation is that the mole fraction solubilities of the vapor of methanol and ethanol in the liquid methyl ethyl ketone is 0.15 [112]. The thermodynamic data [122] are listed as follows:

Specific gravity:

Methanol : 0.792

Acetone : 0.792

MEK : 0.805

Latent heats:

Methanol : 8420.1 cal/mole (60 - 65°C)

Acetone : 7230.96 cal/mole (50 - 60°C)

MEK : 7637.55 cal/mole (78.2°C)

Specific heat:

Methanol : 18.88 cal/mole°C (5 - 20°C)

Acetone : 29.81 cal/mole°C (3 - 22.6°C)

MEK : 39.53 cal/mole°C (20 - 78°C)

The flow rate of MEK is 20 ml/min. which was measured. Thus the molal flow rate of MEK is 0.223 mole/min. The flow rate of the vapor is approximately the same as the total reflux rate which is about 40 ml/min. which also is 0.989 mole/min.

Let the calculation be based on one minute. The moles of methanol or acetone which dissolve into the liquid MEK is 0.03345 mole.

$0.223 \times 0.15 = 0.03345$ moles

For methanol:

0.03345 mole × 8420.1 cal/mole = 281.65 cal (latent heat given up by methanol)

0.223 mole × (70-45°C) × 39.53 cal/mole°C

= 220.38 cal (heat required to heat up liquid MEK from 45°C to 70°C)

281.65 cal - 220.38 cal = 61.27 cal

(61.27 cal)/(7637.55 cal/mole) = 0.008 mole (moles of MEK vaporized which is very small compared with 0.223 mole and compares favorably with measured vapor-phase concentration of MEK).

For acetone:

0.03345 mole × 7230.96 cal/mole = 241.876 cal (latent heat given up by acetone)

241.876 cal - 220.38 cal = 21.496 cal

(21.496 cal)/(7637.55 cal/mole) = 0.003 mole (moles of MEK

vaporized which is very small compared with 0.223 mole and compares favorably with measured vapor-phase concentration of MEK).

MONTANA STATE UNIVERSITY LIBRARIES
3 1762 10023784 9