Separation of acetic acid/4-methyl-2-pentanone, formic acid/4-methyl-2-pentanone and vinyl acetate/ethyl acetate by extractive distillation
by Marc Wayne Paffhausen

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
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Abstract:
Extractive distillation of the acetic acid/4-methyl-2-pentanone, formic acid/4-methyl-2-pentanone and vinyl acetate/ethyl acetate close boiling systems was investigated. Initial screening of potential extractive agents was carried out for each system in an Othmer vapor-liquid equilibrium still. Well over one hundred extractive agents, either alone or in combination with other compounds, were investigated overall. Subsequent testing of selected agents was carried out in a perforated-plate column which has been calibrated to have the equivalent of 5.3 theoretical plates. Relative volatilities for extractive distillation trial runs made in the perforated-plate column were calculated using the Fenske equation. All three systems investigated were successfully separated using chosen extractive agents. The use of polarity diagrams as an additional initial screening device was found to be a simple and effective technique for determining potential extractive agents as well.

Decomposition of acetic acid during one of the test runs in the perforated-plate column was believed to have led to the discovery of ketene gas, which is both difficult to obtain and uniquely useful industrially.

SEPARATION OF ACETIC ACID/4-METHYL-2-PENTANONE, FORMIC ACID/4-METHYL-2-PENTANONE AND VINYL ACETATE/ETHYL ACETATE BY EXTRACTIVE DISTILLATION

by

Marc Wayne Paffhausen

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APPROVAL

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Marc Wayne Paffhausen

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

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TABLE OF CONTENTS

Page

BACKGROUND 1

- Extractive and Azeotropic Distillation 3
- Selection of Extractive Agents 6

THEORETICAL ASPECTS 8

- Thermodynamics of Vapor-Liquid Equilibrium 8
- Relative Volatility 10
- The Fenske Total-Reflux Equation 11
- Altering Relative Volatility 15
- Selectivity 15
- Factors Affecting Selectivity 16
- Use of Solubility Parameters and Polarity Diagrams 18
- Other Methods to Predict Nonideal Solution Behavior 19

RESEARCH OBJECTIVES 20

SYSTEMS TO BE SEPARATED 21

- In General 21
- Acetic Acid/4-Methyl-2-Pentanone 21
- Formic Acid/4-Methyl-2-Pentanone 22
- Vinyl Acetate/Ethyl Acetate 23

EXPERIMENTAL AND ANALYTICAL EQUIPMENT 26

- Othmer Vapor-Liquid Equilibrium Still 26
- The Perforated-Plate Column 28
- Extractive Agent Recovery 31
- The Gas Chromatograph 31

TABLE OF CONTENTS–Continued

EXPERIMENTAL PROCEDURE 33

Operation of the Othmer Still 33
Calibration of the Perforated-Plate Column 33
Extractive Distillation in the Perforated-Plate Column 34

RESULTS 37

Vinyl Acetate/Ethyl Acetate 37
Acetic Acid/4-Methyl-2-Pentanone 40
Formic Acid/4-Methyl-2-Pentanone 47

DISCUSSION 50

The Othmer Still as a Screening Device 50
Polarity Diagrams as a Screening Device 50
Data from the Perforated-Plate Column 56

SUMMARY AND CONCLUSIONS 59

RECOMMENDATIONS FOR FUTURE RESEARCH 60

REFERENCES CITED 61

LIST OF TABLES

Table Page

1. Favorable Characteristics of an Extractive Agent 7
2. Relative Volatility-vs.-Theoretical Plates-vs.-Column Cost 14
3. Effective agents for vinyl acetate/ethyl acetate 37
4. Column results for vinyl acetate/ethyl acetate 38
5. Ineffective agents for vinyl acetate/ethyl acetate 39
6. Effective agents for acetic acid/4-methyl-2-pentanone using DMSO . . 40
7. Effective agents for acetic acid/4-methyl-2-pentanone using DMFA . . 43
8. Ineffective agents for acetic acid/4-methyl-2-pentanone using DMFA . . 44
9. Column results for acetic acid/4-methyl-2-pentanone using DMSO . . . 45
10. Column results for acetic acid/4-methyl-2-pentanone using DMFA . . . 45
11. Results of decomposition in acetic acid/4-methyl-2-pentanone system . 46
12. Effective agents for formic acid/4-methyl-2-pentanone using DMSO . . 47
13. Column results for formic acid/4-methyl-2-pentanone using DMSO . . 49
14. Ineffective agents for formic acid/4-methyl-2-pentanone using DMSO . 49
15. Solubility parameters at 25° C 51

LIST OF FIGURES

Figure Page

1. Fractional distillation column 2
2. Extractive distillation column 5
3. Number of theoretical plates as a function of relative volatility 13
4. Structures and physical data for system components 24
5. Structures and physical data for key extractive agents 25
6. Othmer vapor-liquid equilibrium still 27
7. Batch-wise extractive distillation column 29
8. Agent recovery by simple distillation 32
9. Polarity diagram for acetic acid/4-methyl-2-pentanone 53
10. Polarity diagram for formic acid/4-methyl-2-pentanone 54
11. Polarity diagram for vinyl acetate/ethyl acetate 55

ABSTRACT

Extractive distillation of the acetic acid/4-methyl-2-pentanone, formic acid/4-methyl-2-pentanone and vinyl acetate/ethyl acetate close boiling systems was investigated. Initial screening of potential extractive agents was carried out for each system in an Othmer vapor-liquid equilibrium still. Well over one hundred extractive agents, either alone or in combination with other compounds, were investigated overall. Subsequent testing of selected agents was carried out in a perforated-plate column which has been calibrated to have the equivalent of 5.3 theoretical plates. Relative volatilities for extractive distillation trial runs made in the perforated-plate column were calculated using the Fenske equation. All three systems investigated were successfully separated using chosen extractive agents. The use of polarity diagrams as an additional initial screening device was found to be a simple and effective technique for determining potential extractive agents as well.

Decomposition of acetic acid during one of the test runs in the perforated-plate column was believed to have led to the discovery of ketene gas, which is both difficult to obtain and uniquely useful industrially.

BACKGROUND

Distillation is a mass-transfer operation which separates the components of liquid mixtures containing miscible and volatile substances by vaporization into individual components or, in some cases, into groups of components. The separation of a mixture of alcohol and water into its components; of liquid air into nitrogen, oxygen and argon; and of crude petroleum into gasoline, kerosene, fuel oil, and lubricating stock are examples of distillations [1].

It is believed that distillation was first used around 1500 B.C. thus making it the oldest method for effecting liquid separations [2]. It is also the most widely used technique today mainly due to the ease with which scale-up from the laboratory to an industrial size process can be conducted but also because of its extreme commercial value to the chemical industry [3,4].

Simple fractional distillation is applicable when the liquid feed mixture to be separated forms no azeotrope(s) and the difference in the volatilities of its components is significant, i.e., usually meaning relative volatility values of 1.05 or greater. The components must be capable of vaporizing at feasible temperature and pressure. Also, no reaction can occur between components nor can decomposition or polymerization of one or more of the components occur [5].

Figure 1 on page 2 illustrates a typical fractional distillation column [6]. Feed enters the column at or near a stage which has approximately the same liquid composition as the feed. The "plate" where the feed enters the column is referred to as the feed plate. All plates below and including the feed plate constitute the stripping section of the column. Plates above the feed plate constitute the rectification section. Liquid from the feed plate travels downward through the

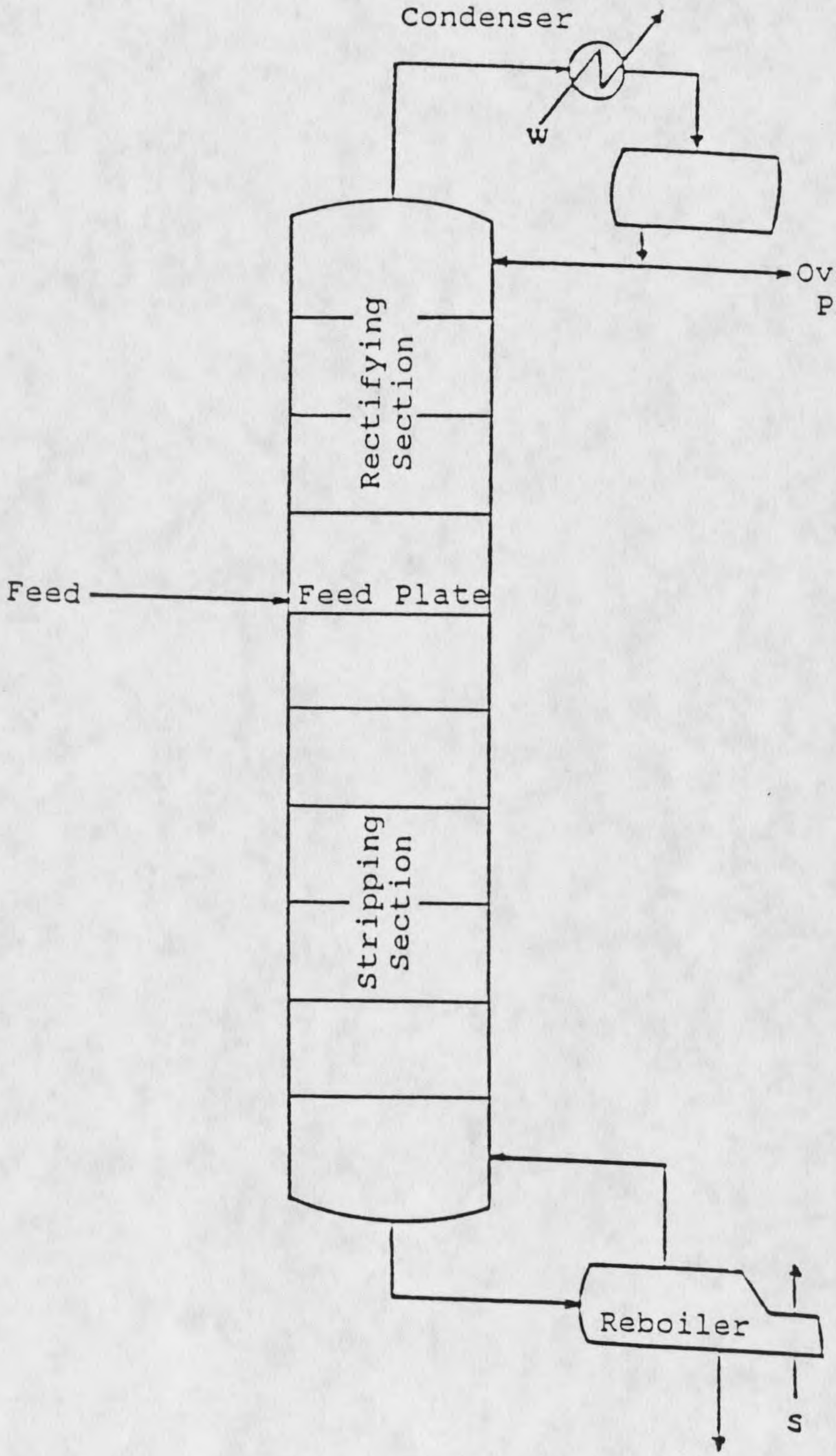
Condenser
W
Overhead
Product
Rectifying
Section
Feed
Feed Plate
Stripping
Section
Reboiler
S
Bottoms
Product

Figure 1. Fractional distillation column.

column and is intimately contacted by rising vapor at each plate. By trading latent heat of vaporization between the high and low boiling components, the vapor deposits its high boiling component in the liquid phase and removes low boiling component from the liquid as vapor to be carried to the overhead condenser. There it is either completely or totally condensed, part is taken off as product, and the rest returned to travel down the column as liquid. Without this liquid returned to the column no rectification would occur in the rectification section. This liquid serves to wash the high boiling component from the vapor as it ascends through the top portion of the column. In this manner, liquids that are separable may be brought to any desired purity at the top and bottom of the column.

In some cases distillation techniques other than simple fractional distillation must be used due to its ineffectiveness. Those cases are (i) when two or more of the components to be separated have only a slight, if any, difference in volatility, i.e., relative volatility is approximately equal to unity; (ii) two or more of the components form homogeneous azeotrope(s) which are not pressure sensitive or which are pressure sensitive but will not provide sufficient relative volatility change; and (iii) where one or more of the components will decompose or change chemically at temperature and pressure well within economic distillation ranges [7]. Fortunately, the technology of distillation has developed two modified forms which are now available for use. They are azeotropic and extractive distillation techniques.

Extractive and Azeotropic Distillation

Both azeotropic and extractive distillation are extremely effective techniques of separation involving the introduction of an additional component to the mixture to be separated. This additional component is referred to as a solvent or an agent.

The purpose of the agent is to change the way the components in the mixture chemically relate to one another. Specifically, the agent alters the relationship between the vapor pressures of the components in the mixture.

Benedict and Rubin have defined extractive and azeotropic distillation [8]. Extractive distillation is carried out in the presence of an agent which is relatively non-volatile compared to the components to be separated. This agent is charged continuously near the top of the column so that an appreciable concentration is maintained on all the plates of the column. The first extractive distillation process was patented by Emile and Guillaume in 1908 for the separation of fusel oil from fermentation alcohol [9]. Azeotropic distillation involves formation of a minimum boiling azeotrope between the agent and one of the components to be separated. The term "azeotrope" means a constant-boiling mixture. It is a very specific mixture of two or more components that boil at a specific temperature and which cannot be readily separated by ordinary distillation.

Figure 2 on page 5 illustrates a typical extractive distillation scheme. Distillation proceeds as described previously in the first column with the exception of the addition of the extractive agent near its top. The extractive agent is usually added a plate or two below the top so as to avoid carryover into the overhead product. The second column is used to recover the extractive agent from the bottoms product which is usually a simple task when the extractive agent being recovered is relatively non-volatile.

Extractive distillation has an advantage over azeotropic distillation in that a larger number of possibilities for successful agents exist and lower energies are required since vaporization of the agent is not necessary. Another advantage of extractive distillation is that the agent is usually easily recoverable. Extractive

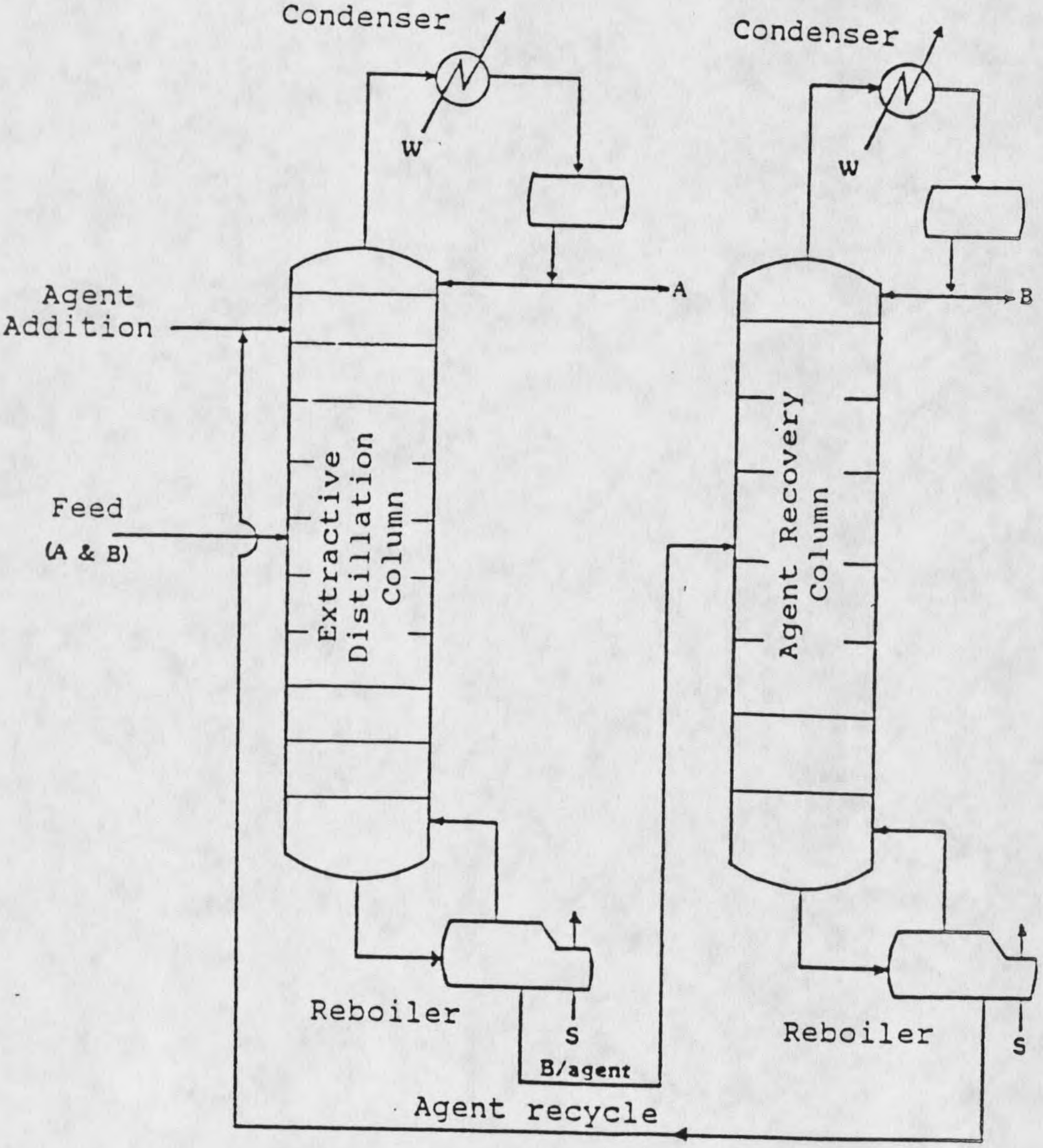
Condenser
W
Condenser
W
A
B
Agent
Addition
Feed
(A & B)
Extractive
Distillation
Column
Agent Recovery
Column
Reboiler
S
B/agent
Reboiler
S
Agent recycle

Figure 2. Extractive distillation column.

distillation is, however, not entirely without shortcomings. The additional volume of liquid on each plate added by the agent requires that columns have larger plates to process the same amount of material. Also, recovery of the agent usually requires an additional column and some additional energy inputs. Still, because of the variety of agents and lower heat requirements, extractive distillation seems to be preferred by industry.

Azeotropic distillation also has a couple of drawbacks. First, this separation technique relies on the formation of an acceptable azeotrope. This greatly reduces the possibility of finding a suitable agent. Secondly, there may still be the difficulty of separating the newly formed azeotrope so that the agent may be reused and the original component made useful.

Selection of Extractive Agents

The final selection of an extractive agent will be affected by many variables such as effectiveness, economics, chemical compatibility and company preference. Table 1 on page 7 contains a modified list of criteria reported by Rall [10] which have been previously suggested by Berg [11] and Yeh [12]. It is apparent after one reviews this list that the task of selecting the right extractive agent is not an easy one. In some instances a company will choose an agent with which it is already familiar or that it is already producing rather than choose the agent with the most favorable characteristics [13]. Fortunately, it is not unusual to have a number of effective agents from which to compare and choose.

Table 1. Favorable Characteristics of an Extractive Agent.

1. It should have a high boiling point, at least 20 degrees centigrade higher than the components to be separated. This is to insure that it is not carried into the overhead product and is easily separable from the bottoms product.
2. It should have a high capacity for the component it is to associate with in the separation. The higher this capacity the less agent may be used. This results in lower recycle rates for the agent, smaller column plates, and less energy consumption.
3. It should be highly selective. That is, it should have a maximum effect on one of the components to be separated and a minimum effect on the other.
4. It should not associate so strongly with either of the components so as to render them inseparable.
5. It should mix well with the feed stream and have a viscosity low enough for pumping and gravity flow within the column.
6. It is desirable that the agent be attracted to the higher boiling component so that the separation may occur in the natural direction.
7. It should be chemically stable at the operating temperatures and pressures of the system so that it will withstand extended recycling through the system without decomposition.
8. It should not be an agent so harsh as to cause decomposition of the components to be separated at the temperatures and pressures of the system.
9. It should be non-toxic, non-corrosive, and not be a serious contaminant to the system being handled.
10. It should not be so expensive as to render the process uneconomical.

THEORETICAL ASPECTS

Thermodynamics of Vapor-Liquid Equilibrium

The most common liquid mixture separation technique used by chemical process industries is distillation, a diffusional operation [14]. Design of these distillation processes requires accurate quantitative data regarding the equilibrium properties of the mixture to be separated. Although many methods for estimation of these properties are available, there is no substitute for reliable experimental data. In the case of extractive distillation, literature concerning estimation of the properties is practically non-existent and of little use since it is unable to predict many of the chemical complications. For this reason, experimental data are a must for designs utilizing extractive distillation.

The distillation process is dependent upon a departure from equilibrium between the liquid and vapor phases coming into contact. If the two phases were in equilibrium, there would be no net diffusion between the phases and no separation would be possible. After intimate contacting of a liquid and gas not originally in equilibrium, under ideal conditions we could bring the two phases to a state of thermodynamic equilibrium. For every component in a mixture, the condition for thermodynamic equilibrium is given by equation (1) [14]:

$$f_i^\ell = f_i^v \quad \text{(for all components } i = 1, 2, \ldots, n) \tag{1}$$

where f_i is the fugacity of component i at the temperature, pressure, and composition of the system, v is the vapor phase, and ℓ is the liquid phase. It is important to note that fugacity is a function of temperature, pressure, and composition only. Although any measure for composition may be used, provided the basis is consistent, the vapor mole fraction y_i is generally used for the vapor phase and the liquid mole fraction x_i is used for the liquid phase. Because fugacity is a function of temperature, pressure, and composition, it is convenient to define some terms relating these conditions. The functions used are the fugacity coefficient for the vapor phase, and the activity coefficient for the liquid phase [14,15]. For the vapor phase:

$$\phi_i = \frac{f_i^v}{y_i P} \tag{2}$$

where ϕ_i is the vapor phase fugacity coefficient of i in the mixture, P is total pressure of the system, and f_i is the fugacity of i in the mixture. For the liquid phase:

$$\gamma_i = \frac{a_i}{x_i} = \frac{f_i^\ell}{x_i f_i^o} \tag{3}$$

where γ_i is the liquid phase activity coefficient, a_i is activity of component i, and f_i^o is the standard state fugacity of component i at the system temperature and at some arbitrary pressure and composition chosen for convenience.

However, it is at this point that the typical thermodynamic development as described by Rall [10] becomes no longer applicable. Although the above development can be valid if used correctly for our extractive distillation scenario, a more simplified view of nonideal mixtures was preferred. What is being done when relative volatility values are obtained for both the Othmer still and the perforated-plate column is simply a comparison of the presence of the two components of interest on an extractive agent free basis. It is only accurate as an "empirical" comparison of the data obtained from the two techniques.

In order to get a more rigorous thermodynamic evaluation of the systems in question, one must look more closely at the total mixture that is present. Upon addition of an extractive agent or an extractive agent mixture to a binary system, a ternary or higher system is formed. In order to obtain valid activity coefficients, vapor-liquid equilibrium data on every possible binary combination should then be obtained at many different compositions and temperatures. Reduction of this data, i.e., by using Barker's method along with an optimization technique such as the Complex Method of Box [16,17], is done in order to fit the data to an equation for the activity coefficient. For instance, the above mentioned reduction method may be used to obtain the binary parameters for the Wilson equation. Once these parameters are known, they are used in the actual equation [18]:

$$\ell n\,\gamma_i = 1 - \ell n \sum_j x_j \Lambda_{ij} - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \tag{4}$$

where Λ is the symbol for a Wilson parameter. Note that $\Lambda_{ij} = 1$ for $i = j$ and so on and also that for each i-j pair there are two parameters since $\Lambda_{ij} \neq \Lambda_{ji}$. For example, in a ternary system the three possible i-j pairs are associated with the parameters Λ_{12}, Λ_{21}; Λ_{13}, Λ_{31}; and Λ_{23}, Λ_{32}. From this an actual activity coefficient, γ_i, for ternary systems or higher is obtained. It was beyond the scope of this thesis project, however, to follow the rigorous analysis. The "empirical" results obtained on the extractive agent free basis were considered sufficient for the goals of this thesis.

Relative Volatility

The single most useful measure of separation for a distillation process is relative volatility. Relative volatility quantitatively shows the ease of separation of a component i from a second component j using the ratio of their volatilities. This ratio is defined as [1]:

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} \tag{5}$$

where α_{ij} is the relative volatility of component i in j, y_i, y_j are vapor mole fractions at equilibrium, and x_i, x_j are liquid mole fractions at equilibrium. By convention, the value of α_{ij} is taken such that the volatility of component j is always less than that of i, i.e., α_{ij} is greater than or equal to unity. Although the relative volatility, given by α, for a nonideal mixture may vary greatly according to liquid composition, for an ideal mixture this value is nearly constant when temperature is constant. For purposes of discussion to be undertaken later, equation (5) above may be put into a more suitable form. Assume that the vapor phase behaves ideally and neglect the Poynting corrections for the pure liquid fugacity. Next, by taking into account the vapor pressures and the liquid and vapor mole fractions in terms of components i and j we obtain:

$$\gamma_i = \frac{y_i P}{x_i P_{vpi}} \tag{6}$$

and

$$\gamma_j = \frac{y_j P}{x_j P_{vpj}} \tag{7}$$

where P is the total pressure of the system, P_{vpi} is the vapor pressure of component i, P_{vpj} is the vapor pressure of the component j, y_i and y_j are vapor mole fractions at equilibrium, and x_i and x_j are liquid mole fractions at equilibrium. Substitution of these values in equation (5) yields the following expression for relative volatility which is also valid:

$$\alpha_{ij} = \frac{\gamma_i P_{vpi}}{\gamma_j P_{vpj}} \tag{8}$$

The Fenske Total-Reflux Equation

Under conditions of total reflux, the minimum number of theoretical plates required to effect a separation is given by the Fenske total-reflux equation [19]:

$$N_m = \frac{\ell n[(x_d/x_b)_i (x_d/x_b)_j]}{\ell n\, \alpha_{ij}} \tag{9}$$

where $(x_d/x_b)_i$ is the mole fraction ratio of component i in the distillate to that in the bottoms, $(x_d/x_b)_j$ is the mole fraction ratio of component j in the distillate to that in the bottoms, and N_m is the minimum number of plates required. It should be noted that the relative volatility in equation (9) must either be constant or represented by the geometric mean to be strictly valid. A good representation of the geometric mean for relative volatility is given by [19]:

$$\alpha_{ij} = \left(\alpha_{ij,\mathrm{top}}\,\alpha_{ij,\mathrm{middle}}\,\alpha_{ij,\mathrm{bottom}}\right)^{1/3} \tag{10}$$

where top, middle, and bottom refer to column position.

Since the work of this thesis involves calculation of relative volatilities using a distillation column, it is convenient to rearrange equation (9) to the form:

$$\alpha_{ij} = \left[(x_d/x_b)_i\,(x_d/x_b)_j\right]^{1/N m} \quad . \tag{11}$$

For use of this equation the number of theoretical plates must be estimated by calibration of the column (see Calibration of the Perforated-Plate Column). Also, when used in this form the relative volatility is not the geometric mean across the column but is the overall average across the column.

Figure 3 on page 13 depicts the number of theoretical plates needed to separate a binary mixture into 99% products as a function of relative volatility. The number of theoretical plates approaches infinity as the relative volatility approaches unity. The number of plates required decreases rapidly when the relative volatility value is in the area of 1.25 and above. Assuming that plate efficiency is 75% and that column cost is linearly proportional to the number of theoretical plates, a comparison of column cost versus relative volatility and plate number is shown in Table 2 on page 14 [12].

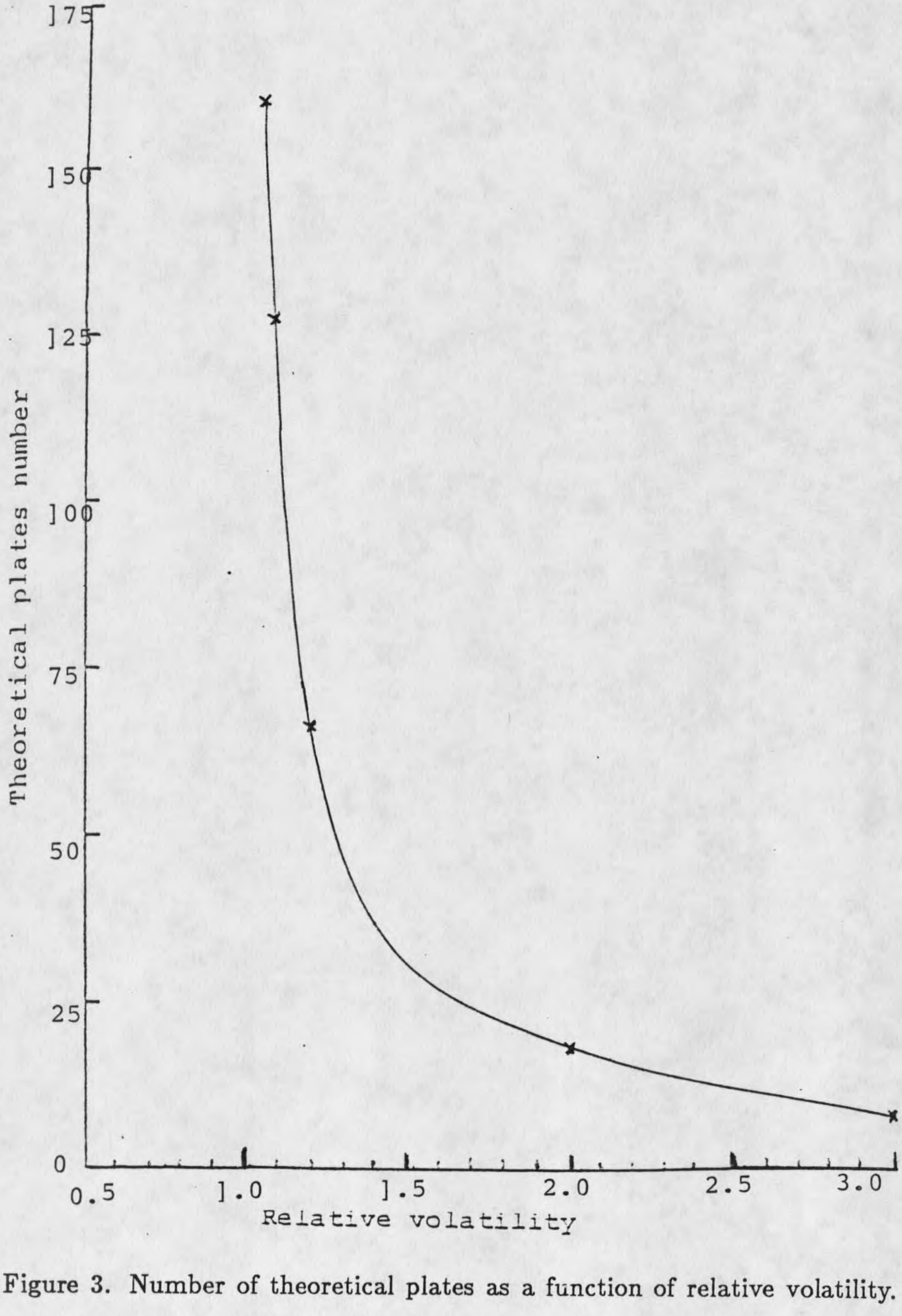

Figure 3. Number of theoretical plates as a function of relative volatility. In a separation of a binary mixture, the overhead and bottoms products are specified 99%.

Table 2. Relative Volatility-vs.-Theoretical Plates-vs.-Column Cost. Plates required to achieve 99% pure overhead and bottom products.

Relative volatility	Theoretical plates required	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	210.3	100.00
1.06	188.4	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
1.20	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 relative volatility value of 1.05.

The column cost is a relative value which is based on a value of relative volatility of 1.05. Using the Fenske equation with geometric mean relative volatilities, the number of theoretical plates required to achieve 99% pure distillate and bottoms products have been calculated. When interpreting Table 2 it is important to understand that the numbers are for total reflux and in terms of theoretical plates. Since neither of these apply to a real industrial process, the number of actual plates would be considerably higher. In practice, mixtures with a relative volatility less than 1.1 are considered extremely difficult to separate and the process is usually uneconomical.

Altering Relative Volatility

By looking at the Fenske equation it is apparent that the key to separating an azeotropic mixture, or one having a very low relative volatility such as in a close boiling mixture, is to increase its separation factor, or its relative volatility. There are three possible means by which this might be accomplished. First, one could alter the correction factors for the components, given by γ_i and ϕ_i, used to obtain equations (6) and (7). However, these values are very close to unity at moderate pressure and do not appreciably affect the relative volatility. By examination of equation (8) the last two alternatives become apparent. One might choose to alter the ratio of the pure component vapor pressures. For instance, as operating temperature of the column is reduced, i.e., reduced column pressure, this ratio will increase which will, in turn, enhance the separation. Unfortunately, this change is usually not appreciable enough to significantly affect the separation [20]. The final alternative is to change the ratio of the liquid phase activity coefficients. This can be achieved by addition of an extractive agent and may significantly affect relative volatility. The latter case provides a basis for extractive distillation.

Selectivity

An important characteristic of an extractive agent based on its relative volatility is one called selectivity. It is defined as the ability of an agent to preferentially enhance the volatility of one component in a mixture over that of another. One expression used to define selectivity is given by Anderson and Prausnitz [20]:

$$S_{ij} = [\alpha_{ij}]_P / [\alpha_{ij}]_A \tag{12}$$

where S_{ij} is the selectivity of agent on component i relative to component j, $[\alpha_{ij}]_P$ is relative volatility in the presence of agent, and $[\alpha_{ij}]_A$ is relative volatility in the absence of agent. It is desirable for the agent to increase the volatility of one component while decreasing the volatility of the other in order to maximize selectivity.

Factors Affecting Selectivity

The selectivity an extractive agent exhibits toward other components is the result of molecular interaction. Work done by Hildebrand and others has resulted in the development of two broad classifications of these interactive forces which are generally recognized to be (i) physical and (ii) chemical forces [21,22]. Physical forces, sometimes called van der Waals forces, are broken into three groups:

(1) Dispersion forces. This is the cause of attractive forces between nonpolar molecules. It is a result of momentarily induced dipoles which occur when the electron clouds of two molecules temporarily overlap.

(2) Induction forces. This is the result of a molecule with a permanent dipole inducing a dipole in another molecule. This is primarily what occurs between polar and nonpolar molecules.

(3) Orientation forces. This causes molecules which have permanent dipoles to interact and orient themselves with respect to one another.

Chemical complexing suitable for extractive distillation occurs as a result of hydrogen bonding and acid-base interactions and of these two, the hydrogen bonding is the most important. Liquids have been classified according to the strength and number of hydrogen bonds that their molecules may form [23]. As a result liquid materials have been placed into one of five classes, which are given here in order of decreasing ability to form strong hydrogen bonds as reported by Berg [24]:

(I) Liquids capable of forming three-dimensional networks of strong hydrogen bonds. Examples of strong hydrogen bonds are: O–HO, N–HO, O–HN.

(II) Liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen, and fluorine).

(III) Liquids composed of molecules containing donor atoms but no active hydrogen atoms.

(IV) Liquids composed of molecules containing active hydrogen atoms but no donor atoms.

(V) All other liquids which have no hydrogen-bond forming capabilities.

By identifying the hydrogen bonding characteristics and polarity of a successful extractive agent, one might be able to identify groups of compounds that might also be used successfully as extractive agents for similar chemical systems.

Two other important effects on agent selectivity are (i) temperature and (ii) fraction of extractive agent present. Higher temperatures tend to disrupt the process of chemical complexing, thus lower temperatures are preferred. This would imply the use of vacuum distillation, the implementation of which would depend upon economics. Increasing the volume fraction of agent in the mixture to be separated also improves selectivity. However, this effect may lead to immiscibility within the system if carried to an extreme. An immiscible system is undesirable in that it will cause unstable operation of the distillation column.

Use of Solubility Parameters and Polarity Diagrams

Intermolecular forces of repulsion are a phenomenon related to the inability of two molecules to occupy the same space. Because the force of repulsion becomes very small as two molecules are separated by distance, it is generally considered insignificant as related to extractive distillation. It is the attractive forces resulting from a molecule's polarity and hydrogen bonding that are important.

When considering extractive distillation using a binary feed mixture, there are three possible attractive molecular interactions to be considered: (i) molecular interactions between components of the feed mixture, (ii) molecular interactions between the extractive agent and one of the feed components, and (iii) molecular interactions between the extractive agent and the second of the feed components. Since interactions between feed components can only be altered by the introduction of extractive agents, only interactions between extractive agents and feed components will be considered.

Yeh [12] reported considerable success in predicting the degree of attraction between extractive agents and mixture components using solubility parameters. In his studies, the dispersion force, δ_d, hydrogen bonding, δ_h, and polarity, δ_p, solubility parameters were used in conjunction with specific volumes of liquids to explore the degree of attractive molecular interactions. However, he found that differences in the dispersion force parameters were negligible and unsuitable for investigation. The remaining factors, δ_h and δ_p, can be plotted on polarity diagrams for the preliminary screening of agents (see Polarity Diagrams as a Screening Device).

Other Methods to Predict Nonideal Solution Behavior

The use of Barker's method and CMBOX as a data reduction technique, as previously mentioned, is not the only way to reduce data to fit an equation like Wilson's. Also, other correlation equations exist [15,25] besides the Wilson equation. These methods were chosen for discussion because of the author's undergraduate and graduate work which utilized these techniques for evaluation of vapor-liquid equilibrium data and also because other methods may have been too time consuming or not as effective.

One such method of predicting nonideal solution behavior is the purely theoretical UNIFAC method. In this method, reduction of experimentally determined activity coefficient data into parameters characterizing structural groups is used to predict activity coefficients for systems not studied experimentally [25]. Two major drawbacks of the UNIFAC method are its inability to be used in electrolyte systems and its lack of accuracy for systems which are very nonideal. Another is the MOSCED model which stands for modified separation of cohesive energy density. It also has been reported to give good results for nonelectrolyte systems.

RESEARCH OBJECTIVES

The objective of this research is to find extractive agents which will effectively separate the following close boiling systems: acetic acid/4-methyl-2-pentanone, formic acid/4-methyl-2-pentanone, and vinyl acetate/ethyl acetate. The agents used could be either pure compounds or mixtures of compounds. They should be chemically as well as thermally stable, easily reclaimable and reusable, and should not react with or cause decomposition of the mixtures to be separated.

It is a further objective of this study to determine whether polarity diagrams are useful in initial screening of potential extractive agents in each of the above mentioned systems when they are considered along with data obtained from the Othmer vapor-liquid equilibrium still for each system.

SYSTEMS TO BE SEPARATED

In General

Figures 4 and 5, which follow the descriptions of the three systems to be separated, are shown on pages 24 and 25, respectively. The chemical structures of the components in all three systems as well as structures for the principle extractive agents used are illustrated for convenience of reference [13,26]. The mixtures were obtained from Hoechst Celanese. The company oxidizes n-butane to obtain both acetic and formic acids. However during this partial oxidation reaction all kinds of other impurities get into the desired product, three of which were studied in this thesis: 4-methyl-2-pentanone, vinyl acetate and ethyl acetate. The ketone and acetates pass through the typical distillation process without being separated. This causes a problem because upon standing, the acids now discolor due to the impurities present. Only clear acids are commercially desirable and so it only makes sense that the company which can do this will control the market.

Acetic Acid/4-Methyl-2-Pentanone

Acetic acid has a molecular weight of 60.05 and a boiling point of 117.9° C. It is used industrially in production of vinyl acetate (52%), acetic anhydride (16%), acetic esters and glycol ether acetates (10%), dimethyl terephthalate/purified terephthalic acid (9%), miscellaneous (7%), textile processing (2%), and the remaining 4% is exported. It currently sells for between 29¢ and 31¢ per pound. Hoechst Celanese's two plants in Clear Lake and Pampa, Texas supply nearly half of the 3.7 billion pounds that are produced annually [13].

4-methyl-2-pentanone has a molecular weight of 100.16 and a boiling point of 117° C. Over 80% of the total compound produced annually is used as a general solvent in coating processes (paints, varnishes, lacquers, etc.) and processes for making adhesives, pesticides and rubber processing chemicals. Fourteen percent is exported annually. Its current value is around 38¢ per pound. The largest producer is Union Carbide in Institute, West Virginia which supplies 65 million pounds per year [13].

Acetic acid and 4-methyl-2-pentanone boil only 0.9° C apart thus having a relative volatility extremely close to 1.0. This is almost as difficult to separate as an azeotrope which suggests that distillation would be nearly impossible without the use of an extractive agent [31].

Formic Acid/4-Methyl-2-Pentanone

Formic acid has a molecular weight of 46.03 and a boiling point of 100.8° C. It has about the same strength as sulfuric acid and may cause severe burns if improperly handled. Industrial uses are in textile dyeing and finishing (21%), pharmaceuticals (20%), rubber intermediates (16%), leather and tanning treatment (15%), and catalysts (12%). It currently sells for 36.5¢ per pound and is provided mainly by Hoechst Celanese's Pampa, Texas plant producing 25 million pounds annually. The 4-methyl-2-pentanone was already discussed [13].

The two components boil 16.2° C apart, however they do form a close boiling mixture. Separation is achieved by distillation with any one of a number of extractive agents being used. The formic acid in this system was unpure due to a water content of about 5%. Some extractive agents caused decomposition to occur in this system [34].