



Separation of formic acid/dioxane and formic acid/3-methyl-2-butanone by extractive distillation
by Richard Randolph Rall

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

Extractive distillation of the formic acid/dioxane and formic acid/3-methyl-2-butanone azeotropes was investigated using dimethylformamide or dimethylacetamide admixed with other oxygenated or nitrogen-containing organic compounds. Initial screening of extractive agents at two concentrations was carried out in an Othmer vapor-liquid equilibrium still. Over eighty extractive agents were evaluated in all. Subsequent testing of selected agents was carried out in a perforated-plate rectification column which was found to have the equivalent of 5.3 theoretical plates. Relative volatilities for extractive distillation runs made in the plate column were calculated using the Fenske equation. Both azeotropes investigated were successfully negated using some of the extractive agents. In all cases formic acid was recovered as a bottoms product.

The use of polarity diagrams was investigated as a means of screening potential extractive agents. Polarity diagrams were found to be a simple and effective technique for determining system behavior in the plate column.

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BY EXTRACTIVE DISTILLATION

by

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of

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in

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MONTANA STATE UNIVERSITY
Bozeman, Montana

March 1989

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APPROVAL

of a thesis submitted by

Richard Randolph Rall

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.

March 15, 1989
Date

Richard Borg
Chairperson, Graduate Committee

Approved for the Major Department

March 27, 1989
Date

John T. Sears
Head, Major Department

Approved for the College of Graduate Studies

March 31, 1989
Date

Henry L. Parsons
Graduate Dean

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ABSTRACT

Extractive distillation of the formic acid/dioxane and formic acid/3-methyl-2-butanone azeotropes was investigated using dimethylformamide or dimethylacetamide admixed with other oxygenated or nitrogen-containing organic compounds. Initial screening of extractive agents at two concentrations was carried out in an Othmer vapor-liquid equilibrium still. Over eighty extractive agents were evaluated in all. Subsequent testing of selected agents was carried out in a perforated-plate rectification column which was found to have the equivalent of 5.3 theoretical plates. Relative volatilities for extractive distillation runs made in the plate column were calculated using the Fenske equation. Both azeotropes investigated were successfully negated using some of the extractive agents. In all cases formic acid was recovered as a bottoms product.

The use of polarity diagrams was investigated as a means of screening potential extractive agents. Polarity diagrams were found to be a simple and effective technique for determining system behavior in the plate column.

INTRODUCTION

Distillation In General

Fractional distillation is the process of separating a mixture of two or more volatile substances into its components by a series of vaporizations and condensations [1]. This process takes advantage of component concentration differences in the liquid and vapor phases at equilibrium. This concentration difference is generally quantified in a term known as the relative volatility of the components.

The distillation process is the oldest and most widely used of all liquid separation techniques [2]. Because it is a simple and effective separation technique that is well understood and easily scaled up from the laboratory bench to commercial design, it is of extreme commercial value to the chemical industry [3]. In 1976, 2.25 trillion pounds of materials were separated by distillation [4]. One of the few drawbacks to the distillation process is its energy intensiveness. Three percent of our nation's energy used in 1976 was consumed by distillation, a total of 2 quads of energy [4].

Figure 1 on page 2 illustrates a typical fractional distillation column [5]. Feed enters the column at or near a stage which has approximately the same liquid composition

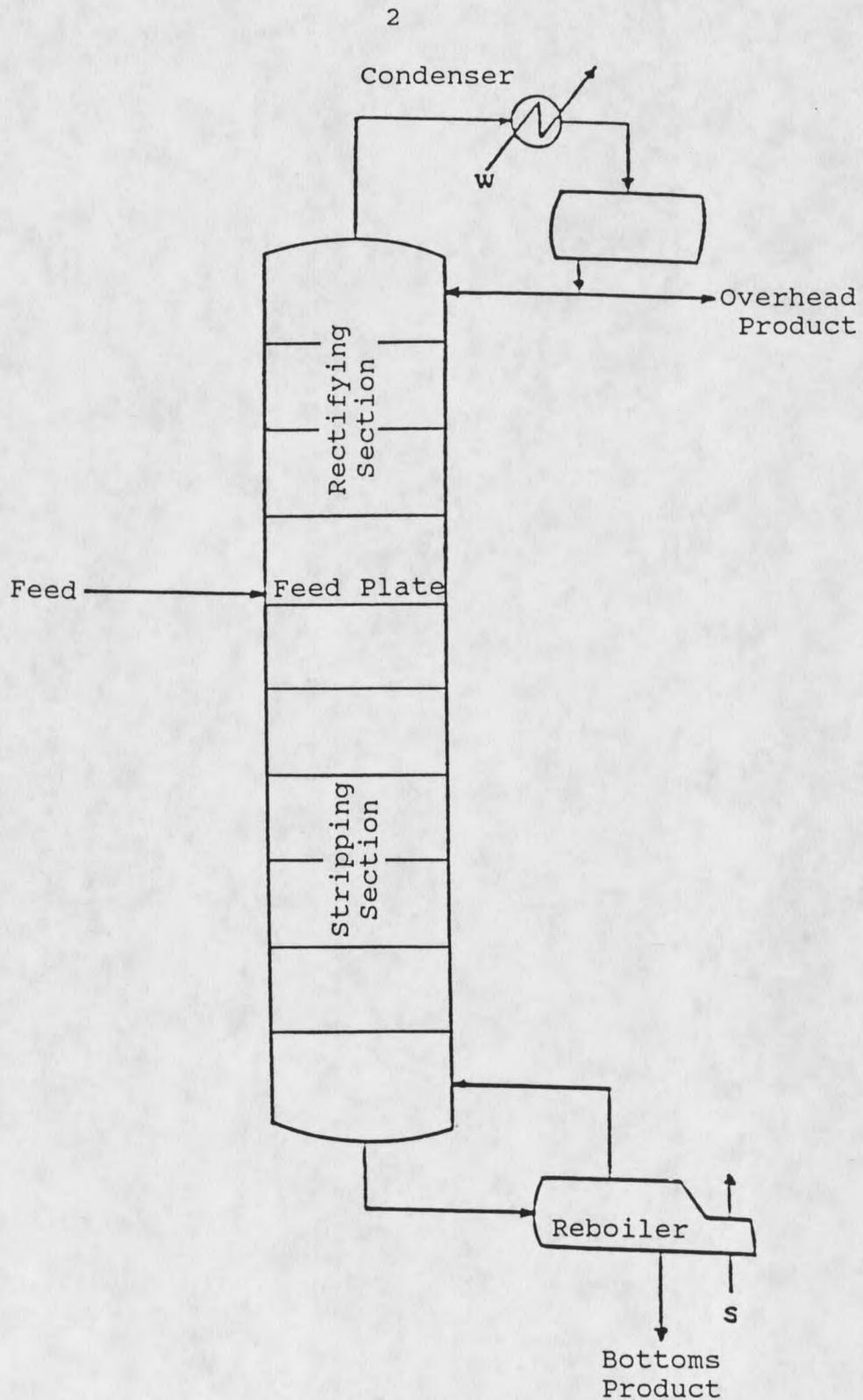


Figure 1. Fractional distillation column.

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 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.

Extractive and Azeotropic Distillation

Although distillation is a very valuable separation technique for volatile liquids, there are occasions where the method described above loses its effectiveness. When two or more components boil at or near the same temperature, i.e., have the same vapor pressures, distillation either becomes

inefficient or all together ineffective, as is the case when an azeotrope is formed. With an azeotrope, liquid and vapor in equilibrium have the same composition and no amount of vaporization and condensation sequences will affect a composition change. Fortunately, the science of distillation has been developed to the point where two modified forms of distillation are available to us. They are azeotropic and extractive 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 solvent is to change the way the components in the mixture chemically relate to one another. Specifically, the solvent alters the relationship between the vapor pressures of the components in the mixture.

Azeotropic distillation, as the name might imply, involves formation of a minimum boiling azeotrope between the solvent and one of the components to be separated. Although effective, this technique has two important drawbacks. First, azeotropic distillation relies on the accidental formation of an 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 solvent may be reused and the original component made useful.

Extractive distillation is carried out in the presence

of a high-boiling solvent which is relatively non-volatile in comparison with components of the original mixture. It has the advantages over azeotropic distillation of having a large number of possibilities for successful agents and lower energy requirements since vaporization of the solvent is not required or desired. Another advantage of extractive distillation is that the solvent is usually easily recoverable. Extractive distillation is, however, not entirely without shortcomings. The additional volume of liquid on each plate added by the solvent requires that columns have larger plates to process the same amount of material. Also, recovery of the solvent usually requires an additional column and some additional energy inputs. Still, because of the variety of agents and lower heat requirements, extractive distillation is generally preferred by industry over azeotropic distillation. Be informed, however, that extractive distillation is not always better than azeotropic distillation [6].

Figure 2, page 6, shows a typical extractive distillation scheme. In the first tower, distillation proceeds as usual with the exception of "extractive agent" addition near the top of the column. The extractive agent is usually added a plate or two below the top of the column to avoid carryover into the overhead product. The second column is used strictly for extractive agent recovery from the bottoms product. Because of the relatively non-volatile nature of the extractive agent

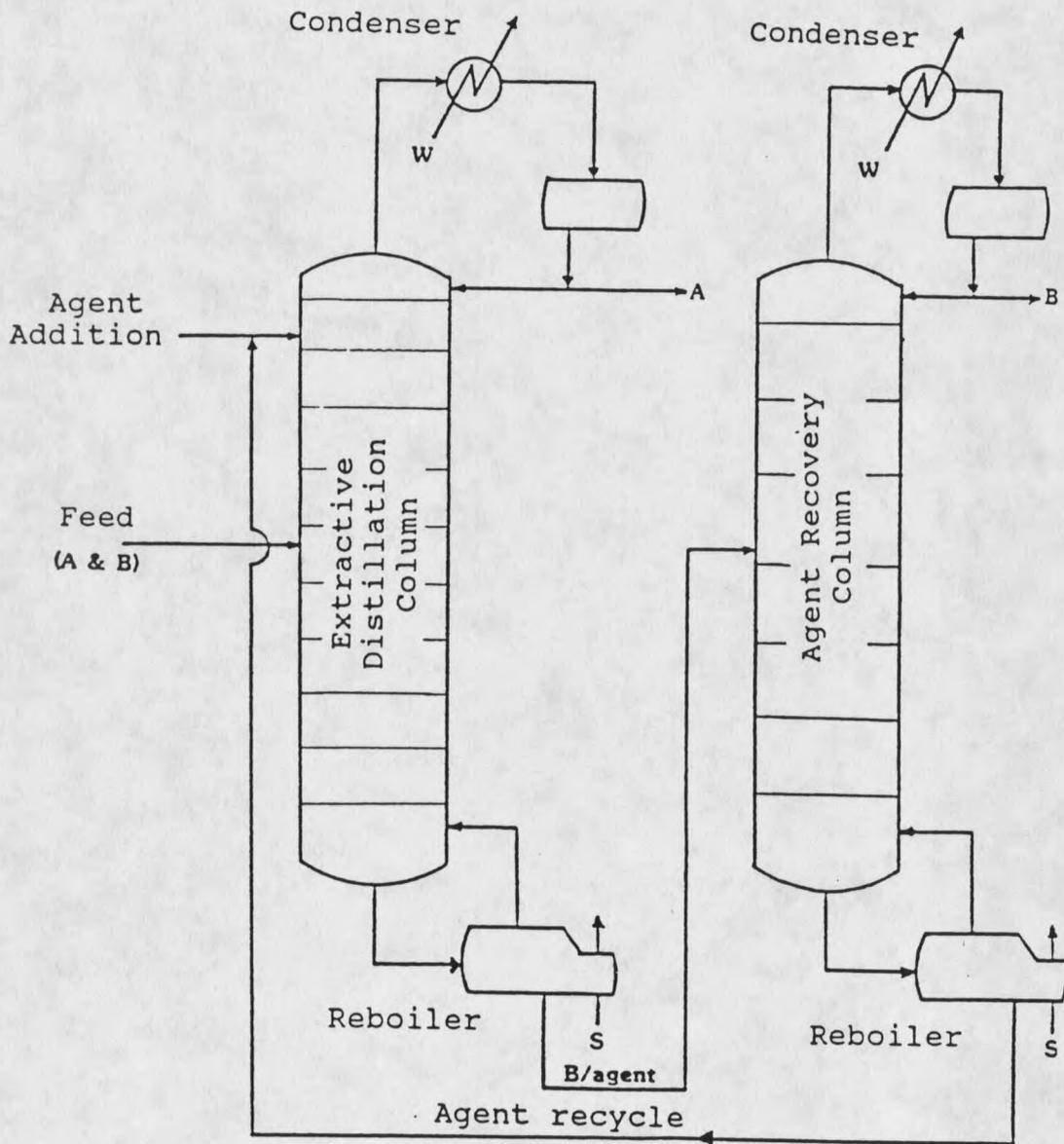


Figure 2. Extractive distillation column.

this second column usually requires only a small number of plates.

Extractive Agent Selection

The hardest part of extractive distillation is finding a suitable solvent. There are many things to consider in finding a solvent that will both work and be economically advantageous to the company implementing it in design. In many instances, a company will not choose a solvent with the most favorable characteristics but will choose one with which it has experience and already uses, or is produced within the company [7]. Table 1 below contains a modified list of some favorable and unfavorable solvent characteristics that have been suggested by Berg [8] and Yeh [9]. Although not of particular importance to this work, they are relevant to design.

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 solvent may be used. This results in lower recycle rates for the solvent, 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.

Table 1-Continued.

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.
-

We can see from this rather lengthy list of agent characteristics that agent selection is not an easy task. Agent selection is a matter of effectiveness, chemical compatibility, economics, and company preference. Fortunately, as mentioned previously, it is not unusual to have a wide variety of agents from which to choose.

THEORETICAL ASPECTS OF DISTILLATION

Thermodynamics of Vapor-Liquid Equilibrium

The most common liquid mixture separation technique used by chemical process industries is distillation, a diffusional operation [10]. 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 is a must for designs utilizing extractive distillation.

The distillation process is dependent upon a lack of 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) [10]:

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

where f_i = fugacity of component i at the temp., press., and composition of the system

v = vapor phase

l = 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 [11,10]. For the vapor phase:

$$\phi_i = \frac{f_i^v}{y_i P} \quad (2)$$

where ϕ_i = vapor phase fugacity coefficient of i in mixture
 P = total pressure of system
 f_i = fugacity of i in the mixture

For the liquid phase:

$$\gamma_i = \frac{a_i}{x_i} = \frac{f_i^l}{x_i f_i^o} \quad (3)$$

where γ_i = liquid phase activity coefficient
 a_i = activity of component i

f_i^0 = standard state fugacity of component i at the system temperature and at some arbitrary pressure and composition chosen for convenience

The most convenient standard state for fugacity is generally taken to be that of the pure liquid component at the system pressure. The fugacity of a pure liquid is given by equation (4) [10]:

$$f_i^l(T, P, x_i=1) = P_{vpi}(T) \phi_i^s(T) \exp \int_{P_{vpi}}^P \frac{V_i^l(T, P)}{RT} dP \quad (4)$$

where P_{vpi} = vapor pressure of component i

ϕ_i^s = fugacity coefficient of the saturated liquid

V_i^l = molar liquid volume of component, this is the ratio of the molecular weight to the density

Substitution of equations (2), (3), and (4) into equation (1) gives:

$$Y_i P = \gamma_i X_i P_{vpi} F_i \quad (5)$$

$$\text{where } F_i = \frac{\phi_i^s}{\phi_i} \exp \int_{P_{vpi}}^P \frac{V_i^l}{RT} dP \quad (6)$$

For components below their critical point and at low pressure, the correction factor F_i is often near unity. Given uncertainties in experimental information, we are sometimes justified in taking F_i as unity even at moderate pressures if only approximate results are required [11]. Since the purpose of this research is to find successful extractive agents and not for determining rigorous thermodynamic data, we will take the value of F_i to be unity.

This leaves us with the equation:

$$Y_i P = \gamma_i X_i P_{vpi} \quad (7)$$

For pure components or ideal solutions the value of γ_i is unity and equation (7) above may be reduced further to obtain Raoult's law:

$$Y_i P = X_i P_{vpi} \quad (8)$$

Equation (7) above will be used later in a qualitative manner to demonstrate the theory behind extractive distillation.

Relative Volatility

Perhaps the 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 [5]:

$$\alpha_{ij} = \frac{Y_i/X_i}{Y_j/X_j} \quad (9)$$

Where α_{ij} = the relative volatility of component i in j
 Y_i, Y_j are vapor mole fractions at equilibrium
 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 one. Although the relative volatility for a nonideal mixture may vary greatly according

to liquid composition, for an ideal mixture this value is constant. For purposes of discussion to be undertaken later, equation (9) above may be put into a more suitable form. By solving equation (7) for liquid mole fraction in terms of components i and j , and substituting these values into equation (9), the following equation for relative volatility is developed:

$$\alpha_{ij} = \frac{\gamma_i P_{vp_i}}{\gamma_j P_{vp_j}} \quad (10)$$

This equation is also valid and adequate for our research work.

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 [12]:

$$N_m = \frac{\ln[(x_d/x_b)_i (x_d/x_b)_j]}{\ln \alpha_{ij}} \quad (11)$$

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
 N_m = minimum number of plates required

It should be noted that the relative volatility in equation (11) 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 [12]:

$$\alpha_{ij} = (\alpha_{ij,top} \alpha_{ij,middle} \alpha_{ij,bottom})^{1/3} \quad (12)$$

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 (11) to the form:

$$\alpha_{ij} = [(x_d/x_b)_i (x_d/x_b)_j]^{1/Nm} \quad (13)$$

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.

Table 2 on page 15 quantitatively illustrates the effect of relative volatility on the distillation process. 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 [9].

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 [5].

Table 2. Relative volatility vs. theoretical plates. Plates required to achieve 99% pure overhead and bottom products.

Relative volatility	Theoretical plates required
1.01	1231.5
1.02	618.8
1.03	414.5
1.04	312.4
1.05	210.3
1.06	188.4
1.08	159.2
1.10	128.5
1.12	108.1
1.15	87.7
1.20	67.2
1.30	46.7
1.40	36.4
1.80	20.8
2.00	17.7
2.40	14.0
2.80	11.9
3.00	11.2
3.50	9.7
4.00	8.8

THEORETICAL ASPECTS OF EXTRACTIVE DISTILLATION

Altering Relative Volatility

We can see from the Fenske equation that the key to separating an azeotropic mixture, or one having a very low relative volatility, is to increase its separation factor, the relative volatility. There are three possible means by which this might be accomplished. The first is by altering the correction factors for the components as given by equation (6). However, these values are very close to one at moderate pressure and do not appreciably effect the relative volatility. By examination of equation (10) the second and third alternatives become apparent. We might choose to alter the ratio of the pure component vapor pressures. As the operating temperature of the column is reduced, i.e., reduced column pressure, this ratio increases which enhances the separation. Unfortunately, this change is } usually not appreciable enough to significantly affect the separation [2]. 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. This is the basis of extractive distillation.

Extractive Agent Selectivity

Perhaps one of the most important characteristics of an extractive agent is its selectivity. Selectivity is 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 Van Winkle [2]:

$$S_{ij} = [\alpha_{ij}]_P / [\alpha_{ij}]_A \quad (14)$$

where S_{ij} is the selectivity of agent on component i relative to component j

$[\alpha_{ij}]_P$ = relative volatility in the presence of agent
 $[\alpha_{ij}]_A$ = relative volatility in the absence of agent

To maximize the selectivity, it is desirable for the agent to increase the volatility of one component while decreasing the volatility of the other.

Factors Affecting Selectivity

The selectivity an extractive agent exhibits towards other components is the result of molecular interaction. Two broad classifications of these interactive forces are generally recognized to be physical and chemical forces [13,14]. Physical forces, sometimes called van der Waals forces, are broken into three groups:

- 1) Dispersion interaction. 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 primary cause of attractive forces between polar and nonpolar molecules. It is the result of a molecule with a permanent dipole inducing a dipole moment on another molecule.

3) Orientation forces. This causes molecules with permanent dipoles to orient themselves with respect to one another.

Chemical complexing suitable for extractive distillation occurs as a result of hydrogen bonding and acid-base interactions. Of these, hydrogen bonding is the most important. Ewell et al. and others have classified liquids based on the strength and number of hydrogen bonds that its molecules may form [15]. As a result of this classification, liquid materials were placed into one of five classes given here in order of decreasing ability to form strong hydrogen bonds [16]:

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) Other 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, i.e., liquids having no hydrogen-bond forming capabilities.

By identifying the hydrogen bonding characteristics and polarity of a successful extractive agent, we may 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 temperature and fraction of extractive agent present. Since higher temperatures tend to disrupt the process of chemical complexing, 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 solvent in the mixture to be separated also improves selectivity. However, this effect produces diminishing returns and 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.

Prediction of Attractive Interactions

Intermolecular forces of repulsion are a phenomenon related to two molecules inability 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.

Yeh [9] has reported considerable success in predicting the degree of attraction between extractive agents and mixture components using solubility parameters. In Yeh's 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, it was found by Yeh that differences in the dispersion force parameters were negligible and unsuitable for investigation. The remaining factors were plotted on a "polarity diagram" for analysis.

When considering extractive distillation using a binary feed mixture there are three possible attractive molecular interactions to be considered: 1) molecular interactions between components of the feed mixture, 2) molecular interactions between the extractive agent and one of the feed components, 3) 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, we will confine our efforts to analysis of interactions between extractive agents and feed components only.

RESEARCH OBJECTIVES

The objective of this research is to find extractive agents which will effectively negate the formic acid/dioxane and/or formic acid/3-methyl-2-butanone azeotropes. The extractive agents may be either pure compounds or mixtures of compounds. They should be chemically and thermally stable, and should not react with or cause decomposition of the mixtures to be separated.

It is a further objective of this study to identify the classes of compounds that are effective agents in negating our azeotropes, and to determine the effectiveness of polarity diagrams in evaluating these agents.

AZEOTROPIC SYSTEMS TO BE SEPARATED

Formic Acid/Dioxane

Formic acid and dioxane are both products encountered in the catalyzed oxidation of n-butane. Formic acid has about the same strength as sulfuric acid and may cause severe burns if improperly handled. It is used industrially in pharmaceutical, leather, textile, dye, rubber, and catalyst processing. Dioxane is mainly used as a solvent in the dye industry. Caution should be taken when handling dioxane since it is listed as a Class I carcinogen by OSHA.

Formic acid has a molecular weight of 46.03, specific gravity of 1.22, and a boiling point of 100.8 °C. Dioxane has a molecular weight of 88.1, specific gravity of 1.033, and a boiling point of 101.2 °C. When together, formic acid and dioxane exhibit negative deviations from Raoult's law producing a maximum boiling azeotrope. The azeotrope consists of 43 weight percent formic acid and 57 weight percent dioxane boiling at 113.4 °C. Distillation of this azeotrope is to be accomplished using amides, a Class I group of compounds, either pure or in mixtures with Class II and III compounds as the extractive agent.

Formic Acid/3-Methyl-2-butanone

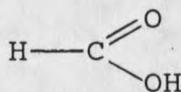
The availability of pure 3-methyl-2-butanone in quantity is relatively new in the chemical market place. It is likely, however, that its use will be found as a solvent in the solvent industry or as a chemical intermediary. Mixtures containing formic acid and 3-methyl-2-butanone result from the catalytic oxidation of n-butane.

3-Methyl-2-butanone has a molecular weight of 86.31, a specific gravity of 0.802, and a boiling point of 94.5 °C. When together, formic acid and 3-methyl-2-butanone exhibit negative deviations from Raoult's law forming a maximum boiling azeotrope. The azeotrope consists of 85 weight percent formic acid and 15 weight percent 3-methyl-2-butanone boiling at 102.2 °C. The azeotrope is to be separated using amides either pure or in mixtures with Class II and III compounds as the extractive agent.

For convenience, the chemical structures of components for both azeotropic systems studied and for the amides used as extractive agents are shown in Figure 3 on page 24.

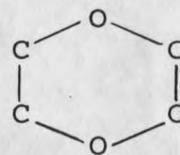
b.pt. = 100.8 °C

m.wt. = 46.03

cm³/g-mole = 37.8Formic acid

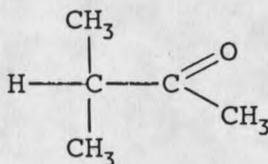
b.pt. = 101.2 °C

m.wt. = 88.1

cm³/g-mole = 85.7Dioxane

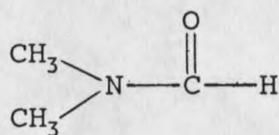
b.pt. = 94.5 °C

m.wt. = 86.31

cm³/g-mole = 107.53-Methyl-2-butanone

b.pt. = 153 °C

m.wt. = 73.09

cm³/g-mole = 77.0Dimethylformamide

b.pt. = 166 °C

m.wt. = 87.12

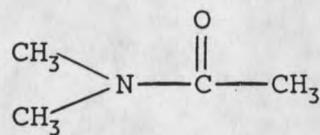
cm³/g-mole = 92.5Dimethylacetamide

Figure 3. Structures and physical data for key components.

EXPERIMENTAL AND ANALYTICAL EQUIPMENT

Othmer Vapor-Liquid Equilibrium Still

Initial investigation to find successful extractive agents for each of the azeotropic systems was done in an Othmer type vapor-liquid equilibrium still. Figure 4 on page 26 illustrates the still.

The azeotrope to be separated is introduced to the still along with a known volume fraction of agent to be tested. Although the total volume introduced to the still is relatively unimportant, the amount must be sufficient to maintain a liquid level between points A and B during operation. Heat for vaporization of the liquid is supplied to the bottom of the still by means of a heating coil. The outside of the still is lagged with insulation to prevent condensation of the vapor leaving the still before it reaches the primary condenser. The condensing vapor continuously flushes the vapor sampling tube and returns to the stillpot by means of an overflow tube. To insure that atmospheric pressure is maintained in the still, the still is equipped with a vent on the overflow tube. This vent is equipped with an additional condenser so that no material is lost from the system to the atmosphere.

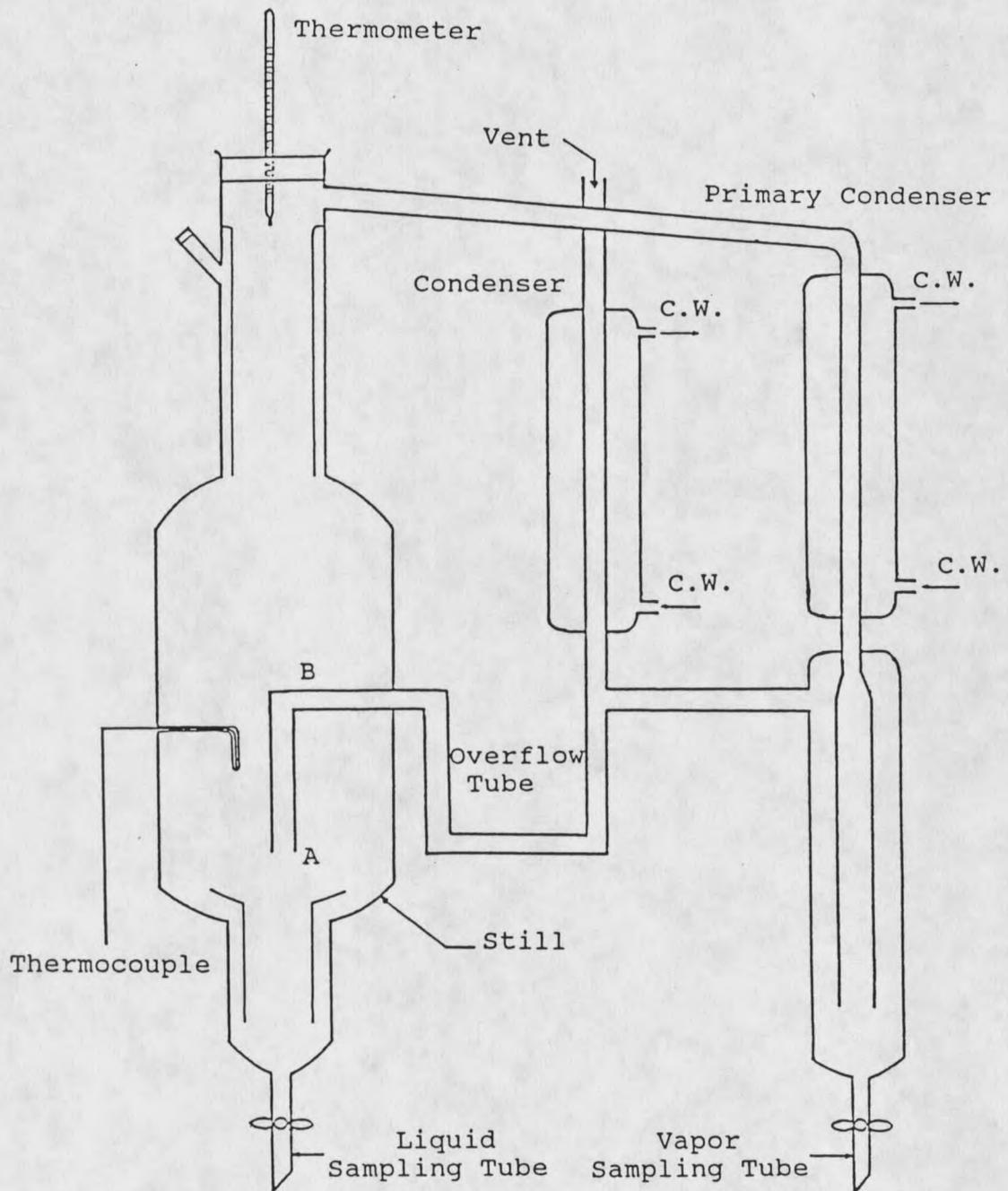


Figure 4. Othmer vapor-liquid equilibrium still.

After allowing the still to reflux its contents for several hours, equilibrium is achieved. Vapor and liquid samples may then be taken from their respective sampling ports for analysis on the gas chromatograph.

The Othmer still in effect represents one equilibrium stage, i.e., one theoretical plate. By analyzing the vapor and liquid samples on the gas chromatograph, the relative volatility of the components for one equilibrium stage may be determined. As a further aid in the analysis of the data, a thermometer and thermocouple are available for measurement of vapor and liquid temperatures respectively.

Perforated-plate Column

After identification of extractive agents which were successful at negating azeotropes in the vapor-liquid equilibrium still, a few of these agents were tested in a perforated-plate column. The distillation column was operated in a semi-batch fashion for reasons of simplicity as well as for conservation of chemical materials. It has been shown by Szabados [17] that batch operation does not significantly affect experimental results. Figure 5 on page 28 illustrates the still setup.

The column in question is strictly a rectification column, i.e., it has no stripping section. The main components of the column and their functions are listed on page 29 following the column illustration.

