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

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.

SEPARATION OF FORMIC ACID/DIOXANE AND FORMIC ACID/3-METHYL-2-BUTANONE BY EXTRACTIVE DISTILLATION

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

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ABSTRACT

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

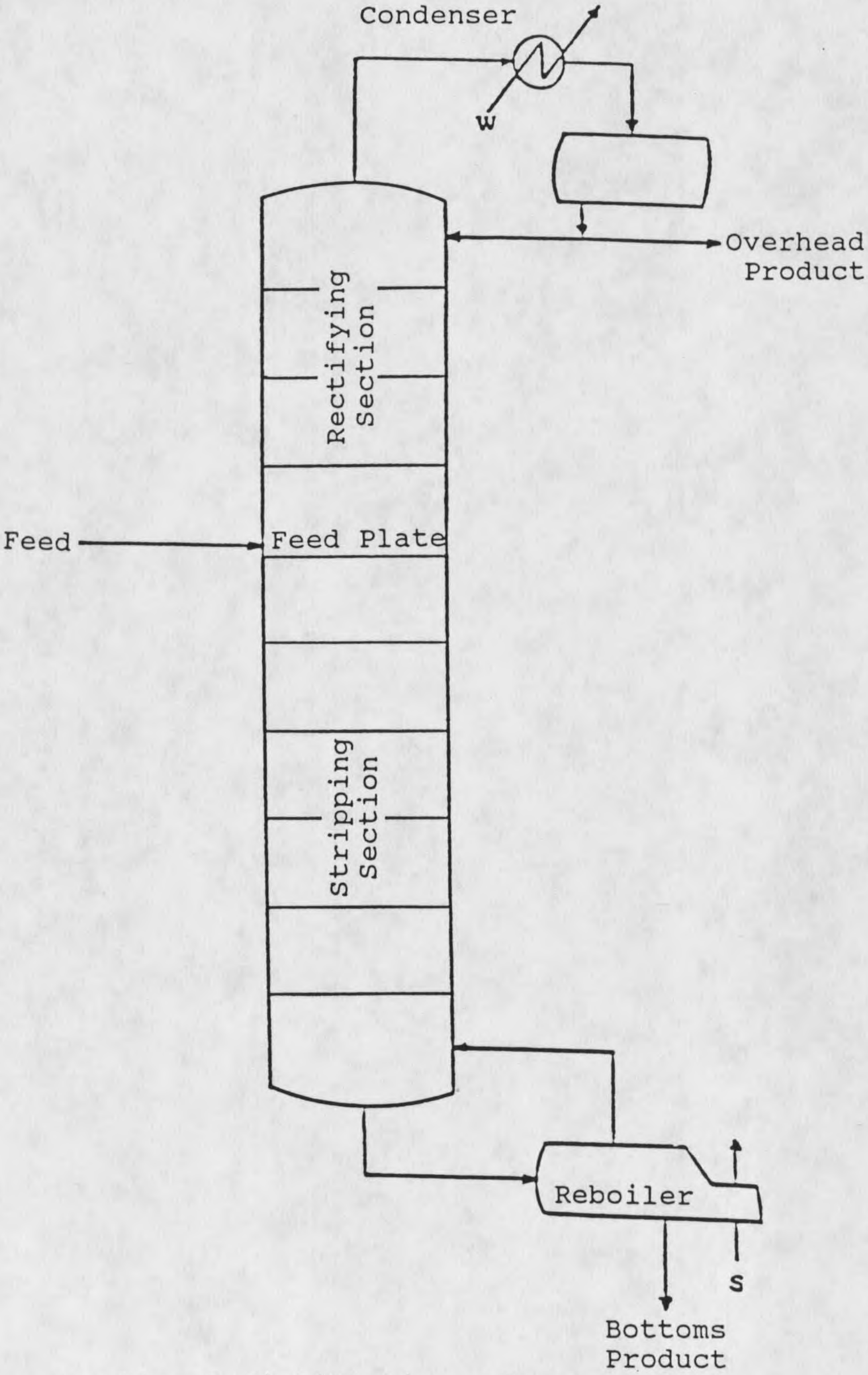


Figure 1. Fractional distillation column.

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

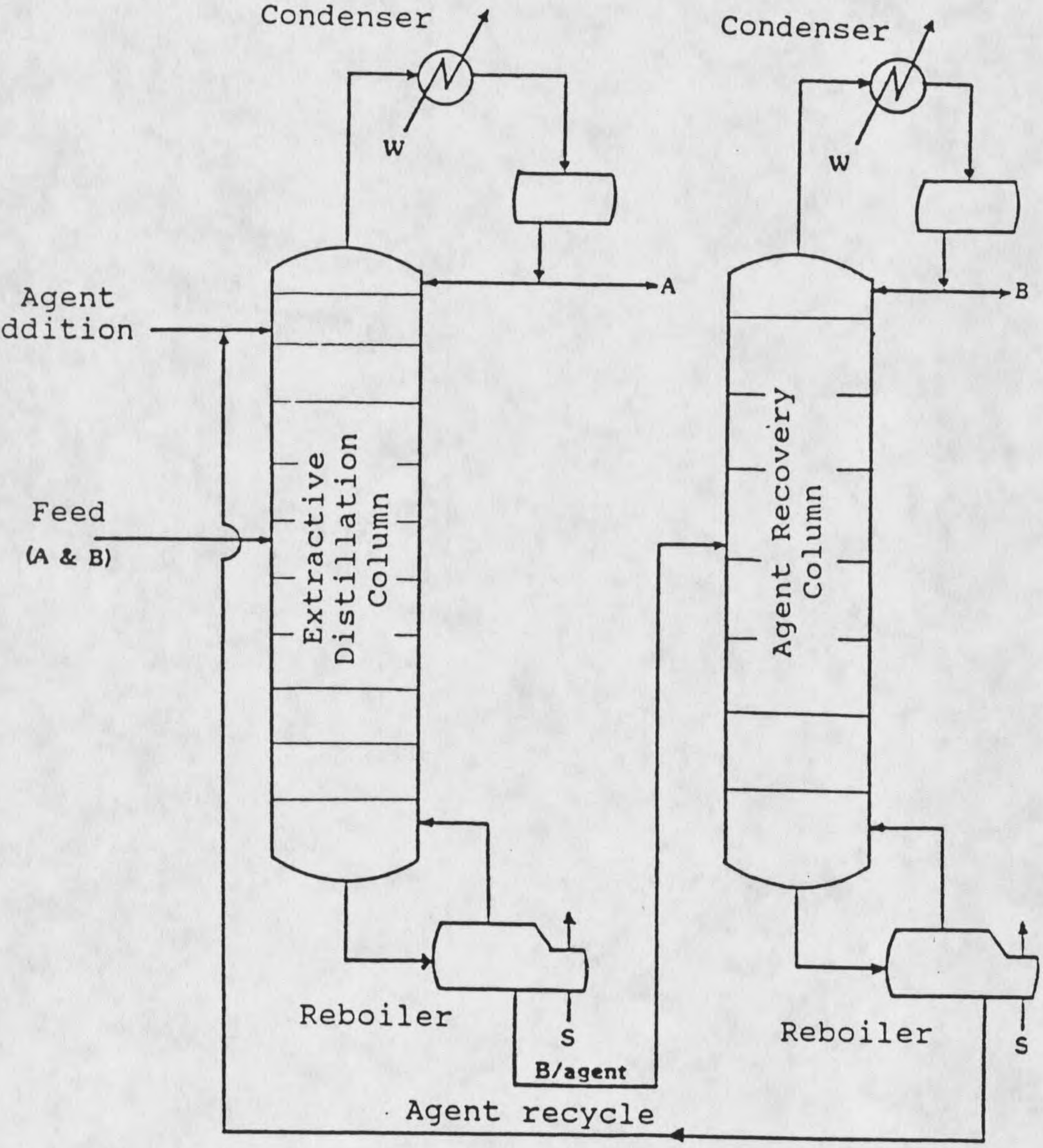


Figure 2. Extractive distillation column.

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]:

$$f^{l}_{i} = f^{v}_{i} \quad \text{(for all components } i=1,2...n) \tag{1}$$

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:

$$\phi_i = \frac{f^{v}_{i}}{y_i P} \tag{2}$$

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:

$$\gamma_i = \frac{a_i}{x_i} = \frac{f^{l}_{i}}{x_i f^{o}_{i}} \tag{3}$$

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

f^o_i = 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]:

$$f^l_i(T,P,x_i{=}1) = P_{vpi}(T)\emptyset^s_i(T)\exp\int^P_{Pvpi}\frac{V^l_i(T,P)}{RT}\,dP \qquad (4)$$

where P_{vpi} = vapor pressure of component i

$\emptyset^s_i$ = fugacity coefficient of the saturated liquid

V^l_i = 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:

$$y_iP = \gamma_i x_i P_{vpi} F_i \qquad (5)$$

where $F_i = \dfrac{\emptyset^s_i}{\emptyset_i}\exp\int^P_{Pvpi}\dfrac{V^l_i}{RT}\,dP \qquad (6)$

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:

$$y_iP = \gamma_i x_i P_{vpi} \tag{7}$$

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:

$$y_iP = x_i P_{vpi} \tag{8}$$

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]:

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} \tag{9}$$

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:

$$\alpha_{ij} = \frac{\gamma_i P_{vpi}}{\gamma_j P_{vpj}} \qquad (10)$$

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]:

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

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]:

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

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:

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

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]:

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

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.

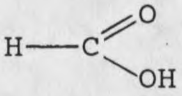
3-Methyl-2-butanone has a molecular weight of 86.31, a specific gravity of 0.802, and a boiling point of 94.5 °C. When together, formic acid and 3-methyl-2-butanone exhibit negative deviations from Raoult's law forming a maximum boiling azeotrope. The azeotrope consists of 85 weight percent formic acid 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

cm^3/g-mole = 37.8

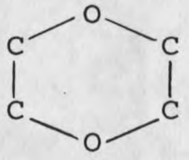


Formic acid

b.pt. = 101.2 °C

m.wt. = 88.1

cm^3/g-mole = 85.7

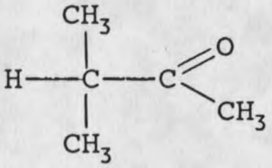


Dioxane

b.pt. = 94.5 °C

m.wt. = 86.31

cm^3/g-mole = 107.5

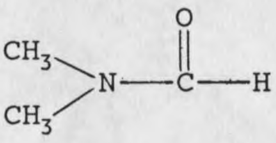


3-Methyl-2-butanone

b.pt. = 153 °C

m.wt. = 73.09

cm^3/g-mole = 77.0

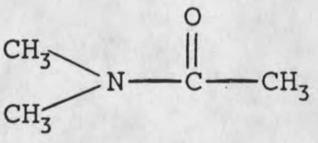


Dimethylformamide

b.pt. = 166 °C

m.wt. = 87.12

cm^3/g-mole = 92.5



Dimethylacetamide

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.

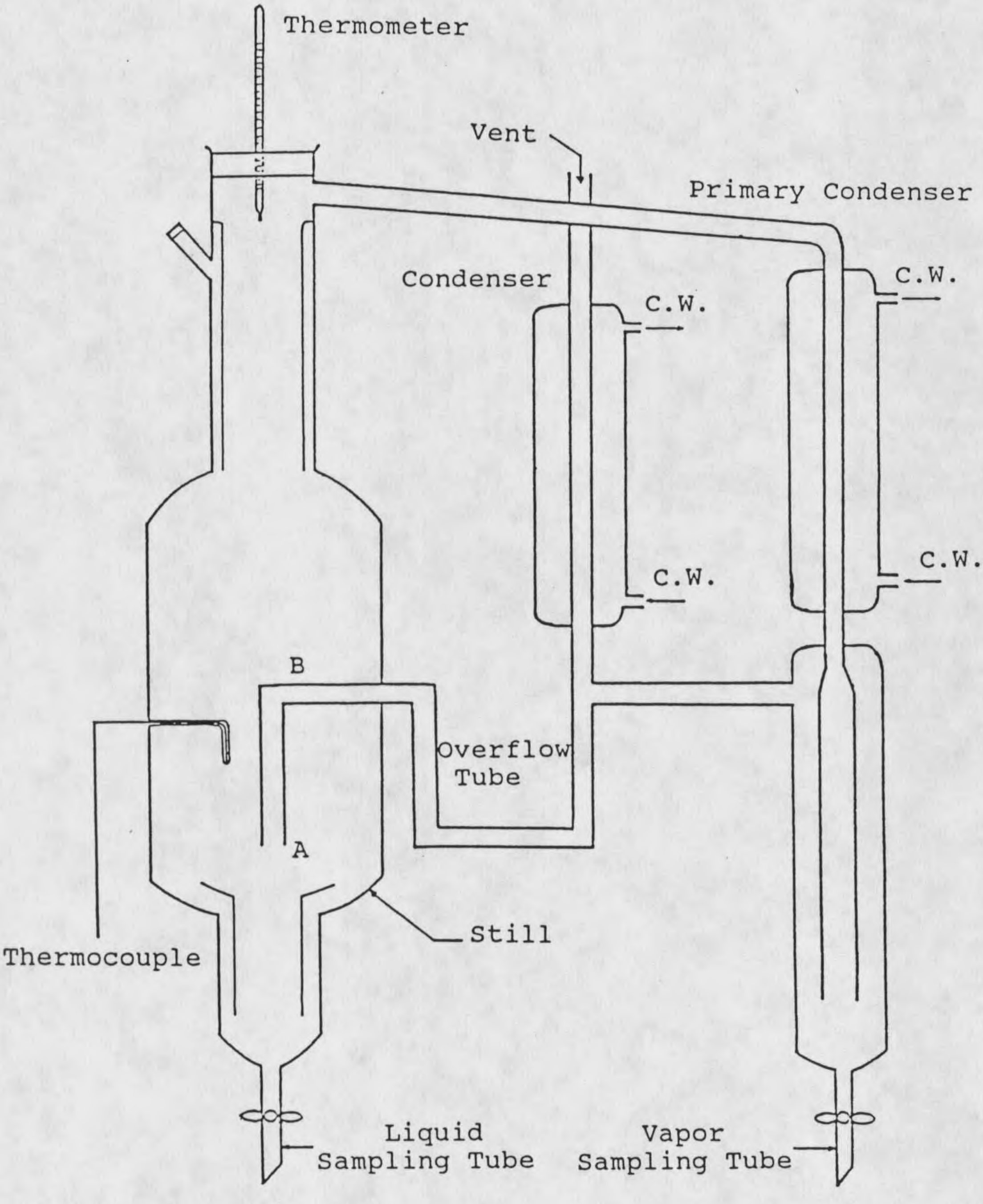


Figure 4. Othmer vapor-liquid equilibrium still.

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.

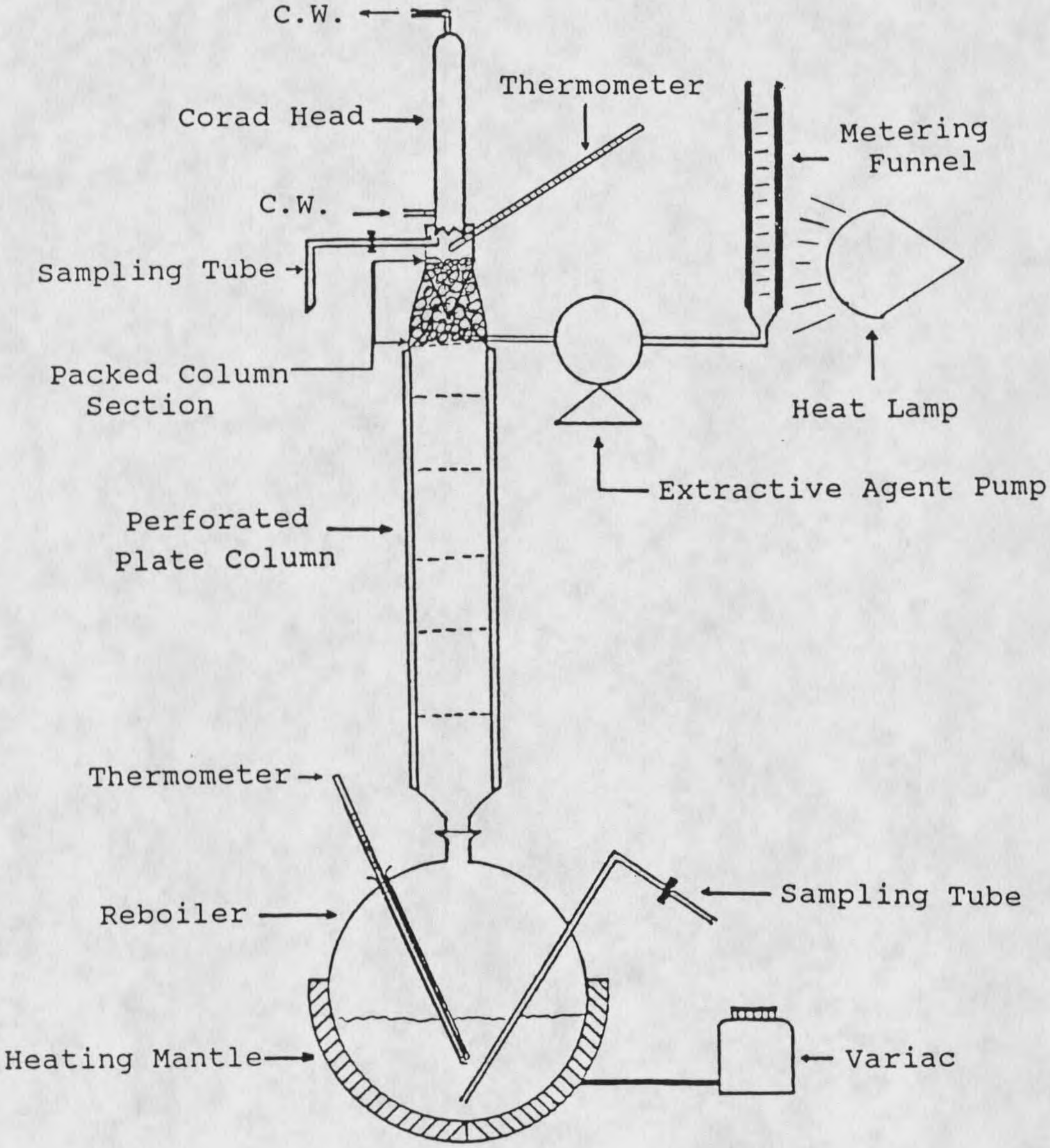


Figure 5. Batch-wise extractive distillation column.

Column components are:

1) A Corad condensing head. Cooling water is channeled through this glass jacketed head to provide a heat sink for condensing the vapor reaching the top of the column. Vertical glass ridges separate various areas on the inside of the head allowing calculation of boil-up rates and reflux ratios. Liquid falling from any of the areas inside the head may be channeled by means of a glass point to the overhead sample collection tube. By changing the area of the Corad head directed at the sample collection tube, the reflux ratio may be changed. Available reflux ratios are: 30:1, 20:1, 10:1, 5:1, 3:1, and 2:1. The head is also fitted with a thermometer port for overhead temperature measurement.

2) Section of packed column. Four inches of insulated packed column separate the corad head from the perforated-plate section of column. The packing is 3/8" X 1/4" bits of glass tubing. Its function is to prevent dynamic carryover of the extractive agent into the overhead product.

3) Perforated-plate column. An Oldershaw perforated-plate column comprised the contacting portion of the column. It is silvered and vacuum jacketed to prevent heat loss. The column is 20 inches long containing 5 actual plates with a 1.5 inch separation between plates. Liquid height on each of the plates is 3/8 inch.

4) Reboiler. The reboiler consists of a 5 liter round bottom flask equipped with a sampling tube and thermal well.

Heat is electrically supplied by a full Glas-Col mantle which also acts as insulation for the flask. Heat through the mantle is controlled using a Variac, an adjustable power transformer. Adjusting the power controls boil-up rates.

5) Extractive agent pump. Preheated extractive agent is supplied to an adjustable micro-bellows metering pump by means of a calibrated 200 ml. glass funnel. The extractive agent enters the column between the packed column and perforated-plate column sections. To assure that the extractive agent does not cool before entering the column, a heating lamp maintains the temperature of extractive agent in the glass funnel and the pumping lines to the column are insulated.

In addition to the components mentioned, three thermometers are required to measure overhead, bottoms, and extractive agent temperatures. It is also advantageous to have a stop watch on hand to aid in measuring flow rates.

Extractive Agent Recovery

When deemed necessary, extractive agents may be recovered using simple distillation. Recovery of extractive agents serves two purposes. One is to conserve the supply of available extractive agent. Another is to verify the stability of the extractive agent since it must be recovered and recycled in an industrial process.

Figure 6 on page 32 is a typical scheme for agent recovery in the laboratory. After an extractive distillation run is made in the perforated-plate column, the resulting agent and azeotropic mixture is emptied into a 2 liter distilling flask. Using a heating mantle and Variac, the azeotropic mixture is driven from the flask as vapor, condensed, and collected in an Erlenmeyer flask. When the distillation is complete, the temperature of the vapor will rise sharply indicating that only extractive agent remains in the flask.

Gas Chromatograph for Sample Analysis

The bottom and overhead products from experimental runs in both the Othmer vapor-liquid equilibrium still and perforated-plate column were analyzed using a gas chromatograph. The gas chromatograph used was a Varian Aerograph model 1400 using a six foot column containing standard Poropak QS packing. Data was output to a Welch-Sargent model SRG recorder in the form of peak heights. Peak height percents for components in the overhead and bottom products were used to calculate relative volatility in the Othmer stills, and were used in conjunction with the Fenske equation to calculate average relative volatility in the perforated-plate column.

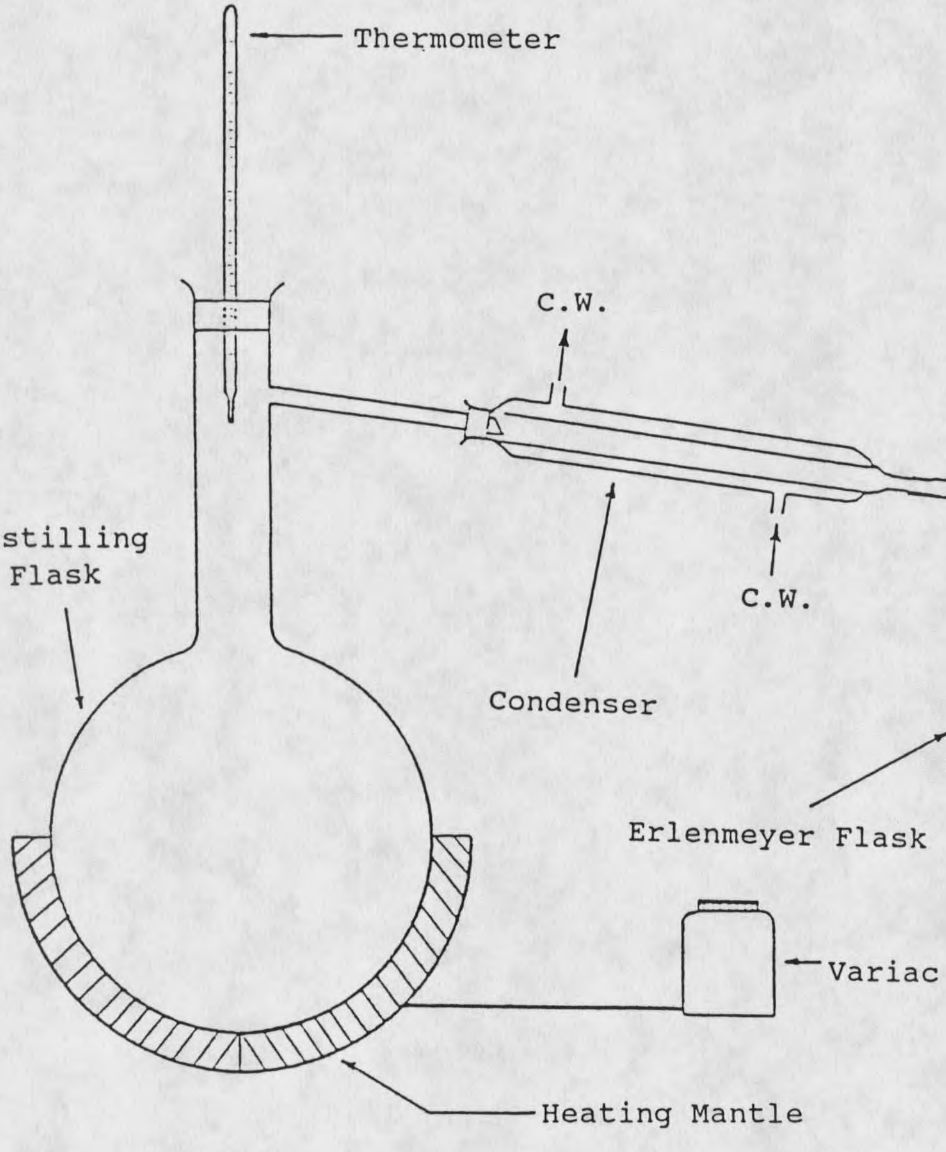


Figure 6. Agent recovery by simple distillation.

EXPERIMENTAL PROCEDURE

Operation of the Othmer Still

Fifty grams of the azeotropic mixture is charged to the Othmer still along with fifty grams of pure extractive agent or extractive agent mixture. The charge is then refluxed in the still for at least six hours to assure that a state of equilibrium has been reached. Samples are then taken for analysis from the condensed overhead vapor and from the bottom product. The still is then flushed with acetone and blown dry with compressed air to prepare it for the next charge.

Analysis of the samples on the gas chromatograph allows us to determine the effectiveness of the extractive agent, and also discloses the amount, if any, of decomposition in the system.

Calibration of the Perforated-plate Column

The purpose of carrying out a separation in the plate column is twofold. One purpose is to reduce separation of the azeotrope to practice. A second reason is to more accurately determine the relative volatility of the azeotrope's components in the presence of the extractive agent. This is done using the Fenske equation. Because use of the Fenske equation for this purpose requires knowledge of the number of theoretical plates involved, we must estimate this number by calibrating the column using ideal mixtures of known relative volatility.

A mixture of 100 grams of toluene (110.6 °C) and methylcyclohexane (100.9 °C) was charged to the Othmer still and refluxed for 4 hours. Analysis of the overhead and bottom products revealed 73.1% toluene and 26.9% methylcyclohexane in the vapor, 80% toluene and 20% methylcyclohexane in the liquid. This gives a relative volatility of 1.47 and compares favorably with a previously reported value of 1.5 [18].

A charge of 134 grams of toluene and 16 grams of methylcyclohexane was charged to the perforated-plate column. The column was operated at total reflux for 2 hours with a boil-up rate of 60 ml. per minute. Product samples were taken and analysis revealed 24% methylcyclohexane and 76% toluene in the vapor, 4% methylcyclohexane and 96% toluene in the liquid. Using the Fenske equation, the number of theoretical plates in the column was found to be 5.3.

Vosburgh [19], Yeh [10], and Szabados [18] have all conducted similar calibration experiments on the very same perforated-plate column. Their calibrations used a variety of ideal test mixtures, and in the case of Yeh included testing with extractive agents present. It was their unanimous conclusion that the number of theoretical plates in the column was very nearly constant at 4.5 plates. However, in calibrating the column for the experiments of this thesis, it was discovered that the column was not plumb during previous calibration experiments [7] causing liquid level to vary across the surface of the plates. After plumbing the column, my experiment showed the column to have approximately 5.3 plates.

Extractive Distillation Using the Plate Column

Extractive distillation runs made in the perforated-plate column were done at total reflux in a semi-batch fashion. The operation is semi-batch in that the azeotropic mixture is introduced as an initial charge, but extractive agent is added continuously throughout the operation.

In each case 200 grams of azeotropic mixture was charged to the stillpot. Heat was applied to the stillpot and the vapors allowed to warm the column to its operating temperature. When vapor reached the top of the column, water was started to the overhead condenser and the column allowed to reflux to achieve operating conditions.

The extractive agent was heated to about 95 °C and introduced to the flask from which the micro-bellows pump would feed. The time at which the extractive agent was introduced to the column was noted. Overhead and bottom samples were taken at 1/2 hour intervals from the time at which agent addition began until equilibrium in the column was established. Extractive agent was fed above the top plate in the column at a rate of 15 ml. per minute. The rate of extractive agent was easily verified since the flask from which the micro-bellows pump fed was calibrated. Heat to the column was adjusted to achieve a boil-up rate of 60 ml. per minute. This gave an agent addition to boil-up ratio of 1:4. Measurement of the boil-up rate was accomplished by counting drops of liquid which fell from any of the points on the Corad head and accounting for the portion of surface area which they represented. It was found that there were approximately 22 drops per ml. and this was used as a conversion factor.

As the distillation progressed, the rising concentration of the extractive agent in the stillpot would increase the bottoms temperature. If the temperature became too high, this would sometimes cause decomposition of the azeotrope's components. For this reason, distillation runs with higher extractive agent addition rates were avoided.

After each run the perforated-plate column was allowed to cool, flushed with acetone, and blown dry with compressed air in preparation for the next run.

RESULTS

The Formic Acid/Dioxane System

The formic/dioxane azeotrope was negated by extractive distillation using certain amides. Initial investigation of extractive agents was accomplished in the Othmer still. Agents or mixtures of agents that were successfully tested in the Othmer still are listed below in Table 3.

Table 3. Agents for formic acid/dioxane.

Compounds	Ratios*		Relative Volatility	
Dimethylformamide(DMFA), Adipic acid	(1/2)^2	(3/5)^2	1.2	1.6
DMFA, Azelaic acid	"	"	1.8	2.5
" , Benzoic acid	"	"	3.9	4.2
" , p-tert. Butyl benzoic acid	"	"	1.6	2.1
" , Cinnamic acid	"	"	4.0	3.5
" , Decanoic acid	"	"	3.3	2.2
" , Dodecanedioic acid	"	"	1.6	1.6
" , Glutaric acid	"	"	2.0	2.1
" , Heptanoic acid	"	"	2.6	3.4
" , Hexanoic acid	"	"	2.3	4.0
" , 4-Hydroxybenzoic acid	"	"	4.4	3.1
" , Itaconic acid	"	"	2.5	2.1
" , Malic acid	"	"	2.5	2.4
" , Neodecanoic acid	"	"	2.0	3.0
" , Octanoic acid	"	"	2.4	5.2
" , Pelargonic acid	"	"	2.2	5.4
" , Salicylic acid	"	"	1.1	4.9
" , Sebacic acid	"	"	1.2	2.4
" , o-Toluic acid	"	"	4.2	5.4
" , m-Toluic acid	"	"	2.1	1.7
" , p-Toluic acid	"	"	2.1	6.2
" , Glycerol triacetate	"		1.7	
" , Hexylene glycol diacetate	"		1.2	
" , Ethylene glycol diacetate	"		2.5	
" , Butoxy propanol	"		3.3	

Table 3-Continued.

Compounds	Ratios*		Relative Volatility	
DMFA, Ethylene glycol butyl ether acetate	$(1/2)^2$		1.2	
" , Diethylene glycol ethyl ether acetate	"		2.3	
" , Propoxy propanol	"		4.7	
" , Adipic acid, Methyl salicylate	$(1/3)^3$	$(2/5)^3$	1.8	1.7
" , Acetyl salicylic acid, Cyclohexanone	"	"	2.7	3.9
" , Azelaic acid, Ethylene glycol diacetate	"	"	4.2	1.5
" , Benzoic acid, Isophorone	"	"	1.6	2.6
" , p-tert. Butyl benzoic acid, 2-Methoxy-ethyl ether	"	"	3.8	4.8
" , Cinnamic acid, Anisole	"		1.3	
" , Decanoic acid, Acetophenone	"	"	1.6	1.7
" , Dodecanedioic acid, Dipropylene glycol dimethyl ether	"	"	1.8	1.8
" , Glutaric acid, Ethyl benzoate	"	"	2.5	2.2
" , Heptanoic acid, Ethyl benzoate	"	"	4.1	6.2
" , Hexanoic acid, Methyl benzoate	"	"	2.1	3.4
" , 4-Hydroxy benzoic acid, Propylene glycol benzoic ether	"	"	1.4	4.2
" , Itaconic acid, Methyl phenyl acetate	"	"	2.5	1.3
" , Malic acid, Diethylene glycol dibenzoate	"	"	1.2	1.5
" , Neodecanoic acid, Adiponitrile	"	"	3.1	1.5
" , Octanoic acid, Butyl benzoate	"	"	3.3	2.3
" , Pelargonic acid, Benzyl benzoate	"	"	1.8	2.6
" , Salicylic acid, Benzyl ether	"	"	1.6	2.4
" , o-Toluic acid, Diethylene glycol diethyl ether	"	"	4.7	3.3
" , Sebacic acid, Benzyl ether	"	"	2.7	1.5
" , p-Toluic acid, Dipropylene glycol dibenzoate	"	"	2.9	2.1
" , m-Toluic acid, Diethylene glycol ethyl ether	"	"	4.2	1.8
Dimethylacetamide (DMAA)	1		1.7	
DMAA, Azelaic acid	$(1/2)^2$	$(3/5)^2$	1.5	3.3
" , Acetyl salicylic acid	"	"	2.7	1.7
" , Benzoic acid	"	"	1.4	2.3
" , Cinnamic acid	"	"	2.7	2.3
" , Decanoic acid	"	"	5.1	4.5
" , Dodecanoic acid	"	"	2.1	3.0
" , Glutaric acid	"	"	2.6	2.5

Table 3-Continued.

Compounds	Ratios*		Relative Volatility	
DMAA, p-tert. Butyl benzoic acid	$(1/2)^2$	$(3/5)^2$	2.1	3.2
" , Heptanoic acid	"	"	1.6	3.8
" , Hexanoic acid	"	"	3.5	2.5
" , p-Hydroxy benzoic acid	"	"	3.5	1.9
" , Itaconic acid	"	"	3.6	2.7
" , Malic acid	"	"	2.3	1.9
" , Octanoic acid	"	"	1.3	2.2
" , Salicylic acid	"	"	1.1	1.7
" , Sebacic acid	"	"	1.6	2.0
" , o-Toluic acid	"	"	2.1	4.3
" , m-Toluic acid	"	"	2.1	1.8
" , p-Toluic acid	"	"	1.3	2.1
" , Adipic acid	"	"	2.1	1.5
" , Adipic acid, Benzyl benzoate	$(1/3)^3$	$(2/5)^3$	2.2	1.6
" , Acetyl salicylic acid, Butyl benzoate	"	"	2.2	2.2
" , Azelaic acid, Isophorone	"	"	2.4	2.2
" , Benzoic acid, Cyclohexanone	"	"	3.7	2.4
" , p-tert. Butyl benzoic acid, Benzyl ether	"	"	1.8	1.8
" , Cinnamic acid, Diethylene glycol diethyl ether	"	"	2.2	2.2
" , Decanoic acid, Ethyl benzoate	"	"	2.9	1.2
" , Dodecanedioic acid, Anisole	"	"	2.1	1.4
" , Glutaric acid, Butyl ether	"	"	4.6	1.5
" , Heptanoic acid, Acetophenone	"	"	2.0	2.1
" , Hexanoic acid, Adiponitrile	"	"	4.6	2.9
" , p-Hydroxybenzoic acid, 2-Octanone	"	"	1.8	1.5
" , Itaconic acid, Dipropylene glycol dibenzoate	"	"	2.1	1.5
" , Malic acid, 2-Methoxy ethyl ether	"	"	1.4	1.4
" , Octanoic acid, Methyl benzoate	"	"	2.7	2.5
" , Salicylic acid, Methyl salicylate	"	"	1.5	1.5
" , o-Toluic acid, Methyl phenyl acetate	"	"	2.9	2.2
" , m-Toluic acid, Ethyl phenyl acetate	"	"	1.7	3.2
" , p-Toluic acid, Anisole	"	"	1.9	1.5

* See explanation of ratios at top of page 40.

The two relative volatilities shown in Table 3 are for the two different ratios of extractive agent mixture investigated. For example, 1/2 part of dimethylformamide plus 1/2 part of azelaic acid with one part of the formic acid/dioxane azeotrope gives a relative volatility of 1.8; 3/5 parts of DMFA plus 3/5 parts azelaic acid with one part of formic acid/dioxane azeotrope gives a relative volatility of 2.5.

After initial screening of the proposed agents, two were selected for use in the perforated-plate column. First a mixture of 50% dimethylformamide and 50% propoxypropanol was used as an extractive agent and later pure dimethylacetamide was used. The results of these runs are given in Table 4 below. The relative volatilities listed were calculated using the Fenske equation with the number of ideal plates being equal to 5.3. Agent addition to boil-up rate was 1:4.

Table 4. Column results: formic acid/dioxane.
OVHDS = Overheads, BTMS = Bottoms

Agent	Column	Time Hrs.	wt.% Dioxane	wt% Formic	Relative Volatility
50% Dimethylformamide	OVHDS	0.5	80.8	19.2	1.72
50% Propoxypropanol	BTMS		26.8	73.2	
"	OVHDS	1.5	81.5	18.5	1.58
	BTMS		36.4	63.6	
Dimethylacetamide	OVHDS	0.75	88.6	11.4	1.71
	BTMS		30.8	69.2	
"	OVHDS	1.5	90.4	9.6	1.71
	BTMS		36.8	63.2	

The Formic Acid/3-Methyl-2-butanone System

Data for the formic acid\3-methyl-2-butanone system was gathered in the same manner as the formic acid/dioxane system. Table 5 below and on the following pages lists extractive agents which were successful at negating the azeotrope in the Othmer still. The convention for listing extractive agent composition and concentration is the same as that used for the formic acid/dioxane system in Table 3.

Table 5. Agents for formic acid/3-methyl-2-butanone.

Compounds	Ratios*		Relative Volatility	
Dimethylformamide (DMFA), Adipic acid	$(1/2)^2$	$(3/5)^2$	4.9	3.1
DMFA, Acetyl salicylic acid	"	"	1.5	3.8
" , Benzoic acid	"	"	2.2	2.4
" , Cinnamic acid	"	"	3.0	3.3
" , Decanoic acid	"	"	2.7	4.0
" , Heptanoic acid	"	"	1.9	1.3
" , Neodecanoic acid	"	"	1.7	1.6
" , Octanoic acid	"	"	2.2	2.5
" , Pelargonic acid	"	"	3.5	2.1
" , Adipic acid, Cyclohexanone	$(1/3)^3$	$(2/5)^3$	3.5	2.5
" , Acetyl salicylic acid, Benzyl benzoate	"	"	1.4	1.8
" , Benzoic acid, Isophorone	"	"	1.6	2.5
" , Cinnamic acid, Butyl ether	"	"	1.9	2.1
" , Decanoic acid, Butyl Benzoate	"	"	3.5	3.2
" , Heptanoic acid, Adiponitrile	"	"	3.9	3.5
" , Neodecanoic acid, Ethyl benzoate	"	"	2.2	3.3
" , Octanoic acid, Acetophenone	"	"	2.8	3.2
" , Pelargonic acid, Methyl benzoate	"	"	2.5	2.1
Dimethylacetamide (DMAA)	1	6/5	1.3	1.4
DMAA, Adipic acid	$(1/2)^2$	$(3/5)^2$	2.8	2.9
" , Acetyl salicylic acid	"	"	2.7	2.6
" , Azelaic acid	"	"	2.5	1.9
" , Benzoic acid	"	"	2.7	1.4
" , 2-Benzoyl benzoic acid	"	"	2.4	2.0
" , 4-tert. Butyl benzoic acid	"	"	1.8	1.7
" , Dodecanoic acid	"	"	2.6	3.0
" , Heptanoic acid	"	"	2.2	2.1

Table 5-Cont'd.

Compounds	Ratios*		Relative Volatility	
DMAA, Dodecanedioic acid	$(1/2)^2$	$(3/5)^2$	2.7	1.7
" , Glutaric acid	"	"	1.2	1.2
" , Hexanoic acid	"	"	1.4	1.4
" , 4-Hydroxybenzoic acid	"	"	1.1	1.1
" , Itaconic acid	"	"	1.1	1.1
" , Malic acid	"	"	1.2	1.2
" , Neodecanoic acid	"	"	2.4	3.3
" , Neopentanoic acid	"	"	1.2	1.6
" , Octanoic acid	"	"	1.6	3.0
" , Pelargonic acid	"	"	2.7	3.6
" , Salicylic acid	"	"	1.0	1.2
" , Sebacic acid	"	"	1.2	1.4
" , o-Toluic acid	"	"	1.0	1.1
" , m-Toluic acid	"	"	1.1	1.2
" , p-Toluic acid	"	"	1.1	1.0
" , Adipic acid, 2-Octanone	$(1/3)^3$	$(2/5)^3$	2.4	2.6
" , Acetyl salicylic acid, Isophorone	"	"	5.0	3.4
" , Azelaic acid, Benzyl benzoate	"	"	1.8	1.4
" , Benzoic acid, benzyl ether	"	"	1.4	1.8
" , 2-Benzoyl benzoic acid, Ethylene glycol butyl ether acetate	"	"	2.1	3.3
" , 4-tert. Butyl benzoic acid, Butyl ether	"	"	3.5	3.5
" , Glutaric acid, Methyl salicylate	"	"	1.1	1.1
" , Heptanoic acid, Methyl benzoate	"	"	2.0	2.5
" , Hexanoic acid, Methyl salicylate	"	"	2.1	2.1
" , 4-Hydroxybenzoic acid, Dipropylene glycol dimethyl ether	"	"	1.2	1.1
" , Itaconic acid, Isobutyl heptyl ketone	"	"	1.1	1.1
" , Malic acid, Ethylene glycol methyl ether acetate	"	"	1.1	1.1
" , Neodecanoic acid, Cyclohexanone	"	"	1.1	1.0
" , Neopentanoic acid, Ethylene glycol methyl ether acetate	"	"	2.2	2.3
" , Octanoic acid, Ethyl benzoate	"	"	2.1	3.9
" , Pelargonic acid, Butyl benzoate	"	"	1.6	2.8
" , Sebacic acid, Propylene glycol dimethyl ether	"	"	1.1	1.1
" , o-Toluic acid, Hexyl acetate	"	"	1.2	1.1
" , m-Toluic acid, Hexyl acetate	"	"	1.1	1.1
" , p-Toluic acid, 2-Ethyl hexyl acetate	"	"	1.2	1.1

* See explanation of ratios at top of page 40.

After initial screening, two of the extractive agents were tested in the perforated-plate rectification column. Pure dimethylacetamide and an equal ratio mixture of heptanoic acid, dimethylformamide, and methyl benzoate were used. The results of these runs are given in Table 6 below. The relative volatilities were calculated in the same manner as for the formic acid/dioxane system. Once again, agent addition to boil-up rate was 1:4.

Table 6. Column results: formic acid/3-methyl-2-butanone.
OVHDS = Overheads, BTMS = Bottoms

Agent	Column	Time Hrs.	wt% 3-methyl-2-butanone	wt% formic acid	Relative Volatility
33% Dimethylformamide	OVHDS	0.75	90.4	9.6	2.28
33% Heptanoic acid	BTMS		17.4	82.6	
33% Methyl benzoate					
	OVHDS	1.5	90.7	9.3	2.37
"	BTMS		15.4	84.6	
Dimethylacetamide	OVHDS	0.75	90.1	9.9	1.52
	BTMS		42.1	57.9	
"	OVHDS	1.5	93.8	6.2	2.42
	BTMS		23.1	76.9	

Although many agents were successful in negating the formic acid/3-methyl-2-butanone azeotrope, some were deficient in that they caused decomposition of the formic acid. Table 7 on page 44 lists some of these deficient agents.

Table 7. Agents which decomposed formic acid.

Dimethylformamide (DMFA)
" , o-tert. Butyl benzoic acid
" , Glutaric acid
" , Itaconic acid
" , Hexanoic acid
" , Salicylic acid
" , Sebacic acid
" , o-Toluic acid
" , Azelaic acid, Benzyl ether
" , Glutaric acid, Diethylene glycol diethyl ether
Dimethylacetamide (DMAA), Cinnamic acid
DMAA, Cinnamic acid, Diethylene glycol diethyl ether

DISCUSSION

Data From the Othmer Still

We can see from Tables 3 and 5 that many extractive agents are effective at negating the formic acid/dioxane and formic acid/3-methyl-2-butanone azeotropes. For most of the extractive agents tested, two concentrations of agent were used. In some cases the higher concentration appears to give increased relative volatility and in some cases the opposite is true. There are many possible reasons for these occurrences.

Small to medium gains in relative volatility can usually be attributed to increases in extractive agent concentration. Increasing agent concentration increases selectivity and results in increased values for relative volatility. The rate at which selectivity increases with concentration depends on the agent or mixture of agents and may only be determined by experimentation.

Large swings in relative volatility between an agent at high and at low concentrations may indicate decomposition. Decomposition of formic acid to H_2O and CO_2 may cause calculated relative volatilities to be higher or lower than actual values. Because H_2O is initially present in the formic acid, and CO_2 is released as a gas, small amounts of decomposition go undetected. The effect of small amounts of decomposition is most apparent in extractive agent tests at higher agent concentrations. After an extractive agent is tested at low concentration in the Othmer still, additional agent is added and the test continued at the higher concentration. Although this saves time and material costs, prolonged exposure of formic acid to harsh extractive agents at high temperatures may cause its partial decomposition.

Small decreases in relative volatility between low and high agent concentrations may result from temporary upset in operation of the Othmer still, decomposition, or an increasingly negative effect by one of the agents in the extractive agent mixture.

The only conclusion which may be drawn from the above discussion is that data taken from the Othmer still is inconclusive. Relative volatility values calculated from data obtained from the stills should not be used in design or in any way be misrepresented as being rigorously determined. These values only represent initial investigation of extractive agents which were shown to negate the azeotropes. They may or may not be suitable for further investigation.

Data From the Perforated-plate Column

Data taken from the plate column far surpasses in accuracy that taken from the Othmer stills. Equilibrium is achieved in a shorter period of time reducing the possibility of decomposition. Because of the shorter period of operation, the plate column may be monitored continuously for evidence of decomposition or system upset. Relative volatilities calculated using the Fenske equation represent the average of 5.3 equilibrium stages and result in much more reliable data.

Two extractive agents were tested on each of the azeotropic mixtures. In all cases an agent addition rate to boil-up rate was maintained at 1:4. Using a 50:50 weight ratio of DMFA and propoxypropanol as extractive agent on the formic acid/dioxane azeotrope gave an average relative volatility of 1.65. The value obtained in the Othmer still using a equal ratio mixture of extractive agent and azeotrope was 4.2. Although this difference could be due to a difference in extractive agent concentration, it is more probable that some decomposition occurred in the Othmer still. With pure DMAA used in the column a relative volatility of 1.71 was attained. This value is nearly identical to the 1.7 attained in the Othmer still with an extractive agent to azeotrope mixture ratio of 1:1. This fact seems to support earlier observations that drastic increases in relative volatility do not usually occur with modest increases in extractive agent concentration.

An equal weight ratio of DMFA, heptanoic acid, and methyl benzoate was used as an extractive agent for the formic acid/3-methyl-2-butanone azeotrope. The average relative volatility was calculated to be 2.3. This extractive agent was not previously tested in the Othmer still. However, a similar extractive agent with DMAA substituted for DMFA was used in the still with an extractive agent to azeotropic mixture ratio of 1:1 and gave a relative volatility of 2.0. Pure DMAA was also used as an extractive agent on the formic acid/3-methyl-2-butanone azeotrope and gave a relative volatility of 1.5 at 0.75 hours and 2.42 at 1.5 hours. Because other systems in the plate column had relative volatilities which did not vary appreciably between 0.75 and 1.5 hours, it is probable that decomposition did occur in this last case. This was probably due to high temperature in the stillpot caused by an ever increasing concentration of extractive agent there.

The effect of increasing concentration of extractive agent in the plate column's stillpot on column operation has been questioned. Yeh [20, 21] has shown that this does in fact have a negligible effect on column operation. The validity of column operation in semi-batch fashion has also been questioned. As stated previously, Szabados has shown that the effects of operating in this fashion are minimal.

Investigation of the various extractive agents shows two facts that generally seem to hold true. First, pure DMAA and pure DMFA both have a tendency to cause decomposition of formic acid, especially at high concentration. Second, DMFA seems to be a stronger extractive agent than DMAA but also has a greater tendency to cause formic acid to decompose.

Solubility Parameters and Polarity Diagrams

Yeh [9] utilized Hansen solubility parameters and a concept he termed the polarity diagram as a means of screening potentially effective agents for various azeotropic systems. Although the technique seems to work well for two component systems with pure extractive agents, it does not lend itself well to multicomponent extractive agents or ternary and greater systems. Table 8 below lists solubility parameters and volumetric data for the azeotropic systems studied and for pure DMFA and DMAA [22].

Table 8. Solubility parameters and volumetric data at 25 °C.

$\delta_t=(\delta_d^2+\delta_p^2+\delta_h^2)^{1/2}$

Compound	δ_t MPa$^{1/2}$	δ_d MPa$^{1/2}$	δ_p MPa$^{1/2}$	δ_h MPa$^{1/2}$	Volume cm^3/g-mol
DMFA	24.8	17.4	13.7	11.3	77.0
DMAA	22.7	16.8	11.5	10.2	92.5
Formic Acid	24.9	14.3	11.9	16.6	37.8
Dioxane	20.5	19.0	1.8	7.4	85.7
3-Methyl-2-butanone	18.4	14.6	8.8	7.0	107.5

In Yeh's studies, the hydrogen bond parameter, δ_h, was plotted against the polar bond parameter, δ_p, on a two dimensional diagram to predict agent effectiveness. The dispersion parameter, δ_d, was not used because values did not differ appreciably between components and extractive agents. To account for the difference in molar volumes of the azeotrope components, the diagram was split into two regions based on molar volumes. In the method, solubility parameters were plotted for components of the azeotrope and for the pure extractive agents to be tested. A line was drawn between the two azeotrope components and bisected with a perpendicular line to create two line segments whose ratio is the same as the molar volume ratio of the components. Because like molecules readily associate, the side of the perpendicular an extractive agent is plotted on will determine which component of the azeotrope it will bring to the bottom of the column.

Figures 7 on page 51 and Figure 8 on page 52 are polarity diagrams for the formic acid/dioxane and formic acid/3-methyl-2-butanone systems respectively. In both cases the formic acid is shown to be more compatible with the extractive agents than are dioxane or 3-methyl-2-butanone. This was indeed the case with all extractive agent runs done in both the Othmer Still and perforated-plate column.

Other experimenters have not had such good success with the polarity diagram method. Szabados reported that the use of polarity diagrams was deficient in his experiments. Yeh also had extractive agent models which did not conform. It is the opinion of Barton [22] that an expanded set of parameters using dispersion, induction, orientation, acid, and base interactions is necessary for reliable quantitative

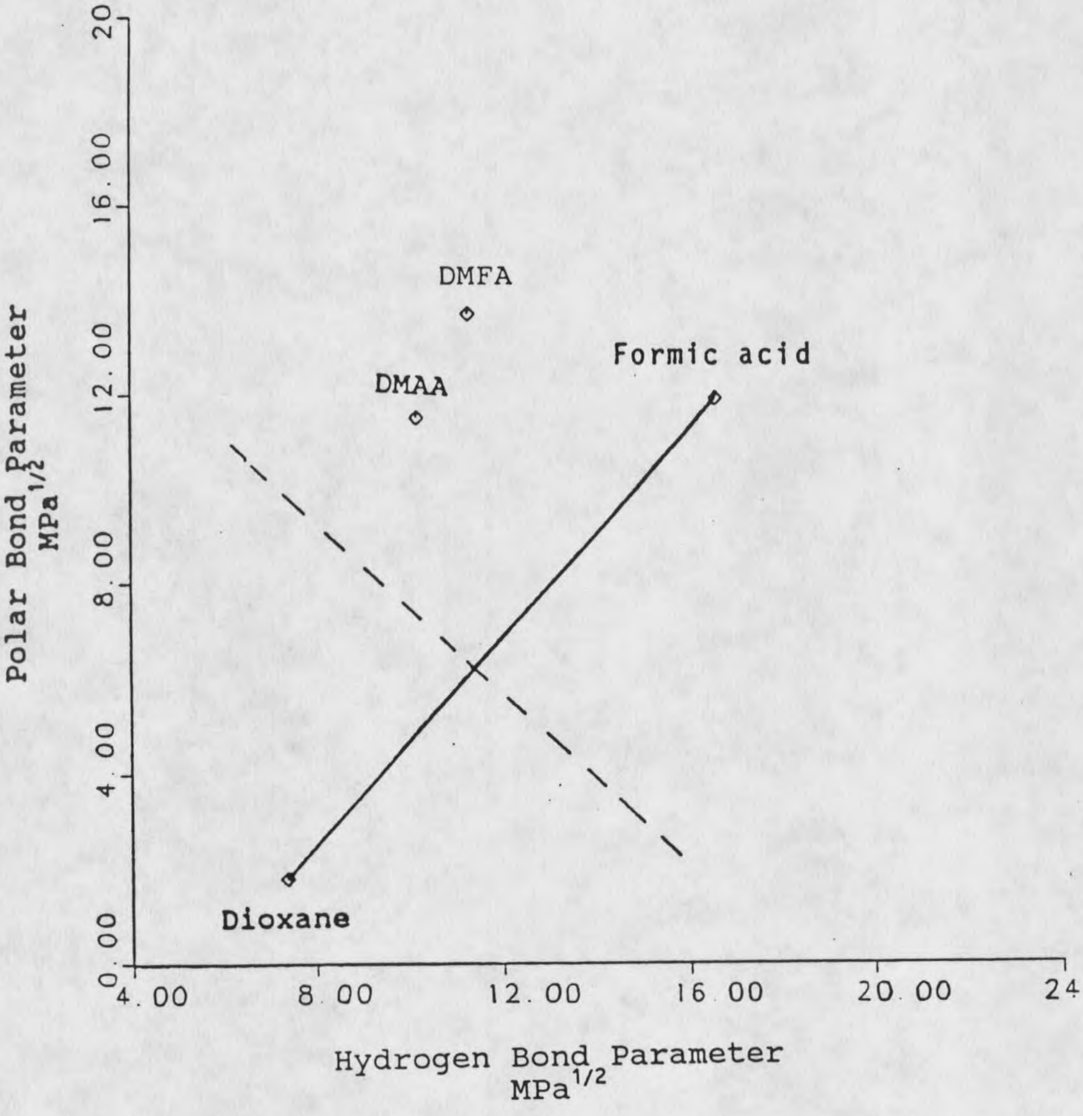


Figure 7. Polarity diagram for formic acid/dioxane system.

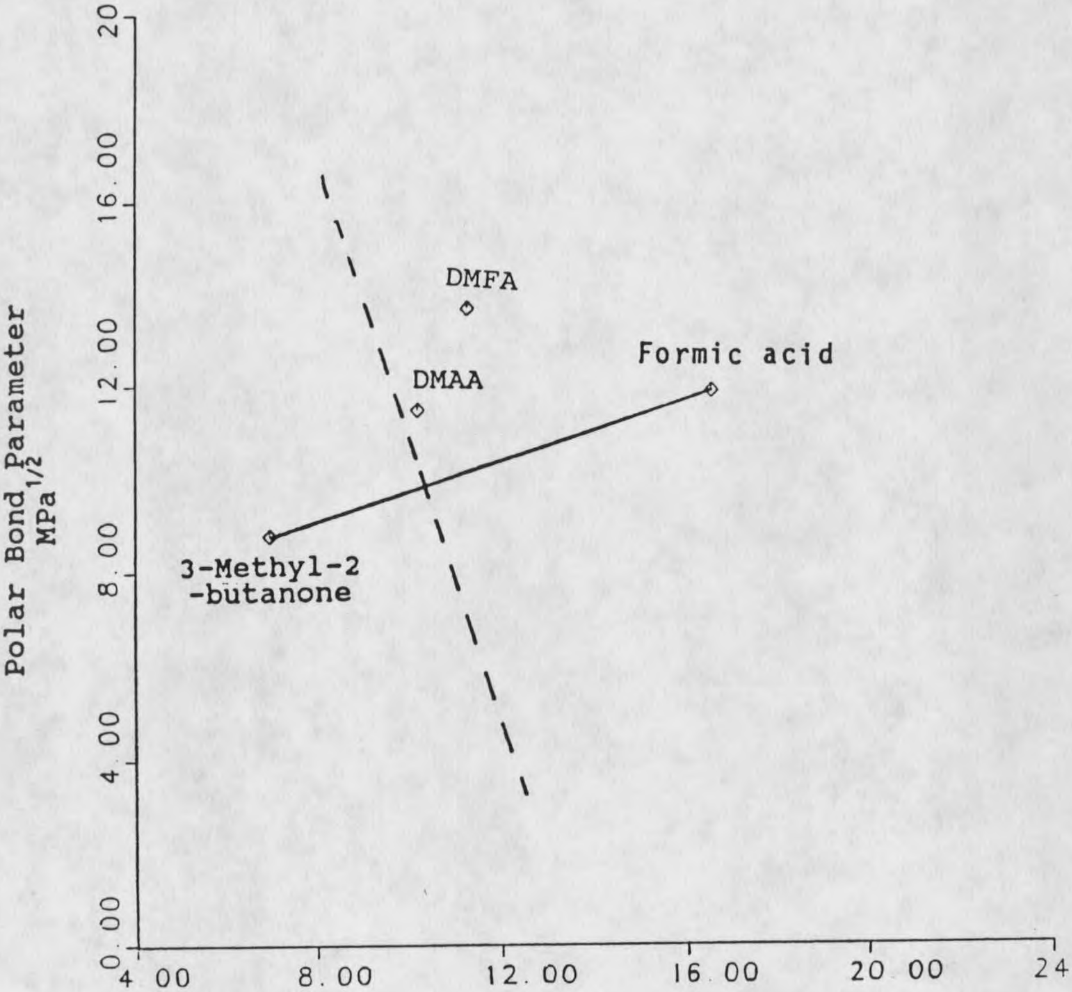


Figure 8. Polarity diagram for formic acid/3-methyl-2-butanone system.

evaluation of behavior in multicomponent systems. Although I must agree with Barton's conclusion, the simplicity of the polarity diagram does seem to warrant its use for initial screening of extractive agents.

Other models for studying non-ideal solutions based on functional group contributions are available. One such model is called the modified separation of cohesive energy density model (MOSCED) [10], another is the UNIFAC method [10]. Although these models are reported to give good results for nonelectrolyte solutions, they only give insight into the outcome of experimentation and do not replace it.

SUMMARY AND CONCLUSIONS

1. Extractive distillation of formic acid/dioxane and formic acid\3-methyl-2-butanone azeotropes can successfully be accomplished if the proper agents are employed.
2. Although dimethylformamide seems to be a more effective agent than dimethylacetamide when used in mixtures, it also has a greater tendency to decompose formic acid.
3. When used in mixtures with DMFA and DMAA, both Class II and Class III compounds seemed to work well as extractive agents.
4. Use of polarity diagrams provides a simple and often very effective method of screening extractive agents. However, this data is often inconclusive and should not be used as the sole basis for investigation.
5. Data taken from the Othmer still provides the surest method for screening possible extractive agents. However, by itself the data is often inconclusive and unsuitable for use in design.
6. The most reliable experimental data is obtained from the perforated-plate column.
7. Although a correlation is known to exist between increased volume fraction of agent and increased selectivity, no definite correlation was noted here.

RECOMMENDATIONS FOR FUTURE RESEARCH

Through the use of polarity diagrams, experience, and occasionally trial and error, it is probable that extractive agents will be found to negate most azeotropes. Although gathering data on effective agents is useful for patenting purposes, in itself it does little to advance the field of extractive distillation.

It is my recommendation that at least one pure extractive agent should be thoroughly tested for each azeotropic system studied. It should be tested at all possible concentrations and agent addition rates in the Othmer still and perforated-plate column respectively. This will allow determination of activity coefficients, checks for thermodynamic consistency of data, and determination of selectivity as a function of agent concentration. To do this, the agent must be gentle enough not to cause decomposition of the azeotrope components at any concentration. It would also be advantageous to choose an agent not so chemically complex as to render analysis of the contribution of chemical groups prohibitive. Although these conditions on the extractive agent would be restrictive, I believe that data gained from such experiments would be of great value to the advancement of extractive distillation.

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