



The separation of azeotropes by extractive distillation
by Rudolph Joseph Szabados

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 in a semi-batch rectification column was used to accomplish the separations of the following maximum-boiling azeotropic mixtures: formic acid/water, formic acid/3-pentanone, formic acid/2-pentanone, formic acid/dioxane, and acetic acid/dioxane. A continuous extractive distillation process was compared with a semibatch process in the separation of a minimum-boiling azeotropic mixture of n-butanol and n-butyl acetate.

Research was conducted in a semi-batch column and a continuous column possessing 4.5 and 3.2 theoretical plates, respectively. The Fenske equation was used for calculation of relative volatilities and for the estimation of the minimum number of theoretical plates required for solvent-free 99% pure products.

All the azeotropes formed by the mixtures studied were negated by using appropriate extractive agents. An extractive agent comprising of DMSO, nanoic acid, and methyl benzoate was utilized for the formic acid/2-pentanone and formic acid/dioxane systems. Successful agents for the formic acid/water and formic acid/3-pentanone systems were certain oxygenated or nitrogen-containing organic compounds. DMSO was used as the agent for the n-butanol/n-butyl acetate system. Certain dimethylamides or DMSO mixed with higher boiling organic compounds were successful in negating the acetic acid/dioxane azeotrope.

The use of polarity diagrams was investigated as a method for evaluating successful agents. Polarity diagrams were found to be deficient in predicting system behavior in the experimental columns except for the dehydration of formic acid.

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MONTANA STATE UNIVERSITY
Bozeman, Montana

November 1988

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APPROVAL

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Rudolph Joseph Szabados

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 in a semi-batch rectification column was used to accomplish the separations of the following maximum-boiling azeotropic mixtures: formic acid/water, formic acid/3-pentanone, formic acid/2-pentanone, formic acid/dioxane, and acetic acid/dioxane. A continuous extractive distillation process was compared with a semi-batch process in the separation of a minimum-boiling azeotropic mixture of n-butanol and n-butyl acetate.

Research was conducted in a semi-batch column and a continuous column possessing 4.5 and 3.2 theoretical plates, respectively. The Fenske equation was used for calculation of relative volatilities and for the estimation of the minimum number of theoretical plates required for solvent-free 99% pure products.

All the azeotropes formed by the mixtures studied were negated by using appropriate extractive agents. An extractive agent comprising of DMSO, nanoic acid, and methyl benzoate was utilized for the formic acid/2-pentanone and formic acid/dioxane systems. Successful agents for the formic acid/water and formic acid/3-pentanone systems were certain oxygenated or nitrogen-containing organic compounds. DMSO was used as the agent for the n-butanol/n-butyl acetate system. Certain dimethylamides or DMSO mixed with higher boiling organic compounds were successful in negating the acetic acid/dioxane azeotrope.

The use of polarity diagrams was investigated as a method for evaluating successful agents. Polarity diagrams were found to be deficient in predicting system behavior in the experimental columns except for the dehydration of formic acid.

INTRODUCTION

Background

Extractive distillation utilizes a multiple plate rectification column with the addition of a solvent to favorably enhance the separation of close boiling mixtures or azeotropes. Distillation in general is a very old process probably first used as a separation technique approximately in 1500 B.C. [1]. Fractional distillation is of extreme commercial value because it is the most common method of separating liquids [2]. Simple fractional distillation is applicable when the feed mixture to be separated forms no azeotrope(s) and the differences in component volatilities is appreciable. No reaction between components or decomposition should occur at the operating column temperature and pressure. This temperature and pressure must be feasibly attainable.

Figure 1 is a schematic of a single rectification column. The feed enters the column near its center at a location which divides the tower into the upper, rectifying and lower, stripping sections. The reboiler at the column bottom is a vaporizer which maintains a liquid level while generating vapor to ascend throughout the tower. A condenser at the column top condenses rising vapors either partially or totally, thereby producing liquid which can be refluxed to the top plate. Within the column, vapor and liquid come in intimate contact on each plate. A portion of the more volatile component vaporizes

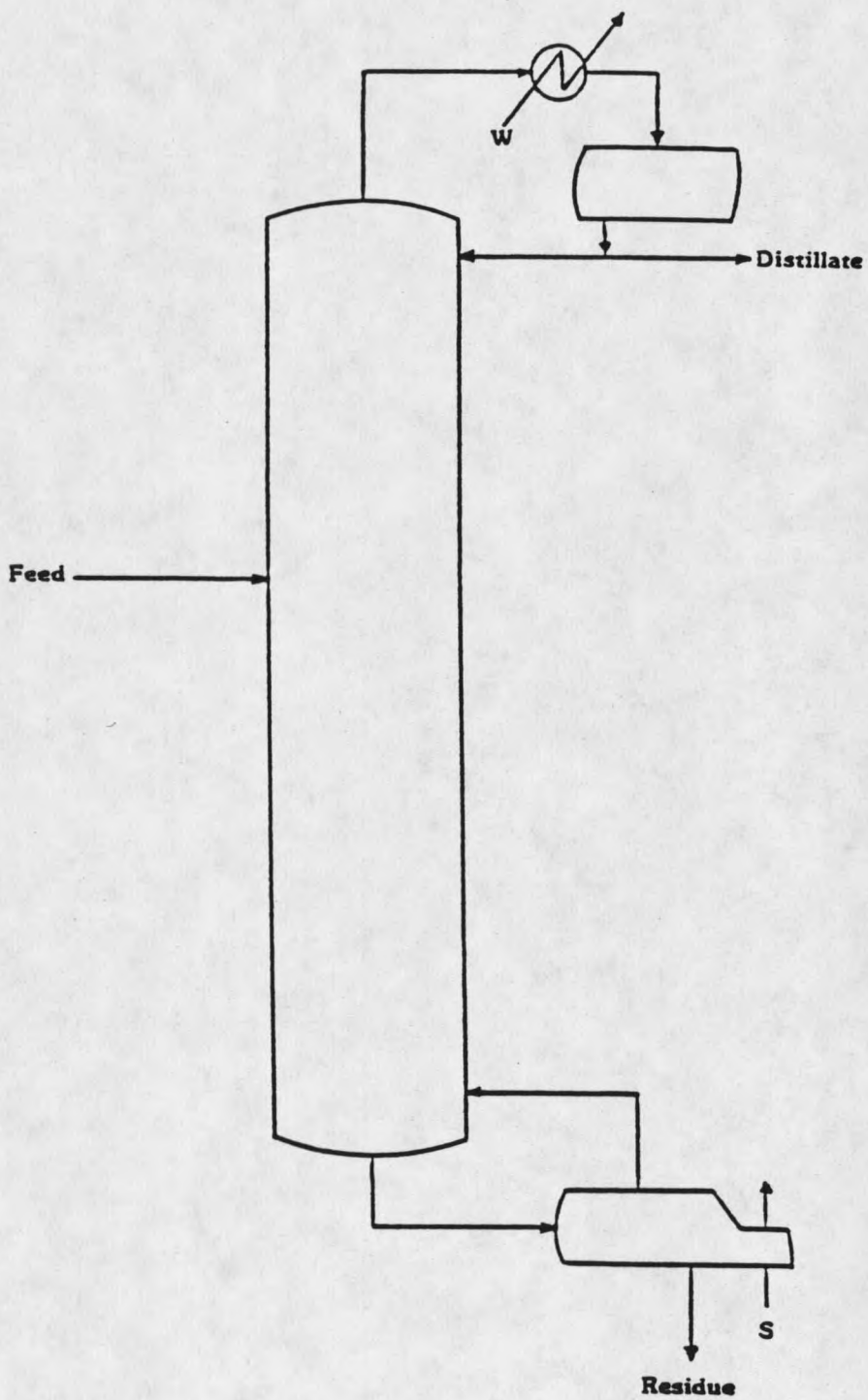


Figure 1. Conventional fractionating column.

from the liquid, enriching the ascending vapor in the low-boiling component while part of the less volatile component condenses, enriching the descending liquid in the high boiling component. Since the bottom tray has the highest concentration of the high boiling component, the temperature there is the highest of any tray in the column and decreases from tray to tray upward throughout the tower.

Azeotropic and Extractive Distillation

As the differences between the volatilities of feed components becomes small, or the formation of an azeotrope occurs, separation using a simple rectification column becomes unfeasible or impossible. In such cases extractive or azeotropic distillation methods must be employed. Both methods are similar in that they utilize the addition of a solvent to favorably increase the difference in component volatilities.

Azeotropic distillation uses a solvent which forms a minimum-boiling azeotrope with the component to be taken off as overhead. This overhead product would normally contain 50 to 80 percent solvent [3]. Extractive distillation alters the volatilities between two components in a direction which improves the possibility of separation by the addition of a solvent which does not form an azeotrope with any of the feed components.

Figure 2 is a schematic representing an extractive distillation process. The solvent is introduced a few plates down from the top plate producing a sufficient concentration of the solvent from plate to plate modifying equilibrium in the desired manner. Allowing a few

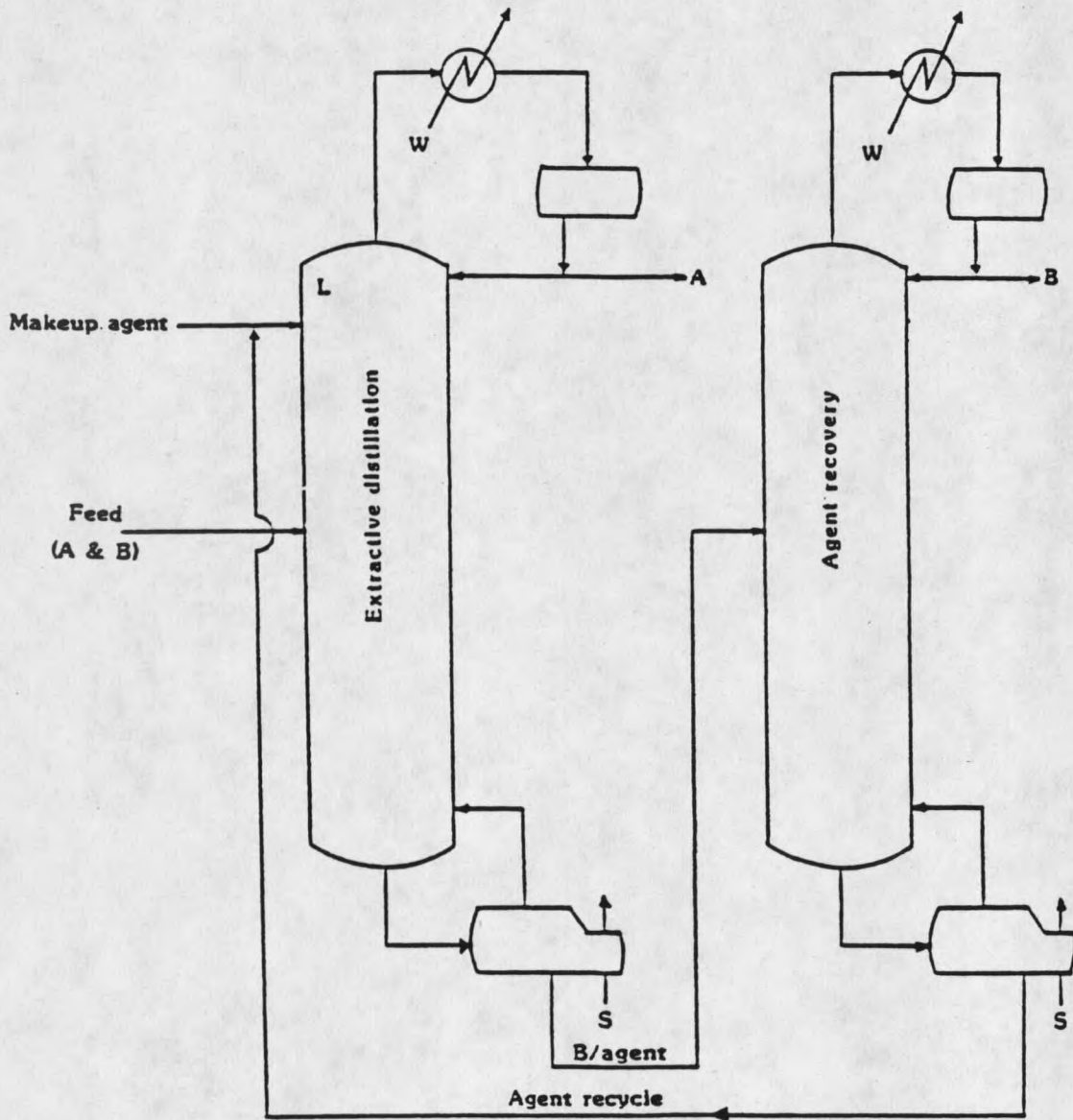


Figure 2. Schematic diagram for an extractive distillation process.

plates above the point of solvent entry helps eliminate the possibility of contamination of the overhead product. Since the solvent is considerably less volatile than the mixture to be separated, its flow can be considered constant at some value throughout the column below its entry point [4]. Typically, the addition of solvent should be at a rate sufficient to allow one to two parts solvent per part of components being separated on each plate [5]. The extractive agent descends through and out of the column where it is then reclaimed by the use of another rectification column.

Agent Selection

The solvent is always chosen so that the column size requirement necessary to reclaim the agent is minimal. This requires that the volatility of the solvent be sufficiently low as to render its recovery in a rectification column simple. Berg [6] has suggested that the solvent boil at least 20 degrees centigrade higher than that of the component mixture to be separated. Yeh [7] has suggested that the following characteristics are favorable in selecting successful agents:

1. It should have a high capacity for the species being separated by it. The higher the agent capacity, the lower the circulation rate required.
2. It should be selective, having a wider range of temperature and concentration of miscibility with one or more of the components being separated while having a small range of miscibility with other components.
3. It should be chemically stable, i.e., it should not undergo irreversible reactions with components of the feed stream or during recovery.

4. It should be easily separable from the components with which it associates. Thus it can be reused again and again.
5. It should be nontoxic and noncorrosive and should not be a serious contaminant to the process stream being handled.
6. It should be inexpensive to keep the cost of maintaining agent inventory and of replacing loss low.
7. It should have a low enough viscosity to be pumped and flow by gravity easily.
8. It should be completely soluble with the components in the distilling system at the temperature and concentrations in the column.

It is obviously a complicated process to determine successful extractive agents. However, the previously mentioned characteristics suggested by Yeh must be examined collectively before a successful process is attainable. This will ensure minimum investment and operating costs for future design considerations if applicable.

Advantages of Using Extractive Distillation

Generally, there are many successful solvents for a given separation using extractive distillation because the volatility of the agent does not have to be matched with the volatility of the feed components. This is not the case in azeotropic distillation where the agent and feed component volatilities must be matched. Extractive distillation may be more attractive than conventional fractional distillation for components that are not close-boiling because of the possible great reduction in the number of plates necessary.

To ensure that ascending vapors in the column do not condense, it is necessary to heat the solvent to approximately the same temperature

as that of the plate onto which it is introduced. This heat requirement is generally smaller than that required for azeotropic distillation, in which case the solvent must be vaporized [3].

THEORETICAL ASPECTS

Vapor-Liquid Equilibrium

Fractional distillation is a separation technique which utilizes the temperature and concentration differences in the vapor and liquid streams on each tray as the driving force for the operation. Since the vapor and liquid are in intimate contact on each plate of the column, a state of equilibrium is approached in temperature and composition. Thus, equilibrium data is essential in order to predict the behavior of systems in a fractionating column. Equilibrium data must be determined experimentally if a high degree of accuracy is required, although approximate methods are available if experimental data is lacking.

The criteria for phase equilibrium in a multicomponent system having (n) nonreacting species is:

$$\hat{f}_i^v = \hat{f}_i^L \quad (i=1,2,\dots,n) \quad (1)$$

where \hat{f}_i is the fugacity of the species in solution and the superscripts v and L stand for the vapor and liquid phases, respectively. Throughout the remainder of this paper, \hat{f}_i^L is identical in meaning to \hat{f}_i . By definition:

$$\hat{\phi}_i = \frac{\hat{f}_i^v}{Y_i P} \quad (2)$$

and

$$\gamma_i = \frac{\hat{f}_i}{X_i f_i} \quad (3)$$

where

- $\hat{\phi}_i$ = fugacity coefficient of component i in the vapor phase
- Y_i = mole fraction of species i in the vapor phase
- γ_i = liquid phase fugacity of component i
- X_i = mole fraction of species i in the liquid phase
- P = total pressure
- \hat{f}_i = fugacity of species i as a liquid
- f_i = standard state fugacity of pure species i.

Simply by mathematics one can write:

$$\hat{f}_i = \hat{f}_i^+ \left(\frac{\hat{f}_i}{\hat{f}_i^+} \right) \quad (4)$$

where the superscript + denotes the fugacity determined at reference temperature and pressure.

Changing equation (3) to represent properties determined at reference conditions and substituting into equation (4) yields:

$$\hat{f}_i = X_i \gamma_i^+ f_i^+ \left(\frac{\hat{f}_i}{\hat{f}_i^+} \right) \quad (5)$$

Again, purely by mathematics:

$$f_i^+ = P_i^{\text{sat}} \left(\frac{f_i^{\text{sat}}}{P_i^{\text{sat}}} \right) \left(\frac{f_i^+}{f_i^{\text{sat}}} \right) \quad (6)$$

where P_i^{sat} = pressure at the equilibrium temperature
 f_i^{sat} = liquid fugacity at the equilibrium temperature and P_i^{sat} .

The fugacity coefficients for saturated vapor and liquid are equivalent and defined as:

$$\phi_i^{\text{sat}} = \frac{f_i^{\text{sat}}}{P_i^{\text{sat}}} \quad (7)$$

Substituting equation (7) into equation (6) and inserting the results into equation (5) yields:

$$f_i = x_i \gamma_i^+ P_i^{\text{sat}} \phi_i^{\text{sat}} \left(\frac{\hat{f}_i}{\hat{f}_i^+} \right) \left(\frac{f_i^+}{f_i^{\text{sat}}} \right) \quad (8)$$

After rearranging, substitution of equation (2) into equation (1) yields:

$$Y_i P \hat{\phi}_i = \hat{f}_i \quad (9)$$

Combining equations (8) and (9) gives:

$$Y_i P \left(\frac{\hat{\phi}_i}{\hat{\phi}_i^{\text{sat}}} \right) \left(\frac{\hat{f}_i^+ / \hat{f}_i}{f_i^+ / f_i^{\text{sat}}} \right) = X_i \gamma_i^+ P_i^{\text{sat}} \quad (10)$$

For systems where the effect of pressure is negligible on liquid fugacity, γ_i^+ becomes γ_i [8]. Also, at low pressures (1 atmosphere) assuming ideal gas behavior for the vapor phase is acceptable. With these assumptions, equation (10) reduces to:

$$Y_i P = X_i \gamma_i P_i^{\text{sat}} \quad (11)$$

A further simplification can be made if one assumes the liquid phase acts ideally. This is then known as Raoult's Law and is mathematically represented by:

$$Y_i P = X_i P_i^{\text{sat}} \quad (12)$$

Equation (11) is sufficient for this work because the assumptions leading to it are valid for the systems studied here.

Relative Volatility

A measure of the ease of separation of a binary mixture by distillation is called relative volatility and is mathematically represented as:

$$\alpha_{ij} = \left(\frac{Y_i}{X_i} \right) \left(\frac{X_j}{Y_j} \right) \quad (13)$$

where

- α_{ij} = relative volatility of component i with respect to component j
- Y_i, Y_j = mole fractions of components i and j, respectively, in the vapor phase
- X_i, X_j = mole fractions of components i and j, respectively, in the liquid phase.

Solving equation (11) first for mole fraction of component i and then for component j in the vapor phase and inserting into equation (13) yields:

$$\alpha_{ij} = \frac{\gamma_i P_i^{\text{sat}}}{\gamma_j P_j^{\text{sat}}} \quad (14)$$

A relative volatility value of one indicates separation is impossible, whereas the greater the value from one, the greater the ease of separation.

Favorably Altering Relative Volatility

Inspection of equation (14) suggests the following methods for favorably altering relative volatility: (i) changing the ratio of liquid activity coefficients in a manner to increase α_{ij} , and (ii) changing the ratio of component vapor pressures in a way which would increase α_{ij} . Pure vapor pressures of compounds are functions of temperature, however, changing the vapor pressure ratio by altering pressure to induce an effect resulting in temperature changes is not very significant [1]. Changing the liquid activity coefficient ratio by altering temperature and pressure is valid although this is usually uneconomical [1]. The ratio of activity coefficients can be changed economically by physical and chemical means. Thus, this is the basis for successful extractive distillation processes.

The liquid activity coefficient is a measure of nonideality in the liquid phase. Positive deviations from Raoult's Law

(equation (12)) arise when two components are insoluble and their corresponding activity coefficient values are greater than one in solution. This results in the formation of minimum-boiling azeotropes at the extreme. Negative deviations from Raoult's Law result when two components have an affinity for one another and their activity coefficient values are less than one in solution [9]. By inspection of equation (14) it would be highly desirable to select a third component which, when added to the component mixture to be separated, would have a positive deviation from ideality with one component and a negative deviation with the other. This gives rise to the possibility of greatly affecting α_{ij} in a favorable manner.

Selectivity

The ability of a solvent to increase the volatility of one component relative to the other is called selectivity [10]. It is represented by:

$$S_{ij} = \frac{[\alpha_{ij}]_P}{[\alpha_{ij}]_A} \quad (15)$$

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

The chemical means by which a solvent affects selectivity is attributed to the formation of molecular chemical complexes or physical bonding between molecules [1]. Hildebrand [11] and others [12] have recognized the physical means by which a solvent affects

selectivity as the following: (i) dispersion forces or nonpolar effects, (ii) induction forces, and (iii) orientation forces. Dispersion forces arise when an instantaneous electrical dissymmetry of electrons in one molecule polarizes the electron clouds in adjacent molecules, inducing instantaneous dipoles of opposite polarity [13]. Induction forces are a result of a molecule having a permanent dipole inducing a dipole in another molecule. Orientation forces are the result of two molecules having permanent dipoles which interact and orient themselves with respect to one another.

Factors Affecting Selectivity

Increasing temperature increases selectivity [12]. Since this would increase the column operating temperature and pressure, it is necessary to determine optimum conditions based on economic and decomposition considerations. Yeh [14] has shown that an increase of the volume fraction of solvent increases selectivity, thereby favorably altering relative volatility. Prausnitz et al. [10] have pointed out that if chemical effects are negligible, selectivity is primarily a function of the differences in molar volumes and polar energies in hydrocarbon systems. Anderson et al. [12] have noted that if chemical complex formation prevails, then the solvent has a large electron affinity and the more stable the complex the greater the selectivity.

Prediction of Nonideal Solution Behavior

Typically, Raoult's Law can be considered no more than a rough approximation in describing vapor-liquid equilibrium. The activity coefficient is then important in the calculation of real behavior in nonideal systems. Liquid activity coefficients can be determined from experimental vapor-liquid equilibrium data. The data is reduced using some method such as the Barker method [15] with an appropriate correlation equation whose constants are determined by an optimization technique such as the Complex Method of Box [16]. Many correlation equations are available [1, 8, 17] but data reduction requires pressure data at many liquid mole fractions for at least one component in a binary mixture examined. The activity coefficients determined from data reduction are approximations which rely heavily on the accuracy of experimental data.

A purely theoretical means of predicting nonideal solution behavior is the UNIFAC method. In this method, reduction of experimentally determined activity coefficient data into parameters characterizing structural groups is used to predict activity coefficients for systems not studied experimentally [17]. Two major drawbacks of the UNIFAC method are its inability to be used in electrolyte systems and its lack of accuracy for systems which are very nonideal.

Polarity Diagrams

Selectivity is a result of molecular interactions. The interaction is a result of attractive and repulsive forces. Two molecules are repulsed when they have a tendency to occupy the same space. This force falls off rapidly as molecules are separated by distance. Attractive molecular interactions are primarily the result of Van der Waal's forces which have a weaker dependence on intermolecular separation than repulsive forces. Thus, intermolecular forces are dominated by attractive forces. When considering extractive distillation, there are three possible scenarios for attractive molecular interaction: (i) interaction between the feed components, (ii) interaction between one feed component and the extractive agent, and (iii) interaction between the other feed component and the agent. If feed component interaction is negligible, then selectivity is confined between the solvent and the two feed components. If the extent of interaction of the solvent with one of the feed components is greater than with the other, the system with the most interaction would flow down the column allowing the other to be removed as overhead. Yeh [7] has proposed using solubility parameters as measures of solvent interactions. He used the following three parameters as a tool to evaluate possible successful agents: (i) dispersion force parameter (δ_d), (ii) polar interaction parameter (δ_p), and (iii) hydrogen bond parameter (δ_h).

Fenske Equation

In the systems studied in this work, it was imperative to know the column theoretical stages in order to calculate relative volatilities. The experimental semi-batch column was operated at total reflux, therefore, the Fenske equation [1] was used to determine relative volatilities:

$$\alpha_{ij}^N = \left(\frac{Y_i}{Y_j} \right)_{OH} \left(\frac{X_j}{X_i} \right)_{BT} \quad (16)$$

where

- α_{ij} = relative volatility
- N = number of theoretical stages
- OH = subscript referring to the overhead
- BT = subscript referring to the bottoms

The assumptions made when using the Fenske equation are: (i) the relative volatility calculated by equation (16) is a value which can be considered constant on each plate throughout the column, and (ii) the value of theoretical stages (N) remains constant for all systems. The constant relative volatility assumption alludes to ideal solution behavior. This is not the case in extractive distillation. It is also unlikely that (N) remained constant for all the mixtures considered because of slightly different feed rates and different column temperature and pressure conditions. Using the Fenske equation yields approximate results. However, since the calibration of the column and the determination of relative volatilities utilized the same assumptions in calculations, all were done on a similar basis.

MIXTURES TO BE SEPARATED

Formic Acid, Water

Formic acid (B.P. 100.8°C) is used extensively in the pharmaceutical, leather and tanning, textile, dyeing, rubber, and catalyst manufacturing industries.

Currently, there are two major commercial methods for producing formic acid. The reaction of caustic soda with carbon monoxide under pressure produces sodium formate which is hydrolyzed with sulfuric acid to yield formic acid. Formic acid is also produced as a by-product from the oxidation of n-butane. Both commercial methods give aqueous mixtures of formic acid.

Water (B.P. 100°C) forms a maximum azeotrope with formic acid. The azeotrope boils at 107.2°C and contains 22.5 wt % water. A possible method for the dehydration of formic acid is extractive distillation.

Formic Acid, 3-Pentanone and Formic Acid, 2-Pentanone

3-Pentanone is used as a chemical intermediate for the production of herbicides and dyestuffs. It is also used in solvent resin formulation. 2-Pentanone is used in the solvent adhesive, magnetic tape, and printing ink industries.

3-Pentanone (B.P. 102°C) forms a maximum azeotrope with formic acid. The azeotrope boils at 105.2°C and contains 33 wt % formic

acid. 2-Pentanone (B.P. 102.4°C) forms a maximum azeotrope boiling at 105.5°C and containing 32 wt % formic acid.

Both ketones and formic acid are by-products from the controlled oxidation of n-butane. Extractive distillation may prove useful in the separation of these ketones from formic acid.

Acetic Acid, Dioxane and Formic Acid, Dioxane

Dioxane is mainly used as a solvent in the stain industry. Acetic acid is used in the production of dietary supplements, vinyl acetate, cellulose acetate, and acetoacetic ester. It is also used in the leather tanning and meat and wood preservation industries.

Acetic acid (B.P. 118.5°C) forms a maximum azeotrope with dioxane. The azeotrope boils at 119.5°C and contains 77 wt % acetic acid. Dioxane (B.P. 101.4°C) forms a maximum azeotrope with formic acid. The azeotrope boils at 113.4°C and contains 43 wt % formic acid.

Mixtures of acetic and formic acids with dioxane occur from the oxidation of n-butane. Extractive distillation is a possible method for their separations.

n-Butanol, n-Butyl Acetate

n-Butanol is used as a solvent in the formulation of nitrocellulose lacquers and for the production of glycol ethers. It is also used for the production of n-butylacetate which is mainly used in the formulation of nitrocellulose lacquer solvents.

n-Butanol (B.P. 117.7°C) and n-butyl acetate (B.P. 126.1°C) form a minimum azeotrope boiling at 117.6°C and containing 67.2 wt % n-butanol.

Mixtures of these compounds arise from the production of n-butylacetate by esterification of n-butanol. Extractive distillation may be an attractive method for their separation.

RESEARCH OBJECTIVES

The objective of this research was to find extractive agents which would successfully eliminate the azeotropes for the systems studied. The agents should be reusable and could be a pure compound or a mixture of compounds.

The use of the polarity diagram for the purpose of evaluating successful agents was examined for its effectiveness.

EXPERIMENTAL EQUIPMENT

Semi-Batch System

Figure 3 is a schematic of the semi-batch extractive distillation column used to accomplish the separation of the acetic acid/dioxane, formic acid/2-pentanone, formic acid/3-pentanone, formic acid/dioxane, and formic acid/water systems. The equipment can be broken down into the following main components:

- (A) A Corad condensing head which condensed vapor inside the inner vertical tube having a trough around its lower inside perimeter. Six different sized strips each having its own downspout lined the inner vertical tube. Reflux ratio could be controlled (30:1, 20:1, 10:1, 5:1, 3:1, 2:1) by rotating the head until the appropriate downspout was located above the sampling cup. A thermometer shaft was located under the downspouts to enable temperature recordings of the overhead.
- (B) A 20-inch long, 1.5-inch diameter, perforated plate Oldershaw column made of Pyrex glass possessing 5 plates and having a silver vacuum jacket of thickness 1.3 in. Tray spacing and wiper height were 1.8 in. and 3/8 in., respectfully.
- (C) A 5-liter round bottom flask with a sampling tube and thermometer shaft fitted at the bottom of the column.

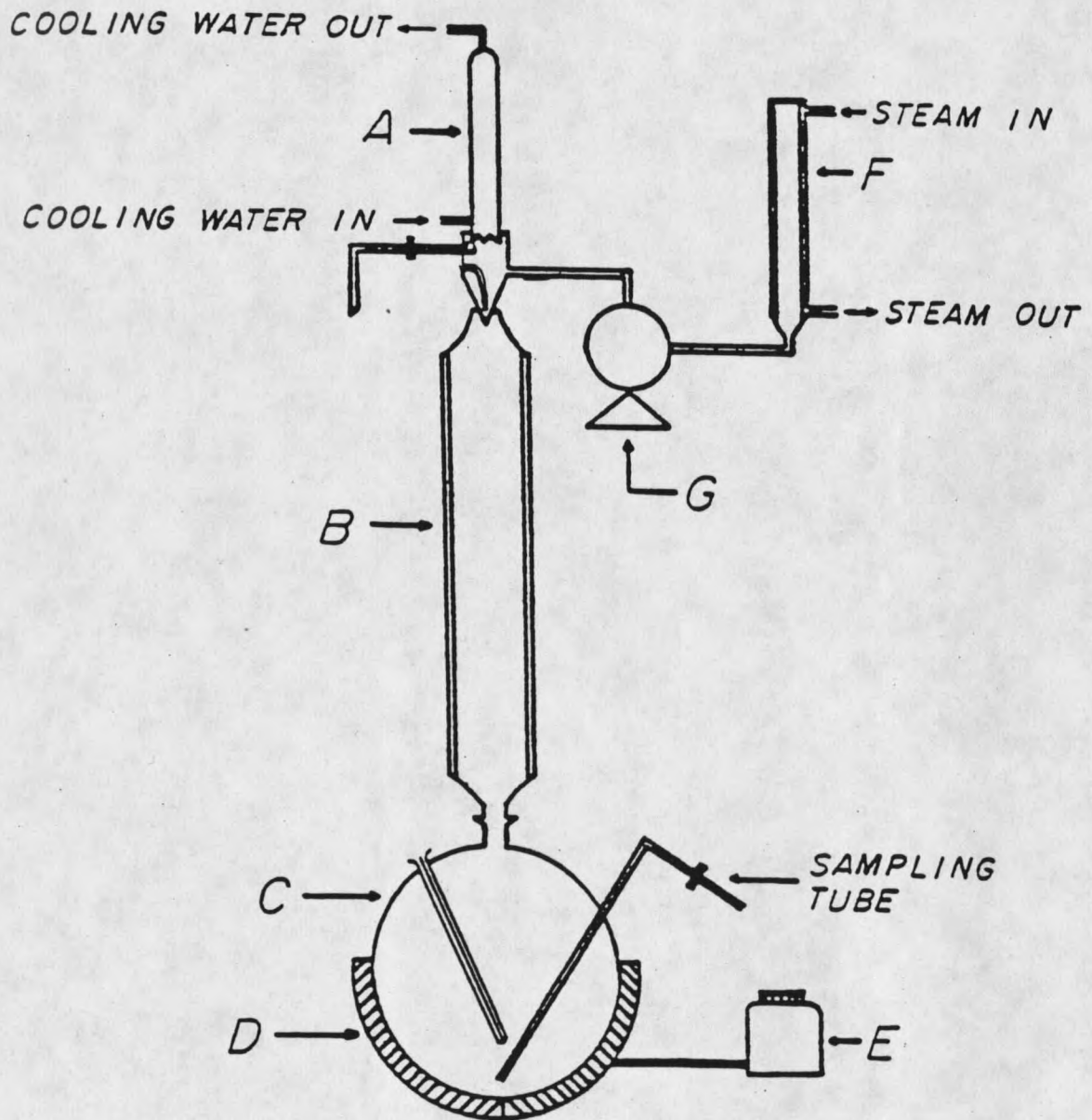


Figure 3. Diagram of the semi-batch extractive distillation column.

- (D) A Glas-Col mantle electrically supplying the heat necessary for vaporation of the bottoms.
- (E) A Variac to adjust the heat output of the Glas-Col mantle.
- (F) A heated Pyrex glass funnel with a capacity of 200 ml. to contain the extractive agent.
- (G) A micro-bellows metering pump made by Research Appliance Company having a 0.5-in. I.D. and 316 stainless steel bellows.

Auxiliary equipment not shown in Figure 3 include: a nichrome heating wire wrapped around the extractive agent pump line, a 65/40 female ball and socket joint having a sidearm for agent entry connected the column with the Corad head, and a 65/40 female ball and socket joint connecting the column with the 5-liter round bottom flask.

Extractive Agent Recovery

The extractive agents were recovered, when necessary, by simple distillation. Figure 4 is a schematic representing the equipment. A 2-liter distilling flask was used as the reboiler. A Pyrex glass condenser condensed vapors rising from the distilling flask. Heat output from the heating mantle was controlled by a Variac.

Recovery of the agent was sometimes necessary for economic reasons and to indicate heat stability of the solvent.

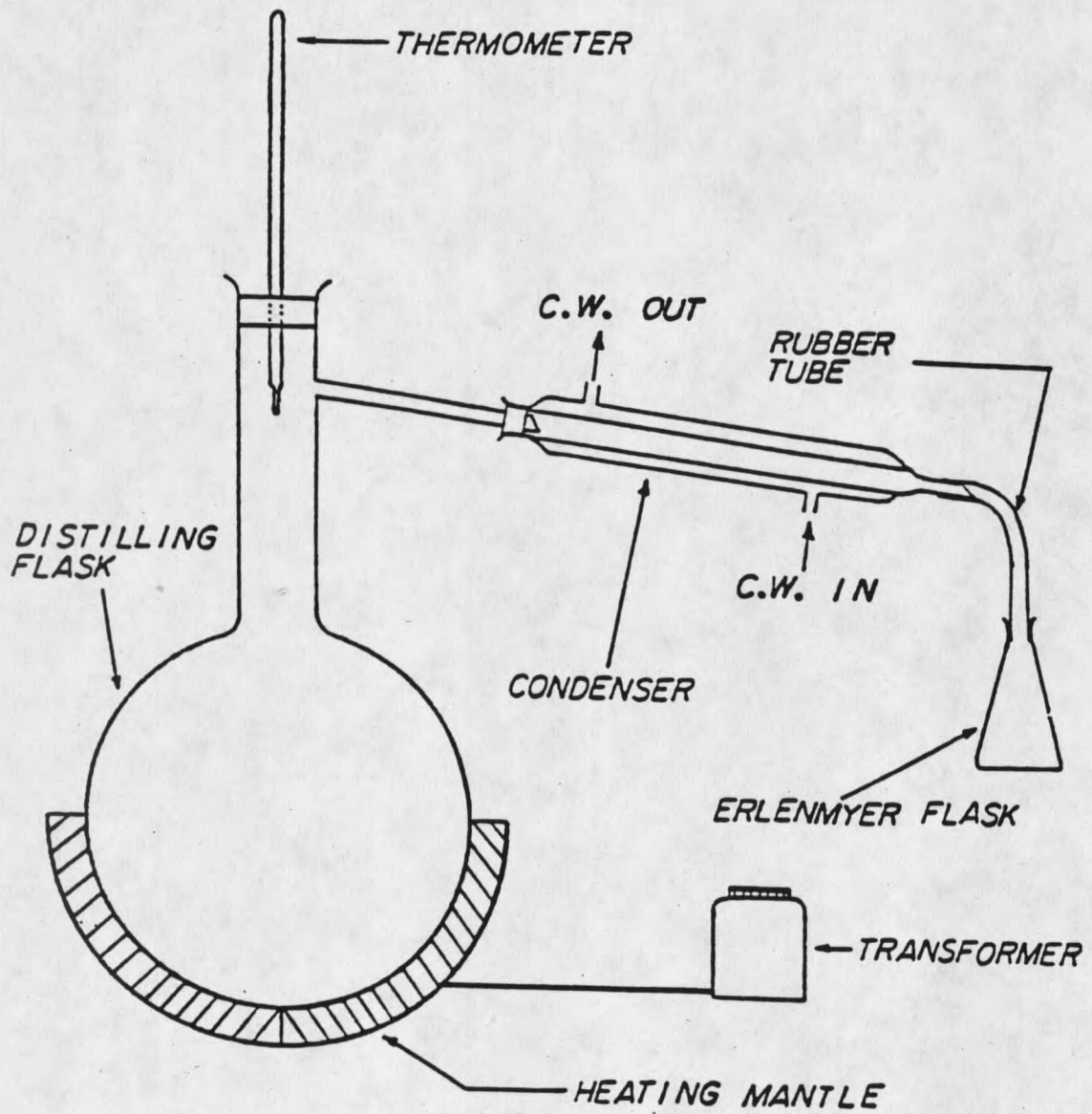


Figure 4. Diagram of the simple distillation system.

Continuous System

Figure 5 is a schematic representing the continuous process used to collect experimental data for the n-butanol/n-butylacetate system. The condensing head, column, Variacs, and micro-bellows pumps used were identical to the equipment used for the semi-batch system. The following additional equipment was necessary in order to make the conversion from a semi-batch to a continuous process:

- (A) A Pyrex glass reboiler fitted with a bottoms product line and a thermometer well. The reboiler was wrapped with nichrome heating wire which was output controlled by the use of a Variac.
- (B) A micro-bellows pump which pumped liquid bottoms product as a continuous rate.
- (C) A 200-ml. Pyrex glass separatory funnel heated by the use of a heat lamp contained the feed mixture.
- (D) A micro-bellows pump pumped the heated liquid feed into the column at a continuous rate.

An additional 65/40 female ball and socket joint having a sidearm for feed entry was added underneath the point of agent entry in the column.

Analytical Equipment

All bottoms and overhead samples were analyzed using gas chromatography. The chromatograph used was an Aerograph model 200 with standard Poropak QS packing. A Sargent model SR recorder was used to record peak heights for the corresponding sample constituents.

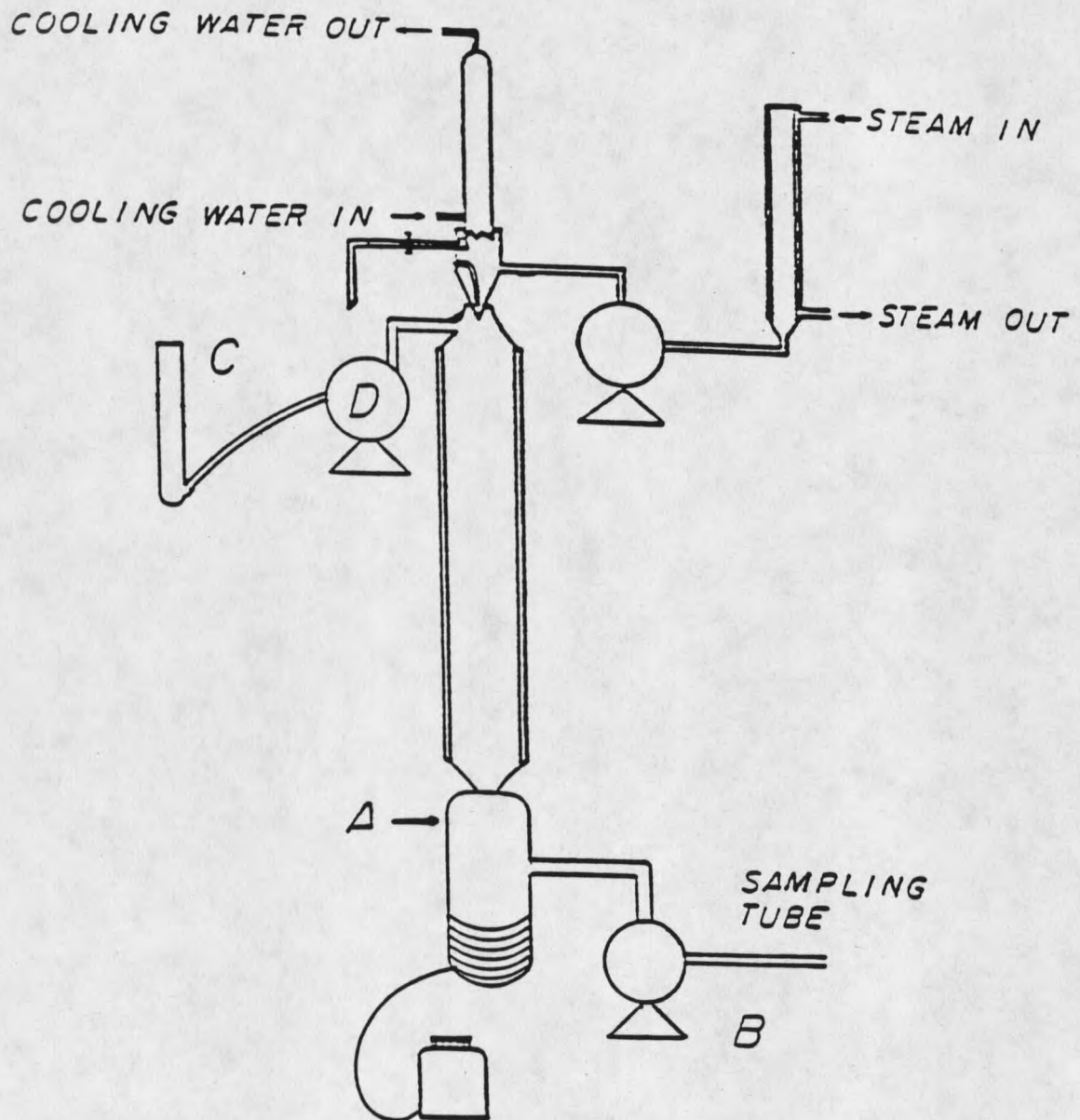


Figure 5. Diagram of the continuous distillation column.

Corresponding sample constituent peak height percents were used in the Fenske equation to calculate relative volatility and average column theoretical plates.

EXPERIMENTAL PROCEDURE

Semi-Batch Experiment

The semi-batch system was calibrated by Ratanapuech [18] using a mixture of ethylbenzene and m-xylene having a known relative volatility of 1.08. The number of theoretical stages calculated using the Fenske equation was 4.5. This value was used to calculate relative volatilities for all the systems studied herein which used the semi-batch column.

The still pot was charged with the material to be studied. Heat was applied to the still pot to initiate vigorous boiling of the charge. The agent was preheated to approximately 100°C and added at a rate of approximately 20 ml./min. after a stable reflux of the condensate was observed. The time the agent was added was recorded as time zero and did not occur until approximately 30 min. after heat was applied to the still pot.

The heat supplied to the reboiler was adjusted to ensure adequate reflux (neither too high or too low) and a uniform boilup rate throughout the column. The system was operated undisturbed at total reflux until samples were collected. Bottoms and overhead samples of 1-2 ml. were collected at 0.5, 1.0, 1.5, and/or 2 hours depending on the results of prior gas chromatography analysis. The extractive agent was pumped continuously during the entire procedure and accumulated in the still pot.

The system was allowed to cool after termination of sample collection. When necessary, the agent was recovered by the use of a simple distilling flask.

The system was flushed with acetone and allowed to dry before further runs were attempted.

Continuous Column Calibration

It was necessary to recalibrate the column after its conversion to a continuous system. The calibration was accomplished by determining the separation at total reflux of a mixture of toluene and benzene having a known relative volatility of 3.0. Analysis of bottoms and overhead samples was taken periodically over a 2 hour time span. This data and the known value for relative volatility was used to determine an average value for the number of theoretical plates using the Fenske equation. Figure 6 is a plot of calculated theoretical plates vs. the time the analyzed samples were taken. An average value of 3.2 can be seen in Figure 6. This value was used to calculate relative volatilities for the separation of n-butyl acetate from n-butanol in the continuous system.

Continuous Experiment

A feed mixture of equal parts by volume of n-butyl acetate and n-butanol was prepared and preheated to 100°C. Dimethyl sulfoxide (DMSO) was used as the extractive agent and preheated to 100°C as well. Both feed and agent were pumped into the column at approximately 20 ml./min.

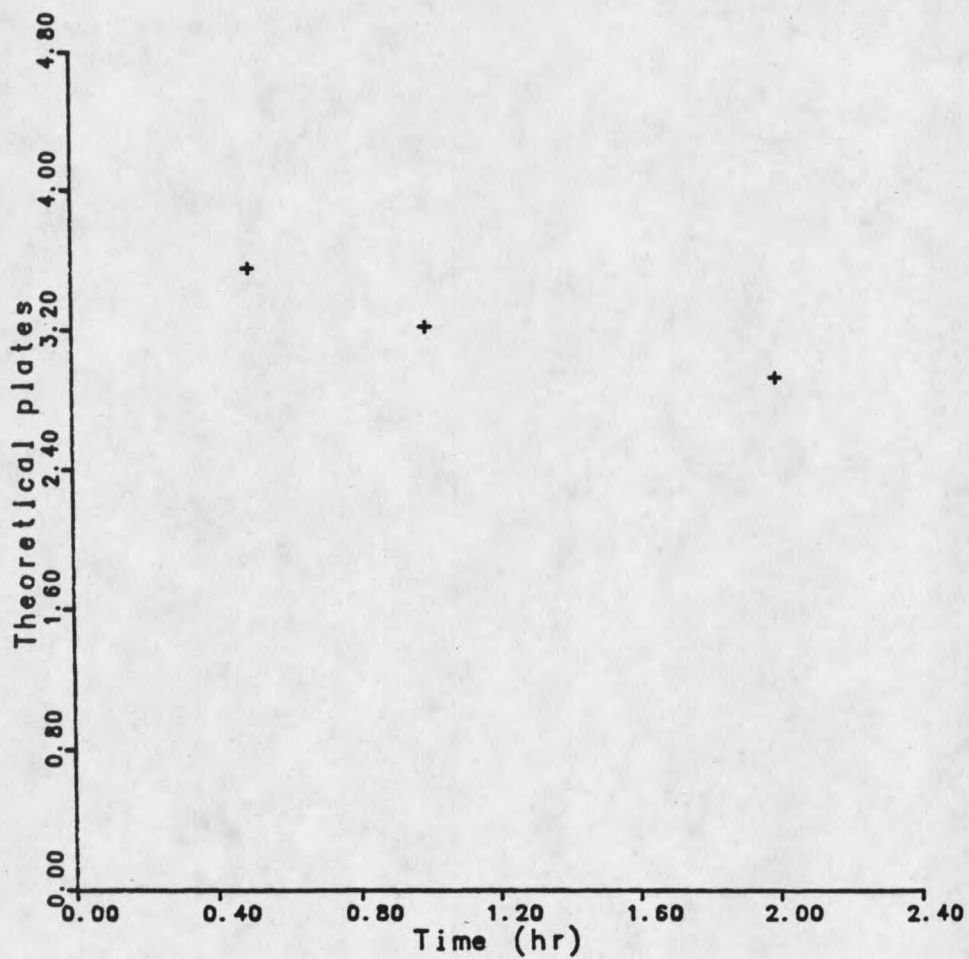


Figure 6. Theoretical plates vs. time for the continuous column calibration using the benzene/toluene system.

Heat was not supplied to the reboiler until liquid could be drawn off the reboiler product sidearm by a micro-bellows pump. The system was allowed to operate undisturbed for approximately 1 hour at which time condensate was observed to appear in the Corad head.

Heat rate was adjusted to the reboiler until the system was stable. At this point, the column was operating under total reflux and was recorded as time zero.

After 30 min. of operation, bottoms and overhead samples of 1-2 ml. were collected. The samples were analyzed by gas chromatography. Overhead product was then taken off at a rate corresponding to a reflux ratio of 2:1. Bottoms and overhead samples were taken again at 1 and 2 hour intervals. All samples were analyzed by gas chromatography.

The system was allowed to cool before being flushed with acetone.

RESULTS

Table 1 lists the results for the experimental runs made in the semi-batch column for the acetic acid/dioxane system. The extractive agents used were certain dimethylamides or dimethylsulfoxide mixed with higher boiling organic compounds.

Table 1. Rectification data for the acetic acid/dioxane system.

Agent	Peak Height Percent Dioxane		Relative Volatility	Time (hr)
	Overhead	Bottoms		
DMSO Nanoic Acid (1:1)*	82.0	17.3	1.96	1.0
DMFA Heptanoic Acid (1:1)	93.5 94.0 90.6	12.5 19.0 10.7	2.80 2.50 2.50	0.5 1.0 1.5
DMAA Heptanoic Acid Diethyl Carbitol (1:1:1)	67.2 95.5 94.5	18.9 16.5 14.3	1.62 3.06 2.80	0.5 1.0 1.5

* Numbers in parentheses () indicate ratios of corresponding compounds which comprised the agent feed.

Table 2 is a compilation of the results obtained in the semi-batch rectification column for the formic acid/dioxane, formic acid/2-pentanone, formic acid/3-pentanone and formic acid/water systems.

Table 2. Rectification data for the (A) formic acid/2-pentanone, (B) formic acid/dioxane, (C) formic acid/water, and (D) formic acid/3-pentanone systems.

System	Agent	Peak % Formic Acid		Relative Volatility	Time (hr)
		Overhead	Bottoms		
A	DMSO				
	Nanoic Acid	4.2	49.4	2.00	0.5
	Methyl Benzoate (1:1:1)*	1.3 2.2	47.5 40.9	2.57 2.15	1.0 2.0
B	DMSO				
	Nanoic Acid	2.7	71.2	2.70	0.5
	Methyl Benzoate (1:1:1)#	1.1 0.9	55.0 74.6	2.90 3.60	1.0 2.0
C	Propylene Carbonate				
	Heptanoic Acid	3.1	43.5	2.06	1.0
	2-Hydroxyl- acetophenone (1:1:1)	2.5 2.1	44.9 46.5	2.14 2.30	2.0 3.0
C	Propylene Carbonate				
	Benzoic Acid	6.2	41.4	1.70	0.5
	Isophorone (2:1:1)	1.9 1.5	46.8 43.9	2.35 2.40	1.0 2.0
C	Ethylene Carbonate	2.5	41.4	2.08	1.0
	Heptanoic Acid	1.1	43.0	2.56	2.0
	(1:1)	0.9	39.1	2.60	2.5
D	Isophorone				
	Methyl Benzoate	13.0	50.8	1.53	0.5
	Diethyl Carbitol (1:1:1)	4.4 1.9	56.5 41.8	2.20 2.60	1.0 2.0

* Numbers in parentheses () indicate ratios of corresponding compounds which comprised the agent feed.

Agent was recovered by simple distillation.

The extractive agents used for the systems consisting of formic acid mixed with 2-pentanone and dioxane consisted of equal mixtures of DMSO, nanoic acid, and methyl benzoate. The formic acid/water and formic acid/3-pentanone system used extractive agents consisting of certain oxygenated or nitrogen containing organic compounds.

Table 3 lists the results for the experiment performed in the continuous column for the n-butanol/n-butyl acetate system. The extractive agent used for this system was DMSO. Values for relative volatility were calculated by using the Fenske equation.

Table 3. Rectification data for the n-butanol/n-butyl acetate system.

Agent	Peak % n-Butanol		Relative Volatility	Time (hr)
	Overhead	Bottoms		
DMSO	40.0	78.0	1.69	0.5*
	45.7	74.5	1.49@	1.0#
	48.9	81.8	1.62@	2.0

* Column operating at total reflux.

Column operating with reflux ratio of 2.0:1 after 0.5 hr.

@ Values are estimates since the column was no longer operating at total reflux.

DISCUSSION

Effects of Extractive Agents on Relative Volatility

The results obtained in the semi-batch distillation column for all the systems studied in it are given in Tables 1 and 2. Examination of these results indicate that in all cases the maximum-boiling azeotropes were negated, significantly improving corresponding relative volatility values. Relative volatility values calculated from data obtained from gas chromatograph analysis of samples taken at specific time intervals were averaged for each system. The averaged relative volatility values for all the systems studied in the semi-batch column are listed in Table 4. All the feed charges studied in the semi-batch column form maximum azeotropes having relative volatility values of 1.0. Table 4 illustrates the effectiveness of the corresponding extractive agents in favorably enhancing each system separation.

Prediction of Minimum Number of Theoretical Plates

Table 5 reports the minimum number of theoretical plates required to obtain solvent-free, 99% pure products as calculated by the Fenske equation. With no extractive agent present, it would be impossible to accomplish the separations even if the number of plates used approached infinity. In other words, these separations would be impossible by a conventional rectification column.

Table 4. Average relative volatility values for corresponding systems studied in the semi-batch column.

System	Agent	Average Relative Volatility
Acetic Acid Dioxane	DMFA Heptanoic Acid (1:1)*	2.60
	DMAA Heptanoic Acid Diethyl Carbitol (1:1:1)	2.49
Formic Acid 2-Pentanone	DMSO Nanoic Acid Methyl Benzoate (1:1:1)	2.24
Formic Acid Dioxane	DMSO Nanoic Acid Methyl Benzoate (1:1:1)	3.07
Formic Acid Water	Ethylene Carbonate Heptanoic Acid (1:1)	2.41
	Propylene Carbonate Heptanoic Acid 2-Hydroxyacetophenone (1:1:1)	2.17
	Propylene Carbonate Benzoic Acid Isophorone (2:1:1)	2.15
Formic Acid 3-Pentanone	Isophorone Methyl Benzoate Diethyl Carbitol (1:1:1)	2.11

* Numbers in parentheses () indicate ratios of corresponding compounds which comprise the agent feed.

Table 5. Number of theoretical plates required for solvent-free, 99% pure products as calculated by the Fenske equation.

System	Agent	Relative Volatility	Theoretical Plates
Acetic Acid Dioxane	50% DMFA	2.60	9.6
	50% Heptanoic Acid		
	50% DMSO	1.96	13.7
	50% Nanoic Acid		
	33% DMAA		
	33% Heptanoic Acid		
	33% Diethyl Carbitol	2.49	10.1
	33% DMSO		
	33% Nanoic Acid		
Formic Acid 2-Pentanone	33% Methyl Benzoate	2.24	11.4
	33% DMSO		
Formic Acid Dioxane	33% Nanoic Acid	3.07	8.2
	33% Methyl Benzoate		
Formic Acid Water	50% Ethylene Carbonate	2.41	10.4
	50% Heptanoic Acid		
	33% Propylene Carbonate	2.17	11.9
	33% Heptanoic Acid		
	33% 2-Hydroxyacetophenone		
	50% Propylene Carbonate	2.15	12.0
	25% Benzoic Acid		
	25% Isophorone		
Formic Acid 3-Pentanone	33% Isophorone	2.11	12.3
	33% Methyl Benzoate		
	33% Diethyl Carbitol		

Continuous Extractive Distillation

The use of the semi-batch column to accomplish separations has raised objections in the determination of relative volatility values because the bottoms composition continually changes as a result of agent addition. Yeh [19] has shown that the composition change in the stillpot resulting from continual agent addition does not alter its effect throughout the column. A comparison of n-butyl acetate/n-butanol system in the semi-batch and continuous columns illustrates the similar effectiveness of the agent to enhance the separation. The alcohol/acetate system separated in the semi-batch column [7] and in the continuous column gave relative volatility values reported in Table 6. These values were calculated by using the Fenske equation.

Table 6. Relative volatility of n-butyl acetate to n-butanol in the semi-batch and continuous columns.

Column	Agent	Reflux Ratio	Relative Volatility
Semi-Batch	DMSO	Total	2.11
Continuous	DMSO	Total	1.69

The lower relative volatility value for the continuous column is probably the result of the system not reaching equilibrium before samples were collected. Inspection of the results for the acetate/alcohol system in the continuous column (Table 3) is in agreement with accepted theory of the behavior of a binary system in an extractive distillation process. At total reflux, a relative

volatility value of 1.69 was reached within 0.5 hr. Relative volatility decreased to 1.49 after an hour of operation with a reflux ratio of 2.0:1. After two hours of operation at this reflux ratio, the system was nearing equilibrium and the relative volatility increased to 1.62.

Agent Stability

The formic acid/2-pentanone and formic acid/dioxane systems utilized the same extractive agents in their corresponding separations in the semi-batch column. In both cases the extractive agents were composed of 33% each of DMSO, nanoic acid, and methyl benzoate. For this reason, the agent was reclaimed by simple distillation after its use as the agent for the formic acid/2-pentanone system. The reclaimed agent was used as the agent for the formic acid/dioxane system. As can be seen from Table 4, its effectiveness was not hindered by being reclaimed and used again for the extractive agent.

The boiling point differences between the agents and feed components for all the systems studied were appreciable enough to make complete recovery and recycle feasibly attainable if necessary. As a result of the boiling point differences between the feed and agent streams, the possibility of contamination of the overhead product by the agent was kept to a minimum.

Polarity Diagrams

The method of Yeh [7] for using polarity diagrams to initially screen potential successful extractive agents was tested. Table 7 is

Table 7. Solubility parameters and specific volumes for feed and agent constituents at 25°C [13].

Compound	$(\delta_d)(\text{MPa})^{1/2}$	$(\delta_p)(\text{MPa})^{1/2}$	$(\delta_h)(\text{MPa})^{1/2}$	$V(\text{cm}^3/\text{mol})$
Acetic Acid	14.5	8.0	13.5	57.1
Dioxane	19.0	1.8	7.4	85.7
Formic Acid	14.3	11.9	16.6	37.8
3-Pentanone	14.5	8.7	7.6	106.4
2-Pentanone	14.6	8.8	7.0	107.5
Water	15.6	16.0	42.3	18.0
DMSO	18.4	16.4	10.2	71.3
DMFA	17.4	13.7	11.3	77.0
DMAA	16.8	11.5	10.2	92.5
Diethyl Carbitol	14.1	7.1	8.0	179.8
Nanoic Acid*	15.4	3.3	8.0	—#
Heptanoic Acid*	16.2	6.3	11.0	—#
Methyl Benzoate	15.9	11.5	7.2	126.0
Propylene Carbonate	20.1	18.0	4.1	85.0
Isophorone	16.6	8.2	7.4	150.5
Ethylene Carbonate	19.4	21.7	5.1	66.0
Benzoic Acid	18.2	7.0	9.8	100.0
2-Hydroxyacetophenone#	—	—	—	—

* Values were estimated by interpolation between higher and lower acids.

No data available.

a listing of solubility parameters for each corresponding system studied herein.

The method of Yeh utilized two dimensional plots of hydrogen bond parameter (δ_h) and polar bond parameter (δ_p) to predict agent behavior in the column. Yeh did not use the dispersion parameter (δ_d) in his evaluations because the difference between δ_d for the feed and agent components was negligible. This was the case for all the systems studied except the acetic acid/dioxane and formic acid/dioxane systems. Differences of molecular size between all the corresponding feed components was appreciable and is believed to affect agent selectivity.

The method of Yeh makes no provision for appreciable differences between feed and agent component δ_d values. Polarity diagrams for the acetic acid/dioxane and formic acid/dioxane systems were made anyway to see if a correlation existed. Figures 7-12 are the polarity diagrams for the formic acid/water, formic acid/2-pentanone, formic acid/3-pentanone, n-butanol/n-butyl acetate, formic acid/dioxane, and acetic acid/dioxane systems.

The method utilizes a plot of δ_h vs. δ_p for all the corresponding system feed and agent components. A line joins the binary feed components and is bisected perpendicularly. This creates two line segments whose ratio with respect to length is equivalent to the ratio of specific volumes of the feed components. This divides the plot into two sections. Each section corresponds to an area where the presence of an agent should signify it has a greater affinity for that feed component than the other. Therefore, feed and extractive

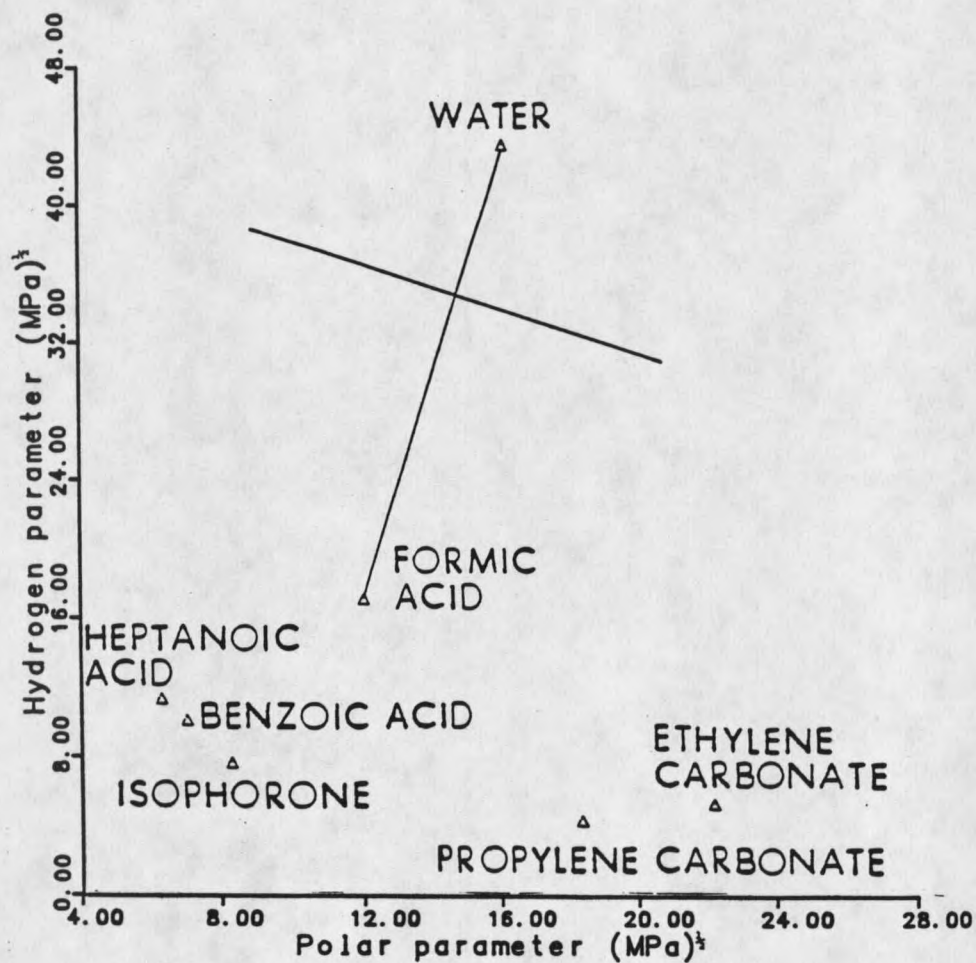


Figure 7. Polarity diagram for the formic acid/water system.

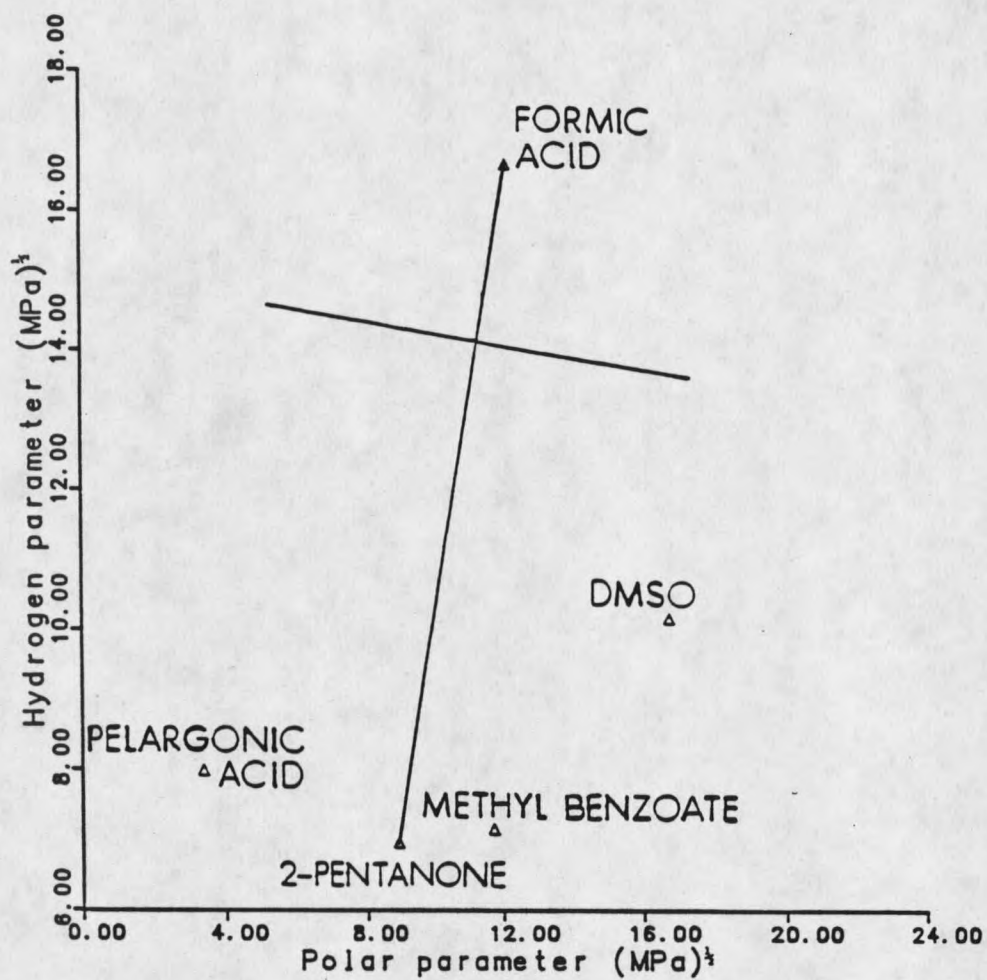


Figure 8. Polarity diagram for the formic acid/2-pentanone system.

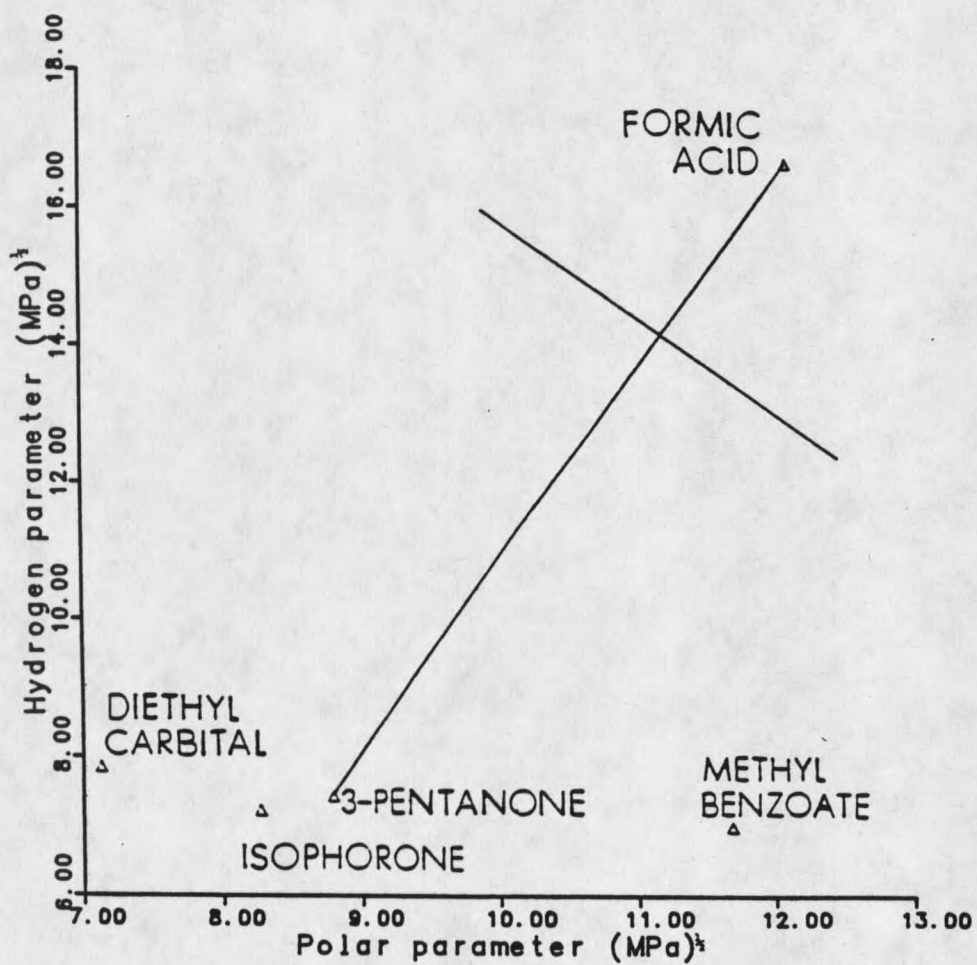


Figure 9. Polarity diagram for the formic acid/3-pentanone system.

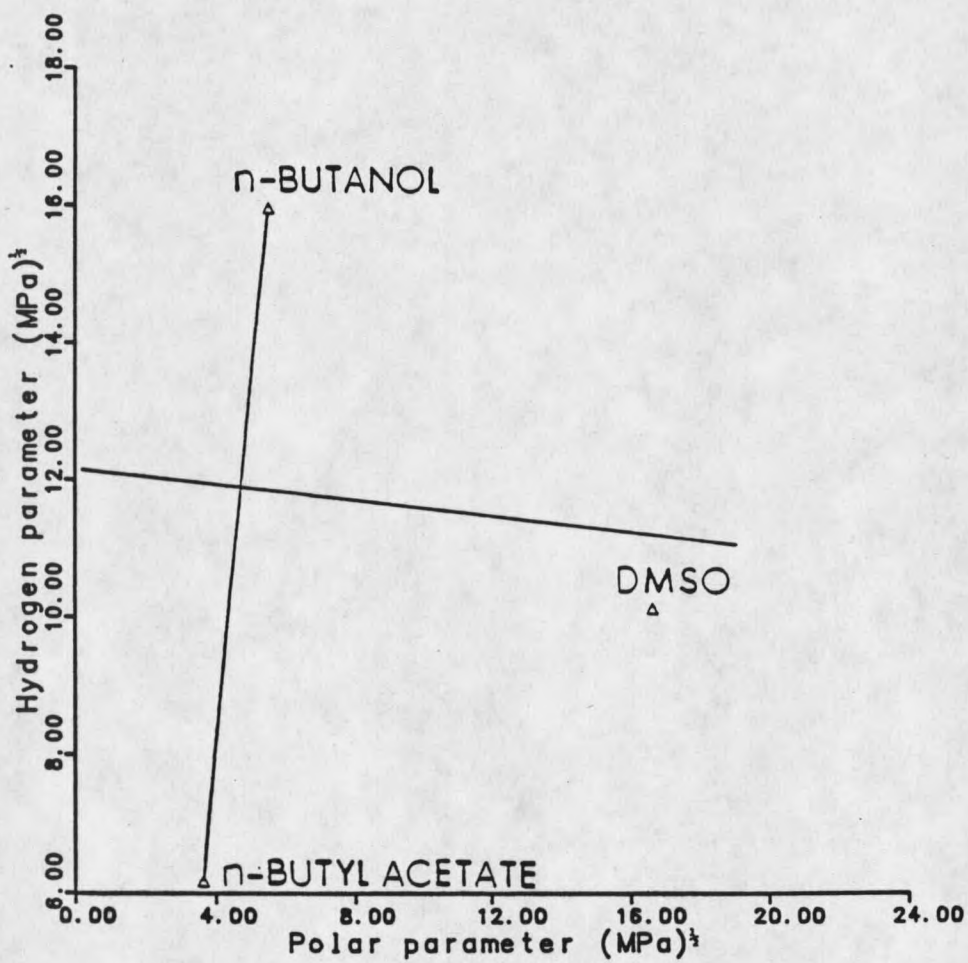


Figure 10. Polarity diagram for the n-butanol/n-butyl acetate system.

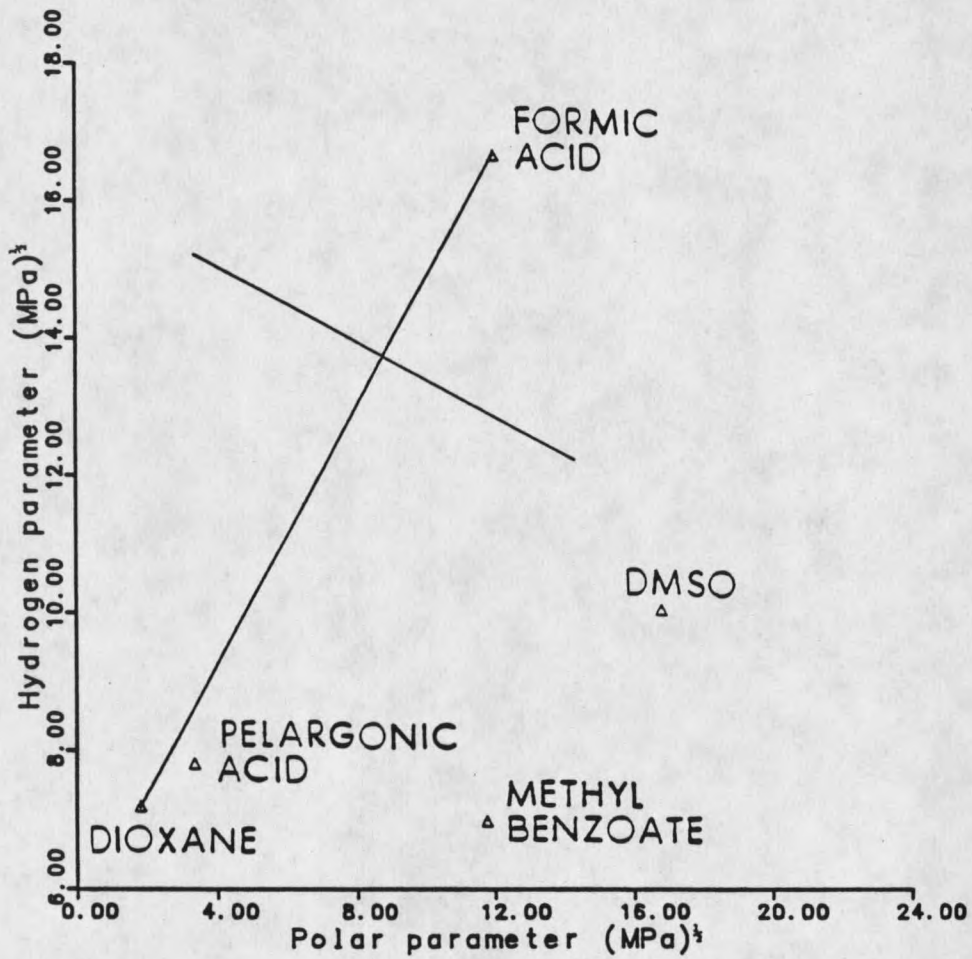


Figure 11. Polarity diagram for the formic acid/dioxane system.

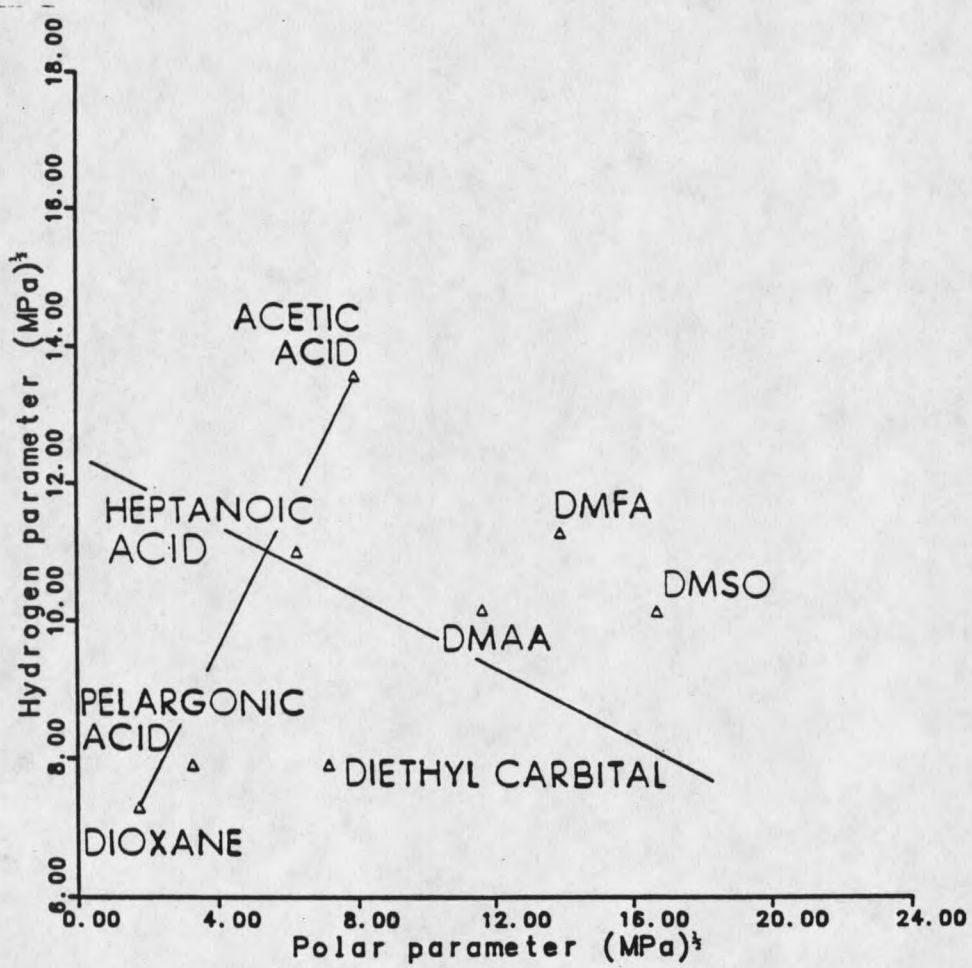


Figure 12. Polarity diagram for the acetic acid/dioxane system.

components in the same section of the plot would be bottoms products in the column allowing the other feed component as overhead. This works very well for the formic acid/water system. As can be seen in Figure 7, all the extractive agents are on the formic acid section of the polarity diagram. The agents should have a greater affinity for the acid and bring it down the column allowing water as the overhead product. This in fact was the case for the experiment made with this system. For the formic acid/2-pentanone, formic acid/3-pentanone, n-butanol/n-butyl acetate, and formic acid/dioxane systems (Figures 8-11), the use of the polarity diagram predicts exactly opposite of what occurs in the distillation column. The polarity diagram for the acetic acid/dioxane system (Figure 12) indicates a random spread of extractive agents on the corresponding feed component sections of the plot.

Clearly, using the polarity diagram for the prediction of successful agents for a separation is greatly deficient. The variables affecting selectivity are numerous and not well understood. Accepted theory of nonideal behavior provides some insight as to the outcome of experimental results but does not adequately explain them.

SUMMARY AND CONCLUSIONS

1. Extractive distillation successfully negated the azeotropes studied when the proper agents were employed.
2. The semi-batch and continuous columns were both effective in accomplishing separations.
3. The agents were reclaimed successfully without losing their effectiveness.
4. Use of the polarity diagram proposed by Yeh was deficient in predicting agent/feed interaction.
5. Accepted nonideal solution theory was deficient in describing experimentally obtained results.
6. No correlation between solubility parameters and specific volumes of the feed and agent components was noted.

RECOMMENDATIONS FOR FUTURE RESEARCH

Systems should be examined in the experimental column which allow calculation of solubility parameters at the column operating temperatures. Group contribution methods are available [13] which allow calculation of solubility parameters at temperatures other than 25°C. However, this limits one to a more narrow range of compounds. A system could be chosen such that approximate solubility parameters could be calculated at the temperature range of the column during operation. This may provide more useful parameter data for use in the polarity diagram method for screening successful agents.

Systems which decompose because of high temperature column operating conditions in the semi-batch column should be studied in the continuous column. The decomposition of the feed component(s) may be eliminated.

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