Extactive distillation in the separation of five close boiling alcohol mixtures, one ternary azeotropic mixture and two close boiling isomer mixtures
by Mark George Vosburgh

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

Abstract:
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Research was conducted in a batch perforated plate extractive distillation column. The column contained 4.5 theoretical plates. The effectiveness of various extractive agents was evaluated by using the Fenske equation to calculate values of relative volatility. The Fenske equation was also used to estimate the minimum number of theoretical plates necessary to obtain 99% pure (agent-free basis) products.

Values of relative volatility for the close boiling alcohol mixtures were improved by the addition of several extractive distillation agents. The ternary azeotrope between isopropyl acetate, isopropanol and water was broken and separation made possible by the addition of extractive agents. In these cases a substantial decrease was noted in the minimum number of theoretical plates estimated to obtain 99% pure products. No extractive agents were found which improved values of relative volatility for the mixtures of isomers.

EXTRACTIVE DISTILLATION IN THE SEPARATION OF FIVE CLOSE BOILING ALCOHOL MIXTURES, ONE TERNARY AZEOTROPIC MIXTURE AND TWO CLOSE BOILING ISOMER MIXTURES

by

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Mark George Vosburgh

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

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TABLE OF CONTENTS

TABLE OF CONTENTS—Continued

LIST OF TABLES

Tables

Appendix Tables

LIST OF FIGURES

ABSTRACT

Extractive distillation was investigated as a method of separating five close boiling alcohol mixtures, one azeotropic mixture and two close boiling isomer mixtures. The close boiling alcohol mixtures included: ethanol and isopropanol, n-propanol and 2-butanol, ethanol and t-butanol, isopropanol and t-butanol, and n-propanol and allyl alcohol. The azeotropic mixture studied was a minimum boiling ternary azeotrope consisting of 76% isopropyl acetate, 13% isopropanol and 11% water. The close boiling isomer mixtures were n-amyl acetate plus isoamyl acetate and 1-methyl-2-butanol plus n-amyl alcohol. All of these mixtures are difficult or impossible to separate by ordinary rectification.

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INTRODUCTION

Distillation is the process of separating the components of a solution by taking advantage of concentration differences in the liquid and vapor phases at equilibrium. This process [1] is the most widely used method of separating liquid mixtures and is at the heart of the separation process in many chemical and petroleum plants.

Distillation, however, loses its ability to separate mixtures as differences in volatilities of the components of the mixture decrease. In the case of close boiling mixtures or azeotropes, separation by ordinary distillation is difficult or impossible. Under these circumstances it may be possible to modify the distillation process to more readily achieve a desired separation.

Two possible modifications which involve the addition of a solvent to the column are azeotropic and extractive distillation. While azeotropic distillation is extremely effective in certain instances, extractive distillation is generally considered to be more widely useful. Among its advantages are the large number of possible effective solvents. Unlike azeotropic distillation the precise nature of phase relationships in mixtures of solvent and key components is not critical to the success of the process, that is, extractive distillation does not rely upon the accident of azeotrope formation. Other advantages [2] include a lower heat requirement and a more simple solvent recovery procedure.

Extractive distillation can be described as distillation in the presence of a high-boiling component. This component is referred to as a solvent or an extractive agent. Figure 1 [3] is a sketch of an extractive distillation column. As is seen in this illustration, the extractive agent is added near the top of the column. Space is provided above the addition point to

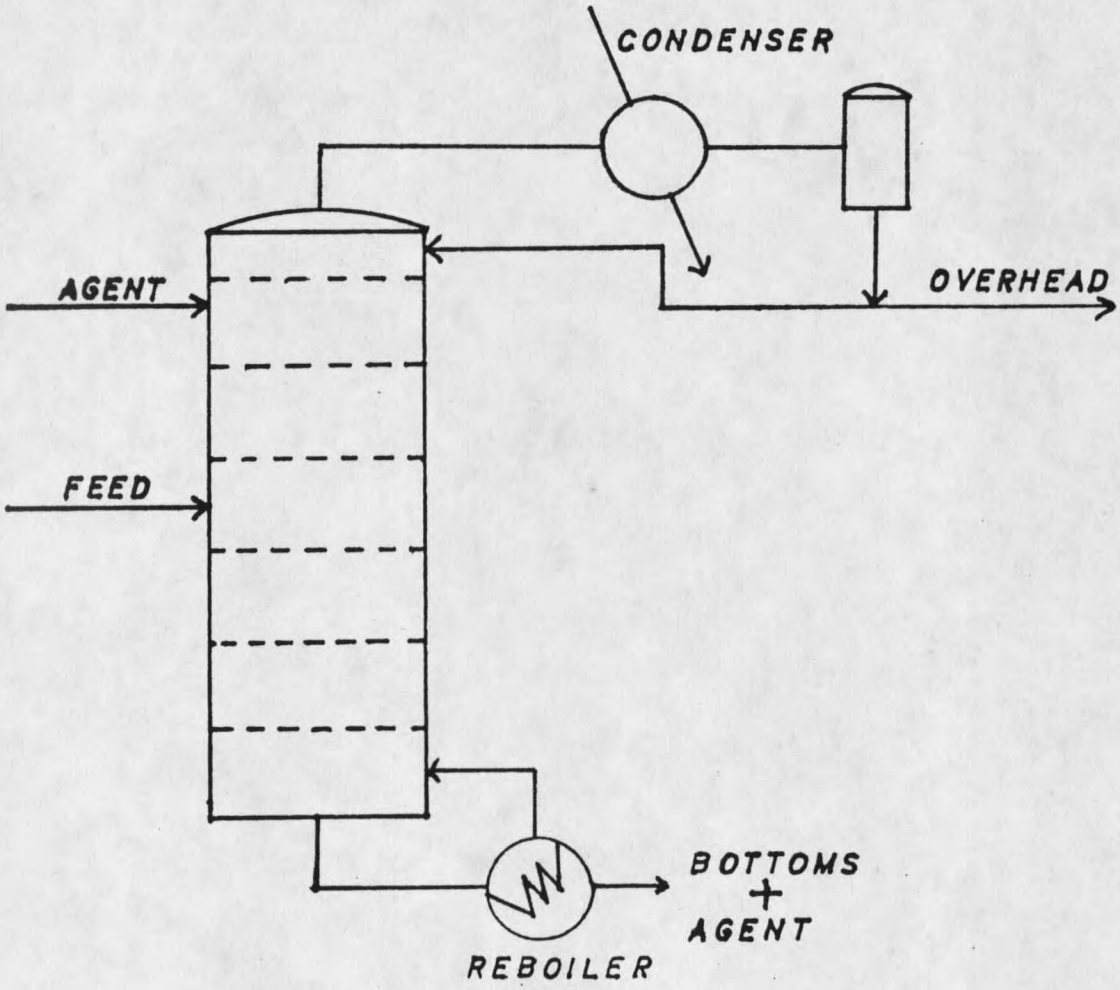

Figure 1. Extractive distillation column.

prevent the agent from being carried overhead. Since the agent is, by definition, less volatile than the components of the mixture, it flows downward through the column from stage to stage at a fairly constant rate until it reaches the reboiler. The presence of the solvent on the column plates effects the separation by altering the vapor pressure relationships between the components of the mixture. The desired result is to reduce the number of plates required for a given separation or to increase the separation for a given number of plates.

The improvements offered by extractive distillation do not come without tradeoffs. The advantage of fewer theoretical plates is partially offset by an increase in the plate diameter necessary to handle the increased liquid flow. As a rule of thumb, 1 to 4 moles of solvent per mole of feed is required [4]. The agent must be heated to approximately the same temperature as the plate to which it is introduced. The heat requirement is therefore larger than that of an ordinary distillation column. Also, extractive distillation requires extra time and energy in the separation of the bottoms product from the agent. In considering extractive distillation for commercial use one must balance these opposing factors.

An example of a continuous extractive distillation process which has commercial applications is given in Figure 2 [5]. Here the less volatile components of the mixture along with the extractive agent are removed and sent to a second column. In the solvent recovery unit the agent is recovered and recycled back to the main column. This separation scheme serves to illustrate some of the desirable properties of an extractive agent.

First, the agent must reduce the number of plates necessary to obtain a desired separation in the main column. Second, it must have a volatility low enough to minimize the size of the agent recovery column. It is suggested [6] that the boiling point of the solvent be at least 20 Celsius degrees higher than those of the components in the mixture. Third, azeotrope formation between the solvent and the mixture is undesirable since this would

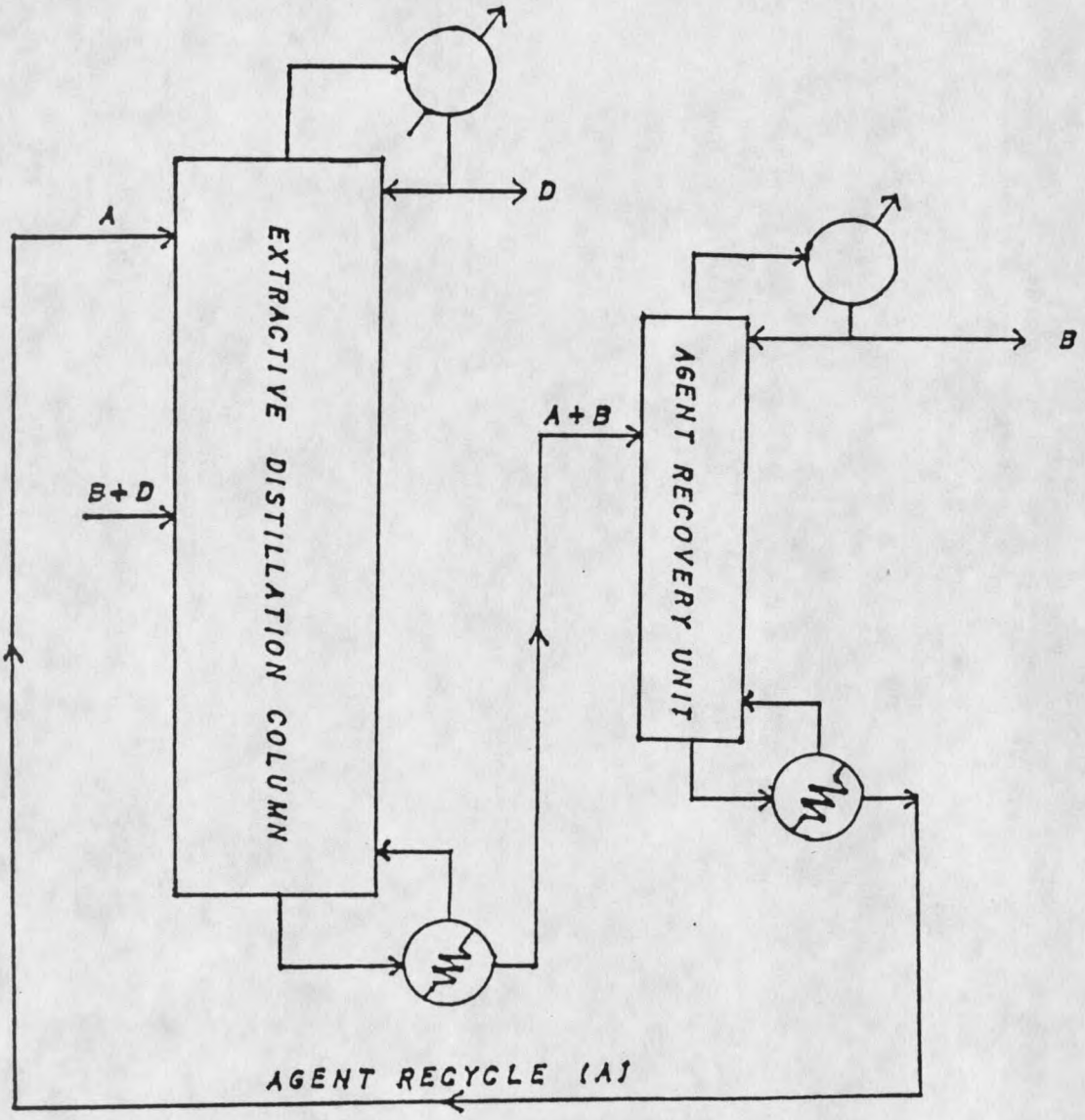

Figure 2. Continuous extractive distillation flowsheet.

complicate the recovery of the solvent. Fourth, the agent must be stable enough to withstand repeated recycle between the two columns. Other important solvent properties which must be evaluated include solvent cost, toxicity, corrosiveness, and potential for undesired reactions.

Extractive distillation has been shown to be effective in separating mixtures that would be difficult or impossible to separate by normal rectification. Berg and Yeh [7] used extractive distillation to provide a method for recovering essentially pure methanol from acetone. Because of the presence of a minimum boiling binary azeotrope in this system, complete separation of methanol from acetone is impossible with ordinary rectification. A close boiling mixture of benzene (80.1°C) and cyclohexane (80.7°C) would require more than 460 plates to separate to 99% purity at total reflux. With extractive distillation [8] the vapor pressure relationship is altered to the point where the same separation could be accomplished with approximately 8 plates. In both examples the feasibility of separation is greatly enhanced with the addition of an extractive agent.

THEORETICAL ASPECTS

Relative Volatility

Ordinary distillation attempts to exploit concentration differences between vapor and liquid phases to effect the separation of components of a mixture. A liquid mixture is heated to its boiling point at which time a vapor is formed which is richer in the more volatile component. The concentration of this key component increases with the height of a distillation column as the cycle of vaporization and condensation repeats itself. The difficulty of a given separation of components i and j can be measured by values of relative volatility, α [9]. This value is the ratio of mole fraction (x and y) ratios in one phase to that in another phase.

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \qquad (1)$$

A relative volatility of one indicates that the vapor formed from a liquid mixture has the same concentration as that mixture; therefore, no separation is possible. As values of α increase above unity separation becomes easier. Values of relative volatility were used to measure the effectiveness of various extractive agents in separating the mixtures under consideration.

Since the column in this work was operated at total reflux, values of relative volatility were calculated by the Fenske equation [9].

$$\alpha_{Ave}^{N} = \left[\frac{y_i}{y_j}\right]_O \left[\frac{x_j}{x_i}\right]_B \qquad (2)$$

where α is the average relative volatility,

N is the number of theoretical plates, — should be stages

subscripts O and B represent overhead and bottoms respectively.

The use of this equation requires several assumptions. First, the value of relative volatility is assumed to be constant throughout the entire concentration range. Second, the number of theoretical plates (N) used in this equation was found by calibration of the column with a mixture of known α (ethylbenzene + p-xylene). This value of N was assumed constant for all of the various mixture and extractive agent combinations studied.

The validity of these assumptions is somewhat in question in parts of this work. For instance, it is unlikely that values of relative volatility remained constant throughout the entire concentration range for all of the mixtures studied. Also, the number of theoretical plates (N) present in the column would likely vary slightly for the various mixture agent considerations. From this discussion it is clear that the values of α calculated in this work contain the errors caused by deviations from the above assumptions; nonetheless, this method of calculation provided a means to compare the effectiveness of various extractive agents.

"Concentrations" reported in this work are peak height (P.H.) percentages referring to size of the peaks on the gas chromatograph output. Peak height percents [10] have been found to be acceptable for use in the Fenske equation.

Another method of quantifying the improvement in separation provided by an extractive agent is to use values of selectivity. Selectivity (sel.) is defined as the ratio of the relative volatility of a system in the presence of an agent to that in which no agent is used. This value has also been called the relative improvement factor [8].

$$\mathrm{Sel}_{ij} = \frac{(\alpha_{ij})_P}{(\alpha_{ij})_A} \tag{3}$$

where subscripts P and A indicate the presence and absence of an agent respectively.

Vapor-Liquid Equilibrium

The study of both ordinary and extractive distillation relies heavily on classical solution thermodynamics. Of specific interest is the topic of vapor-liquids equilibria. In beginning an explanation of the effect of extractive agents on the vapor-liquid equilibria of a system, a general criterion of phase equilibrium is often used. That is, the fugacity of a component in a multicomponent, multiphase system must be the same in all phases in which it is present at equilibrium [11]. This statement can be expressed as

$$\hat{f}_i^V = \hat{f}_i^L \tag{4}$$

or

$$\phi_i \times y_i \times P = \gamma_i \times x_i \times p_i^{SAT} \tag{5}$$

where ϕ_i is the fugacity coefficient of component i,

P is the total pressure,

γ_i is the activity coefficient of component i,

p_i^{SAT} is the pure-component vapor pressure of i.

Another important form of this equation can be written if the gas phase is considered to be ideal. In this case $\phi = 1$. Also $(y_i \times P)$ can be written as p_i^* the equilibrium partial pressure of component i.

$$p_i^* = \gamma_i x_i p_i^{SAT} \tag{6}$$

This equation can be further simplified to the familiar form of Raoult's Law.

$$p_i^* = p_i^{SAT} \times x_i \tag{7}$$

where p_i^* is the pure state vapor pressure of component i.

Raoult's Law holds true when the following restrictions apply to the system in question.

1. The vapor phase is an ideal gas.

2. The liquid phase is an ideal solution.

3. The liquid phase fugacities are independent of pressure.

Possible Methods of Improving Relative Volatility

Insight into the effect of extractive agents on a given mixture is obtained by rewriting Equation (1) by substituting Equation (5).

$$\alpha_{ij} = \frac{\gamma_i p_i^{SAT} \phi_j}{\gamma_j p_j^{SAT} \phi_i} \tag{8}$$

This expression can be further simplified since values of ϕ, the vapor-phase fugacity coefficient, are close to one at moderate pressures.

$$\alpha_{ij} = \frac{\gamma_i p_i^{SAT}}{\gamma_j p_j^{SAT}} \tag{9}$$

Equation (9) suggests several possibilities for increasing the relative volatility of a liquid mixture. An increase in the ratio of the pure component vapor pressures for example would result in an increase in α. Although variation in the temperature may change this ratio it is unlikely that the resulting change would be large enough to have much influence on the relative volatility. In effect the ratio of pure component vapor pressures can be considered constant.

Another possible method [12] of increasing α would be to increase the ratio of activity coefficients. The activity coefficient is a meausre of the nonideality of the liquid phase and can be changed by the addition of certain liquids to the mixture. This is the theoretical basis for extractive distillation. The desired effect of an extractive agent is therefore to form nonideal solutions with one or both of the components of a mixture in such a manner that the relative volatility of the mixture is increased.

These remarks are illustrated in Figures 3 and 4 [2] which refer to the separation of a paraffin-toluene mixture. As shown in Figure 3 the addition of the extractive agent

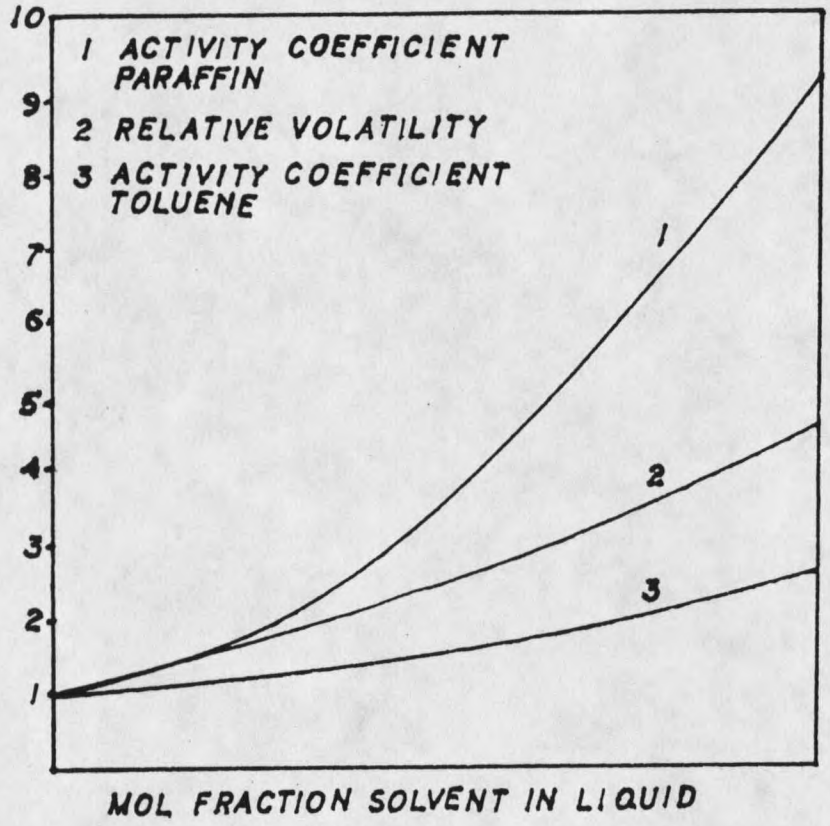

Figure 3. Effect of phenol on paraffin-toluene relative volatility.

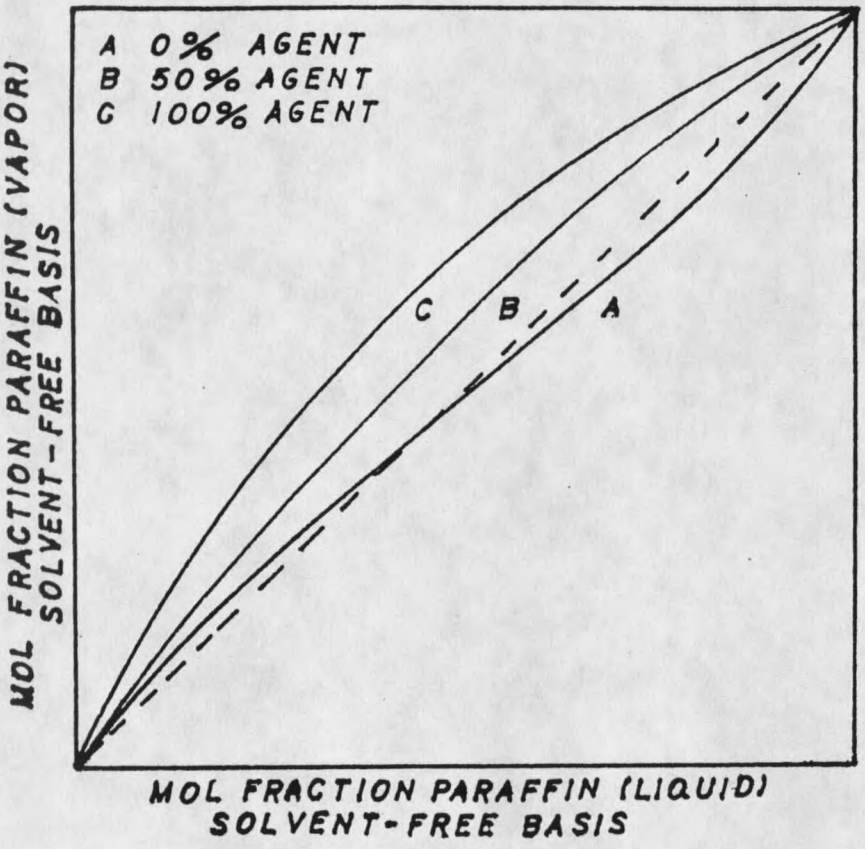

Figure 4. Effects of phenol on paraffin-toluene x-y diagram.

phenol increases the activity coefficient of both components but it increases that of the paraffin to a greater extent than that of toluene. This change leads to an increase in the ratio of activity coefficients and from Equation (9) an increase in the relative volatility. Figure 4 shows the results on an x-y diagram. With no agent there exists an azeotrope between the paraffin and toluene. This corresponds to the initial relative volatility of one in Figure 3. As phenol is added to the system the azeotrope is broken and the x-y line moves away from the 45 degree line indicating an easier separation.

Methods for Predicting Activity Coefficients

At this point the question might be asked: How is it possible to predict the effect of various extractive agents on the activity coefficients of components of a mixture? Numerous attempts have been made in this regard; however, the goal of predicting activity coefficients from pure component data remains elusive. Historically, values of activity coefficients were calculated from experimental equilibrium data [13]. Recent attempts [14] have resulted in "semi-theoretical" approximations of activity coefficients in multicomponent mixtures. The use of such methods requires binary equilibrium data.

In short, even with all the successes of modern solution thermodynamics it is currently not possible to predict values of relative volatility for the nearly limitless number of mixture and extractive agent combinations. For this reason all work in this research was based on experimental data.

Even though it is not yet possible to predict activity coefficients and/or relative volatilities from pure component data, advances in this area provide insights into the workings of extractive distillation. What follows is a summary of some of this work, especially that which pertains to this research.

Deviations From Ideality

A necessary condition for ideality of a solution is for Raoult's Law to hold. As seen by comparing Equations (6) and (7), activity coefficients must be one in this case. Non-ideality of a solution occurs when γ's differ from 1, positive deviation from ideality occurs when γ's are greater than one and negative deviations when γ's are less than 1. From Equation (6) it can be seen that variations in activity coefficients effectively change partial pressures of the component. As expected these changes in partial pressures alter volatility of one component of a mixture with respect to another, i.e., the relative volatility.

Changes in activity coefficients appear to be the result of interactions between a solvent and components of a mixture. Two types of interactions have been identified, namely chemical and physical.

Chemical effects [15] can be described as changes caused by the formation of new species or complexes when a solvent is added. Hydrogen bonding is a chemical effect which appears to be a major source of nonideality. Hydrogen bonding has been used to predict positive or negative deviations from Raoult's Law [16] and has been described [17] as being an important criterion for successful extractive agents.

Physical effects [15] are those deviations from ideal behavior caused by intermolecular (van der Waals) forces. These physical effects are often measured by dielectric constants and dipole moments. Attempts to evaluate the effectiveness of extractive agents using these quantities as parameters have met with only limited success.

In short, the separate consideration of physical and chemical effects has seen some success but has not resulted in the ability to predict values of either activity coefficients or relative volatility. It seems likely that the effect of a given agent on a component of a mixture is a highly complex mixture of these two extreme viewpoints.

MIXTURES TO BE SEPARATED

Ethanol, Isopropanol

Ethanol and isopropanol are the two most widely used alcohols in commerce today. Their use as solvents frequently results in a mixture of solvents. In this case it may be desirable to separate the mixture before re-use. Ethanol boils at 78.3°C, isopropanol at 82.4°C. A mixture of these two alcohols has a relative volatility of 1.09 making it very difficult to separate by normal distillation. Ethanol and isopropanol are both manufactured by the hydration of the corresponding olefin, respectively ethylene and propylene. Normally the ethylene and propylene are separated to high purity before reaction with sulfuric acid and water to make the alcohol. An alternative procedure might be to react the mixtures of olefins and separate the resulting alcohols.

In the separation of ethanol from isopropanol Carlson and Smith [20] reported sulfolane to be an effective extractive agent with relative volatilities of 2.22 and 2.47 for two of their runs. Berg [10] reports a relative volatility of 1.05 for this agent. It is suspected that the high relative volatility reported by Carlson and Smith is the result of low accuracy analytical equipment available in 1948. Sulfolane is not an effective extractive agent for this mixture.

n-Propanol, 2-Butanol

n-Propanol (97.2°C) and 2-Butanol (99.5°C) are common alcohols. As with isopropanol and ethanol their use as solvents frequently results in their mixture as solvents. A mixture of these alcohols possesses a relative volatility of 1.07 making it very difficult to separate. Extractive distillation offers a possible method of separation.

Smith and Carlson [20] again reported sulfolane to an effective agent for this mixture claiming a relative volatility of 2.22. Berg [10] showed this result to be in error and reported a relative volatility of 1.05. Sulfolane does not increase the relative volatility of this mixture.

Ethanol, t-Butanol

Ethanol is an extremely widely used alcohol and it is often required that it be relatively pure. Separation of ethanol (78.3°C) from t-butanol (82.9°C) is difficult because of the low relative volatility (a = 1.11) of a mixture of the two. These two alcohols can come into contact either by their use as solvents or in their manufacture by the hydration of a mixture of ethylene and isobutylene.

Isopropanol, t-Butanol

Isopropanol (82.5°C) and t-butanol (82.9°C) can come into contact by their use as solvents or in their manufacture by the hydration of a mixture of propylene and isobutylene. Separation of these alcohols by rectification is nearly impossible because of a relative volatility of 1.01 between them. Extractive distillation offers a possible method of separation.

n-Propanol, Allyl Alcohol

n-Propanol is a common commercial organic solvent. In cases where it is practical, it is desirable to recover and re-use it. Often n-propanol must be separated from a mixture of other solvents to be suitable for re-use. Allyl alcohol is one of the most difficult components of a solvent mixture to separate from n-propanol. Aside from being added from another source, allyl alcohol can originate from the dehydrogenation of part of the n-propanol. The boiling points, respectively, of n-propanol and allyl alcohol are 97.2°C and

96.9°C. A mixture of these compounds possesses a relative volatility of 1.01 making them virtually impossible to separate by conventional rectification.

Several attempts have been made to separate n-propanol from allyl alcohol using azeotropic distillation [18,19]; however, no reference to the use of extractive distillation was found.

Isopropyl Acetate, Isopropanol, Water

One commercial method of manufacturing isopropyl acetate is by the catalytic esterification of isopropanol with acetic acid to form a mixture of isopropanol, isopropyl acetate and water. A mixture of these compounds is impossible to separate by simple distillation since this system has three binary and one ternary azeotrope to contend with. The lowest boiling of these is the ternary azeotrope which will come off overhead as the initial product. Extractive distillation provides a possible method for separating isopropanol from isopropyl acetate in this system.

The breaking of the isopropyl acetate, isopropanol, water azeotrope [27] has been achieved with extractive distillation. In this case isopropyl acetate was the overhead product.

The boiling points [1] of the pure compounds and relative volatilities for the mixtures that were studied in this investigation are summarized in Table 1.

Table 1. Boiling Points and Relative Volatility of Mixtures.

Compound	Boiling Pt. °C	Relative Vol. Mixture
Ethanol	78.3	1.09
Isopropanol	82.4	
n-Propanol	97.2	1.07
2-Butanol	99.5	
Ethanol	78.3	1.11
t-Butanol	82.9	
Isopropanol	82.4	1.01
t-Butanol	82.9	
n-Propanol	97.2	1.01
Allyl Alcohol	96.9	
Isopropyl Acetate (76%)	88.7	1.00
Isopropanol (13%)	82.4	Ternary azeotrope
Water (11%)	100.0	

RESEARCH OBJECTIVES

The objective of this research was to identify, by experimentation in a perforated plate rectification column, extractive agents which would increase the relative volatility of the mixtures listed. An increase in the relative volatility of a given mixture would result in fewer plates required to effect a given separation or increase the separation obtained with a fixed number of plates. The extractive agent could be either a pure compound or a mixture of compounds. It is a further objective of this research to identify agents meeting several requirements including ease of recovery from bottoms product, stability, reusability, low toxicity and nonreactivity. Since this work was based on preliminary investigations [21,22, 23,24,25,26] by Berg and Vosburgh, it serves to reduce to practice these results by providing actual working examples in an extractive distillation column.

PHYSICAL PROPERTIES OF AGENTS

The boiling point, melting point, and chemical formula [1] of the extractive agents that were used in this research are listed in Table 2.

Table 2. Physical Properties of Extractive Agents.

Compound	Formula	Boiling Point °C	Melting Point °C
Adiponitrile	$NC(CH_2)_4CN$	295	—
Cinnamic Acid	$C_6H_5CH{=}CHCOOH$	300	133
Diisooctyl phthalate	$(C_8H_{17}COO)_2C_6H_4$	370	—
Dimethylformamide (DMFA)	$HCON(CH_3)_2$	152.8	-61
Dimethyl Sulfoxide (DMSO)	$(CH_3)_2SO$	189	18.5
Hexahydrophthalic Anhydride (HHPA)	$C_6H_{10}(CO)_2O$	158 @	35-36 17 mm
Methyl Benzoate	$C_6H_5COOCH_3$	198.6	-15
Methyl Hexahydrophthalic Anhydride (MHHPA)	$C_6H_9CH_3(CO)_2O$	Not listed in handbooks	
Methyl Salicylate	$C_6H_4(OH)COOCH_3$	222.2	—
Phthalic Anhydride	$C_6H_4(CO_2)O$	285	131.16
Salicylic Acid	$C_6H_4(OH)(COOH)$	211 @ 20 mm	158-161

APPARATUS

Experimental data from this work was collected from a batch extractive distillation column. The column [3] is shown in Figure 5. The apparatus that was used consisted of the following main components:

1. stillpot
2. heating system
3. gas-liquid contacting section
4. extractive agent feed system
5. condenser
6. agent recovery system
7. additional equipment

Each of the individual components are described separately.

Stillpot

A five liter capacity round bottom flask served as a stillpot in this work. The flask was fitted with two joints and a thermocouple well. One joint connected the stillpot to the gas-liquid contacting section while the other was used to attach a sidearm for sampling of the bottoms product.

Heating System

Heat input to the stillpot was provided by an electrical Glas-col mantle. The mantle was designed to fit a five liter flask and included insulation which was helpful in reducing

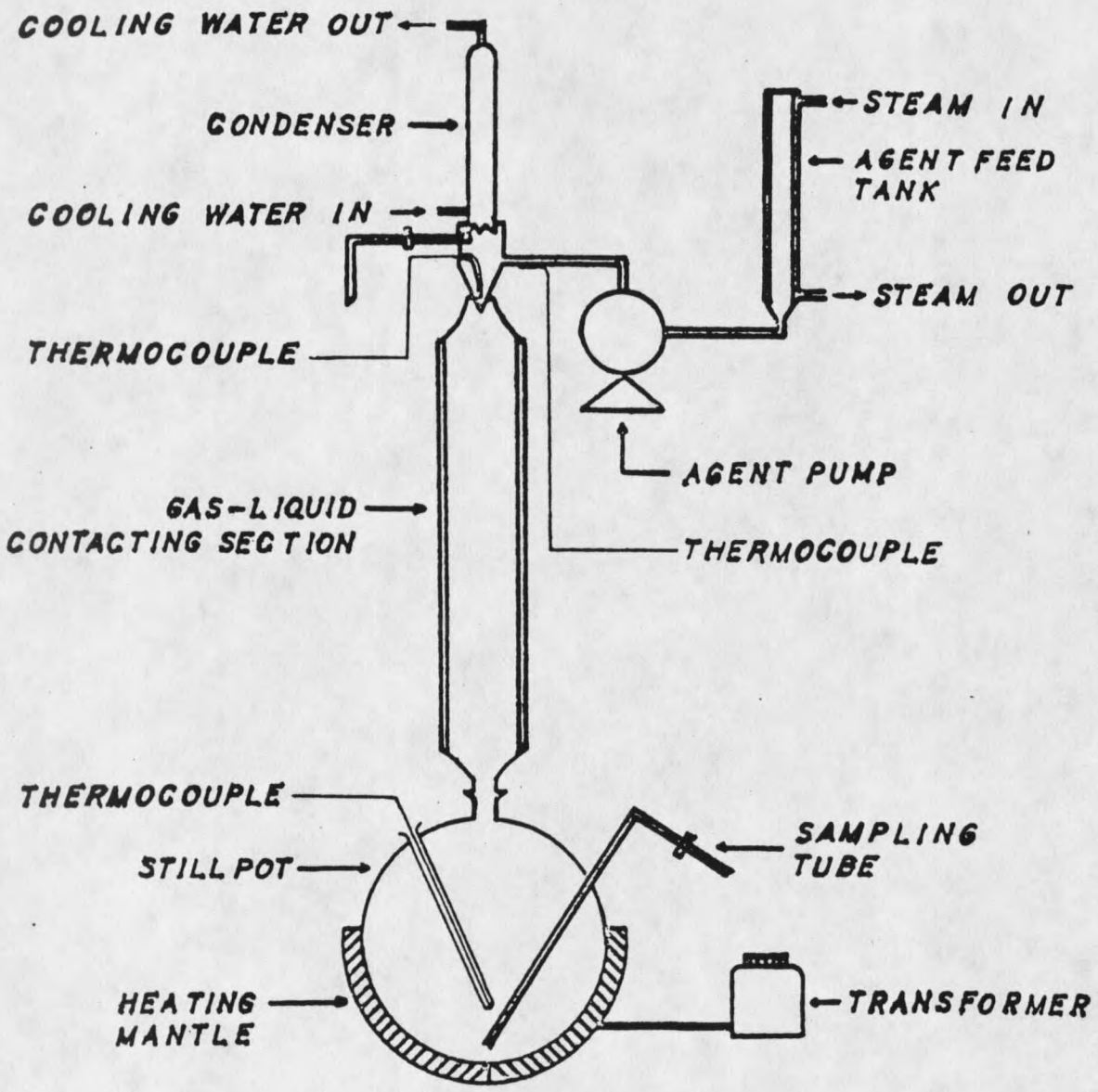

Figure 5. Experimental apparatus.

heat loss. Power input to the mantle and therefore the boil-up rate was controlled by a transformer.

Gas-Liquid Contacting Section

Effective gas liquid contact was achieved in a 20 inch long, 1.5 inch diameter perforated plate column. A silvered vacuum jacket was placed around the column to reduce heat loss. The contacting section contained five Oldershaw perforated plates with tray spacings of 1.8 inches and weir weights of 3/8 inches. An additional section of packed column was added above the agent entrance to prevent agent from being carried overhead with the products.

Extractive Agent Feed System

The extractive agent was fed to the column from a cylindrical steam jacketed separatory funnel. Steam was used to control the temperature of the agent entering the column. The funnel was made of Pyrex glass and had a capacity of 200 ml. Feed lines in the system were copper and measured 0.375 inches outside diameter. The lines were wrapped in heating wires, the temperatures of which were controlled by transformers. The addition rate of agent was controlled with a positive displacement pump. The pump was a microbellows metering pump which was manufactured by Research Appliance Company. It was a standard model, 0.5 in. inside diameter bellows.

Condenser

The condenser used was a water cooled Corad condensing head. Vapor condensed on the inside surface of the Corad head. This was surface divided into six different sized parallel parts by means of vertical glass ridges. The condensate from any one section could be

taken off as product by positioning that section over the side arm sampling port. The remainder of the condensate returned to the column as reflex.

Agent Recovery System

Due to the large differences in boiling points between the extractive agents and the mixtures that were investigated, it was possible to reclaim the agents by simple distillation. The recovery stillpot consisted of a two liter round bottom flask. The vapor exited a side-port of the flask and was condensed in a simple water cooled condenser. The overhead vapor temperature was measured with a mercury thermometer. The arrangement [3] of the agent recovery system is shown in Figure 6.

Additional Equipment

Additional equipment included a digital thermometer OMEGA 2176a connected to K-type thermocouples. With this equipment it was possible to record temperatures in the stillpot, at the overhead, and in the agent feed line.

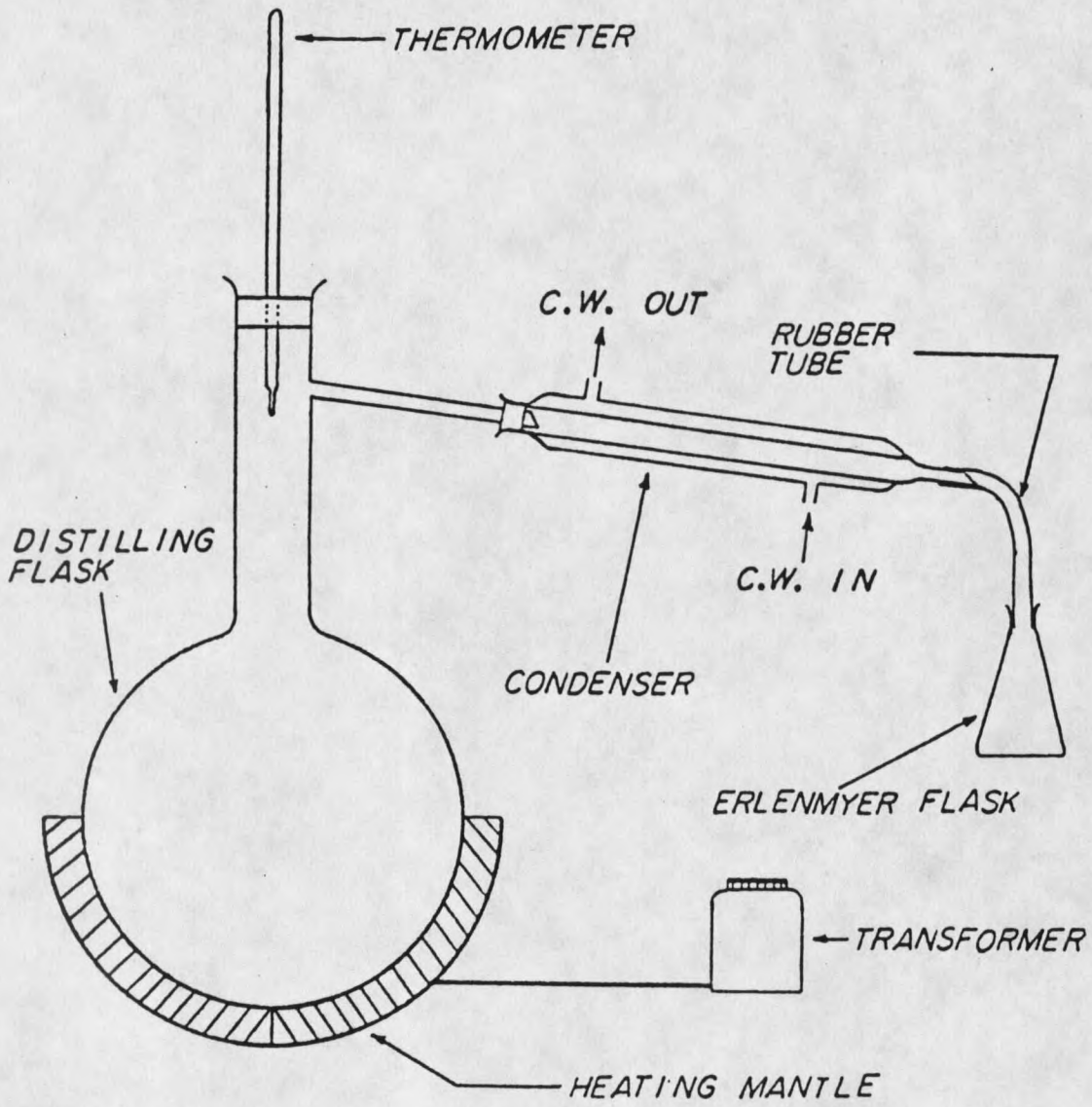

Figure 6. Agent recovery system.

EXPERIMENTAL PROCEDURE

Calibration of the Perforated Plate Column

Before beginning an experimental study of the effects of extractive agents on the relative volatility of various mixtures, it was necessary to determine the number of theoretical plates or stages present in the column. This calibration was accomplished by determining the separation at total reflux of a mixture of ethylbenzene (136.2°C) and p-xylene (138.5°C). The mixture of ethylbenzene and p-xylene has a known relative volatility of 1.06 which is uniform throughout the entire concentration range. With knowledge of both the relative volatility of the mixture and the concentration of samples from the overhead and stillpot at total reflux, the number of theoretical plates could be determined from Equation (5), the Fenske equation. From this analysis [5] the number of theoretical plates in the experimental column was found to be 4.5.

Two Hour Experimental Runs

To begin an experimental run the stillpot was charged with the mixture to be investigated. With the exception of the isopropanol–isopropyl acetate–water mixture, 400 grams of feed were used, 200 grams of each of the components. In the case of the ternary mixture, 400 grams of a mixture were used; however, the composition was that of the ternary azeotrope. Extractive agents were prepared. In the case of a liquid mixture of agents, weight ratios of 1:1 or 1:1:1 were used. If one or more of the agents were solids, the ratios used depended strongly on the solid-liquid solubility. The extractive agents were heated to within approximately 10 degrees of the overhead temperature. If solid agents were being studied, it was sometimes necessary to use higher agent temperatures to keep the solid in

solution and prevent clogging of the pump and feed lines. In extreme cases it was necessary to apply heat lamps as an additional heat source.

Heat was applied to the mixture in the stillpot until refluxing began. At this point the agent or mixture of agents was pumped into the column at a rate of 20 ml per minute. The start of agent flow was considered to be time zero. After establishing the feed rate of the agent, the heat input to the mixture in the stillpot was adjusted to give a reflux rate of 10-20 ml per minute. The reflux rate was determined by counting drops from the Corad condensing head.

The runs were conducted at total reflux. No overhead or bottoms products were removed during normal operation of the column. The extractive agent, however, was continually pumped into the column and accumulated in the stillpot. This buildup of agent caused an increase in the stillpot temperature and required frequent adjustments in the heat input to maintain the desired boil-up rate.

After one hour of operation, samples of approximately 2 ml were collected from the overhead and stillpot. Samples were again collected at 1.5 and 2.0 hours. All samples were analyzed by gas chromatography. By using the Fenske equation, it was possible to calculate values of relative volatility.

Three Hour Experimental Runs

The presence of chemical reaction or azeotrope formation is extremely undesirable in extractive distillation. Both problems complicate or make impossible the separation to pure components. In the case of unwanted reaction the actual separation may be substantially different than that shown from analysis of overhead and bottoms products. For example, if one of the components of the mixture reacts to form a noncondensable gas, the resulting low concentration of this component in the product analysis could be mistaken

for legitimate separation. Azeotrope formation between an agent and a component of the mixture would prevent the recovery of agent by simple distillation.

A second set of operational procedures was used to detect the presence of these phenomena. In these experiments the column was operated for three hours with samples taken each half hour. During the first hour of operation extractive agent was pumped into the column as previously described. In the second hour the addition of agent was discontinued, however, the boil-up rate was held constant. For the third hour extractive agent was again added to the column.

Agent Recovery

Following an experimental run the contents of the stillpot were transferred to the recovery flask to be reclaimed. Since the column was operated at total reflux, these contents consisted essentially of the original mixture plus the agent that was added in during the run. This mixture was distilled until the vapor temperature in the recovery flask was approximately 20 Celsius degrees higher than the highest boiling compound in the mixture. At this point the liquid left in the flask was ready for re-use as an agent.

RESULTS AND DISCUSSION

Effects of Agents on Relative Volatility

The results obtained from two hour experimental runs are shown in Tables 3-8. Relative volatilities were significantly increased for the following mixtures: ethanol + isopropanol, n-propanol + 2-butanol, ethanol + t-butanol, isopropanol + t-butanol, n-propanol + allyl alcohol, isopropanol + isopropyl acetate + water. In each case the separation obtained for a given number of plates was increased and the number of plates required for a given separation decreased. The relative improvement factor or selectivity (sel.) varied for each individual mixture and corresponding agent.

None of the extractive agents tested were successful in improving the relative volatility of n-amyl acetate + isoamyl acetate or 2-methyl-1-butanol + n-amyl alcohol. The results for these mixtures of isomers are given in Appendix A.

Although values of relative volatility cannot be predicted from the structure of either the agents or the mixtures, it is sometimes possible to make qualitative generalizations. For instance, agents of similar structure were seen to have similar effects on the values of relative volatility. In the ethanol plus isopropanol system (Table 3) an increase in α was reported for the agent methyl benzoate, an aromatic compound with an attached ester group. Methyl salicylate, which differs from methyl benzoate only in the addition of a hydroxy group in the two position, is also an effective agent. Salicylic acid and cinnamic acid, aromatic compounds with attached carboxylic acid groups were also effective in increasing relative volatilities when mixed with methyl benzoate and methyl salicylate. The pattern of similar extractive agents producing similar changes in relative volatility was also

Table 3. Data From Runs Made in Rectification Column: Ethanol From Isopropanol.

Agent	Peak Height % Ethanol		Relative Volatility	Selectivity
	Overhead	Bottoms		
None	61.7	52.0	1.09	1.00
Methyl Benzoate (2)*	72.8	50.1	1.25	1.15
Methyl Benzoate (1) Salicyclic Acid 4:1	69.7	48.3	1.22	1.12
Methyl Salicylate (2) Cinnamic Acid (1) 5:1	70.6	49.6	1.22	1.12
Methyl Benzoate (1) Cinnamic Acid (1) 5:1	72.3	55.6	1.17	1.07
Methyl Salicylate	73.8	53.8	1.22	1.12
Methyl Salicylate (1) Salicylic Acid (1) 5.7:1	70.3	51.0	1.20	1.10

*Numbers in parenthesis ( ) indicate the number of times the agent was reclaimed. The ratio of agents was 1:1 unless otherwise noted. All values represent an average of three samples taken during the run.

Table 4. Data From Runs Made in Rectification Column: n-Propanol From 2-Butanol.

Agent	Peak Height % n-Propanol		Relative Volatility	Selectivity
	Overhead	Bottoms		
None	49.0	42.3	1.07	1.00
Methyl Salicylate	63.3	42.0	1.21	1.13
Methyl Benzoate (2)* Salicylic Acid (1) 4:1	59.3	41.0	1.18	1.10
Methyl Salicylate (1) Cinnamic Acid 5:1	64.0	41.7	1.22	1.14
Methyl Benzoate (1)	64.7	42.1	1.23	1.15
Methyl Benzoate (2) Cinnamic Acid (2) 5:1	61.6	43.0	1.18	1.10
Methyl Salicylate Salicylic Acid	63.1	41.4	1.22	1.14

*Numbers in parenthesis ( ) indicate the number of times the agent was reclaimed. The ratio of agents was 1:1 unless otherwise noted. All values represent an average of three samples taken during the run.

Table 5. Data From Runs Made in Rectification Column: Ethanol From t-Butanol.

Agent	Peak Height % Ethanol		Relative Volatility	Selectivity
	Overhead	Bottoms		
None	74.6	64.7	1.11	1.00
Methyl Benzoate (3)*	83.4	63.7	1.26	1.14
Methyl Benzoate (3) Cinnamic Acid (3) 5:1	84.3	64.3	1.27	1.15
Methyl Benzoate (3) Salicylic Acid (2) 4:1	85.9	62.7	1.34	1.21
Methyl Benzoate HHPA Phthalic Anhydride 5:3:1**	76.6	55.6	1.24	1.12
Methyl Salicylate	81.4	59.6	1.27	1.15
Methyl Salicylate Salicylic Acid	79.4	58.7	1.25	1.13
Methyl Salicylate Cinnamic Acid	77.8	65.4	1.25	1.13

*Numbers in parenthesis ( ) indicate the number of times the agent was reclaimed. The ratio of agents was 1:1 unless otherwise noted. All values represent an average of three samples taken during the run.
**90 minute sample. Unwanted reaction was observed between 90 and 120 minutes.

seen in the separation of n-propanol from 2-butanol (Table 4) and ethanol from t-butanol (Table 5).

Unfortunately it was not possible to relate the importance of the various functional groups of the agents to the numerical values of relative volatility. The improved relative volatilities fell in a narrow range of values and differences between them might have been the result of slightly different operating conditions such as boil-up rate, agent rate or agent temperature rather than differences in chemical structure.

Effects of Mixture Chemical Structure

Mixtures of chemically dissimilar liquids have been shown to be good candidates for separation by extractive distillation [2]. Because of the differences in mixture chemical

Table 6. Data From Runs Made in Rectification Column: Isopropanol From t-Butanol.

Agent	Peak Height % Isopropanol		Relative Volatility	Selectivity
	Overhead	Bottoms		
None	62.4	62.2	1.01	1.00
Methyl Benzoate	69.9	59.3	1.11	1.10
Methyl Benzoate Cinnamic Acid 5:1	69.3	60.3	1.09	1.08
HHPA	***** Undesired Reaction *****			
MHHPA	***** Undesired Reaction *****			
Phthalic Anhydride HHPA Methyl Benzoate 3:2:1	***** Undesired Reaction *****			
HHPA Methyl Benzoate 1:1**	60.9	44.8	1.16	1.15*
Methyl Benzoate HHPA Phthalic Anhydride 5:3:2**	57.3	38.3	1.19	1.18

*Numbers in parenthesis ( ) indicate the number of times the agent was reclaimed. The ratio of agents was 1:1 unless otherwise noted. All values represent an average of three samples taken during the run.
**90 minute sample. Unwanted reaction was observed between 90 and 120 minutes.

structures, it is likely that an added agent could be selectively nonideal with one component of a dissimilar mixture. This situation leads to a change in the ratio of activity coefficients and therefore a change in relative volatilities.

Anderson et al. [28] examined the effects of chemical dissimilarity on the component volatility of mixtures being separated by extractive distillation. It was found that the volatility for a series of cyclical C_6 hydrocarbons decreased with an increase in the degree of unsaturation when mixed with potential extractive agents. That is, volatility decreased from normal hexane to hexene to hexadiene to hexyne to benzene. These results were explained by the fact that olefins have highly polarizable pi electrons which can form a loose bond or chemical complex with electrophilic groups.

Table 7. Data From Runs Made in Rectification Column: n-Propanol From Allyl Alcohol.

Agent	Peak Height % n-Propanol		Relative Volatility	Selectivity
	Overhead	Bottoms		
None	63.1	61.9	1.01	1.00
DMSO	91.6	60.4	1.55	1.53
DMFA	91.4	61.9	1.52	1.50
DMSO (1)* DMFA (1)	86.9	60.2	1.40	1.39
Adiponitrile	87.1	60.3	1.39	1.38
Adiponitrile (1) DMSO (1)	89.9	61.9	1.46	1.45
Adiponitrile (1) DMFA (1) 3:1	85.9	61.3	1.35	1.34
Adiponitrile (1) DMSO (2) DMFA (2)	89.9	61.9	1.46	1.45

*Numbers in parenthesis ( ) indicate the number of times the agent was reclaimed. The ratio of agents was 1:1 unless otherwise noted. All values represent an average of three samples taken during the run.

Table 8. Data From Runs Made in Rectification Column: Isopropanol From Isopropyl Acetate.

Agent	Peak Height % (water free)		Relative Volatility	Selectivity
	Overhead	Bottoms		
None	42.0	43.5	0.99**	——
Methyl Benzoate	56.1	15.0	1.55	1.55
Methyl Benzoate Diisooctyl Phthalate	74.3	35.7	1.45	1.45

*Numbers in parenthesis ( ) indicate the number of times the agent was reclaimed. The ratio of agents was 1:1 unless otherwise noted. All values represent an average of three samples taken during the run.

**Experimental value. Selectivities were calculated with the values of $\alpha = 1.00$ since composition of the feed was that of the minimum boiling azetrope.

Similar results were seen in this research (Table 7). Allyl alcohol and n-propanol differ in structure only by the double bond in the two position. The volatility of allyl alcohol relative to n-propanol was dramatically decreased when extractive distillation was used. A possible explanation for this result is the formation of a chemical complex between the double bond in the allyl alcohol and, for an example, the electrophilic cyano group in adiponitrile. The formation of such a complex would hold the allyl alcohol in the column while allowing the n-propanol to pass overhead. The end result is an increase in the ratio of activity coefficients and therefore an increase in relative volatility.

The trend noted by Benedict and Rubin [2] that chemically dissimilar mixtures are more likely candidates for extractive distillation was definitely seen in this work. Isomers iso-amylacetate and n-amylacetate along with isomers n-amyl alcohol and 2-methyl-1-butanol were the two most chemically similar mixtures in this study. The mixtures of alcohols isopropanol plus ethanol, 2-butanol plus n-propanol, ethanol plus t-butanol and t-butanol plus isopropanol might be said to have been one step more dissimilar than the isomers. The double bond in allyl alcohol could be considered to have added another degree of dissimilarity to its mixture with n-propanol. Finally isopropanol and isopropyl acetate were probably the most chemically dissimilar components that were studied. The closer the chemical structure of the mixtures being separated the more difficult it was to separate by extractive distillation. No agents were found that could significantly increase the relative volatility of the mixtures of isomers (Appendix A). Moderate success was seen improving the relative volatility of the close boiling alcohols listed in the second category (Tables 3-6). The relative volatility of the allyl alcohol, n-propanol mixture was increased from 1.01, a value so low that separation is practically impossible, to 1.55 which is a relatively easy separation (Table 7). Isopropanol and isopropyl acetate existed in a ternary azeotrope with water which was impossible to separate by normal distillation. Extractive

distillation effectively broke this azeotrope and made possible the separation of isopropanol from isopropyl acetate as shown in Table 8.

Prediction of Minimum Number of Theoretical Plates

As stated earlier, an increase in the value of relative volatility decreases the number of theoretical plates necessary to achieve a desired separation. Tables 9-14 report the results of this research in terms of the number of theoretical plates required to obtain 99% pure (solvent-free basis) overhead and bottoms products as calculated by the Fenske equation.

Table 9. Number of Theoretical Plates Required for 99% Purity (Solvent-Free Basis): Ethanol From Isopropanol.

Agent	Relative Volatility	Number of Plates
None	1.09	106.6
Methyl Benzoate	1.25	41.2
Methyl Benzoate Salicylic Acid	1.22	46.2
Methyl Salicylate Cinnamic Acid	1.22	46.2
Methyl Benzoate Cinnamic Acid	1.17	58.5
Methyl Salicylate	1.22	46.2
Methyl Salicylate Salicylic Acid	1.20	50.4

Table 10. Number of Theoretical Plates Required for 99% Purity (Solvent-Free Basis): n-Propanol From 2-Butanol.

Agent	Relative Volatility	Number of Plates
None	1.07	135.8
Methyl Salicylate	1.21	48.2
Methyl Benzoate Salicylic Acid	1.18	55.5
Methyl Salicylate Cinnamic Acid	1.22	46.2
Methyl Benzoate	1.23	44.4
Methyl Benzoate Cinnamic Acid	1.18	55.5
Methyl Salicylate Salicylic Acid	1.22	46.2

Table 11. Number of Theoretical Plates Required for 99% Purity (Solvent-Free Basis): Ethanol From t-Butanol.

Agent	Relative Volatility	Number of Plates
None	1.11	88.1
Methyl Benzoate	1.26	39.8
Methyl Benzoate Cinnamic Acid	1.27	38.4
Methyl Benzoate Salicylic Acid	1.34	31.4
Methyl Benzoate HHPA Phthalic Anhydride	1.24	42.7
Methyl Salicylate	1.27	38.5
Methyl Salicylate Salicylic Acid	1.25	41.2
Methyl Salicylate Cinnamic Acid	1.25	41.2

Table 12. Number of Theoretical Plates Required for 99% Purity (Solvent-Free Basis): Isopropanol From t-Butanol.

Agent	Relative Volatility	Number of Plates
None	1.01	923.6
Methyl Benzoate	1.11	88.1
Methyl Benzoate Cinnamic Acid	1.09	106.6
Methyl Benzoate HHPA Phthalic Anhydride	1.19	52.8
Methyl Benzoate HHPA	1.16	61.9

Table 13. Number of Theoretical Plates Required for 99% Purity (Solvent-Free Basis): n-Propanol From Allyl Alcohol.

Agent	Relative Volatility	Number of Plates
None	1.01	923.6
DMFA	1.55	21.0
DMSO	1.52	21.9
DMSO DMFA	1.40	27.3
Adiponitrile	1.39	27.9
Adiponitrile DMSO	1.46	24.3
Adiponitrile DMFA	1.35	30.6
Adiponitrile DMSO DMFA	1.46	24.3

Table 14. Number of Theoretical Plates Required for 99% Purity (Solvent and Water-Free Basis): Isopropanol From Isopropyl Acetate.

Agent	Relative Volatility	Number of Plates
None	1.00	∞
Methyl Benzoate	1.55	21.0
Methyl Benzoate Diisooctyl Phthalate	1.45	24.7

Agent Stability

One important consideration of an agent for industrial use would be its stability. In a commercial situation it is likely that an agent would be required to withstand many recyclings. The stability of several agents and mixtures of agents was tested and the results listed in Table 15. The agents in this table were repeatedly used to separate liquid mixtures and were then recovered. After having been used with several systems, the agent was then retested with the system for which it was originally mixed. As shown in these results no substantial decrease in effectiveness was detected for any of the agents tested.

Table 15. Comparison of Results Between Fresh and Recycled Agents.

Times Reclaimed	System	Agent	Average Relative Volatility
0	Isopropanol t-Butanol	Methyl Benzoate Cinnamic Acid	1.09
4	" "	" "	1.10
0	Isopropanol Ethanol	Methyl Benzoate Salicylic Acid	1.22
4	" "	" "	1.20
0	Isopropanol t-Butanol	Methyl Benzoate	1.11
4	" "	" "	1.10
0	Isopropyl Acetate Isopropanol Water	Methyl Benzoate Diisooctyl Phthalate	1.43
1	" "	" "	1.45
0	2-Butanol n-Propanol	Methyl Salicylate Salicylic Acid	1.19
4	" "	" "	1.22

Unwanted Chemical Reaction and Azeotrope Formation

The presence of either azeotrope formation or chemical reaction is undesirable in extractive distillation. A series of experiments were conducted to detect the presence of these phenomena. During the first and third hours of operation extractive agents were added to the column as previously described. In the second hour distillation continued but no agents were added. In the absence of azeotrope formation and chemical reaction, relative volatilities in the first and third hours would be increased while values in the second hour would approach those of the "blank" runs performed earlier. This pattern is expected since extractive distillation requires a concentration of agent on each plate in order to be effective.

In the case of azeotrope formation a deviation from this pattern would be expected. Should azeotrope formation occur, the values of relative volatility would remain high since the formation of azeotropes would not rely on the presence of agent on the plates.

Chemical reaction has the potential for causing the disappearance of one component of a mixture thereby altering product compositions and giving the false impression of improved separation. If chemical reaction did occur there is no reason that simply stopping the flow of agent during the second hour of operation would result in the product compositions' return to those of the "blank" runs.

From these comments it appears likely that no azeotrope formation or undesired reaction occurred in the experiments represented by the first five entries of Table 16. In these cases values of relative volatility for the second hour of operation approached those of "blank" runs. Furthermore, these results support the prediction that effective extractive distillation requires the presence of agent on each plate.

In several cases it was not possible to rule out chemical reaction as a factor in improved relative volatilities. Perliminary work in vapor-liquid equilibrium stills predicted several anhydrides to be effective extractive agents in the separation of isopropanol from t-butanol and ethanol from t-butanol. Attempts at verifying these results in a perforated plate column were unsuccessful. As noted in the final two entries of Table 16, completion of successful runs did not occur when hexahydrophthalic anhydride (HHPA), methylhexahydrophthalic anhydride (MHHPA), Phthalic Anhydride (Pht. Anh.), or mixtures of these agents were used. Undesired reaction appeared to be occurring whenever these agents were used. Attempts to dilute the anhydrides with methyl benzoate met with limited success. Observation of undesired reaction was delayed by these attempts; however, it was not possible to complete a 2 hour run without evidence of reaction.

The most likely reaction which could have occurred in these cases is the dehydration of t-butanol to form isobutylene and water. This reaction was suspected since tertiary

Table 16. Results From Three Hour Runs (No Agent Added in Second Hour).

Time	Overhead	Bottoms	Relative Volatility	Selectivity
	System: Allyl Alcohol + n-Propanol Agent: Dimethylformamide + Dimethyl Sulfoxide			
	Peak Height % n-Propanol			
30	86.0	61.0	1.38	1.37
60	85.9	60.5	1.36	1.35
90	72.3	59.7	1.13	1.12
120	71.3	59.1	1.13	1.12
150	85.6	59.4	1.36	1.35
180	90.2	59.9	1.49	1.48
	System: 2-Butanol + n-Propanol Agent: Methyl Benzoate			
	Peak Height % n-Propanol			
30	57.7	43.1	1.14	1.07
60	63.9	42.8	1.21	1.13
90	53.7	43.2	1.10	1.03
120	53.3	42.3	1.10	1.03
150	65.6	41.7	1.23	1.15
180	64.7	41.7	1.23	1.15
	System: Ethanol + t-Butanol Agent: Methyl Salicylate			
	Peak Height % Ethanol			
30	80.6	58.2	1.27	1.14
60	80.8	60.3	1.25	1.13
90	70.9	60.7	1.11	1.00
120	70.9	61.1	1.11	1.00
150	80.9	59.1	1.25	1.13
180	82.4	59.1	1.30	1.17
	System: Isopropanol + Ethanol Agent: Methyl Salicylate			
	Peak Height % Ethanol			
30	80.6	58.2	1.27	1.14
60	80.8	60.3	1.25	1.13
90	70.9	60.7	1.11	1.00
120	70.9	61.1	1.11	1.00
150	80.9	59.1	1.25	1.13
180	82.4	59.1	1.30	1.17

Table 16 (continued).

Time	Overhead	Bottoms	Relative Volatility	Selectivity
	System: Isopropyl Acetate + Isopropanol + Water Agent: Methyl Benzoate + Diisooctyl Phthalate			
	Peak Height % Isopropanol Water-free basis			
30	68.1	45.1	1.24	1.24
60	75.1	34.2	1.44	1.44
90	44.6	43.5	1.01	1.01
120	42.5	42.9	0.99	0.99
150	74.3	35.1	1.45	1.45
180	75.1	35.7	1.45	1.45
	System: Isopropanol + t-Butanol Agents*: HHPA, MHHPA, Ph Anh + HHPA + Methyl Benzoate, HHPA + Methyl Benzoate			
	Peak Height % Isopropanol			
	Unable to complete these runs without evidence of unwanted reaction. Runs with Methyl Benzoate and Methyl Benzoate + Cinnamic Acid showed no signs of decomposition.			
	System: Ethanol + t-Butanol Agent*: Methyl Benzoate + HHPA			
	Peak Height % Ethanol			
	Unable to complete run without reaction.			

*Refer to Tables 3-8 for composition of agent mixtures.

butanol is relatively unstable and susceptible to this dehydration reaction [1]. Also, the anhydrides used in these experiments have an affinity for water and may tend to pull water molecules off the alcohol. Other evidence pointing to this reaction include several sightings of the evolution of a noncondensable gas (isobutylene B.P. -6.9°C) and uncharacteristically low levels of t-butanol in produce samples. In any case the anhydrides do not appear to be effective extractive distillation agents in separations involving t-butanol.

SUMMARY AND CONCLUSIONS

1. The following close boiling alcohol mixtures showed improved relative volatilities upon the addition of extractive agents to a perforated plate column: ethanol + isopropanol, n-propanol + 2-butanol, ethanol + t-butanol, isopropanol + t-butanol, and n-propanol + allyl alcohol.
2. The ternary azetrope between isopropyl acetate + isopropanol + water was broken and the separation of isopropanol from isopropyl acetate made possible by the use of extractive distillation.
3. The effectiveness of extractive agents remained high throughout repeated recovery and reuse.
4. Improved values of relative volatility occurred only when an agent was present on the plates.
5. Phthalic anhydride, hexahydrophthalic anhydride, and methyl hexahydrophthalic anhydride were not effective in separations involving t-butanol. It is suspected that these compounds promoted the dehydration of this alcohol.
6. Agents of similar chemical structure gave similar values of relative volatility in mixtures of: ethanol + t-butanol, ethanol + isopropanol, and n-propanol + 2-butanol. The effective agents included methyl benzoate, methyl salicylate, cinnamic acid and salicylic acid.
7. Extractive agents were least effective when components of the mixtures had similar structures.

RECOMMENDATIONS FOR FURTHER RESEARCH

Experiments in this work were performed in a batch distillation column at total reflux. Commercial application of extractive distillation would likely occur in a continuous column. Laboratory scale research of a continuous set-up could provide important information on this type of operation. Specifically, the effects of variations in reflux ratios could be examined. Also, since the residence time for a mixture in a continuous column would be shorter than that in a batch column, it might be possible to avoid the dehydration of t-butanol that was observed in this work.

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APPENDICES

APPENDIX A

RESULTS FOR MIXTURES OF ISOMERS

Table 17. Separation of Amyl Acetate Isomers: n-Amyl Acetate + Isoamyl Acetate.

Agent	Relative Volatility
None	1.28
DMSO	1.29
Sulfolane	1.26
Polyethylene Glycol 300	1.28
DMSO, Polyethylene Glycol 300, Sulfolane	1.28
Dipropylene Glycol Dibenzoate	1.27
Methyl Benzoate	1.27
Dipropylene Glycol Dibenzoate, Me-p-Hydroxy-benzoate	1.25
Ethylene Glycol 300, DMFA	1.30

Table 18. Separation of Amyl Alcohols: 1 Methyl-2-Butanol + n-Amyl Alcohol.

Agent	Relative Volatility
None	1.43
Methyl Benzoate	1.32
Methyl Benzoate, Phthalic Anhydride	1.32

APPENDIX B

SAFETY FACTORS AND COMMENTS ON AGENTS

Table 19. Ease/Difficulty of Experimental Runs.

Agent	Comments
Methyl Benzoate	Moderately toxic by ingestion. Easy to run and handle.
Salicylic Acid	Moderately toxic by ingestion. Solid at room temperature. Difficult to run at concentrations listed, tendency to crystallize out of solution.
Methyl Salicylate	Toxic by ingestion. Easy to run and handle.
Cinnamic Acid	Combustible. Solid at room temperature. Somewhat difficult to keep in solution.
Hexahydrophthalic Anhydride	Strong irritant to eyes and skin. Solid, turning to liquid at just above room temperature. Easy to run by itself, but fairly difficult when solid agents are added.
Methyl Hexahydrophthalic Anhydride	Not listed in handbooks. Liquid at room temperature. Easy to run and handle.
Phthalic Anhydride	Toxic and skin irritant. Solid at room temperature. No problems keeping in solution at concentrations studied.
Dimethyl Sulfoxide	Readily penetrates skin and other tissues. Low toxicity. Easy to run and handle.
Dimethylformamide	Strong irritant to skin and tissue. Easy to run and handle.
Adiponitrile	Toxic by ingestion and inhalation. Easy to run and handle.
Sulfolane	Combustible. Easy to run and handle.
Polyethylene glycol	Combustible; nontoxic. Easy to run and handle.
Dipropylene glycol	Combustible. Easy to run and handle.
Diisooctyl Phthalate	Low toxicity. Easy to run and handle. Slightly viscous at room temperature.