



Extractive 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
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Montana State University
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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
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MIXTURE AND TWO CLOSE BOILING ISOMER MIXTURES

by

Mark George Vosburgh

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Mark George Vosburgh

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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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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.

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

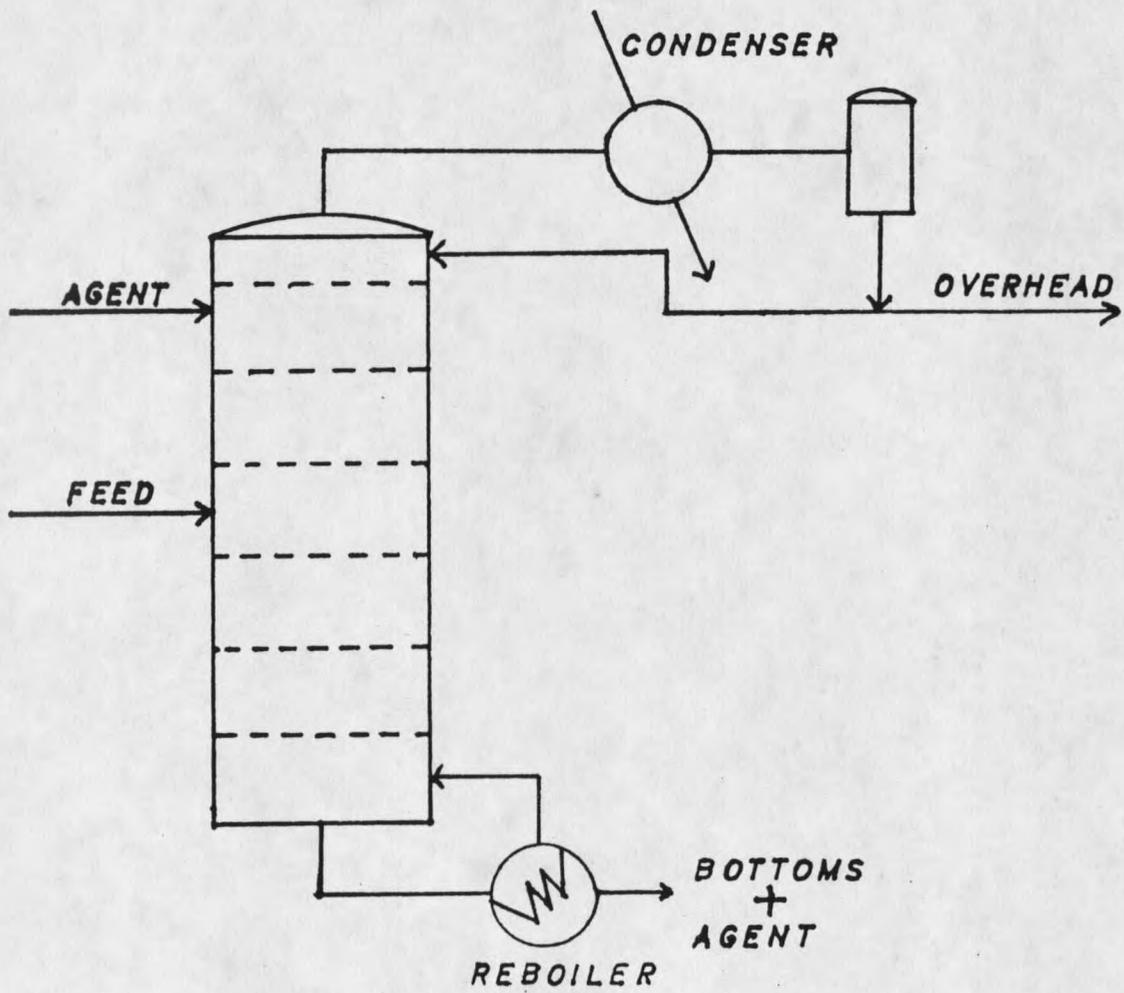


Figure 1. Extractive distillation column.

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

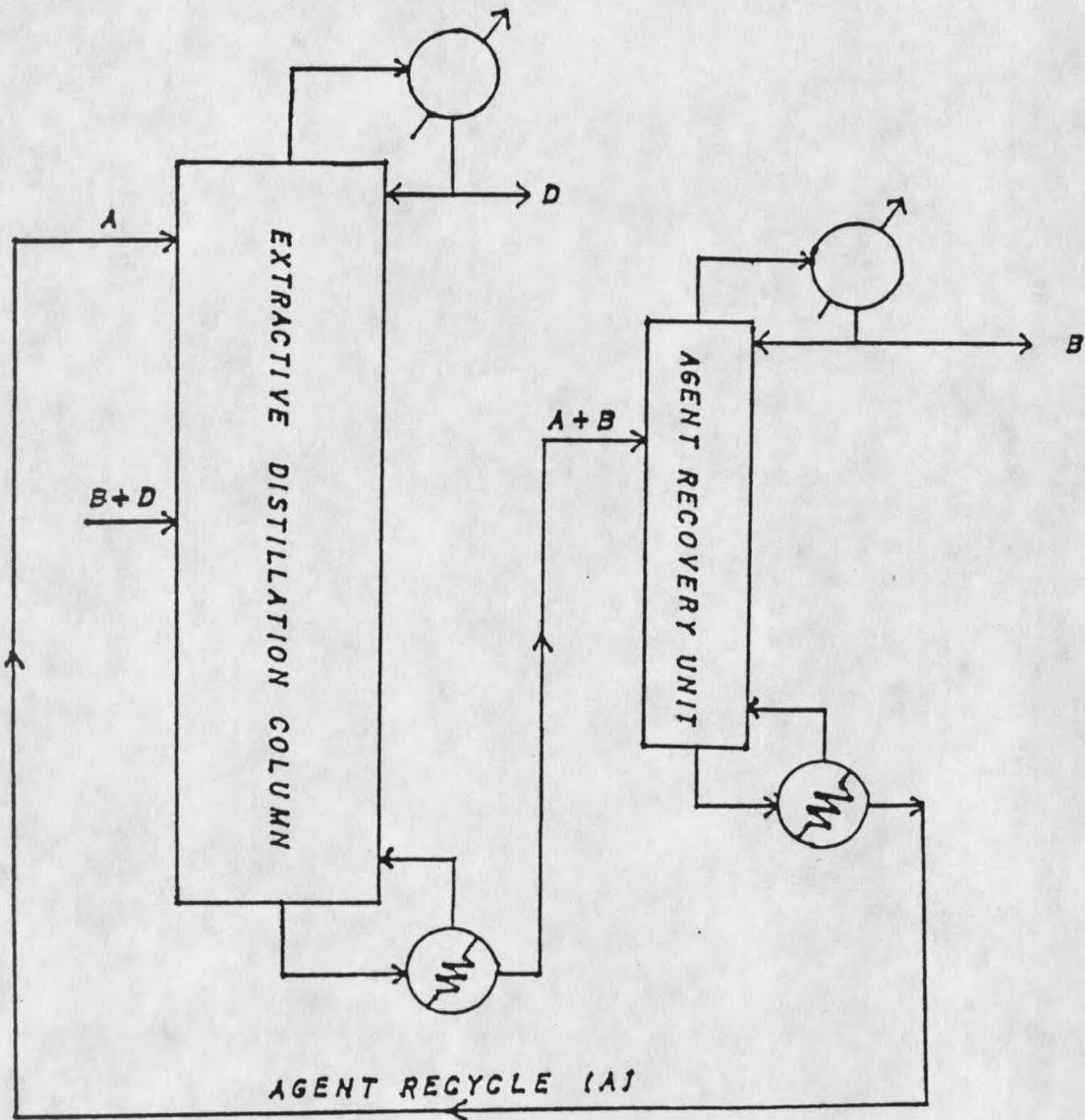


Figure 2. Continuous extractive distillation flowsheet.

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.

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

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].

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

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].

$$Sel_{ij} = \frac{(\alpha_{ij})_P}{(\alpha_{ij})_A} \quad (3)$$

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

$$\hat{f}_i^V = \hat{f}_i^L \quad (4)$$

or

$$\phi_i \times y_i \times P = \gamma_i \times x_i \times p_i^{\text{SAT}} \quad (5)$$

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 .

$$p_i^* = \gamma_i x_i p_i^{\text{SAT}} \quad (6)$$

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

$$p_i^* = p_i^{\text{SAT}} \times x_i \quad (7)$$

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).

$$\alpha_{ij} = \frac{\gamma_i p_i^{\text{SAT}} \phi_j}{\gamma_j p_j^{\text{SAT}} \phi_i} \quad (8)$$

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

$$\alpha_{ij} = \frac{\gamma_i p_i^{\text{SAT}}}{\gamma_j p_j^{\text{SAT}}} \quad (9)$$

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 measure 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

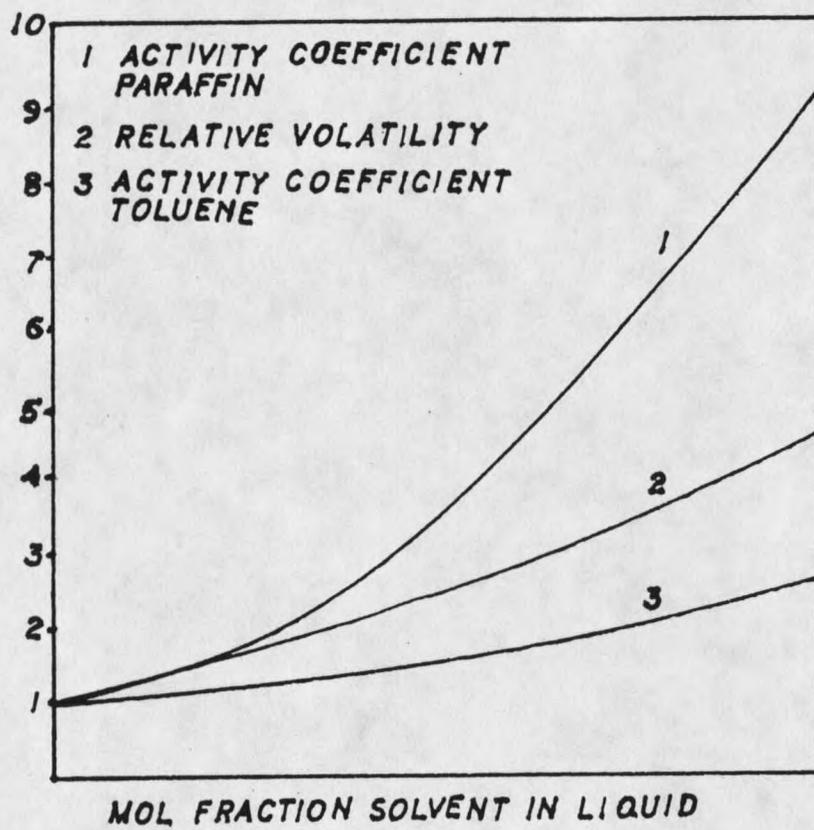


Figure 3. Effect of phenol on paraffin-toluene relative volatility.

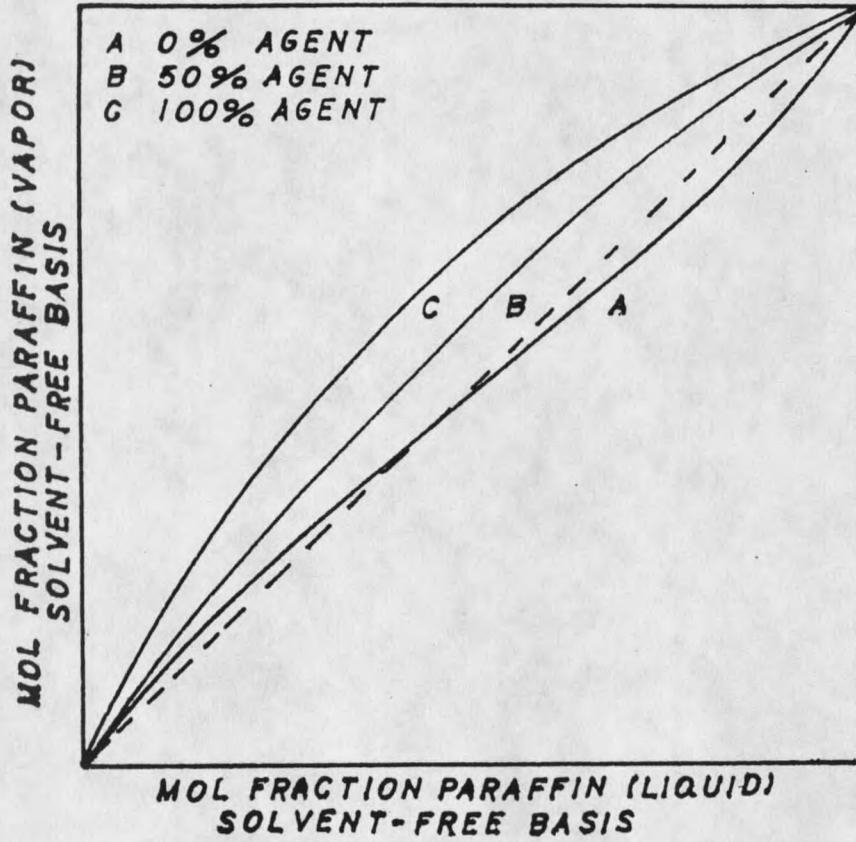


Figure 4. Effects of phenol on paraffin-toluene x-y diagram.

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 ($\alpha = 1.11$) 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.

