



The separation of three azeotropes by extractive distillation
by An-I Yeh

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

Several different kinds of extractive distillation agents were investigated to affect the separation of three binary liquid mixtures, isopropyl ether - acetone, methyl acetate - methanol, and isopropyl ether - methyl ethyl ketone. Because of the small size of the extractive distillation column, relative volatilities were assumed constant and the Fenske equation was used to calculate the relative volatilities and the number of minimum theoretical plates.

Dimethyl sulfoxide was found to be a good extractive distillation agent. Extractive distillation when employing a proper agent not only negated the azeotropes of the above mixtures, but also improved the efficiency of separation. This process could reverse the relative volatility of isopropyl ether and acetone. This reversion was also found in the system of methyl acetate and methanol when nitrobenzene was the agent. However, normal distillation curves were obtained for the system of isopropyl ether and methyl ethyl ketone undergoing extractive distillation.

In the system of methyl acetate and methanol, the relative volatility decreased as the agents' carbon number increased when glycols were used as the agents. In addition, the oxygen number and the locations of hydroxyl groups in the glycols used were believed to affect the values of relative volatility.

An appreciable amount of agent must be maintained in the column to affect separation. When dimethyl sulfoxide was an agent for the three systems studied, the relative volatility increased as the addition rate increased.

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MONTANA STATE UNIVERSITY
Bozeman, Montana

August 1983

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APPROVAL

of a thesis submitted by

An-I Yeh

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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ACKNOWLEDGEMENT

The author wishes to thank the faculty and staff of the Chemical Engineering Department at Montana State University for their encouragement and help. A special thanks goes to Dr. Lloyd Berg, director of this research, for his guidance.

The author wishes to thank Montana State University Engineering Experiment Station for its financial support of this project.

Appreciation is extended to Lyman Fellows for his fabrication and maintenance of research equipment and Dr. Pisant Ratanapuech for his suggestions. A special appreciation goes to my brother, Angong Yeh, for his encouragement and suggestions.

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ABSTRACT

Several different kinds of extractive distillation agents were investigated to affect the separation of three binary liquid mixtures, isopropyl ether - acetone, methyl acetate - methanol, and isopropyl ether - methyl ethyl ketone. Because of the small size of the extractive distillation column, relative volatilities were assumed constant and the Fenske equation was used to calculate the relative volatilities and the number of minimum theoretical plates.

Dimethyl sulfoxide was found to be a good extractive distillation agent. Extractive distillation when employing a proper agent not only negated the azeotropes of the above mixtures, but also improved the efficiency of separation. This process could reverse the relative volatility of isopropyl ether and acetone. This reversion was also found in the system of methyl acetate and methanol when nitrobenzene was the agent. However, normal distillation curves were obtained for the system of isopropyl ether and methyl ethyl ketone undergoing extractive distillation.

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INTRODUCTION

Azeotropic And Extractive Distillation

Separation is an important industrial process. Fractional distillation is one of the commonest methods for separating liquid mixtures. However, it is very difficult or impossible to separate azeotropic mixtures or mixtures whose components boil very close together. The separation can be sometimes greatly facilitated by adding a third component, called herein an "agent". In these cases two methods, namely azeotropic and extractive distillation, have been developed commercially. In azeotropic distillation the agent has about the same vapor pressure as the feed components and is removed with the overhead product with which it forms a minimum azeotrope. One kind of azeotropic distillation columns is shown in Figure 1 [1]. In extractive distillation the agent has a low vapor pressure, so the agent is added near the top of the column and removed with the bottom product. The agent flows down the column, washing the ascending vapors and absorbing one of the components preferentially. There are four sections in an extractive distillation column as illustrated in Figure 2 [1].

Obviously, for azeotropic or extractive distillation to be economically attractive, the improvement in relative volatility, and resulting savings in column height and steam and water costs, should more than offset the added costs of recirculating the agent, recovering

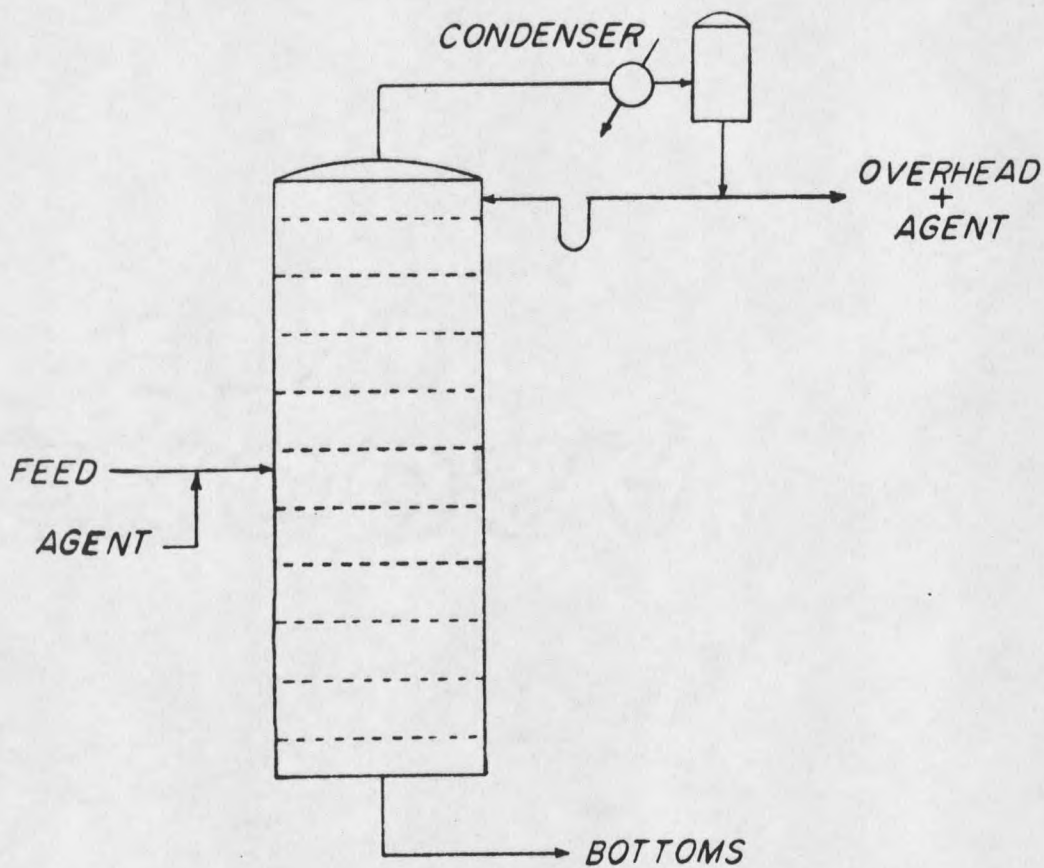


Figure 1. Azeotropic distillation column

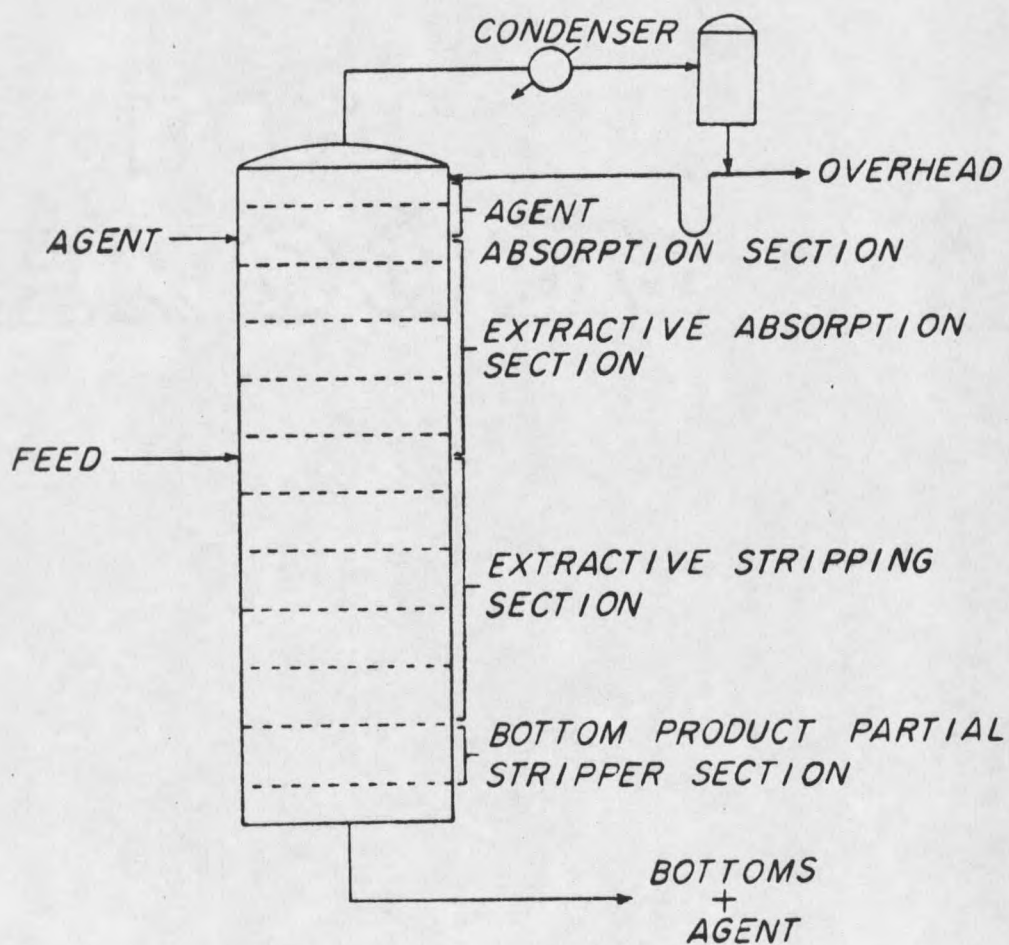


Figure 2. Extractive distillation column

it from the products, and providing makeup agent because of losses in recirculation. In extractive distillation, agent recovery from the bottom product is easily affected in a separate stripping column because of the agent's low vapor pressure. In azeotropic distillation an agent immiscible with the overhead product can be separated by decantation, and with a hydrocarbon overhead product a water-soluble agent can be used and then recovered by washing the overhead with water. The principal difference between the processes of azeotropic and extractive distillation is that the agent is almost entirely recovered in the distillate in azeotropic distillation, and in extractive distillation the agent is recovered in the residue or bottoms. Also, the optimum point of addition of the agent to the column is different for the two types of processes. Gerster [2] illustrated the difference between these two methods by the various special-agent distillations required at Celanese's Bishop, Texas plant. If the feed is a close-boiling hydrocarbon pair, the difference in the nature of the feed components are usually comparatively small, so that the agent is required to improve the relative volatility over the entire height of the column. This is achieved best in extractive distillation where the agent enters at, or near, the top and is discharged at the bottom of the column. Azeotropic distillation is particularly useful when the feed component selected to come overhead as an azeotrope with the agent is present in the feed in small amount. In such an instance the amount of agent needed to be circulated is small, resulting in only small additional steam costs because of the presence of the agent and in a low-agent recovery cost.

Treybal [3] has pointed out that extractive distillation is generally considered to be more desirable than azeotropic distillation since (i) there is a greater choice of agent because the process does not depend upon the accident of azeotrope formation and (ii) generally smaller quantities of agent must be volatilized. Due to the increase in energy costs, extractive distillation is worth considering even when the conventional approach is feasible. Sucksmith [4] has shown that 42 million Btu/h are required to separate the mixture of n-heptane and toluene by conventional distillation; 18 million Btu/h are required for the same separation by extractive distillation. If an agent provides approximately 40% greater relative volatility, Bojnowski and Hanks [5] suggested that the extractive distillation could be considered instead of conventional fractional distillation. Thus extractive distillation would be an attractive method to separate three liquid binary mixtures, isopropyl ether - acetone, methyl acetate - methanol, and isopropyl ether - methyl ethyl ketone.

Selection of Azeotropes

One of the commercially important ways to manufacture acetone is by the catalytic dehydrogenation of isopropanol. Since acetone does not form an azeotrope with isopropanol (normal b.p.=82.4°C), acetone is relatively easy to separate from the unreacted isopropanol by rectification. However, a concurrent reaction takes place in which isopropanol dehydrates to form isopropyl ether (IPE). Acetone and isopropyl ether form a minimum azeotrope [6] boiling at 54.2°C at one atmosphere. It is therefore impossible to produce pure acetone from

the acetone -isopropyl ether mixture by conventional rectification. This system is a good candidate for extractive distillation.

One way to manufacture methyl acetate (MeAc) is by the catalytic esterification of methanol with acetic acid. Methyl acetate and methanol (MeOH) form a minimum binary azeotrope [6] boiling at 53.5°C at one atmosphere. Methyl acetate also forms with water a binary azeotrope which boils at 56.1°C at one atmosphere. The binary-azeotrope contains 95 wt.% methyl acetate. Methyl acetate, methanol, and water do not form a ternary azeotrope. Thus, in the esterification of methanol with acetic acid to form methyl acetate and water, the rectification of this mixture yields the lowest boiling constituent, namely the methyl acetate - methanol azeotrope. It is therefore impossible to produce pure methyl acetate from methanol - methyl acetate mixture by conventional rectification because the lowest boiling azeotrope will always come off overhead as the initial product. This mixture also might be extractively distilled.

Two of the most commonly used solvents in the chemical industry are isopropyl ether and methyl ethyl ketone (MEK). Normally mixtures of solvents are recovered by fractionation in a multiplate rectification column, and the ease of separation depends upon the difference in boiling points of the compounds to be separated. However isopropyl ether and methyl ethyl ketone form a minimum azeotrope [7] boiling at 65°C at one atmosphere. It is therefore impossible to produce pure isopropyl ether from isopropyl ether - methyl ethyl ketone mixture by conventional rectification. This would be the third mixture to be

examined. The properties of these compounds and azeotropes at one atmosphere are as follows:

	B.P., <u>°C</u>	Azeotrope <u>Composition</u>
Isopropyl ether	68.5	
Acetone	56.5	
Methyl acetate	57.1	
Methanol	64.7	
Methyl ethyl ketone	79.6	
Isopropyl ether-Acetone Azeotrope	54.2	39 wt.% IPE
Methyl acetate-Methanol Azeotrope	53.5	81 wt.% MeAc
Isopropyl ether-Methyl ethyl ketone Azeo.	65.0	88 wt.% IPE

Research Objectives

The first objective of this research was to find the agents which (i) would break the azeotropes listed and (ii) were easy to recover from the bottom product. The agent could be a pure compound or a mixture of compounds. A desirable agent must meet many requirements, such as low toxicity, noncorrosiveness, low viscosity, high stability, low price, etc. The second objective was to study the effects of agents on relative volatility in extractive distillation and the stability of the agents.

THEORETICAL ASPECTS

Vapor-Liquid Equilibrium

Distillation is a method of separating the components of a solution. It depends upon the distribution of the substances between a gas and a liquid phase applied to cases where all components are present in both phases at the pressure and temperature of the system. Instead of introducing a new substance into the mixture in order to provide the second phase, as is done in gas absorption or desorption, the new phase is created from the original solution by vaporization or condensation. This process is concerned with the separation of solutions where all the components are appreciably volatile. When the two (or more) phases are in a state of physical equilibrium, the maximum relative difference in concentration of the materials in the phases occurs. Therefore, attainment of equilibrium condition is desirable in the distillation process. The application of distillation methods depends greatly upon an understanding of the equilibria existing between the vapor and liquid phases of the mixtures encountered.

Vapor-liquid equilibrium data, except in the special situations of ideal and regular solutions, must be determined experimentally. Phase diagrams are used to describe two-component systems by plotting two of the three independent variables, composition, temperature, and pressure, at a constant value of the remaining one. In Figure 3 [8], the a, e, i diagrams are typical of regular or normal systems. The b,

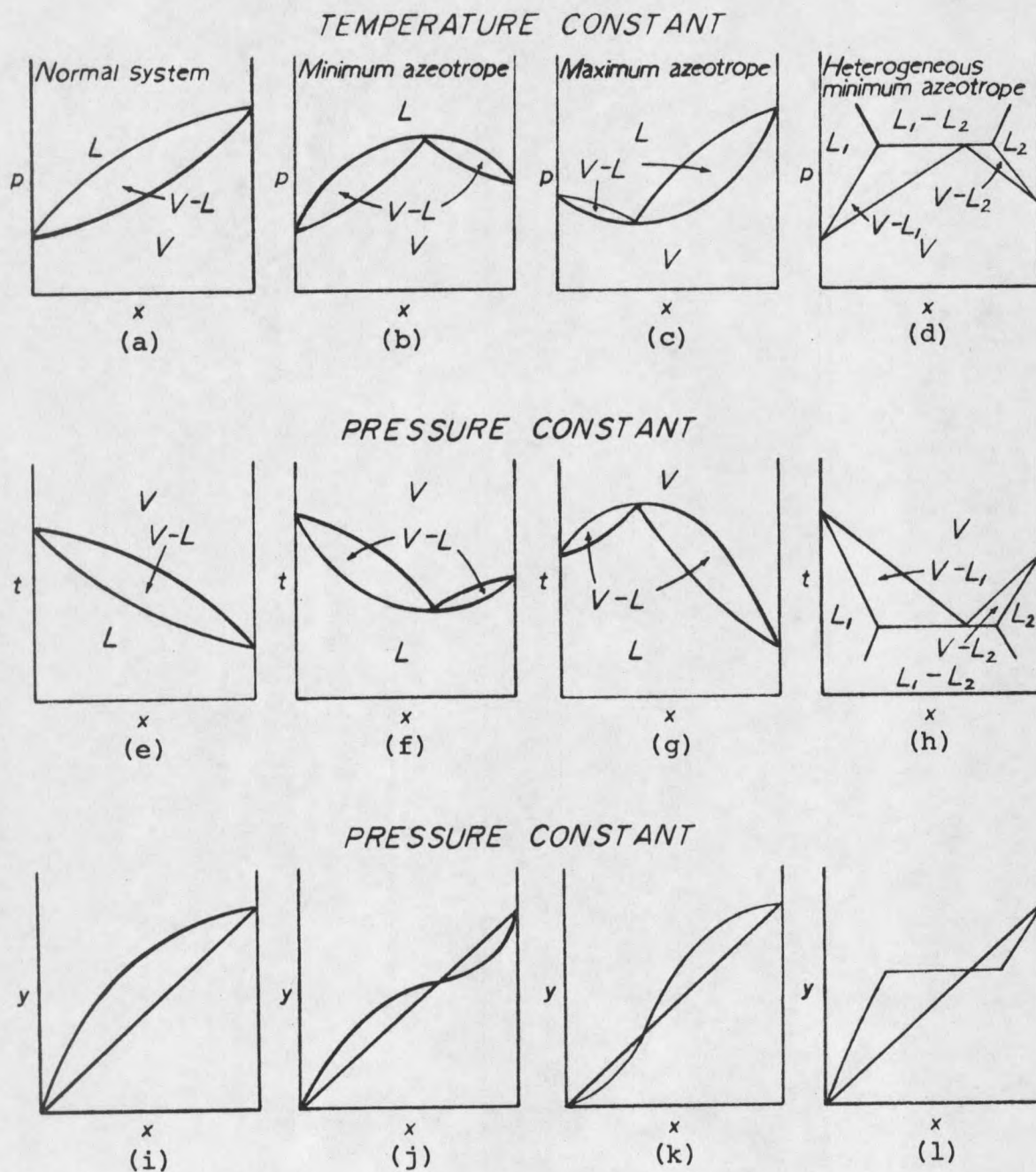


Figure 3. Phase diagrams for various types of binary systems

f, j diagrams are typical of minimum-boiling homogeneous azeotropes, the c, g, k diagrams of maximum-boiling homogeneous azeotropes, and the d, h, l diagrams of minimum-boiling heterogeneous azeotropes. In the first three systems only one liquid phase exists; whereas in the fourth, two liquid phases can exist at and below the azeotrope temperature.

For an ideal solution, the equilibrium pressure p_i^* of a constituent at a fixed temperature equals the product of its vapor pressure p_i when pure at this temperature times its mole fraction, x_i , in the liquid phase. This is Raoult's law

$$p_i^* = p_i * x_i \quad (1)$$

In a nonideal solution, the extent of deviation from nonideality of components in liquid mixtures is measured by the activity coefficient, γ . Applying this correction factor to Raoult's law results in

$$p_i^* = \gamma_i * x_i * p_i \quad (2)$$

Here we say that the standard state fugacity, f_i^0 , can be approximated by the pure-component vapor pressure, p_i , at low-to-moderate pressures and temperatures. At equilibrium, the fugacities of any component i in the vapor and liquid phases must be equal. This can be expressed as:

$$\phi_i * y_i * P = \gamma_i * x_i * p_i \quad (3)$$

where ϕ_i is the fugacity coefficient of component i ,

P is the total pressure of the system, and

y_i is the mole fraction of i in vapor phase.

The greater the distance between equilibrium curves and diagonals of Figure 3 i, j, k, l, the difference in vapor and liquid compositions

is greater and the easier the separation by distillation. One numerical measure of this is called the separation factor, or, particularly in the case of distillation, the relative volatility, α . This is the ratio of the concentration ratio of i and j in one phase to that in the other phase and is a measure of the separability.

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} = \frac{y_i p_i \phi_j}{y_j p_j \phi_i} \quad (4)$$

The value of α will ordinarily change as x varies from 0 to 1.0. If $y_i = x_i$ (except at $x = 0$ or 1.0), $\alpha = 1.0$ and no separation is possible by conventional rectification. The larger the value of α above unity, the greater the degree of separability.

The Fenske Equation

In an ideal case the ratio of vapor pressures of the key components is very close to a constant, i.e., the relative volatility is constant. If this case can be assumed without introducing excessive error in a distillation process, the number of theoretical plates required at total reflux may be calculated by the Fenske equation [9]

$$N_{av} = \left(\frac{y_i}{y_j} \right)_0 \left(\frac{x_j}{x_i} \right)_B \quad (5)$$

where N are the minimum theoretical plates at total reflux and subscripts 0 and B denote the overhead and bottom products.

α_{av} may be evaluated as the arithmetic average between the overhead and bottom temperatures.

$$\alpha_{av} = (\alpha_{t0} + \alpha_{tB})/2$$

where α_{t0} is the relative volatility at the overhead temperature and

α_{tB} is the relative volatility at the bottom temperature.

However, α_{av} may also be evaluated as the geometric average of the values of the overhead and bottom products [3].

The weight percent can be expressed in terms of molecular weight and mole fraction as follows: for the vapor phase,

$$W_{yi} = \frac{W_{i0}}{W_{T0}} = \frac{m_i y_i}{m_i y_i + m_j y_j} \quad (6)$$

where W_{i0} is the weight of component i in vapor phase,

W_{T0} is the total weight in vapor phase, and

m_i is the molecular weight of component i ;

for the liquid phase,

$$W_{xi} = \frac{W_{iB}}{W_{TB}} = \frac{m_i x_i}{m_i x_i + m_j x_j} \quad (7)$$

where W_{iB} is the weight of component i in liquid phase and

W_{TB} is the total weight in liquid phase.

Substituting Eq. (6) and (7) into Eq. (5) yields

$$\alpha_{av}^N = \left(\frac{W_{yi}}{W_{yj}}\right)_0 \left(\frac{W_{xj}}{W_{xi}}\right)_B \quad (8)$$

Eq. (8) was used to do the calibration of the rectification column and also to calculate the relative volatilities in this investigation. Thus everything was done on a consistently comparable basis.

Effect of Adding An Agent

Examination of Eq. (4) indicates that the relative volatility may be changed by three ways:

1. Alter the ratio of pure-component vapor pressures. This ratio increases slightly as temperature is reduced, but not usually enough to enhance separation to a significant degree.
2. Alter the ratio of vapor-phase fugacity coefficients. These are measures of the nonideality of the vapor-phase mixture. At moderate pressures, these coefficients are usually close to one and do not provide a practical means of changing relative volatility.
3. Alter the ratio of liquid-phase activity coefficients. Many liquid mixtures are highly nonideal, and therefore these coefficients can be much greater than one. The ratio of the two coefficients can be changed substantially by adding an agent that is chemically more similar to one component than to the other. This approach is the basis of extractive distillation.

Scheibel [10] has pointed out three main ideas on selecting a proper agent: (i) the agent must not form an azeotrope with any components in the mixture to be separated, (ii) it must be less volatile than any components, (iii) the agent must have a different effect on the partial pressure of each of the components in mixture. Berg [11] suggested that the boiling point difference between the compounds being separated and the agent should be twenty degrees Celsius or more.

