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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A thesis submitted in partial fulfillment
of the requirement for the degree

of

Master of Science

in

Chemical Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

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July 8, 1983
Date

Lloyd Berg
Chairperson, Graduate Committee

Approved for the Major Department

July 8, 1983
Date

John T. Sears
Head, Major Department

Approved for the College of Graduate Studies

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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.

# 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 minimun 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

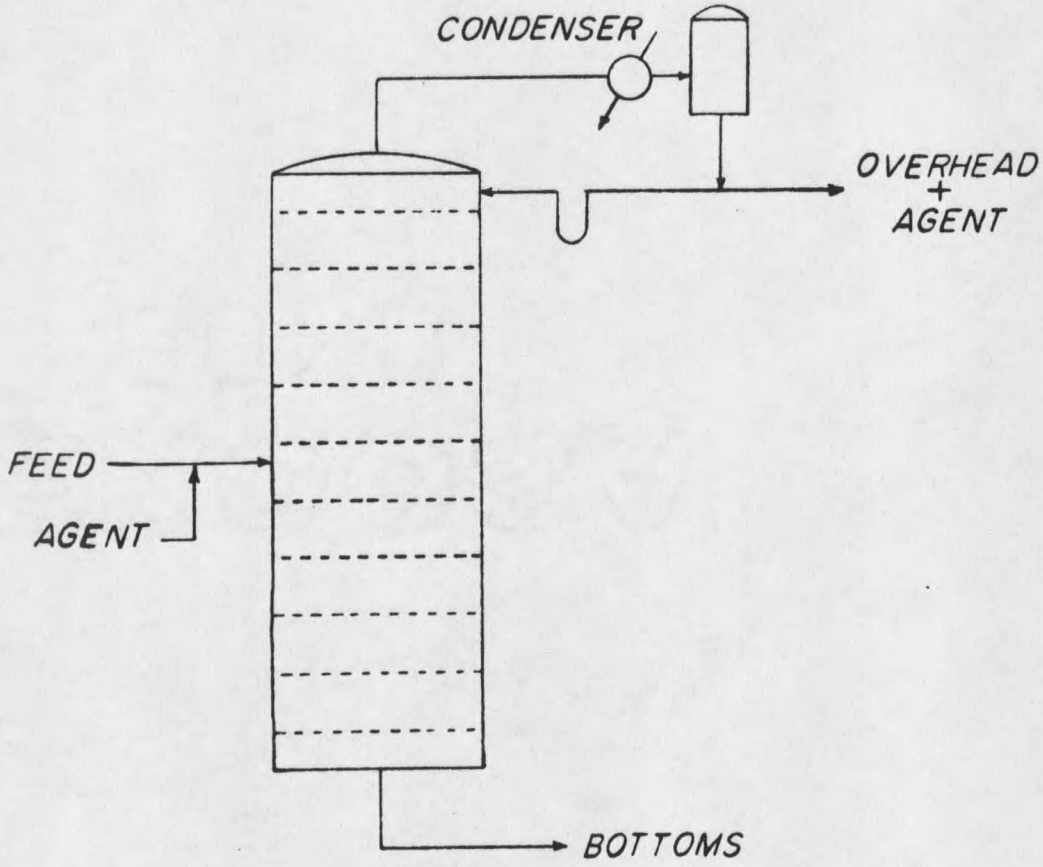



Figure 1. Azeotropic distillation column

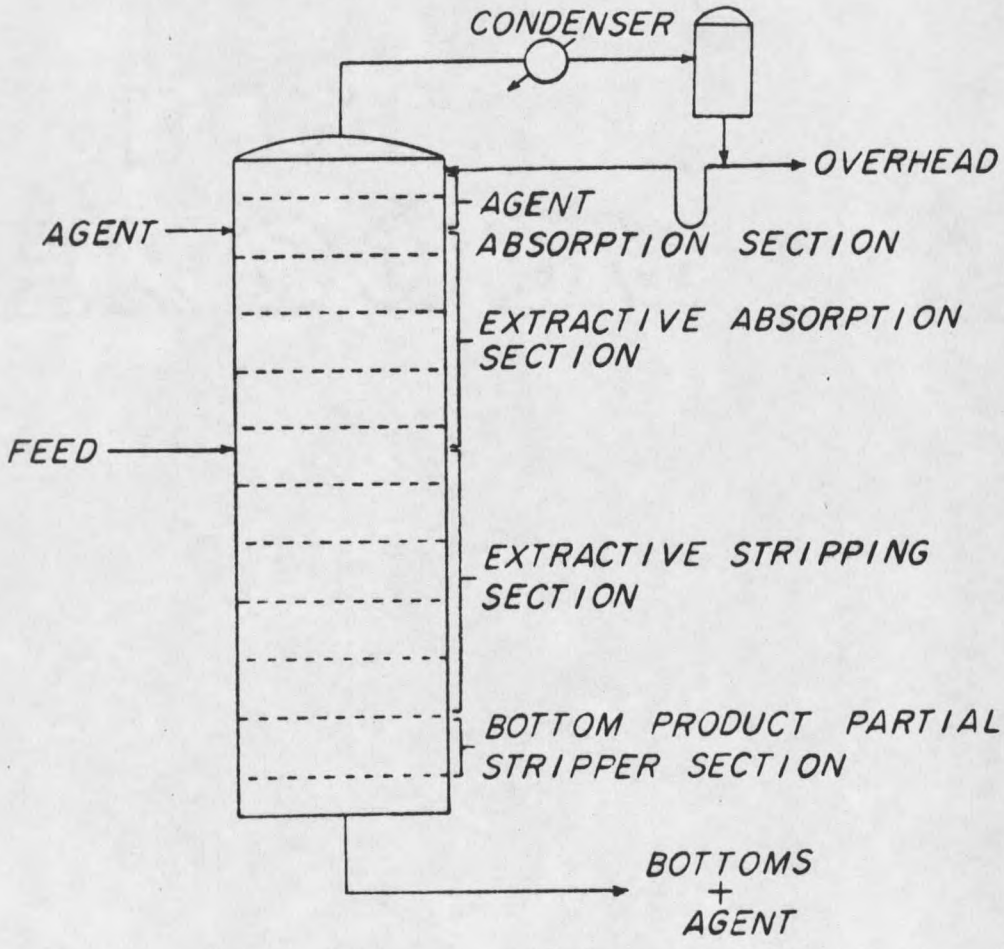



Figure 2. Extractive distillation column

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 (noraml 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 constitutent, 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 minimun 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., °C | Azeotrope Composition |
|---|---|---|
| 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,

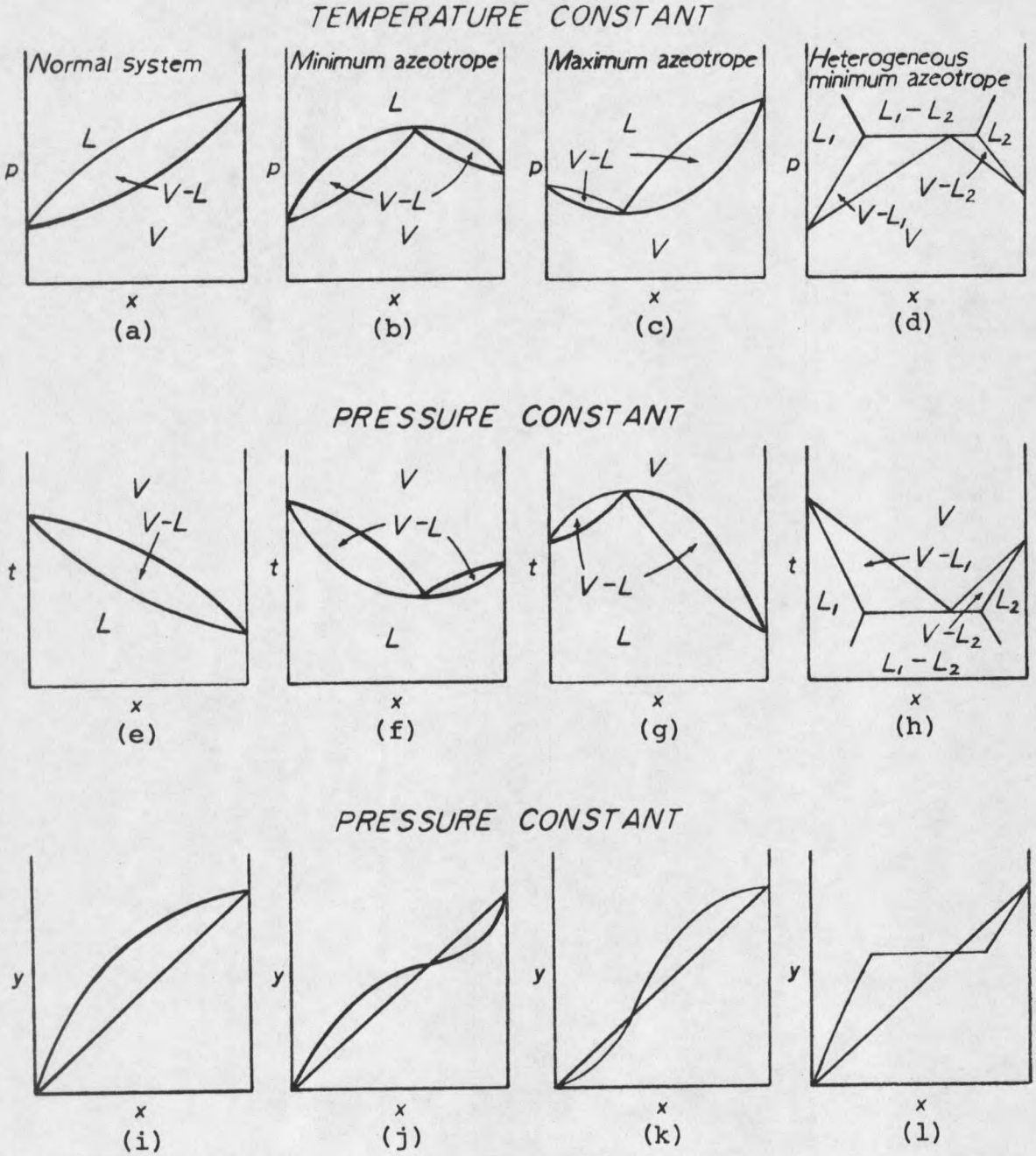



**Figure 3. Phase diagrams for various types of binary systems**

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 constitutent 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

$$p_i^* = p_i * x_i \tag{1}$$

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

$$p_i^* = \gamma_i * x_i * p_i \tag{2}$$

Here we say that the standard state fugacity, $f_i^o$, 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:

$$\phi_i * y_i * P = \gamma_i * x_i * p_i \tag{3}$$

where $\phi_i$ 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, $\alpha$. 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.

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} = \frac{\gamma_i p_i \phi_j}{\gamma_j p_j \phi_i} \tag{4}$$

The value of $\alpha$ 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 $\alpha$ 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]

$$\alpha_{av}^{N} = \left(\frac{y_i}{y_j}\right)_0 \left(\frac{x_j}{x_i}\right)_B \tag{5}$$

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

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

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

where $\alpha_{t0}$ is the relative volatility at the overhead temperature and

$\alpha_{tB}$ is the relative volatility at the bottom temperature.

However, $\alpha_{av}$ 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,

$$W_{yi} = \frac{W_{io}}{W_{TO}} = \frac{m_i y_i}{m_i y_i + m_j y_j} \tag{6}$$

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

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

$m_i$ is the molecular weight of component i;

for the liquid phase,

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

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

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

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.

Besides the relative volatility, selectivity can be used to indicate the effect of an agent on separation. Quantitatively, selectivity is defined as the ratio of the relative volatility of the key components in the mixture which are to be separated in the presence of the separating agent to their relative volatility before the addition of the agent. One expression used to define selectivity [8] is

$$S_{ij} = \frac{[\alpha_{ij}]_P}{[\alpha_{ij}]_A} = \frac{[(y_i/x_i)/(y_j/x_j)]_P}{[(y_i/x_i)/(y_j/x_j)]_A} = \frac{[\gamma_i p_i \phi_j / \gamma_j p_j \phi_i]_P}{[\gamma_i p_i \phi_j / \gamma_j p_j \phi_i]_A} \quad (9)$$

where the subscript P indicates the presence of agent and the subscript A indicates the absence of agent.

To obtain the selectivity on a strictly comparable basis, it should be evaluated for the same relative liquid composition of the key components; and, if the temperature is widely different, the activity coefficients and vapor pressures of the components should be corrected to the same basis. If the agent used in extractive distillation is added at the bubble point of the agent-free mixture, and if the temperature is far below the boiling point of the agent (i.e., its vapor pressure is low), the correction is small and negligible.

Selectivity or the ability of a compound to affect the behavior of other compounds in solution to the extent that their relative volatilities are changed is the result of molecular interaction. The work of Hildebrand [12], van Arkel [13], London [14], and others has resulted in the recognition of two broad forms of molecular interaction, namely physical and chemical force.

The physical forces causing molecular interactions in which energy effects are thermodynamically positive in sign (endothermic) are classified by Hildebrand [12] as:

1. Dispersion forces which tend to cause a perturbation in the electronic motion of one molecule as the result of its being within the field of influence of another. This is considered a nonpolar effect.
2. Induction forces which are exerted by one molecule on another, the first having a permanent dipole moment which makes it capable of inducing a polarization or induced dipole in the other. This is an attractive force.
3. Orientation forces which are exerted by the action of one permanent dipole on another permanent dipole causing molecules to orient with respect to one another.

It has been shown [12, 13, 14] that molecules which are nonpolar in makeup or electroneutral - such as the saturated hydrocarbons -when forming a nonideal solution with other nonpolar molecules evidence only endothermic energy effects or positive heats of mixing, since only dispersion forces are involved. Where nonideal mixtures of nonpolar and polar molecules are formed, both dispersion and induction forces are involved with the mixture formation accompanied by an endothermic heat of mixing. When polar-polar mixtures are formed, all three physical effects of dispersion, induction, and orientation are evidenced to contribute to a positive endothermic heat of mixing.

The chemical forces are usually attributed to hydrogen bonding or complexing of the molecules in a solution. These forces cause

molecular interactions in which the energy effects are thermodynamically negative in sign or exothermic. Ewell et al. [15] concluded that hydrogen can coordinate between two molecules of $O_2$, $N_2$ and/or F, and can coordinate between $O_2$, $N_2$, F and C if a number of negative atoms are attached to the carbon atom. They suggested the following classification of hydrogen bonds as "strong" or "weak", and classified all liquid materials into five classes.

| Strong | Weak |
|---|---|
| O-HO | N-HN |
| N-HO | HCCl |
| | O HCl -CCl |
| O-HN | N HCNO |
| | HCCN |

Prausnitz et al. [16, 17] qualitatively considered evidence of physical and chemical interaction of compounds when mixed as liquids, and they discussed three criteria - heat of mixing, volume change on mixing, and change in ultraviolet spectra of the compounds alone and in solution.

## Factors Affecting Selectivity

The variables affecting selectivity of one compound for another are numerous, and the quantitative extent, and in some instances even the qualitative extent, and direction of the effects are little understood. Experimental study of the effects of some of the variables has given some insight to the problem for some systems, but in the study

of some systems the experimental results are not readily explained by accepted theory.

Temperature

Temperature is believed to affect selectivity in that an increase in temperature tends to increase mutual solubility of compounds in a liquid mixture and thus decrease the selectivity of one component for another. This may be referred to as a physical effect as contrasted to a chemical effect. In addition to the physical effect of solubility, the chemical effect of complexing is generally considered to be affected by temperature. Prausnitz [16] and others observe that the complex stability decreased with an increase in temperature and, therefore, the selectivity attributed to complexing was decreased by an increase in temperature. This is consistent with the generalization that exothermic reactions are favored by lower temperature level.

Pressure

In general, the specific effect of pressure on activity coefficients is negligible, and therefore pressure can be said to have no effect on selectivity at low-to-moderate range.

Volume Fraction of Agent

The quantity of agent relative to the quantity of original mixture (as volume fraction, mole fraction, or weight fraction) can exert a strong effect on the selectivity. It is possible for the dilution effect of further additions of agent to break complexes formed in the

more concentrated solutions, to reduce the absolute values of $(y_i/x_i)/(y_j/x_j)$ to insignificance, and to reduce the solubility of the less soluble component to the point of immiscibility.

Relative Size of Molecule

Prausnitz [17] pointed out that the logarithm of the activity coefficient for individual paraffin hydrocarbons mixed with a polar agent increased approximately linearly with the number of carbon atoms in the paraffin molecule where there is no hydrogen bonding or chemical effect. In addition, the larger molecule will have the greater activity coefficient of that of two differently sized paraffin molecules in the same agent.

Chemical Effect of Hydrogen Bonding

The hydrogen-bonding theory accounts for molecular association between like and also unlike molecules, usually designated as the chemical effect in nonideal behavior of liquids. H-bond energies vary from 2 to 8 Kcal/mole compared to regular bond strength of 87 Kcal for C-H bonds and 84 Kcal for N-H bonds. This accounts for easy breaking of H bonds.

Predicting the effect of an agent on the components in a mixture needs to know the activity coefficients of key components in liquid phase. Some theoretical or empirical methods were applied by using the van Laar, Margules, or other equations. Unfortunately, the theory of nonideal liquid mixtures is not sufficiently well developed to allow a sound prediction to be made on the performance of a

proposed extractive agent. Thus the choice of the agents in this investigation was based on the experimental data.

# APPARATUS

## Equipment for Extractive Distillation

In order to carry out the necessary operations for batch extractive distillation, an apparatus was designed incorporating a condenser, a vapor-liquid extractive distillation contacting section, a heat source for introducing vapor to the bottom of the contacting section, and a means of feeding the agent to the top of the extractive distillation section. The general assembly of the equipment is shown in Figure 4. It consisted of eight parts as described below.

(1). A Corad condensing head, A, condensed the vapor to the liquid phase. The vapor was condensed on the inside surface of the inner tube. The inside surface of the inner tube was divided by means of vertical strips into six different sized parallel parts. The condensate from any one part could be taken off as product while the remainder was returned as reflux to the column. A sidearm sampling port was suspended from the Corad condensing head.

(2). A contacting section which was 20 inch long and 1.5 inch in diameter, B, contained five Oldershaw perforated plates. It was made of Pyrex glass. The arrangement of the glass-perforated plate is shown in Figure 5. The tray spacing was 1.8 inch and the weir was 3/8 inch high. Figure 6 illustrates the direction of liquid flow on the plate. The column was equipped with a

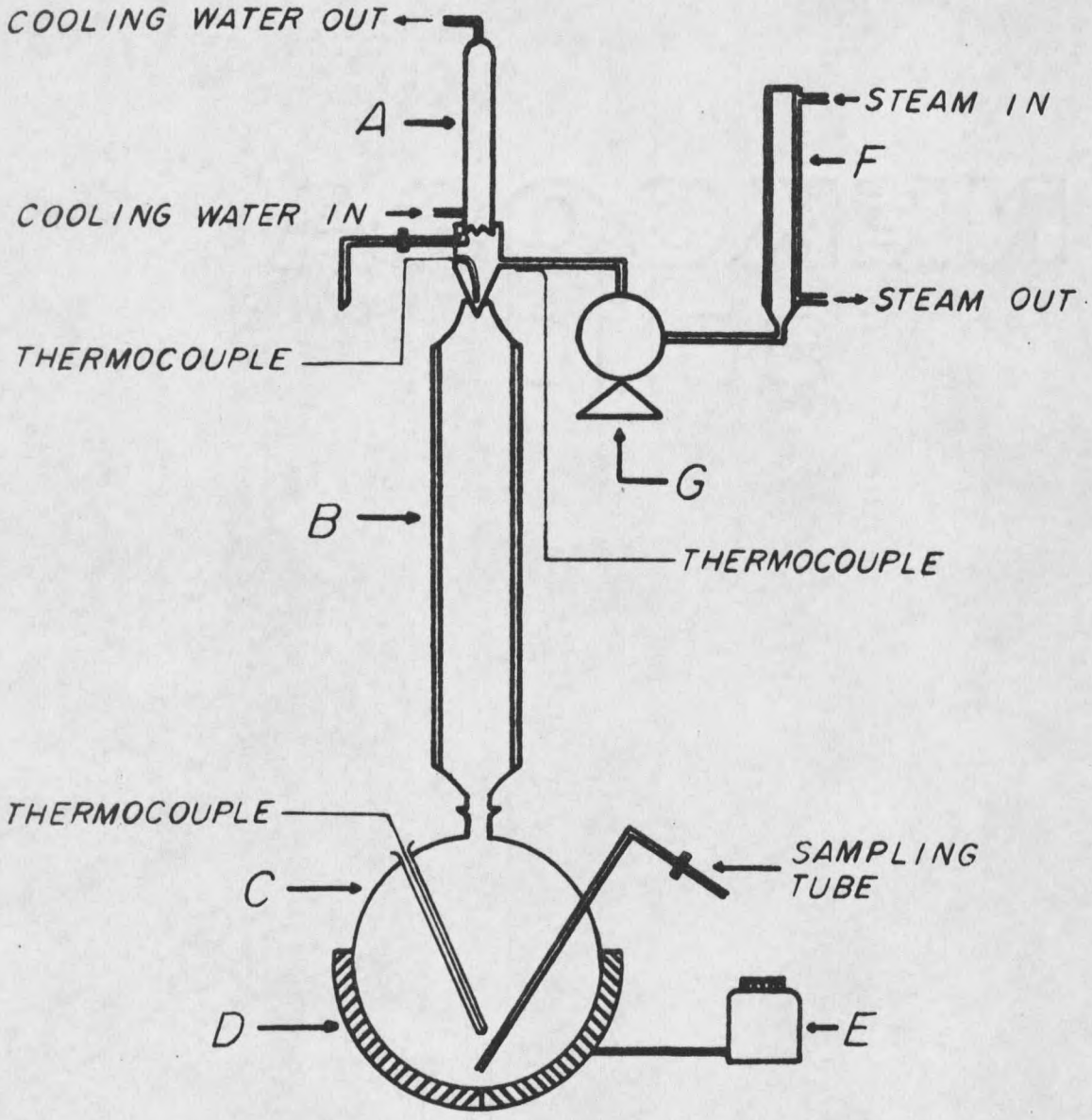



Figure 4. Diagram of the experimental appratus

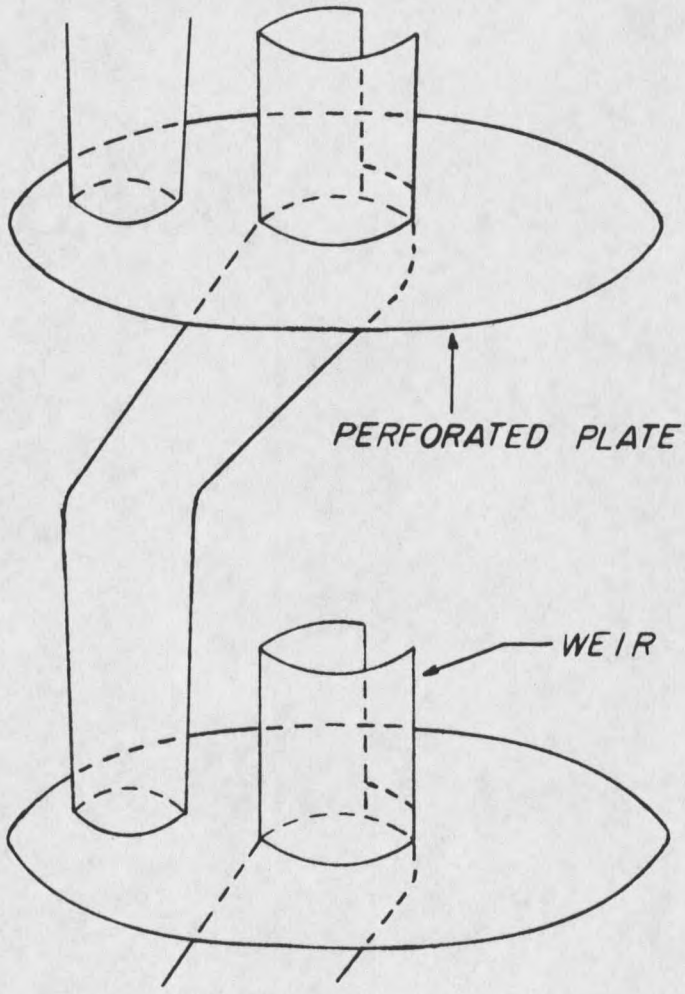



Figure 5. Perforated plate arrangement

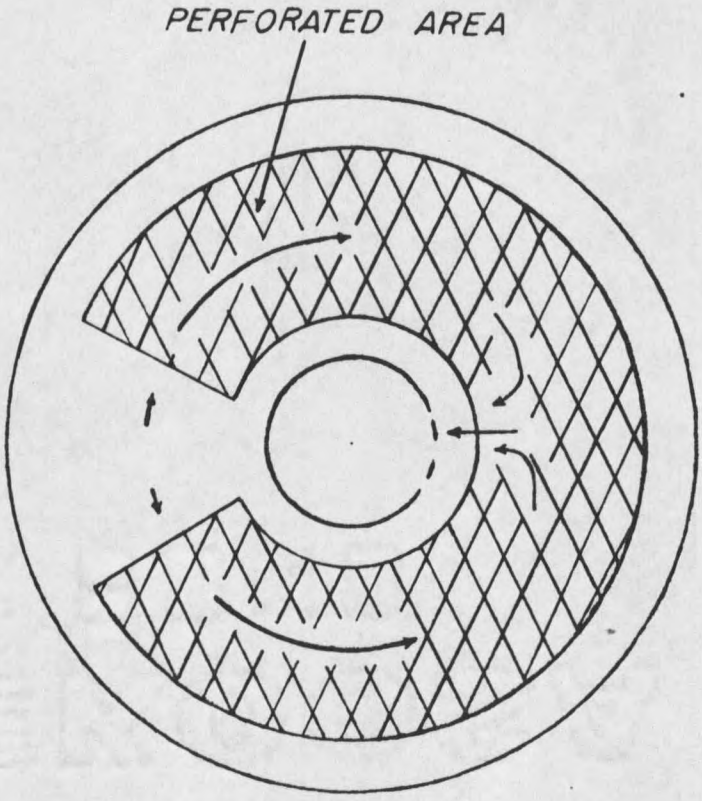



Figure 6. Perforated plate schematic. Arrows show direction of liquid flow.

silvered vacuum jacket in a thickness of 1.3 in. The silvered vacuum jacket effectively reduced heat loss from the column to a negligibly small value.

(3). A 5-liter round-bottom flask served as a reboiler or stillpot, C. It was fitted with a thermocouple well and sampling tube.

(4). Column heat was supplied electrically by means of a Glas-Col mantle, D, which was further lagged to reduce the heat loss from the stillpot.

(5). A transformer, E, adjusted the heat input into the stillpot and controlled the boil-up rate.

(6). Agent was stored in a cylinder, F, steam-jacketed separatory funnel. It was made of Pyrex glass and had a capacity of 200 ml. The steam jacket was used to control the temperature of the agent entering the column.

(7). A fluid metering pump, G, adjusted the addition rate of agent. The pump was a micro-bellows metering pump made by Research Appliance Company. It was a standard model, 0.5 inch I.D., 316-stainless bellows.

(8). Three K-type thermocouples were used to measure the temperatures at the overhead, stillpot and agent entrance to the column.

Auxiliaries not shown on the drawing included a nichrome heating wire wrapped on the pump line, a Glas-Col mantle connected to the heating wire, a digital thermometer, OMEGA 2176A, connected to the K-type thermocouples, and two ball-and-socket joints. The first two were used to control the temperature of the agent entering the column. The thermometer was used to record the temperatures at the overhead,

stillpot, and pump line. A 65/40 female ball-and-socket joint and 65/40 male ball-and-socket joint connected the column with the Corad condensing head and stillpot, respectively.

## Analytical Equipment

A gas chromatograph was used to analyze the samples. The actual apparatus included an Aerograph 1800 ionization gas chromatograph hooked to a Sargent recorder, Model SR. The column in the chromatograph was 15 feet long and 1/8 inch in outside diameter. The column packing was made up as follows: 0.5 g. each of Bentone 34 (an organo clay complex, National Lead Bariod Division) and dissodecyl phthalate were deposited on 9.0 g. of chromosorb P using the conventional vaporization and slurry techniques. The operating conditions used were: column temperature, 75°C; injection port temperature, 200°C; detector temperature, 140°C; helium flow rate, 20-30 ml. per minute; hydrogen flow rate, 20-30 ml. per minute; air flow rate, 250-400 ml. per minute.

## Equipment for Agent Recovery

The agents were reclaimed by simple distillation. Figure 7 illustrates the assembly of the apparatus. A 2-liter distilling flask served as a stillpot. A mercury thermometer was used to indicate the temperature of vapor in the stillpot.

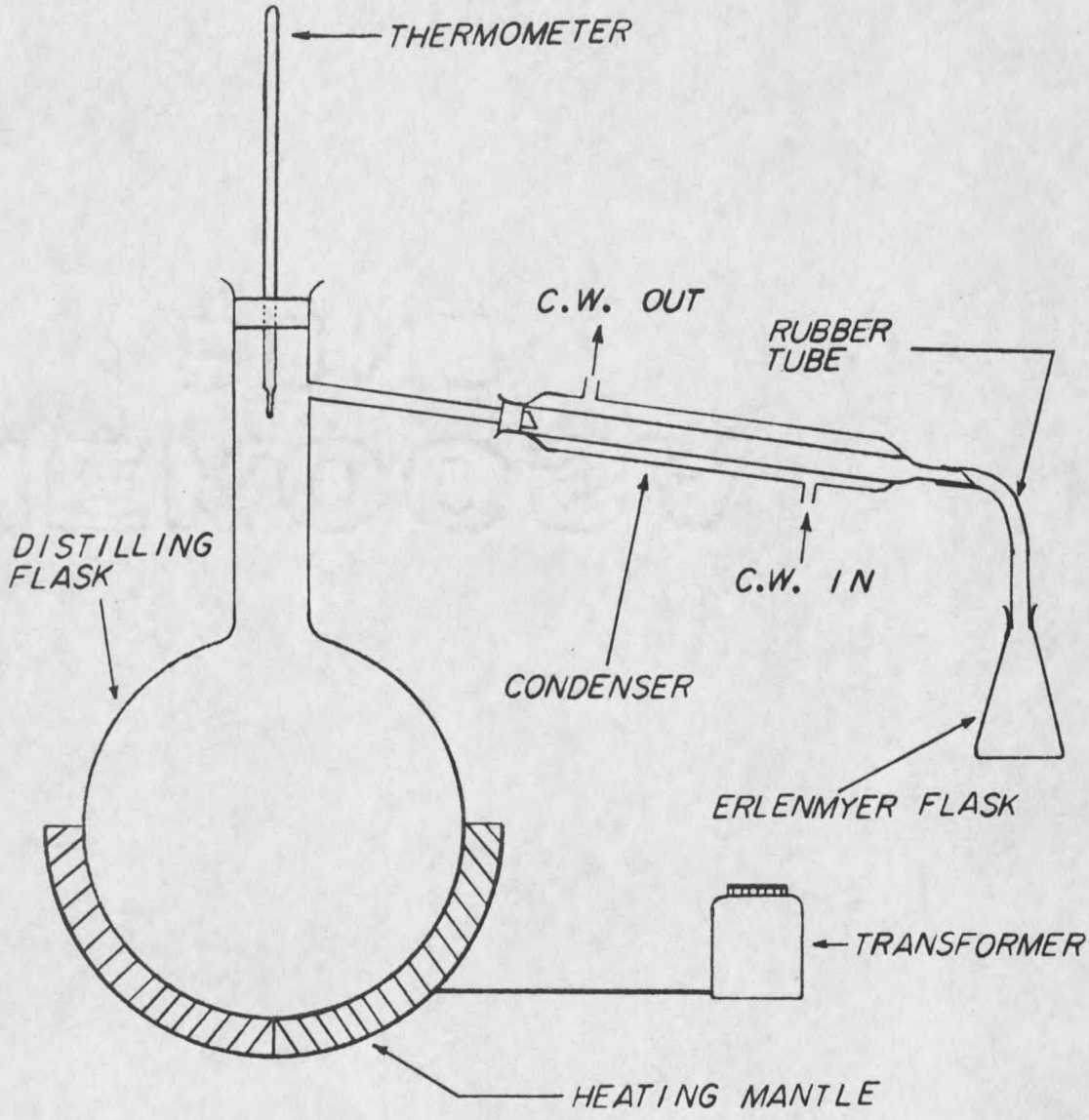



Figure 7. Diagram of the simple distillation system

# OPERATIONAL PROCEDURES

The operational procedures can best be explained in four sections.

## Gas Chromatograph Calibration

A series of known composition mixtures were made up and analyzed on the gas chromatograph. The peak height percents of the chromatographs tracing of the components in the mixtures were correlated to the actual weight percents of the components in the mixtures. These calibrations are shown in Figures 8, 9, and 10. From these figures, we could obtain the weight percents of the components in the samples.

## Calibration of Glass-Perforated Distillation Column

The glass-perforated plate rectification column was calibrated with a ethylbenzene and p-xylene mixture which possesses a relative volatility of 1.06. The column was found to have 4.5 theoretical plates [18].

## Studies on the Different Agents

Four methods were used to investigate the effects of the agents on the separation of three azeotropes by extractive distillation. The agents were added at 52±2°C, 48±2°C, and 58±2°C for the systems isopropyl ether - acetone, methyl acetate - methanol, and isopropyl ether - methyl ethyl ketone, respectively. If the agent was a mixture

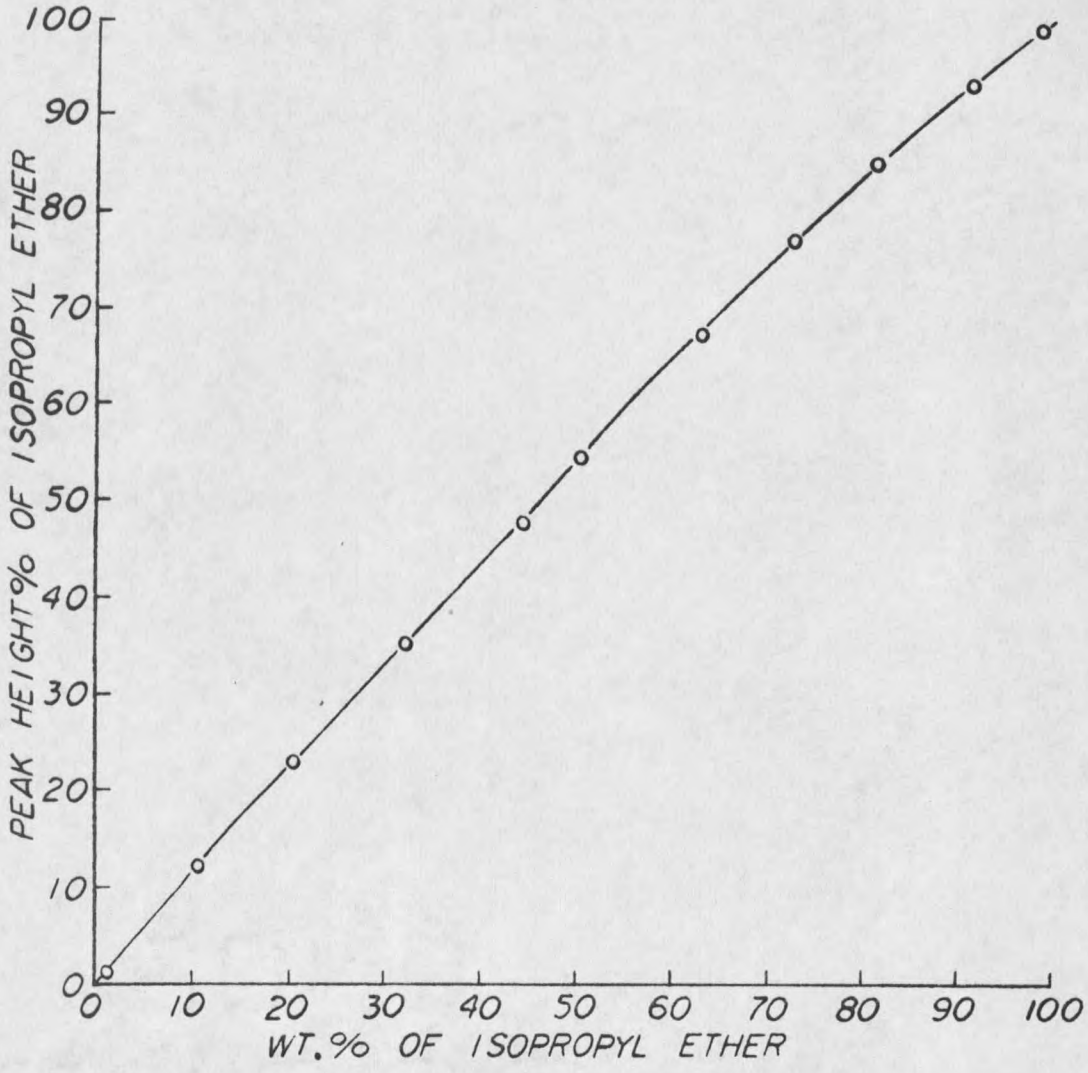



Figure 8. Calibration curve for the mixture Isopropyl ether - Acetone

Notes: Column packing was chromosorb P and column temperature was 75°C.

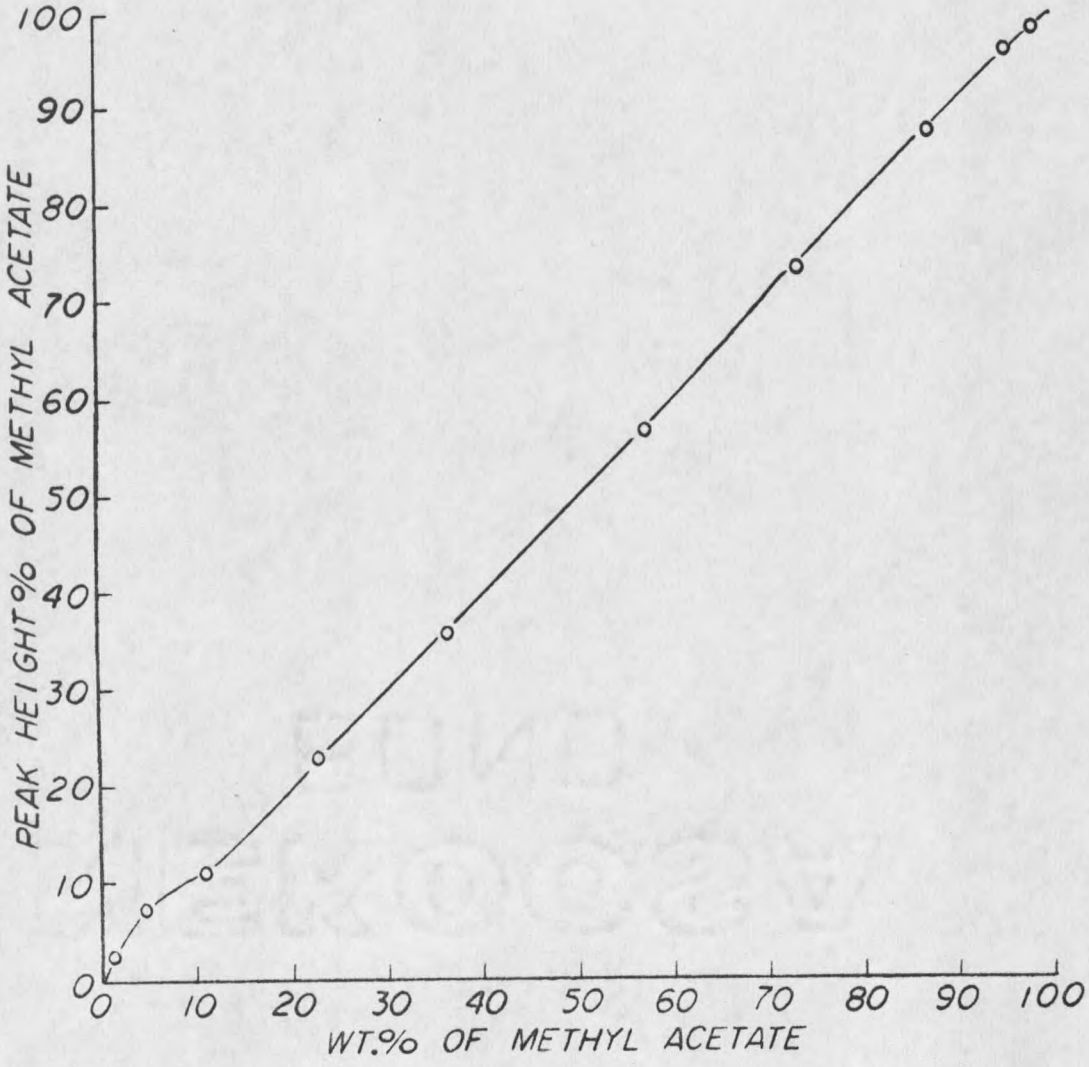



Figure 9. Calibration curve for the mixture Methyl acetate - Methanol

Notes: Column packing was chromosorb P and column temperature was 75°C.

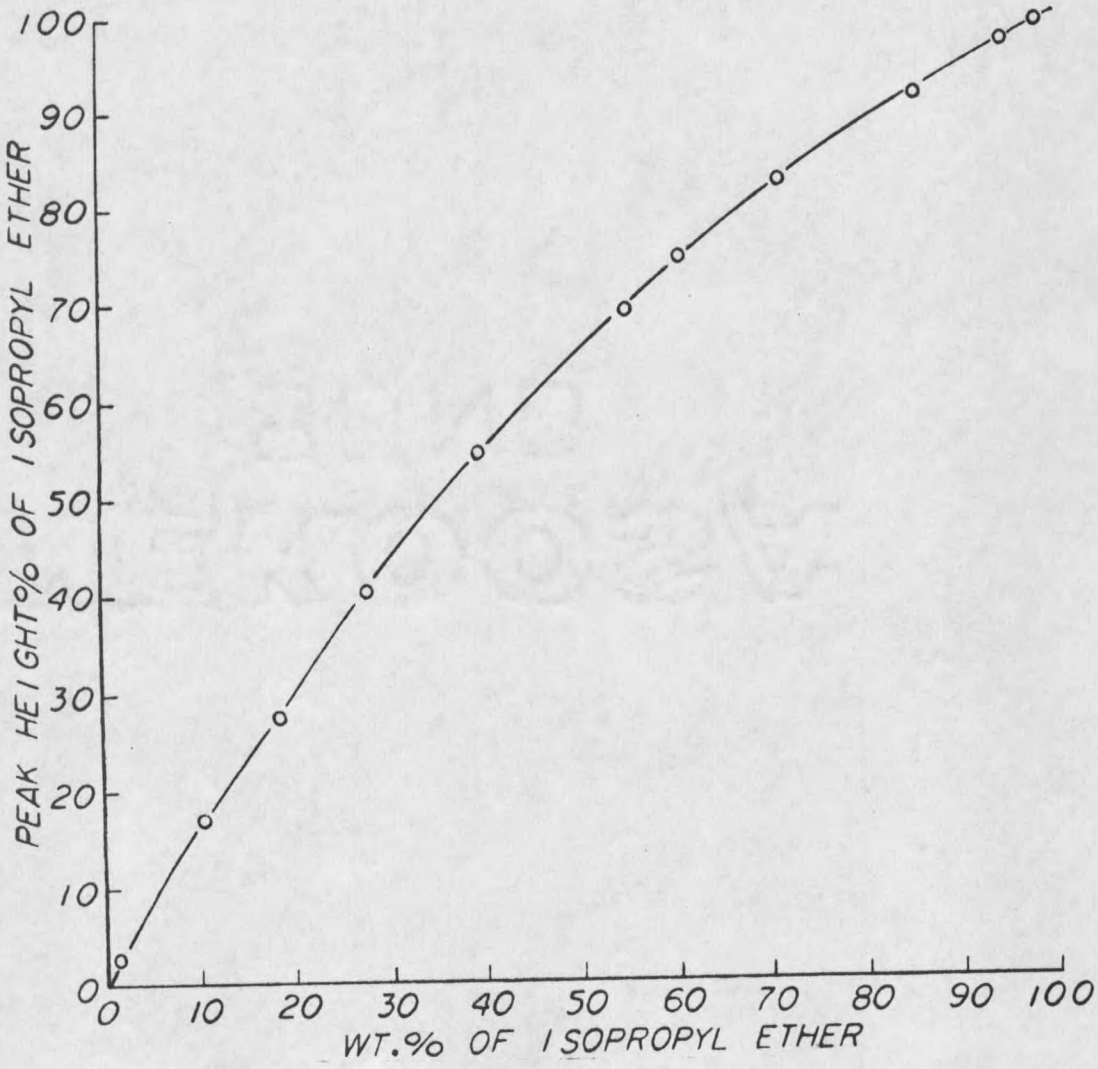



Figure 10. Calibration curve for the mixture Isopropyl ether - Methyl ethyl ketone

Notes: Column packing was chromosorb P and column temperature was 75°C.

of two or three compounds, the weight ratio of compounds was 1:1 or 1:1:1. When refluxing began, the agent was pumped into the top of the column. That was the time zero. The temperatures at the overhead, bottoms, and agents entering the column were recorded every ten minutes. The overhead temperature could be used to check the time required to reach equilibrium. Around 2 ml. samples were taken from the overhead and stillpot every half hour.

Method 1. Berg [19, 20, 21, 22] had found some effective agents for those three systems by means of a vapor-liquid equilibrium still. During the course of this research, 12 different agents, 14 different agents, and 11 different agents were investigated for the systems isopropyl ether-acetone, methyl acetate-methanol, and isopropyl ether-methyl ethyl ketone, respectively. In the systems of isopropyl ether-acetone and isopropyl ether-methyl ethyl ketone, one-and-a-half hours were allowed for the column to reach equilibrium. In the system methyl acetate-methanol, two hours To determine the minimum theoretical plates required, total reflux ratio was applied. The agents were added at a rate of 20 ml/min. The boil-up rate was controlled at 10-16 ml/min. The feed compositions used are as follows:

| System | Weight of Components |
|---|---|
| IPE-Acetone | 40 g. IPE + 460 g. Acetone |
| MeAc-MeOH | 75 g. MeAc + 425 g. MeOH |
| IPE-MEK | 25 g. IPE + 475 g. MEK |

Method 2. The studies of the unusual behavior occurring in the system isopropyl ether-acetone were made in a manner of batch extractive distillation. Dimethyl sulfoxide (DMSO) was the agent. The addition rate and boil-up rate were the same as those in method 1. The reflux ratio was 2.5:1. The feed compositions are shown in Tables IV and V (page 45 and 48). Two systems, isopropyl ether-acetone and isopropyl ether - methyl ethyl ketone, were studied. In these studies, the samples were taken only from the overhead. The weight of distillate and the changes in temperatures at the overhead and bottoms were recorded.

Method 3. The possibility of azeotrope formation between agent and feed components was studied by a serial of experiments. DMSO was used as a test agent for the three systems. The addition rate, boil-up rate, feed compositions, and reflux ratio were the same as those in method 1. The experiments were carried out for three hours continuously. During the first and third hour, the agent (DMSO) was added. During the second hour, the column was operated as an ordinary fractional distillation with no agent added.

Method 4. In order to study the effect of the addition rate of the agent on relative volatility, DMSO was used again. The boil-up rate, feed compositions, and reflux ratio were the same as those in method 1. The experiments were carried out in a series. For each run after the first, DMSO was reclaimed and reused. If it was necessary, about 2 wt.%

make-up DMSO was added. There were four different runs made of 20, 10, 5, and 20 ml/min. for each of the systems methyl acetate-methanol and isopropyl ether-methyl ethyl ketone. Eight individual runs were made for the system isopropyl ether-acetone with addition rates of 20, 20, 10, 10, 30, 30, 20, and 20 ml/min.

## Agent Recovery

After every run made in section 3, the agent was recovered by distilling off everything boiling below 100°C in the simple distillation system. The operation was typically carried out in one hour for each batch.

# RESULTS

The data obtained by method 1 are listed in Tables I, II, and III. In these tables, "Blank" means that the system was operated by ordinary fractional distillation with no extractive distillation agent employed, and "(R)" indicates that the agent was reclaimed and reused. Generally the agents used effectively negated the azeotropes and permitted the separation of high purity components from the mixtures by extractive distillation. DMSO was found to be a good agent for the three systems studied. It offered a relative volatility of 5.67 for the system isopropyl ether - acetone, 7.72 for the system methyl acetate - methanol, and 9.51 for the system isopropyl ether - methyl ethyl ketone. In the system of isopropyl ether - acetone, the less volatile isopropyl ether came off overhead when the system was subjected to extractive distillation with the agents studied. We also found similar phenomenon in the system methyl acetate - methanol when nitrobenzene was the agent.

Figure 11 and Table IV show the data obtained when the isopropyl ether - acetone mixtures were subjected to batch extractive distillation with DMSO as the agent. First no agent was added. The normal distlillation curve was obtained as shown in Figure 11 (page 38). The azeotrope came off overhead until acetone was exhausted and then the temperature rose as the overhead composition changed to be isopropyl ether. When mixture No. 2, containing 30 wt.% isopropyl ether, and

Table I. Rectification data for the system Isopropyl ether - Acetone

| Agent | Overhead Temp., °C | Stillpot Temp., °C | | wt.% of IPE | | REL. VOL. | SEL. |
|---|---|---|---|---|---|---|---|
| | | Start | 1.5hrs. | Oh. | Bt. | | |
| Blank | 49 | 53 | 53 | 26.3 | 7.0 | 1.41 | - |
| DMSO | 63 | 53 | 86 | 98.7 | 3.0 | 5.67 | 4.02 |
| Adiponitrile | 62 | 53 | 85 | 98.1 | 3.1 | 5.16 | 3.66 |
| Sulfolane | 62 | 53 | 84 | 95.5 | 3.1 | 4.24 | 3.01 |
| Ethylene Glycol | 56 | 53 | 77 | 72.7 | 3.5 | 2.60 | 1.84 |
| Glycerine | 49 | 53 | 69 | 40.0 | 5.1 | 1.75 | 1.24 |
| DMSO(R) + Adiponitrile(R) | 62 | 53 | 87 | 97.2 | 3.5 | 4.60 | 3.26 |
| DMSO(R) + Sulfolane(R) | 62 | 53 | 84 | 96.0 | 3.05 | 4.37 | 3.10 |
| Sulfolane(R) + Adiponitrile(R) | 61 | 53 | 82 | 95.2 | 3.5 | 4.06 | 2.88 |
| DMSO + Glycerine | 57 | 53 | 70 | 76.3 | 3.3 | 2.75 | 1.95 |
| Sulfolane + Glycerine | 56 | 53 | 76 | 79.5 | 4.9 | 2.61 | 1.85 |
| DMSO(R) + Sulfolane(R) + Adiponitrile(R) | 61 | 53 | 83 | 94.6 | 3.9 | 3.85 | 2.73 |
| DMSO(R) + Sulfolane(R) + Glycerine(R) | 60 | 53 | 76 | 85.7 | 3.9 | 3.03 | 2.15 |

Notes: Blank means the run was operated with no agent added.
(R) indicates the agent was reclaimed and reused.

Table II. Rectification data for the system Methyl acetate - Methanol

| Agent | Overhead Temp., | Stillpot Temp., °C | | wt.% of MeAc | | REL. VOL. | SEL. |
|---|---|---|---|---|---|---|---|
| | | Start | 2hrs. | Oh. | Bt. | | |
| Blank | 48.2 | 58.0 | 58.2 | 76.9 | 10.4 | 2.11 | - |
| DMSO | 57.2 | 60.8 | 103.2 | 99.9 | 9.2 | 7.72 | 3.66 |
| Ethylene Glycol | 52.2 | 61.2 | 93.8 | 99.4 | 2.2 | 7.23 | 3.43 |
| Propylene Glycol | 53.2 | 60.4 | 90.2 | 99.3 | 6.7 | 5.40 | 2.56 |
| Diethylene Glycol | 52.8 | 60.8 | 89.6 | 99.0 | 4.9 | 5.37 | 2.55 |
| 1,4-Butanediol | 51.8 | 60.8 | 88.6 | 99.2 | 7.2 | 5.15 | 2.44 |
| Triethylene Glycol | 51.8 | 60.4 | 85.4 | 98.1 | 9.1 | 4.01 | 1.90 |
| Dipropylene Glycol | 52.6 | 60.8 | 86.6 | 95.7 | 11.9 | 3.11 | 1.47 |
| Ethylene Glycol(R) + DMSO(R) | 53.2 | 61.6 | 91.0 | 99.7 | 6.3 | 6.62 | 3.14 |
| Ethylene Glycol(R) + Propylene Glycol(R) | 52.4 | 62.8 | 91.8 | 99.0 | 8.0 | 4.78 | 2.27 |
| Propylene Glycol(R) + Glycerine(R) | 51.6 | 62.8 | 86.2 | 98.5 | 7.1 | 4.49 | 2.13 |
| Ethylene Glycol(R) + 1,4-Butanediol(R) | 51.8 | 62.0 | 89.9 | 97.3 | 6.0 | 4.09 | 1.94 |
| Ethylene Glycol(R) + DMSO(R) + Glycerine(R) | 52.2 | 61.6 | 91.6 | 99.5 | 5.0 | 6.24 | 2.96 |
| Diethylene Glycol(R) + DMSO(R) + Glycerine(R) | 51.8 | 62.6 | 87.8 | 99.2 | 8.1 | 5.01 | 2.37 |
| Nitrobenzene* | 60.6 | 56.0 | 90.2 | 23.5 | 89.0 | 0.48 | 0.23 |
| Nitrobenzene(R)* | 60.0 | 53.2 | 89.6 | 22.8 | 87.7 | 0.49 | 0.23 |

* : The feed composition was 85 wt.% MeAc and 15 wt.% MeOH.
Blank : The run was operated with no agent added.
(R) : The agent was reclaimed and reused.

Table III. Rectification data for the system Isopropyl ether - Methyl ethyl ketone

| Agent | Overhead Temp., °C | Stillpot Temp., °C | | wt.% of IPE | | REL. VOL. | SEL. |
|---|---|---|---|---|---|---|---|
| | | Start | 1.5hrs. | Oh. | Bt. | | |
| Blank | 63 | 78 | 76 | 66.0 | 2.8 | 2.55 | - |
| Adiponitrile | 64 | 78 | 115 | 99.8 | 1.5 | 10.08 | 3.95 |
| DMSO | 63.6 | 78.2 | 115.8 | 99.7 | 1.3 | 9.51 | 3.73 |
| Sulfolane | 64 | 78 | 112 | 97.1 | 1.7 | 5.38 | 2.11 |
| Ethylene Glycol | 61.6 | 78.6 | 93.8 | 91.9 | 1.3 | 4.49 | 1.76 |
| DMSO + Adiponitrile | 63.2 | 75.8 | 115.8 | 99.7 | 1.3 | 9.51 | 3.73 |
| DMSO(R) + Adiponitrile(R) | 62.6 | 75.6 | 109.2 | 99.6 | 1.0 | 9.46 | 3.71 |
| DMSO + Sulfolane | 63.0 | 76.8 | 116.2 | 99.0 | 1.7 | 6.84 | 2.68 |
| Sulfolane(R) + Adiponitrile | 62.2 | 77.6 | 112.6 | 98.5 | 1.2 | 6.75 | 2.65 |
| DMSO(R) + Sulfolane(R) + Adiponitrile(R) | 62.8 | 77.8 | 112.0 | 98.8 | 1.1 | 7.24 | 2.84 |
| DMSO(R) + Sulfolane(R) + Ethylene Glycol(R) | 62.0 | 77.4 | 103.8 | 97.0 | 1.2 | 5.77 | 2.26 |
| DMSO(R) + Glycerine + Adiponitrile(R) | 61.6 | 78.8 | 104.0 | 94.4 | 1.1 | 5.09 | 2.00 |

Notes: Blank means the run was operated with no agent added.
(R) indicates the agent was reclaimed and reused.

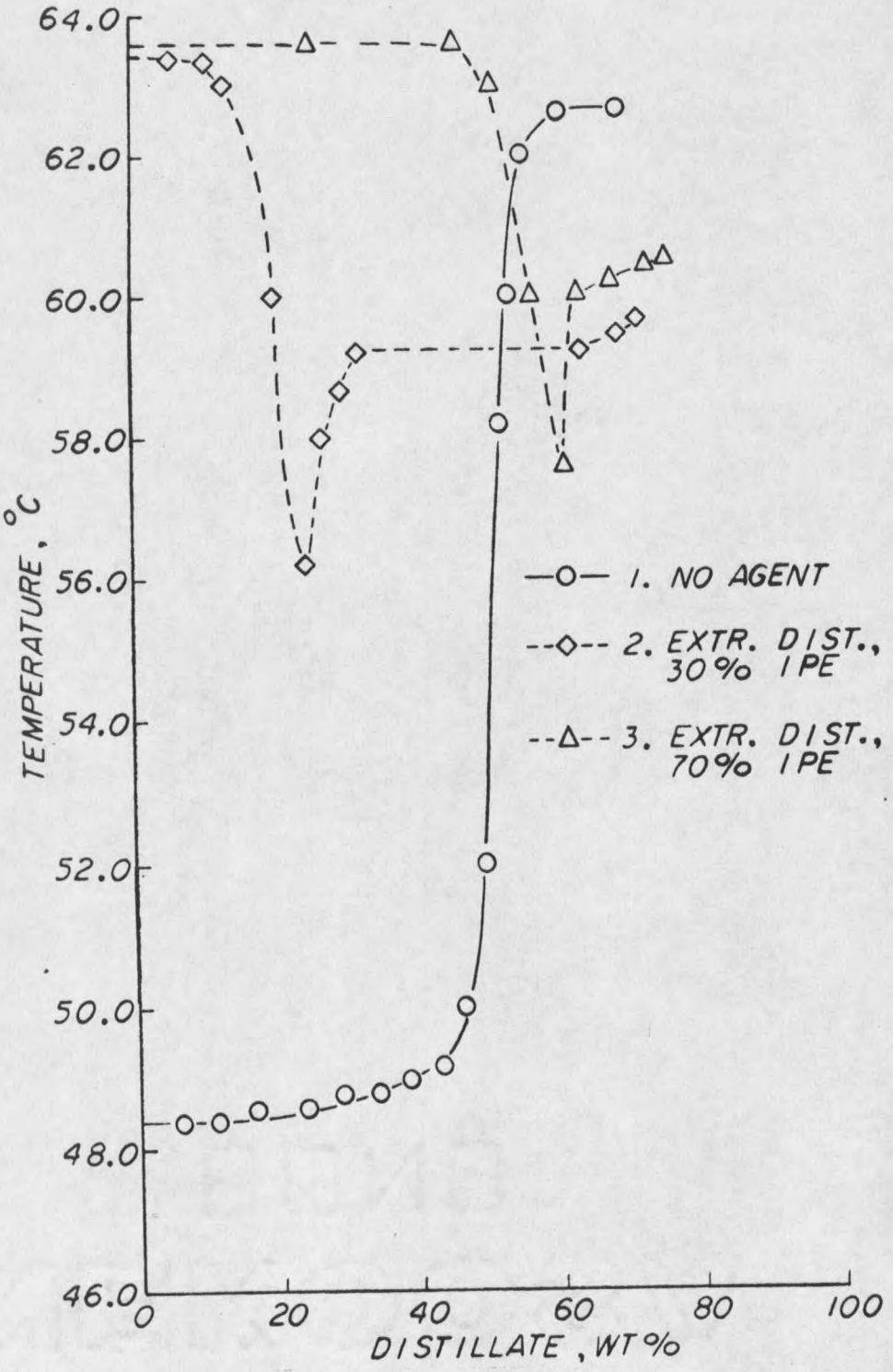



Figure 11. Distillate wt.% vs. temperature for Isopropyl ether - Acetone system

Table IV. Compositions and temperatures vs. time for the system Isopropyl ether - Acetone

| Time, min. | Temperature, °C | | Composition (wt.%) In Overhead | |
|---|---|---|---|---|
| | Overhead | Stillpot | Isopropyl ether | Acetone |
| Mixture 1.: IPE (225g.) + Acetone (90g.); Agent: None | | | | |
| 40 | 48.4 | 51.8 | 45.4 | 54.6 |
| 190 | 52.0 | 63.2 | 65.9 | 34.1 |
| 205 | 58.2 | 64.6 | 76.1 | 23.9 |
| 210 | 60.0 | 64.8 | 88.8 | 11.2 |
| 220 | 62.2 | 65.2 | 97.4 | 2.6 |
| 240 | 62.6 | 65.4 | 98.9 | 1.1 |
| 305 | 63.0 | 70.8 | 100.0 | 0.0 |
| Mixture 2.: IPE (30g.) + Acetone (70g.); Agent: DMSO | | | | |
| 13 | 63.4 | 115.2 | 99.7 | 0.3 |
| 24 | 63.0 | 128.2 | 98.9 | 1.1 |
| 37 | 60.0 | 140.2 | 91.8 | 8.2 |
| 43 | 56.2 | 145.6 | 21.5 | 78.5 |
| 47 | 58.6 | 151.2 | 3.9 | 96.1 |
| 50 | 59.2 | 157.4 | 0.8 | 99.2 |
| 95 | 59.4 | 184.4 | 0.0 | 100.0 |
| Mixture 3.: IPE (70g.) + Acetone (30g.); Agent: DMSO | | | | |
| 35 | 63.6 | 141.6 | 99.4 | 0.6 |
| 65 | 63.0 | 169.8 | 97.1 | 2.9 |
| 70 | 60.0 | 172.6 | 89.9 | 10.1 |
| 77 | 57.6 | 176.0 | 27.5 | 72.5 |
| 83 | 60.0 | 179.2 | 3.7 | 96.3 |
| 95 | 60.2 | 182.4 | 0.1 | 99.9 |
| 100 | 60.4 | 185.4 | 0.0 | 100.0 |

mixture No. 3, containing 70 wt.% isopropyl ether, were subjected to batch extractive distillation with DMSO as the agent, the unusal distillation curves shown in Figure 11 were obtained. The less volatile isopropyl ether came off overhead first. When the isopropyl ether disappeared from the stillpot, the overhead temperature and composition dropped to those of the azeotrope and then acetone came off overhead.

The rectification data for the system isopropyl ether - methyl ethyl ketone are shown in Figure 12 and Table V. When no agent was employed as in mixture No. 4, the isopropyl ether - methyl ethyl ketone azeotrope came off overhead until isopropyl ether was exhausted and then the remaining methyl ethyl ketone came off overhead at its normal boiling point. In mixtures No. 5 and 6, the isopropyl ether - methyl ethyl ketone azeotrope appeared to be negated by the agent (DMSO) and the more volatile isopropyl ether came off overhead until it was exhausted in the stillpot. The temperature rose and methyl ethyl ketone was produced in about 100% purity.

The results from method 3 are listed in Tables VI, VII, and VIII. During the second hour the overhead temperatures and relative volatilities dropped and were very close to those of the blank runs in method 1.

The values of relative volatility obtained by using different addition rates of DMSO are listed in Tables IX, X, and XI. We found that the relative volatility increased as addition rate increased. This showed the importance of using the proper addition rate in extractive distillation.

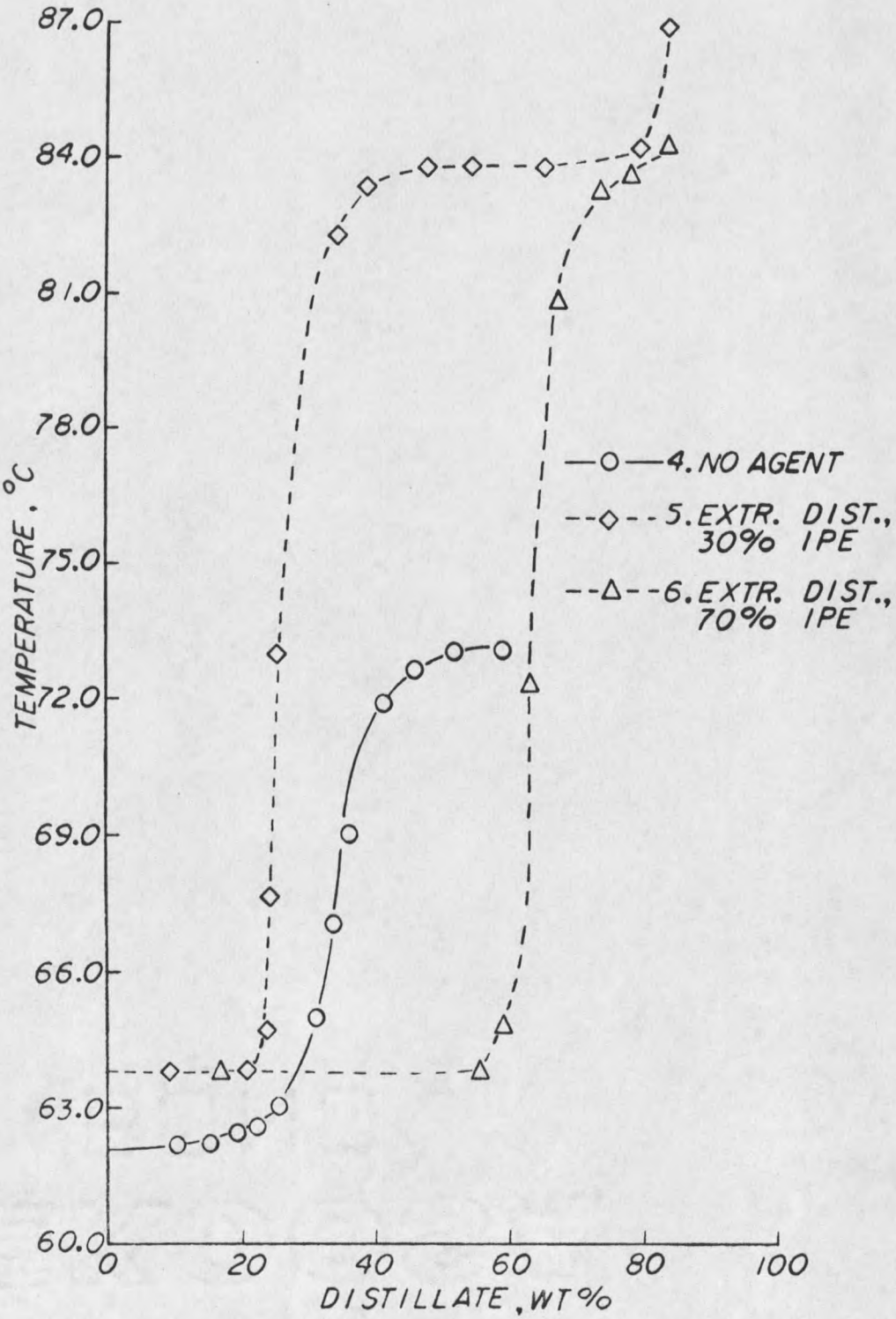



Figure 12. Distillate wt.% vs. temperature for Isopropyl ether - Methyl ethyl ketone system

Table V. Compositions and temperatures vs. time for the system Isopropyl ether - Methyl ethyl ketone

| Time, min. | Temperature, °C | | Composition (wt.%) In Overhead | |
|---|---|---|---|---|
| | Overhead | Stillpot | Isopropyl ether | MEK |
| Mixture 4.: IPE (90g.) + MEK (225g.); Agent: None | | | | |
| 30 | 62.2 | 69.0 | 71.1 | 28.9 |
| 95 | 63.0 | 71.8 | 65.0 | 35.0 |
| 127 | 67.2 | 73.2 | 41.4 | 58.6 |
| 150 | 70.8 | 73.8 | 19.1 | 80.9 |
| 175 | 72.6 | 74.4 | 5.4 | 94.6 |
| 200 | 73.2 | 74.6 | 1.9 | 98.1 |
| 225 | 73.2 | 74.6 | 0.3 | 99.7 |
| Mixture 5.: IPE (30g.) + MEK (70g.); Agent: DMSO | | | | |
| 12 | 63.8 | 144.0 | 100.0 | 0.0 |
| 27 | 64.6 | 157.6 | 88.9 | 11.1 |
| 29 | 67.6 | 158.2 | 76.0 | 24.0 |
| 32 | 73.0 | 161.0 | 44.1 | 55.9 |
| 44 | 82.2 | 166.6 | 2.0 | 98.0 |
| 58 | 83.2 | 169.6 | 0.5 | 99.5 |
| 68 | 83.8 | 174.6 | 0.0 | 100.0 |
| Mixture 6.: IPE (70g.) + MEK (30g.); Agent: DMSO | | | | |
| 55 | 63.8 | 174.2 | 100.0 | 0.0 |
| 60 | 64.8 | 176.2 | 94.9 | 5.1 |
| 62 | 72.2 | 178.2 | 55.9 | 44.1 |
| 65 | 80.8 | 180.2 | 9.3 | 90.7 |
| 70 | 83.2 | 182.8 | 1.1 | 98.9 |
| 73 | 83.6 | 183.6 | 0.7 | 99.3 |
| 78 | 84.2 | 185.0 | 0.0 | 100.0 |

Table VI. The rectification data obtained by method 3 for the system Isopropyl ether - Acetone

| Time, hrs. | Distillation Method | Overhead Temp., °C | Stillpot Temp., °C | wt.% of IPE Oh. | Bt. | REL. VOL. |
|---|---|---|---|---|---|---|
| ½ | Extractive | 61.2 | 69.6 | 96.0 | 3.9 | 4.13 |
| 1 | Extractive | 62.8 | 77.2 | 98.7 | 2.9 | 5.71 |
| 1½ | No Agent | 48.6 | 77.2 | 39.8 | 4.0 | 1.85 |
| 2 | No Agent | 48.6 | 78.4 | 35.0 | 3.8 | 1.79 |
| 2½ | Extractive | 62.2 | 90.4 | 96.0 | 1.9 | 4.87 |
| 3 | Extractive | 62.8 | 97.6 | 98.2 | 1.9 | 5.84 |

Table VII. The rectification data obtaind by method 3 for the system Methyl acetate - Methanol

| Time, hrs. | Distillation Method | Overhead Temp., °C | Stillpot Temp., °C | wt.% of MeAc Oh. | Bt. | REL. VOL. |
|---|---|---|---|---|---|---|
| ½ | Extractive | 58.4 | 80.6 | 99.0 | 8.5 | 4.71 |
| 1 | Extractive | 58.4 | 90.6 | 99.8 | 8.1 | 6.82 |
| 1½ | No Agent | 48.6 | 90.8 | 79.0 | 8.6 | 2.27 |
| 2 | No Agent | 48.6 | 91.2 | 77.5 | 8.1 | 2.26 |
| 2½ | Extractive | 57.2 | 99.8 | 99.8 | 5.1 | 7.62 |
| 3 | Extractive | 58.6 | 106.2 | 99.8 | 5.0 | 7.65 |

Table VIII. The rectification data obtained by method 3 for the system Isopropyl ether - Methyl ethyl ketone

| Time, hrs. | Distillation Method | Overhead Temp., °C | Stillpot Temp., °C | wt.% of IPE Oh. | Bt. | REL. VOL. |
|---|---|---|---|---|---|---|
| ½ | Extractive | 63.4 | 95.8 | 94.9 | 1.9 | 4.60 |
| 1 | Extractive | 63.4 | 103.8 | 99.7 | 1.1 | 9.87 |
| 1½ | No Agent | 57.8 | 104.4 | 77.2 | 1.1 | 3.56 |
| 2 | No Agent | 57.8 | 104.8 | 76.0 | 1.0 | 3.59 |
| 2½ | Extractive | 63.4 | 112.8 | 98.2 | 0.6 | 7.57 |
| 3 | Extractive | 63.4 | 118.8 | 99.3 | 0.6 | 9.36 |

Table IX. The effect of the addition rate of DMSO on the system Isopropyl ether - Acetone

| Run No. | Addition Rate ml/min. | Overhead Temp., °C | wt.% of IPE | | REL. VOL. | SEL. |
|---|---|---|---|---|---|---|
| | | | Oh. | Bt. | | |
| AR-1 | 20 | 62.8 | 98.7 | 3.0 | 5.67 | 4.02 |
| AR-2 | 20 | 62.8 | 98.8 | 3.3 | 5.65 | 4.01 |
| AR-3 | 10 | 60.8 | 90.9 | 2.0 | 3.96 | 2.81 |
| AR-4 | 10 | 60.6 | 91.1 | 1.7 | 4.13 | 2.93 |
| AR-5 | 30 | 62.6 | 99.4 | 2.9 | 6.90 | 4.89 |
| AR-6 | 30 | 62.4 | 99.3 | 2.0 | 7.14 | 5.06 |
| AR-7 | 20 | 62.4 | 98.2 | 2.4 | 5.54 | 3.93 |
| AR-8 | 20 | 62.6 | 98.3 | 2.4 | 5.61 | 3.98 |

Table X. The effect of the addition rate of DMSO on the system Methyl acetate - Methanol

| Run No. | Addition Rate ml/min. | Overhead Temp., °C | wt.% of MeAc | | REL. VOL. | SEL. |
|---|---|---|---|---|---|---|
| | | | Oh. | Bt. | | |
| BR-1 | 20 | 57.2 | 99.9 | 9.2 | 7.72 | 3.66 |
| BR-2 | 10 | 56.4 | 99.8 | 8.1 | 6.82 | 3.23 |
| BR-3 | 5 | 54.6 | 98.9 | 8.2 | 4.65 | 2.20 |
| BR-4 | 20 | 57.8 | 99.9 | 8.4 | 7.89 | 3.74 |

Table XI. The effect of the addition rate of DMSO on the system Isopropyl ether - Methyl ethyl ketone

| Run No. | Addition Rate ml/min. | Overhead Temp., °C | wt.% of IPE | | REL. VOL. | SEL. |
|---|---|---|---|---|---|---|
| | | | Oh. | Bt. | | |
| CR-1 | 20 | 63.6 | 99.7 | 1.3 | 9.51 | 3.73 |
| CR-2 | 10 | 63.0 | 98.0 | 1.1 | 6.45 | 2.53 |
| CR-3 | 5 | 62.8 | 94.9 | 1.4 | 4.93 | 1.93 |
| CR-4 | 20 | 63.2 | 99.7 | 1.3 | 9.51 | 3.73 |

# DISCUSSION

From the results obtained, we could say that the agents used negated the azeotropes and made the separation by rectification possible. For example, in the system of isopropyl ether and acetone, the weight percent of isopropyl ether in the overhead was 26.3 when no agent was added. After applying the agent (DMSO), 98.7 wt.% isopropyl ether was obtained in overhead. With DMSO a recovery of 39 wt.% isopropyl ether was possible, and the azeotrope was broken; thus allowed the collection of isopropyl ether beyond the azeotrope limit.

Tables XII, XIII, and XIV present the results obtained with the 4.5 theoretical glass-perforated rectification column. Number of plates are the theoretical plates required to produce overhead and bottom products of 99.9% purity as calculated by the Fenske equation. The run designated "Blank" in each table was operated with no agent present. Here the separation was between the minimum-boiling azeotrope as overhead and the excess constitute as bottoms - acetone, methanol, or methyl ethyl ketone. Thus it is impossbile to get 99.9% purity products by conventiaonal fractional distillation. The calculation shows a relative volatility of 1.41 for the isopropyl ether - acetone azeotrope versus acetone, 2.11 for the methyl acetate - methanol azeotrope versus methanol, and 2.55 for the isopropyl ether - methyl ethyl ketone azeotrope versus methyl ethyl ketone. The remainder of the data in these tables are for the systems obtained in the extractive

Table XII. Theoretical plates requirement for the system Isopropyl ether - Acetone

| Agent | Relative Volatility | Number of Plates |
|---|---|---|
| Blank | 1.41 | impossible |
| DMSO | 5.67 | 8.0 |
| Adiponitrile | 5.16 | 8.4 |
| Sulfolane | 4.24 | 9.6 |
| Ethylene Glycol | 2.60 | 14.5 |
| Glycerine | 1.75 | 24.7 |
| DMSO(R) + Adiponitrile(R) | 4.60 | 9.1 |
| DMSO(R) + Sulfolane(R) | 4.37 | 9.4 |
| Sulfolane(R) + Adiponitrile(R) | 4.06 | 9.9 |
| DMSO + Glycerine | 2.75 | 13.7 |
| Sulfolane + Glycerine | 2.61 | 14.4 |
| DMSO(R) + Sulfolane(R) + Adiponitrile(R) | 3.85 | 10.2 |
| DMSO(R) + Sulfolane(R) + Glycerine(R) | 3.03 | 12.5 |

Theoretical plate is defined as one where the effluent phases are in equilibrium.

Table XIII. Theoretical plates requirement for the system Methyl acetate - Methanol

| Agent | Relative Volatility | Number of Plates |
|---|---|---|
| Blank | 2.11 | impossible |
| DMSO | 7.72 | 6.8 |
| Ethylene Glycol | 7.23 | 7.0 |
| Propylene Glycol | 5.40 | 8.2 |
| Diethylene Glycol | 5.37 | 8.2 |
| 1,4-Butanediol | 5.15 | 8.4 |
| Triehtylene Glycol | 4.01 | 9.9 |
| Dipropylene Glycol | 3.11 | 12.2 |
| Ethylene Glycol(R) + DMSO(R) | 6.62 | 7.3 |
| Ethylene Glycol(R) + Propylene Glycol(R) | 4.78 | 8.8 |
| Propylene Glycol(R) + Glycerine(R) | 4.49 | 9.2 |
| Ethylene Glycol(R) + 1,4-Butanediol (R) | 4.09 | 9.8 |
| Ethylene Glycol(R) + DMSO(R) + Glycerine(R) | 6.24 | 7.5 |
| Diethylene Glycol(R) + DMSO(R) + Glycerine(R) | 5.01 | 8.6 |
| Nitrobenzene | 0.48 | 18.8 |

Theoretical plate is defined as one where the effluent phases are in equilibrium.

Table XIV. Theoretical plates requirement for the system Isopropyl ether - Methyl ethyl ketone

| Agent | Relative Volatility | Number of Plates |
|---|---|---|
| Blank | 2.55 | impossible |
| Adiponitrile | 10.08 | 6.0 |
| DMSO | 9.51 | 6.1 |
| Sulfolane | 5.38 | 8.2 |
| Ethylene Glycol | 4.49 | 9.2 |
| DMSO + Adiponitrile | 9.51 | 6.1 |
| DMSO(R) + Adiponitrile(R) | 9.46 | 6.1 |
| DMSO + Sulfolane | 6.84 | 7.2 |
| Sulfolane(R) + Adiponitrile(R) | 6.75 | 7.2 |
| DMSO(R) + Sulfolane(R) + Adiponitrile(R) | 7.24 | 7.0 |
| DMSO(R) + Sulfolane(R) + Ethylene Glycol(R) | 5.77 | 7.9 |
| DMSO(R) + Glycerine + Adiponitrile(R) | 5.09 | 8.5 |

Theoretical plate is defined as one where the effluent phases are in equilibrium.

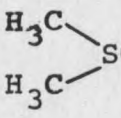
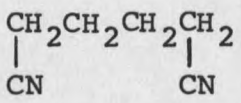
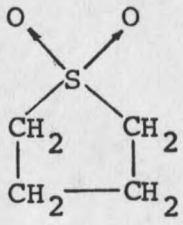
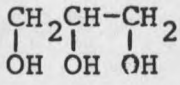
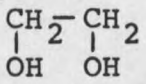
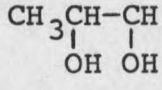
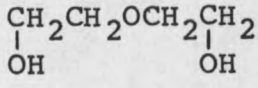
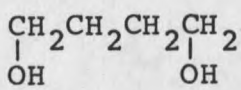
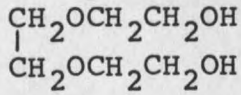
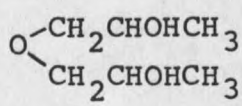
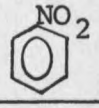
distillation mode. Relative volatilities were calculated from actual overhead and bottoms analyses using 4.5 theoretical plates. For example, when DMSO was the extractive distillation agent, it affected the separation of isopropyl ether from acetone with a relative volatility of 5.67, of methyl acetate from methanol with a relative volatility of 7.72, and of isopropyl ether from methyl ethyl ketone with a relative volatility of 9.51.

The extractive distillation agent was pumped into the top of the column through the Corad head, and thus the agent was closer to the overhead product than it would be in a commercial column. However the vapor pressures of the agents used were so low, see Table XV [24, 25, 26], that the carry over into the overhead product was negligible.

In each of the three systems in these tables, the agents' temperatures were maintained constant during the runs. Analyses were performed every half hour and the relative volatilities were calculated. When the relative volatility and overhead temperature became constant, the system was deemed to have reached equilibrium. The operational hours were kept long enough to allow the column to reach equilibrium.

Berg et al. [23] have shown that packed columns are as effective as plate column in extractive distillation. Thus these results, although obtained in a perforated plate column, could be validly applied to packed columns. Extractive distillation makes the separation of these mixtures commercially possible by rectification.

Table XV. Molecular structures and physical properties of the agents

| Compound | Molecular Structre | B.P. °C | M.P. °C | Vapor Pressure (mm Hg) |
|---|---|---|---|---|
| DMSO |  | 189 | 18.5 | 5.11 at 56.6°C |
| Adiponitrile |  | 308 | 1.0 | 10 at 154°C |
| Sulfolane |  | 285 | 27.6 | - |
| Glycerine |  | 290 | 17.9 | 1.0 at 125.5°C |
| Ethylene Glycol |  | 197.6 | -13 | 3.0 at 70°C |
| Propylene Glycol |  | 188 | - | 1.0 at 45.5°C |
| Diethylene Glycol |  | 244.8 | -6.5 | less than 0.01 at 20°C |
| 1,4-Butanediol |  | 230 | 19 | 10.0 at 120°C |
| Triethylene Glycol |  | 290 | -5 | 14.0 at 165°C |
| Dipropylene Glycol |  | 231.8 | - | 0.03 at 20°C |
| Nitrobenzene |  | 210.9 | 5.7 | 2.2 at 50°C |

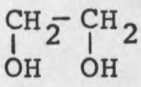
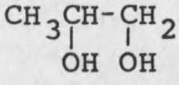
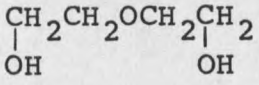
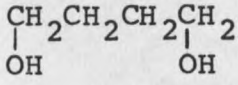
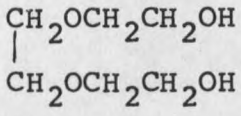
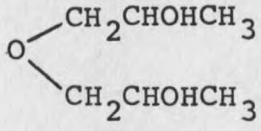
## Effect of Molecular Structure

Black et al. [27] have found that the activity coefficient of a solute increases as the carbon number of the solute increases. A similar phenomenon was found in the system methyl acetate - methanol when glycols listed in Table XVI were used as the agents. The relative volatility decreased as the carbon number of the agent increased. We need to consider other factors when agents have the same carbon number. For example, both diethylene glycol and 1,4-butanediol have four carbons. However, diethylene glycol has an oxygen in the straight chain. The oxygen could form hydrogen bond with another molecule. That could cause diethylene glycol to be more active than 1,4-butanediol. Thus diethylene glycol produced a larger relative volatility than 1,4-butanediol. The similar phenomenon was found between triethylene glycol and dipropylene glycol. We also need to consider the locations of hydroxyl groups. In triethylene glycol, the hydroxyl groups are located at both ends of the straight chain; and those of dipropylene glycol are located in the straight chain. That would be another reason to cause dipropylene glycol to be less active than triethylene glycol. Therefore the molecular structures did affect the relative volatility in extractive distillation.

## Reversion of Relative Volatility

The curves 2 and 3 in Figure 11 and the results listed in Table IV seem to show that isopropyl ether came off overhead as long as there was any isopropyl ether in the stillpot. The separation taking

Table XVI. The molecular structures and relative volatilities of the glycols used in the system Methyl acetate - Methanol

| Compound | Molecular Structure | Relative Volatility |
|---|---|---|
| Ethylene Glycol |  | 7.23 |
| Propylene Glycol |  | 5.40 |
| Diethylene Glycol |  | 5.37 |
| 1,4-Butanediol |  | 5.15 |
| Triethylene Glycol |  | 4.01 |
| Dipropylene Glycol |  | 3.11 |

place appeared to be between isopropyl ether and the azeotrope. When isopropyl ether disappeared from the stillpot, the separation became between the azeotrope and acetone and the overhead temperature and composition dropped to those of the azeotrope. However, since isopropyl ether had been exhausted in the stillpot, the azeotrope could not be replenished and was pushed out by acetone. The temperature and composition indicated that acetone then came off overhead until it was exhausted and some extractive agent began to appear in the overhead. The results obtained for the system isopropyl ether - methyl ethyl ketone were normal distillation curves. Therefore extractive distillation sometimes could reverse the relative volatility of two compounds and bring out overhead what was normally the less volatile compound, but not always. The more volatile compound remained in the column and stillpot at a temperature much above its normal boiling point. Ewell et al. [28]have shown similar distillation curves when rectificating ternary mixtures containing binary azeotropes. Buell et al. [29] have reported the reversion of the relative volatility of compounds when separating $C_4$ hydrocarbons by extractive distillation.

The molecular size of acetone is much smaller than that of isopropyl ether. In addition, there is one carbonyl group, C=O, in acetone. Due to the carbonyl group, acetone had a higher polarity than isopropyl ether. The oxygen in isopropyl ether has electronic interference by other atoms and is less active in forming hydrogen bonds than that in acetone. Thus acetone was more active than isopropyl ether. In the extractive distillation column the agent

flowed down the column, washing and absorbing the ascending vapors. Because acetone was more active, the agent would absorb acetone preferentially and bring it down the stillpot. This could explain why isopropyl ether came off overhead in the extractive distillations studied. However, we need further experiments to verify the cause.

In extractive distillation, the agents used should not form an azeotrope with any of the feed components. Tables VI, VII, and VIII present the data to demonstrate this with the three systems studied. DMSO was the extractive distillation agent employed. For the first hour with extractive agent being pumped, the overhead was essentially high-purity isopropyl ether, as shown by the boiling point of 61 - 62.8°C. For the second hour, the extractive agent was turned off and the column was operated as a conventional rectification. The temperature dropped to 48.6°C which corresponded to the isopropyl ether - acetone azeotrope. For the third hour, DMSO was again pumped in and the overhead again became high-purity isopropyl ether boiling at 62.2 - 62.8°C. Tables VII and VIII show similar pheonomena for methyl acetate - methanol and isopropyl ether - methyl ethyl ketone systems. During the second hour there was DMSO in the stillpot. If DMSO formed an azeotrope with any of the feed components, the overhead temperatures during the first and second hours would be the same or very close to each other. Therefore we could say that DMSO did not form an azeotrope with any of the feed components.

The experiments also indicated that DMSO could be separated easily from the mixture of DMSO and the feed components due to the low vapor pressure of DMSO. During the second hour, no DMSO was maintained

in the column and the relative volatilities were very low. Obviously, an appreciable amount of DMSO or agent must be maintained in the column to affect the separation by extractive distillation.

## Stability of the Agents

The stability of DMSO can be seen from Tables IX, X, and XI (page 44). In the system isopropyl ether - acetone, DMSO had been reclaimed seven times without losing its effect on separation. In the systems methyl acetate - methanol and isopropyl ether - methyl ethyl ketone, DMSO had been reclaimed three times without losing its effect on separation. Thus DMSO could be reclaimed and reused in extractive distillation. Other agents used in this study had been reclaimed and reused as shown in Tables I, II, and III (page 35, 36, and 37). They did not lose their effect on separation. Therefore we could say that the agents used could be reclaimed and reused.

## Effect of Addition Rate of DMSO

The relative volatility was found to increase as the addition rate of DMSO increased in the three systems studied. Under the conditions studied, three equations were developed to express the relative volatility in terms of addition rate using linear regression [30]. The statistical analyses are listed in Tables XVII, XVIII, and XIX. The equations fit the experimental data are as follows:

For the system of isopropyl ether and acetone, the equation was

$$\alpha = 1.41 + 0.5409V^{0.6861} \qquad (10)$$

where V is the addition rate in ml/min.

Table XVII. Statistical analysis for the system Isopropyl ether - Acetone to express relative volatility as a function of addition rate of DMSO

| Fit: | Var | R-Part | B | Se(B) | T | P-Value |
|---|---|---|---|---|---|---|
| | 4 | 0.9969 | 0.6861 | 0.2223E-01 | 30.87 | 0.000 |

Intercept = -0.6146

R-Squared = 0.9937

Analysis of Variance:

| Source | DF | S.S. | M.S. | F-Value | P-Value |
|---|---|---|---|---|---|
| Regress | 1 | 0.5877 | 0.5877 | 953.0 | 0.000 |
| Residual | 6 | 0.3700E-02 | 0.6167E-03 | | |
| Total | 7 | 0.5914 | | | |

Table XVIII. Statistical analysis for the system Methyl acetate - Methanol to express relative volatility as a function of addition rate of DMSO

| Fit: | Var | R-Part | B | Se(B) | T | P-Value |
|---|---|---|---|---|---|---|
| | 4 | 0.9609 | 0.5543 | 0.1129 | 4.908 | 0.39E-01 |

Intercept = 0.1178

R-Squared = 0.9233

Analysis of Variance:

| Source | DF | S.S. | M.S. | F-Value | P-Value |
|---|---|---|---|---|---|
| Regress | 1 | 0.4060 | 0.4060 | 24.08 | 0.39E-01 |
| Residual | 2 | 0.3371E-01 | 0.1686E-01 | | |
| Total | 3 | 0.4397 | | | |

Table XIX. Statistical analysis for the system Isopropyl ether - Methyl ethyl ketone to express relative volatility as a function of addition rate of DMSO

| Fit: | Var | R-Part | B | Se(B) | T | P-Value |
|---|---|---|---|---|---|---|
| | 4 | 0.9992 | 0.7797 | 0.2238E-01 | 34.83 | 0.000 |

Intercept = -0.4032

R-Squared = 0.9984

Analysis of Variance:

| Source | DF | S.S. | M.S. | F-Value | P-Value |
|---|---|---|---|---|---|
| Regress | 1 | 0.8031 | 0.8031 | 1213.0 | 0.000 |
| Residual | 2 | 0.1324E-02 | 0.6619E-03 | | |
| Total | 3 | 0.8045 | | | |

For the system of methyl acetate and methanol, the equation was

$$\alpha = 2.11 + 1.125V^{0.5543} \quad (11)$$

For the system of isopropyl ether and methyl ethyl ketone, the equation was:

$$\alpha = 2.55 + 0.6682V^{0.7797} \quad (12)$$

The experimental measurements and correlated curves of relative volatilities for three systems are shown in Figure 13. The correlated curves fitted the experimental data very well. Under the conditions studied, a general formula expressing relative volatility in terms of addition rate of DMSO was found to be

$$\alpha = c + aV^{b} \quad (13)$$

where a, b, and c are empirical coefficients.

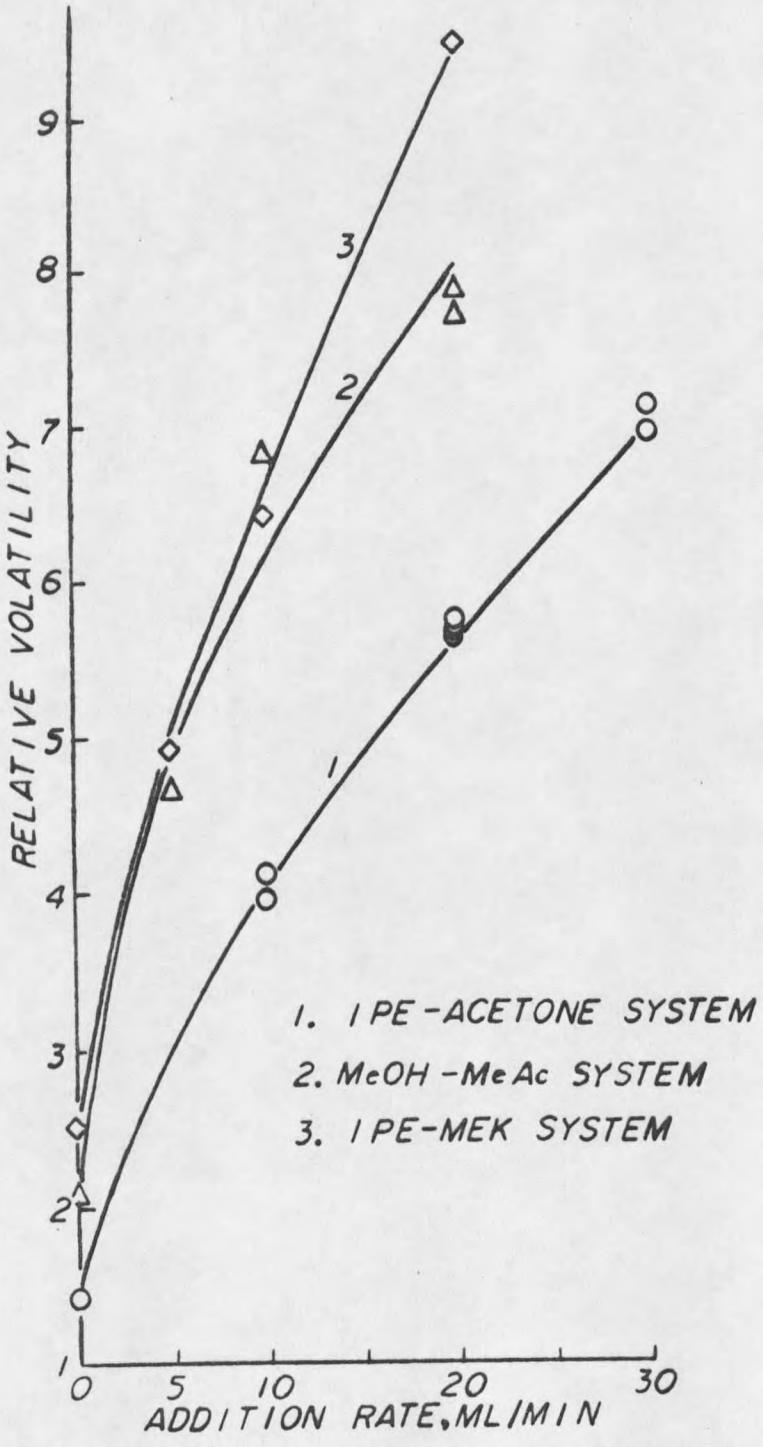



Figure 13. Relative volatility as a function of addition rate of DMSO. ○, △, and ◇ represent the experimental measurements and solid lines are calculated from equation (10), (11), and (12)

## SUMMARY AND CONCLUSIONS

1. Extractive distillation when employing a proper agent not only negated the azeotropes, but also improved the efficiency of separation.
2. The molecular structures of glycols had an effect on separation by extractive distillation.
3. Extractive distillation sometimes could reverse the relative volatility of two compounds.
4. Dimethyl sulfoxide(DMSO) was a good agent for separating three liquid binary mixtures, isopropyl ether-acetone, methyl acetate-methanol, and isopropyl ether-methyl ethyl ketone, by extractive distillation.
5. The agents used could be reclaimed and reused without losing their effect on separation.
6. An appreciable amount of agent must be maintained in the column to affect the separation by extractive distillation.
7. A general formula was found to describe the relationship between relative volatility and addition rate of DMSO for the three systems studied. It can be expressed as

$$\alpha = c + aV^b$$

# RECOMMENDATION FOR FUTURE RESEARCH

A systematic study on the compositions and temperatures on each plate is suggested. That would be a good way to study the behavior of agents in an extractive distillation column. This information can be then used for commercial design.

## ABBREVIATIONS

Azeo. : Azeotrope

B : Slope Coefficient

Bt. : Bottom

B.P. : Boiling Point

C.W. : Cooling Water

DF : Degree of Freedom

DMSO : Dimethyl Sulfoxide

EXTR. DIST. : Extractive Distillation

IPE : Isopropyl ether

MeAc : Methyl acetate

MEK : Methyl ethyl ketone

MeOH : Methanol

M.P. : Melting Point

M.S. : Mean of Squares

normal b.p. : normal boiling point

Oh. : Overhead

R-Part : Partial Correlation

REL. VOL. : Relative Volatility

Se(B) : Standard Error

SEL. : Selectivity

S.S. : Sum of Squares

T : t-tests for zero slopes

Var : Variable

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