PHASE EQUILIBRIUM DATA AND EXTRACTION KINETICS IN THE 95 PER CENT AQUEOUS PHENOL-CETANE-1-METHYLNAPHTHALENE SYSTEM

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PREFACE

As liquid-liquid extraction has become more important and the number of industrial applications of extraction has grown, the basic data for proper design of contacting equipment have become essential. With the exception of the wetted-wall column, nearly all types of liquid-liquid extraction units work by dispersing one phase as droplets in another phase. Therefore, a study of extraction from liquid drops in a second liquid phase should provide basic knowledge and understanding for proper equipment design.

Among many operating variables, the effects of temperature, of solute concentration, and of the direction of mass transfer on mass transfer rates were investigated. Also, the combined end effect and Korchinski's correlation factor for mass transfer were evaluated.

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CHAPTER I

INTRODUCTION

Phenol extraction is chiefly concerned with the manufacture of lubricating oils from fractionated crude stocks. Originally, acid treatment followed by clay refining was used for this purpose. But, the quality of lubricating oil so obtained was poor. As the mechanical industry grew rapidly, demands for higher quality lubricating oils increased. In 1928, Imperial Oil Company in Canada started a research program in an attempt to find a satisfactory solvent to replace sulfuric acid. A review of literature at that time revealed two patents dealing with the use of phenol for the refining of mineral and other oils. (8) (26). This may be referred to as the beginning of the use of phenol as a selective solvent in industry.

At the present time, phenol extraction is one of the more important processes for refining lubricating oils. A number of other extraction processes using solvents such as furfural, sulfur dioxide, and propane-cresol (Duo-Sol Process) are also in widespread use.

There are a number of criteria to be met by a satisfactory solvent. The major conditions may be summarized as follows:

1. Ability to treat a large variety of distillates to different degrees of improvement.
2. Low operating cost, including the cost of solvent due to loss in handling.
3. Stability, particularly toward heat, and very easy separation from solvent-oil mixtures.
4. Resistance to oxidation due to the small amounts of dissolved moisture or oxygen generally present in the feed stocks.
5. Ready availability.

At the same time, qualities of the product oil should meet certain standards. Stratford summarized the general results of phenol treating. (6).

1. Viscosity index. Phenol has been used successfully in the treatment of oils with viscosity indices below zero as well as for oils with viscosity indices of 100. Oils with a viscosity as low as 80 Saybolt Universal at 100° F. and as high as 200 Saybolt Universal at 210° F. have been satisfactorily treated by phenol.
2. Flash-point. Phenol-treated oils in general have the same flash-point as the stock from which they are prepared. As the viscosity is reduced more by phenol treatment than is the case with acid, the flash-point of the oil is higher for a given viscosity than can be obtained from the same stock by acid treating.

3. Conradson Carbon Residue. In general, the Conradson carbon residue of lubricating oils is reduced between 60 per cent and 95 per cent by phenol treatment. The extent of the improvement is governed by the width of initial cut as well as the viscosity of the oil.
4. Gravity and Color. The improvement in API gravity can be very great with solvent extraction. It has been frequently found that as oil will continue to improve in gravity by additional treatment with phenol even after there is no further improvement in viscosity index. Phenol is an excellent solvent for volatile coloring material in lubricating oil. While it removes a great deal of color from the residual oil, it does not appreciably improve the cast or bloom of the oil.
5. Reduction of Sligh Oxidation Number. Phenol treatment of a lubricating oil greatly improves its stability towards oxidation as measured by the Sligh test and many other oxidation tests. The Sligh number is frequently reduced over 90 per cent.
6. Sulfur Reduction. The sulfur content is reduced between 60 and 80 per cent, depending upon the stock and the treating conditions.
7. Steam Emulsification Number. By treating an oil with phenol followed by proper finishing, very

low steam emulsification numbers can be obtained.

Factors Influencing the Quality of Oil

The temperature of treating has a direct bearing on the operabiltiy of the process as well as on the quality of the lubricating oil. The treating temperatures are limited by the temperature at which miscibility occurs between the oil and phenol, and the temperature at which the phenol crystallizes from the phenol-oil mixture. In this connection, anhydrous phenol cannot be used in practice at temperatures much below 110° F. In general, an increase in temperature gives an improvement in the raffinate quality, but lowers the yield.

The proportion of phenol to oil usually varies between one volume of phenol to two volumes of oil and one volume of phenol to one volume of oil. An increase in the proportion of phenol to oil gives results similar to those obtained by increasing the temperature.

The treatment of oil with phenol can be made either by single batch, multiple batch, or continuous countercurrent extraction. The quantity of solvent necessary to produce a given improvement in the oil by countercurrent treating is approximately one-half that which is required for batch treatment. While it is true that multiple batch treatments can give results approaching those obtained by countercurrent treating, nevertheless, neither the yield nor the improvement in stability, color, etc., are as good as with countercurrent treating.

The higher the viscosity index and viscosity of the oil being treated, the higher the temperature at which treatment can be made without adversely affecting the yield.

Statement of Problem

In the design of liquid extraction process equipment, accurate data and methods for the prediction of mass transfer rates are needed. At the same time, relationships between the process operating variables and the mass transfer rates are desirable.

The purpose of this investigation was to evaluate the effect of the temperature, solute concentration and direction of mass transfer on mass transfer rates in the 95 per cent aqueous phenol-cetane-1-methylnaphthalene system.

CHAPTER II

PHASE EQUILIBRIA

Selection of a Ternary System

Since the process of refining to produce lubricating oil, in essence, is the separation of aromatic hydrocarbons of low viscosity index from straight chain hydrocarbons of higher viscosity index, the ternary system to be considered should include one aromatic hydrocarbon, one aliphatic hydrocarbon and phenol as a selective solvent. The 95 per cent aqueous phenol-cetane-1-methylnaphthalene system was chosen on the following bases:

1. Both hydrocarbons have high boiling points minimizing evaporation loss during the determination of phase equilibrium data.
2. The two components forming the raffinate and extract phases were liquid at the room temperature.
3. There was an appreciable difference between the densities of the two components forming the extract and raffinate phases facilitating the phase separation.
4. The refractive index of the two hydrocarbons was sufficiently different so that refractive

index was an acceptable means of analysis.

Anhydrous phenol possesses characteristics and limitations very similar to those of anhydrous cresol. In the case of cresol, the effects of the solvent have been modified in the Duo-Sol process by introducing liquid propane into the oil-cresol system, which influences the physical properties of the oil being treated, but does not affect the properties of the solvent. In the phenol-water process, the introduction of water into the phenol-oil system modifies the solvent treatment effects by modifying the properties of the solvent only. At the same time, the result of adding water to anhydrous phenol has the same effect as raising the temperature. For this reason, 95 per cent aqueous phenol is usually used in industry. To simulate actual plant process conditions, 95 per cent aqueous phenol was used as the selective solvent in this study.

Physical properties of the three components are tabulated in Table I. Densities and refractive indices were measured by using a pycnometer and a AO Spencer 1591 refractometer, respectively.

Phenol, analytical reagent grade, loose crystal, was used as received from the Mallinckrodt Chemical Works. 1-Methylnaphthalene, practical grade, was used as received from Eastman Organic Chemicals. Cetane for determining phase equilibrium data was obtained from the Continental Oil Company, Ponca City, Oklahoma. Cetane, practical grade, was used for mass transfer study as received from

Eastman Organic Chemicals, and once distilled city tap water was used as a diluent of the solvent.

Selection of the Method for Determining the Binodal Curve

The most frequently used methods for determining binodal curves of ternary systems are the titration method, the construction method, and the analysis method. (1). The titration, or synthetic, method was tried first, but difficulty was encountered in determining the points on the binodal curve because the color of 1-methylnaphthalene obscured the titration end points. (24) (25). The construction method was rejected because this method is based on the assumption that the physical properties involved in the construction change additively with composition of the mixture. (1). The construction method is a very quick method and can be applied satisfactorily to a system forming an ideal solution or when only a rough sketch of the binodal curve is needed. The method for predicting ternary liquid equilibria from activity coefficients of binary solutions proposed by Hildebrand (16) and applied to a number of systems by Treybal (27) was considered, but the results were found to be reliable only at low concentrations. For these reasons, the analysis method was employed. The principle of this method is to prepare heterogeneous mixtures of various compositions, agitate, and let them settle into the coexisting phases, after which these phases are separated and analyzed. The analysis reveals the composition of

TABLE I

PHYSICAL PROPERTIES OF THE THREE COMPONENTS

	95 per cent aqueous phenol	Cetane		1-Methylnaphthalene
		Continental Oil Co.	Eastman	
Boiling point, °C.*	---	286.793		244.642
Melting point, °C.*	---	18.165		-30.57
Density, d_4^{20}	---	0.77344*		1.02015*
	1.0665**	0.7682**	0.7695**	1.01525**
Refractive Index 160° F. **	---	1.4130	1.4135	1.5872
140° F. **	---	1.4176	1.4182	1.5930
20° C. *	---	1.4345	1.4350	1.6174

* Taken from (7)

** Measured

the phases and, hence, their position on the ternary diagram.

Experimental Apparatus

A 250 ml, ground glass stoppered, Erlenmeyer flask with a water jacket around it was used as an equilibrium cell. A thermometer was inserted into the water jacket so that variations in temperature could be observed. This cell was mounted on a shaker with a speed regulator.

A constant temperature water bath was adjusted to the desired temperature and a small centrifugal pump circulated water through the refractometer and the water jacket, maintaining the constant temperature desired. A 1/70 HP centrifugal pump, immersion type, 3000 rpm, Model BL 94, purchased from Redmond Company, was used. The constant temperature bath was heated by one 200 watt, immersion type, tubular heater controlled by a mercury-to-wire regulator connected to a Fisher-Serfass Electronic Relay. An auxiliary 200 watt heater was also installed and connected directly to the power source. The bath was insulated with asbestos paper so that variations in room temperature had little effect on the bath operation.

Since water evaporated from the constant temperature bath, a make-up water tank was installed. It supplied water by siphon action.

The phase equilibrium cell and auxiliary equipments are shown schematically in Figure 1.

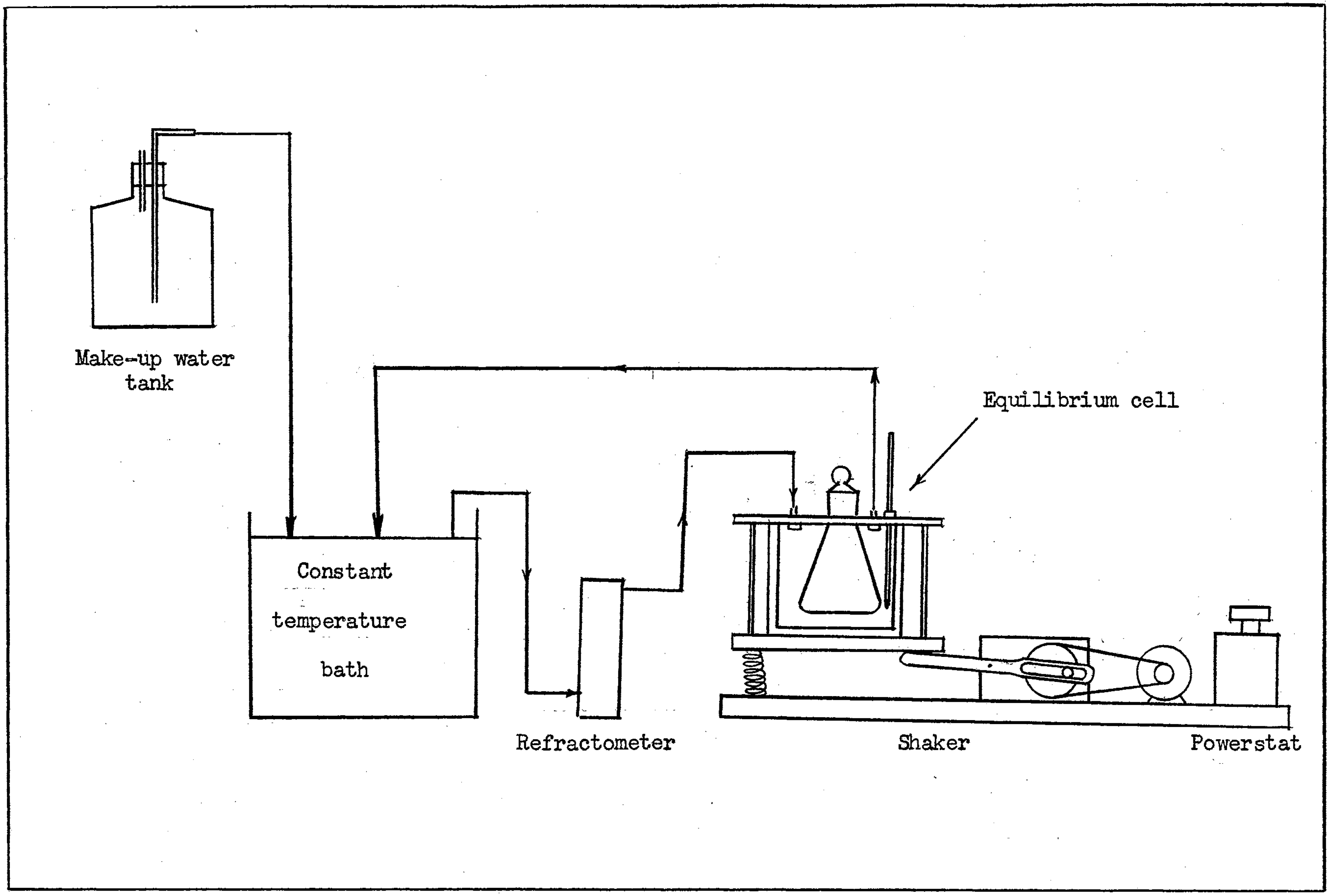


Figure 1. Schematic Diagram of Phase Equilibrium Cell

Experimental Procedure

Sufficient amounts of the three components to form 20-30 ml. of a mixture of known composition were pipetted into the equilibrium cell. The cell was agitated for six hours to ensure that equilibrium was reached. The phases were allowed to settle and were separated using a rubber-bulb pipette. They were then weighed, and analyzed. Densities of the three components were measured at two temperatures. Densities at temperatures between these were found by straight-line interpolation. Plots of the densities are shown in Appendix B.

Graphs of refractive index as a function of composition at the operating temperatures, i. e., 140° F. and 160° F. and of density as a function of composition at room temperature were prepared. Copies of these graphs are included in Appendix B.

For the analysis of the equilibrium phases, about 10 ml. of both phases were pipetted out of the equilibrium cell into tared Babcock bottles and weighed. These samples were treated with 10 ml. of 20 per cent sodium hydroxide aqueous solution to remove the phenol in the form of a water-soluble sodium phenolate. These mixtures were shaken for 10 minutes and another 10 ml. of 20 per cent sodium hydroxide aqueous solution was added. This ensured that all the phenol was converted into its sodium derivative and was dissolved in the water phase. These two-phase mixtures were transferred to separatory funnels where the water phase containing sodium phenolate was separated from the mixture of cetane and 1-methylnaphthalene. The volumes and refractive indices of the oil phases were measured. The compositions and the densities of the oil phases were read from the two charts prepared previously, and the weights of both aromatic and straight-chain hydrocarbons were calculated. The weight of phenol was assumed to be the difference between the weight of original sample pipetted into the Babcock bottle and the sum of both hydrocarbons present in the oil phase.

To see if above-mentioned method of analysis was acceptable, two check runs were made. The results checked within ± 0.2 per cent.

Six points at 160° F. and seven points at 140° F. on each branch of the binodal curves were determined. The results are given in Chapter IV.

To check the reproducibility of the experimental results, one duplicate determination of one point and one triplicate determination of another point were made. The results are given in Tables II and III.

During agitation of the equilibrium cell, the shaker was so controlled that the liquid mixture did not touch the ground glass stopper. There was always a slight build-up of pressure in the equilibrium cell during shaking. If some of the mixture was allowed to splash onto the stopper, droplets of the liquid would be blown off by the escaping vapors when the stopper was opened.

After equilibrium had been reached, the phases were removed by rubber-bulb pipette. The pipette was warmed to equilibrium temperature so that the components would not separate due to lower temperature as it was dipped into a phase of the mixture. A relatively large portion of each phase was taken so that any phase separation errors would be small. Temperatures 140° F. and 160° F. were chosen to simulate actual plant operating conditions.

Due to the peculiar motion of the shaker, there was an optimum shaking stroke below or above which the liquid mixture became rather calm. In this connection, a magnetic stirrer is recommended for agitation of the mixture. The temperature at the water jacket outside the cell was maintained constant within ± 0.2° F. A mercury thermometer which had been calibrated against a standard thermometer which had an accuracy of 0.1° C. was used.

If the mercury-to-wire regulator received any vibratory motions caused by stirrer or pump, it would give a very poor temperature regulation. Therefore, it is not desirable to install a regulator together with any source of vibratory motion on the same rack or frame.

Tie-Line Correlation

As Othmer and Tobias (23) pointed out, the triangular diagram for representing the solubility curve of the ternary systems has the advantage of giving easily the weight ratios of the two conjugate phases formed from a mixture of known composition. It has the rather serious defect of requiring considerable data for the entire range of concentrations. Unless an observed tie line coincides exactly with the composition of a mixture for which distribution data are desired, interpolation between adjacent tie lines must be used. If the plait point is displaced from the apex of the binodal curve, the slope of the tie lines will not be horizontal, and usually will vary with concentration. This variation makes accurate interpolation of the tie-lines difficult unless a considerable number of tie-lines have been determined. Therefore, it is necessary to have some method of correlating tie-line data by which the distribution data at any composition can be predicted satisfactorily.

Attempts at correlation were made by earlier investigators such as Brancker, Hunter, and Nash (4), Bachman (2), Hand (14), following Bancroft (3), and Othmer and Tobias (23). Though the correlations of Othmer and Tobias and of Hand usually apply, Bachman's method gives a better correlation for certain systems.

The correlation of Bachman, Hand, and Othmer and Tobias were tried for the system under consideration. It was concluded that the method of Othmer and Tobias gave the best results. This method consists of plotting the conjugate values of $(1 - X_{AA})/X_{AA}$ as ordinate against $(1 - X_{BB})/X_{BB}$

as abscissa on logarithmic coordinates which gives a straight line. Here, X_{AA} is the mole or weight fraction of A in the A-rich phase and X_{BB} is the mole or weight fraction of B in the B-rich phase. The derivation of the tie-line equation in terms of $(1 - X_{AA})/X_{AA}$ and $(1 - X_{BB})/X_{BB}$ given in Othmer and Tobias' article (23) was based on Nernst's distribution law (21) which was later generalized by Hand (14) to apply to any system.

Correlation plots for the system under consideration are included in Chapter IV, Figures 7 and 8.

Estimation of the Plait Point

A plot of the concentration of component C in the A-rich phase, X_{CA}, as abscissa against equilibrium concentrations of component C in the B-rich phase, X_{CB}, as ordinate on arithmetic coordinates gives the simplest distribution curve. At the same time, the curve meets the 45° diagonal line at the plait point composition. (29). This method for estimating the plait point was tried and rejected. It was almost impossible to determine the intersection of the distribution curve and the 45° diagonal line, due to negligible selectivity. The use of mole fractions instead of weight fractions gave a better correlation, but was still unsatisfactory. This method may be recommended for a system which includes a highly selective solvent. The curve of such a system will form a sharp angle with the diagonal line making the result obtained by extrapolation satisfactory.

Treybal, Weber, and Daley (28) plotted solubility data evaluated at various points along the binodal curve on logarithmic coordinates using X_C/X_A as the abscissa and X_C/X_B as the ordinate. This method of plotting gave a smooth curve, which intersected the rectilinear tie-line data at the plait point. The point of intersection divides the solubility curve into two parts; one of them representing extract phase compositions and the other raffinate phase compositions.

This method was useful in evaluating the plait point of the system under consideration, although the tie-line data did not form a straight line (see Figures 9 and 10). The tie-line data were extrapolated using the Othmer and Tobias' correlation (see Figures 7 and 8). The extrapolated data was then used to extend the experimental tie-line data to determine the intersection of the curves as shown in Figure 9.

CHAPTER III

MASS TRANSFER TO AND FROM DROPLETS

As liquid-liquid extraction as a means of refining has become more important and the number of applications has grown, the basic data for the proper design of equipment have become essential. With the exception of wetted-wall and packed columns, nearly all types of liquid-liquid extraction units work by dispersing one phase as droplets in another phase. Therefore, a study of mass transfer rates to and from liquid drops in a second liquid phase should provide basic information for proper design.

Many extensive studies on heat and mass transfer rates to and from drops passing through another liquid have been made. (5) (9) (10) (11) (15) (17) (18) (19) (20).

Mechanisms for mass transfer many be classified according to the chronological history of the drop, i. e., during drop formation, free-rise, and coalescence. Since mass transfer during the free-rise period was of primary interest, mass transfer during drop formation and coalescence was evaluated in terms of the combined end effect, E_F.

Pioneer work in this field was done on the assumption that a liquid droplet traveling through another fluid assumes a rigid spherical form. The data so obtained resulted in the overdesign of equipment, suggesting invalidity of the assumption. If the fluids have practically the same density, the droplets may be assumed to be at rest, and the problem is one of simple diffusion. If the fluids have considerably different densities, one liquid may rise or fall through the other by the gravity action, the velocity ultimately becoming constant. Due to shear stresses between the two fluids, circulation currents are set up in the droplets which increase the extraction rate.

Visual observations of oscillations as well as circulating currents inside a droplet as it rose or fell through continuous media were made by several investigators by suspending aluminum or bentonite dust in the dispersed phase and by photographic studies. (9) (10) (17) (20).

Gröber (11) (12), in his study of cooling and heating of a rigid sphere moving through fluid with continuous phase resistance, developed a relationship between the rate of heat loss, operating conditions, and physical properties of both sphere material and continuous medium. His equation can readily be transformed for mass transfer:

$$E = 1 - \frac{M(t)}{M(0)} = 1 - 6\sum_{n=1}^{\infty} B_n \exp\left[-\lambda_n^2 \frac{Dt}{a^2}\right] \qquad (1)$$

where a = drop radius

M(t) = the mass of solute at any time, t, in the droplet

$M(0)$ = the mass of solute at the beginning, $t = 0$

t = free-rise or free-fall time

λ_n, B_n = constants (λ_n = eigenvalue) .

As was pointed out earlier, this relation based on the use of the molecular diffusivity does not predict results satisfactorily in any case where fluid drops are involved. The predicted efficiencies would be expected to result in serious overdesign. The situation can be corrected by replacing the molecular diffusivity by an eddy diffusivity.

Newman (22) developed a mass transfer rate equation for the case of no resistance to transfer in the continuous phase and for stagnant drops:

$$E = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[\frac{-n^2 D \pi^2 t}{a^2} \right] \qquad (2)$$

Vermeulen (30) showed that Newman's model could be accurately represented by the following empirical equation:

$$E = \sqrt{1 - \exp \frac{-D\pi^2 t}{a^2}} \qquad (3)$$

As the exact modes of circulation currents were not known, many investigators developed mathematical models by assuming a certain mode of circulation inside drops. Each of these models is satisfactory in limited regions of operating conditions and physical properties of both continuous and dispersed phases. Among circulation models assumed, the most widely known may be Hadamard's (13) model and the Handlos-Baron (15) model. These two models are compared schematically in Figure 2.

Hadamard's model assumes the streamlines as shown in the cross section at the left. Handlos and Baron's model, in which the streamlines of Hadamard are replaced by a system of tori, is shown in the cross section at the right. A particle is considered initially at a radius ρ. After a time sufficient for one circuit along a streamline, the particle is presumed to be displaced to a point ρ' as a result of the assumed random radial motions.

Using Hadamard's circulation model and an assumption that a droplet falling or rising in a fluid under the influence of gravity retains its spherical shape during the steady state of motion, Kronig and Brink (19) derived the following equation for diffusion into a circulating drop with no continuous phase resistance:

$$E = 1 - \frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp \left[- \mu_n \frac{16Dt}{a^2} \right] . \qquad (4)$$

This relationship holds only for negligible interfacial tension and for a drop Reynolds number less than unity when the drop is assumed to have a constant spherical shape. Calderbank and Korchinski (5) found that Equation (4) was accurately represented by the following empirical equation (5):

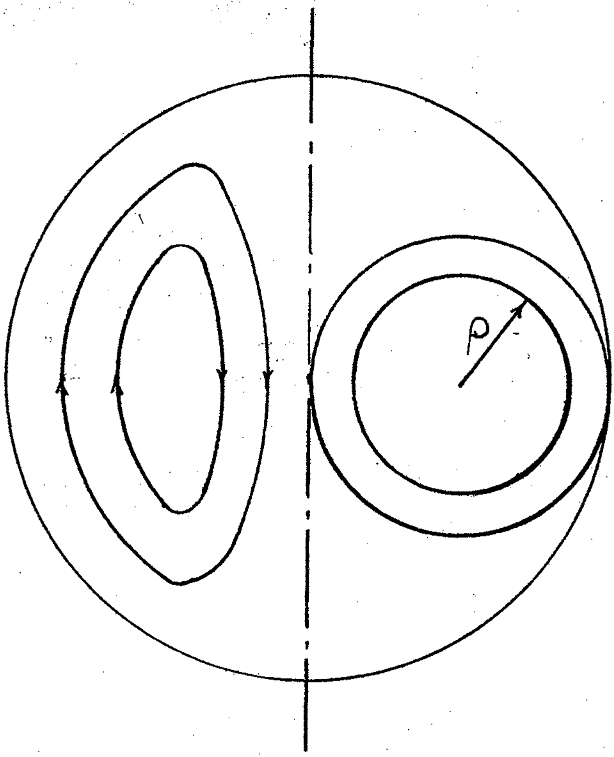


Figure 2. Circulation Models (15)

$$E = [1 - \exp (-2.25 \frac{D\pi^2 t}{a^2})]^{1/2} . \qquad (5)$$

If Equations (3) and (5) are compared, it is readily seen that the influence of circulation inside liquid drops is to raise the effective diffusivity to a value equal to 2.25 times the molecular diffusivity.

Handlos and Baron developed an extraction model based on the assumption that the circulation in the drop is fully developed and there is radial motion. They assumed that the circulation pattern in a drop is a system of tori instead of Hadamard's streamline pattern. Under these assumptions they obtained following equation (15):

$$E = 1 - 2 \sum_{n=1}^{\infty} A_n^2 \exp \left[\frac{-16 \lambda_n Dt \, Pe_i'}{2{,}048 \, d^2} \right] \qquad (6)$$

where d = drop diameter

Pe_i' = modified Peclet number.

They claimed that only one term of this series with λ_1 = 2.88 needs to be used. They also derived the effective diffusivity in terms of drop radius for the case when the transfer process can be described by eddy diffusion:

$$E(r) = \frac{dV}{2{,}048} \; \frac{(6a^2 - 8a + 3)}{(1 + \mu_i/\mu_o)} \qquad (7)$$

where V = drop velocity

μ_i = viscosity of droplet

μ_o = viscosity of continuous phase

In order to be able to compare the mass transfer rate given by the various mathematical models, a correlation factor, R, proposed and used by Korchinski (5), can be used as a multiplier of the molecular diffusivity. If the rate of mass transfer within a stagnant drop is taken as the standard for comparison, R may be defined in the following fashion (5):

$$E = [1 - \exp (-R \frac{D\pi^2 t}{a^2})]^{1/2} . \qquad (8)$$

It is apparent from the definition of the factor R that the correlation factor, R, should be equal to unity for stagnant drops. For drops with circulation and radial oscillation, R should be larger. Korchinski tabulated the relationship between correlation factor, R, and type of drop behavior.

Johnson and Hamielec (18) defined another correlation factor which is somewhat different from Korchinski's. They presented methods for evaluating the correlation factor, one for high transfer efficiency and the other for low transfer efficiency ($E_m < 0.5$).

As the mechanisms of mass transfer to and from droplets were not completely known, Handlos and Baron tried numerous empirical models in an attempt to predict the mass transfer coefficients. Among many mathematical models they tried, the following were found to best represent the available data for mass transfer from the main body of the continuous phase to the interface of the drop and within the drop, respectively (15):

$$Nu_o = 1.13 \sqrt{Pe_o} \tag{9}$$

$$Nu_i = 0.00375\ Pe_i' \tag{10}$$

where Nu_o = Nusselt number of continuous phase

Nu_i = Nusselt number inside droplet

Pe = Peclet number .

In the calculation of over-all mass transfer coefficients predicted by Handlos and Baron's mathematical model, the individual mass transfer coefficients were calculated from Equations (9) and (10). Using the relation:

$$\frac{1}{K_D} = \frac{m_{io}}{k_o} + \frac{1}{k_i} \tag{11}$$

the over-all mass transfer coefficient based on dispersed phase concentration, K_D, was evaluated.

Experimental over-all mass transfer coefficients were estimated in the following fashion (15). The equation for transfer is:

$$\frac{dC_i}{dt} = \frac{6K_D}{d} (C_i - C^*) \tag{12}$$

where C is defined in terms of the concentration of dispersed phase in equilibrium with the solute concentration in the bulk phase. Assuming that K_D is constant in the concentration range where actual extraction process takes place, Equation (12) may be integrated to give:

$$N_D = \frac{6K_D t}{d} = \ln \frac{(C_i - mC_o)_1}{(C_i - mC_o)_2} . \qquad (13)$$

As the number of transfer units based on the dispersed phase concentration, N_D, obtained in this way includes end effects, it is necessary to study at least two column heights for the evaluation of K_D. Then, the over-all mass transfer coefficient for the free-rise period is determined by:

$$K_D = \frac{d}{6} \frac{\Delta N}{\Delta t} . \qquad (14)$$

To check the validity of assuming K_D constant, a study of three column heights is required.

Experimental Apparatus

Figure 3 is a schematic diagram of the simple apparatus used in this study. The continuous phase flowed down from a large aspirator bottle in which the level of liquid was maintained constant within one-half inch by installing a make-up tank. The jacketed column was three inches I.D. and twenty-six inches high.

In determining the diameter of the column, wall effect on the drop behavior was considered. In an attempt to eliminate wall effect, Licht and Narasimhamurty (20) collected data on carbon tetrachloride drops in water in a three inch diameter glass column up to drop diameter, D = 0.448 cm. and compared with the data on the same system in a six inch diameter Lucite column, observing no noticeable difference in the fall-velocity data. Calderbank and Korchinski (5) found that the effect of column diameter had disappeared when the column diameter was about ten times that of the drop. Considering these observations, it was decided to use a column of three inches diameter.

The dispersed phase was pushed out through the nozzle by using a slight positive air pressure. The use of a funnel to collect the dispersed phase has a disadvantage as some drops miss it and a change in level of the interface may change the contact area between the continuous phase and the coalesced dispersed phase. The collecting mechanism was designed so as to keep the contact area between two phases as small as possible decreasing the end effect. The contact area remained constant in spite of changes in the height of the interface. The inside diameter of the collecting device was five-eighths inch.

Beveled glass capillaries of 2 mm. diameter and different length were used as nozzles. A Teflon stopper was used at the bottom so that the height of the nozzle, and, therefore, the column height, could be changed.

The tubing used was one-half inch stainless steel tubing purchased from McMaster Company. As it was known

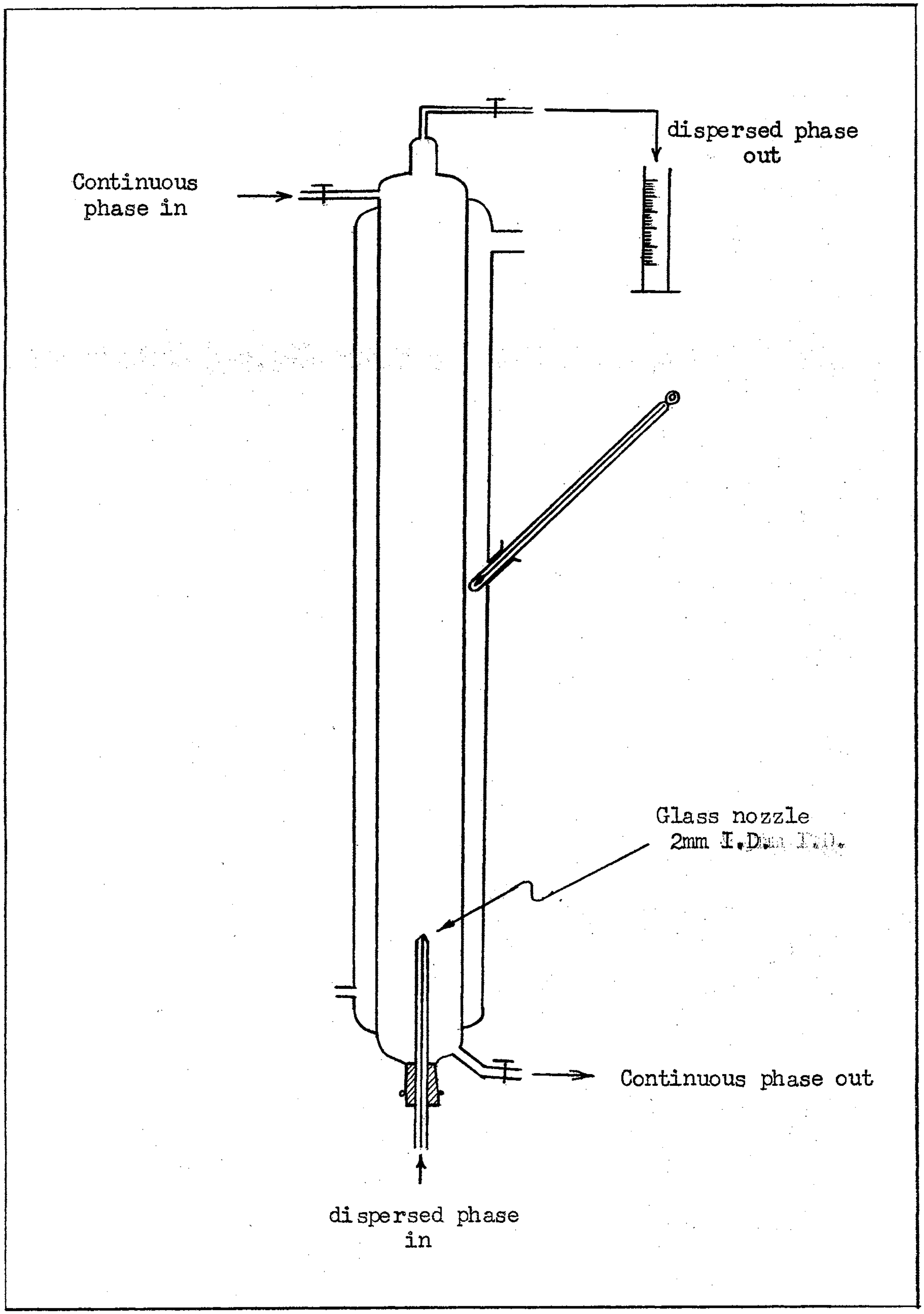


Figure 3. Extraction Column

that the presence of materials extracted from plastic tubing or gaskets could have an effect on the rate of mass transfer, use of such materials was avoided.

The phases were analyzed by the same method used in the determination of the phase equilibria.

Systems Under Consideration

The effects of changing temperature, solute concentration, and the direction of mass transfer on the rates of mass transfer were the object of this study. The following systems were chosen for investigation:

1. Transfer of Phenol to Cetane Droplets at 140° F.
   Dispersed phase = pure cetane
   Continuous phase = 95 per cent aqueous phenol saturated with cetane.
2. Transfer of Phenol to Cetane Droplets at 160° F.
   Dispersed phase = pure cetane
   Continuous phase = 95 per cent aqueous phenol saturated with cetane.
3. Transfer of 1-Methylnaphthalene from Droplets at 140° F.
   Dispersed phase = cetane saturated with phenol containing 0.1015 gm. of 1-Methylnaphthalene per ml. of solution.
   Continuous phase = 95 per cent aqueous phenol saturated with cetane.

4. Transfer of 1-Methylnaphthalene from Droplets at 140° F.

   Dispersed phase = cetane saturated with phenol containing 0.2030 gm. of 1-Methylnaphthalene per ml. of solution.

   Continuous phase = 95 per cent aqueous phenol saturated with cetane.

5. Transfer of 1-Methylnaphthalene to Droplets at 140° F.

   Dispersed phase = cetane saturated with phenol

   Continuous phase = 95 per cent aqueous phenol saturated with cetane containing 0.2030 gm. of 1-Methylnaphthalene per ml. of solution.

The effect of changing temperature on mass transfer and drop behavior can be shown by comparing systems (1) and (2). The effects of changing the concentration and the direction of mass transfer can be shown by comparing systems (3) and (4), and systems (4) and (5), respectively.

CHAPTER IV

RESULTS AND DISCUSSION

Phase Equilibria

Ternary Diagram

Comparing Figures 4 and 6, it is evident that the zone of miscibility decreased considerably from 140° F. to 160° F. The tie-lines were essentially horizontal indicating that 95 per cent aqueous phenol did not show much selectivity for 1-Methylnaphthalene over cetane. The change of temperature from 140° F. to 160° F. did not have any apparent effect on the selectivity of the phenol. This was indicated by the essentially horizontal tie-lines at both temperatures. Such is generally not the case in phenol extraction of lubricating oil stock.

Figure 5, a plot of solute concentration in dispersed phase as a function of solute concentration in continuous phase, illustrates the selectivity of phenol better than Figure 4.

The density differences between equilibrium layers in the range of concentration ordinarily encountered were large except in the close vicinity of the plait point. The interfacial tensions were such that the settling of insoluble phases was rapid and complete.

Tie-Line Correlation

Figures 7 and 8 show tie-line correlations at 140° F. and 160° F., respectively. The slope of these lines is essentially the same, indicating again that phenol is not a selective solvent for this system evaluated on the basis of weight fractions. Although the Othmer and Tobias correlation gave a straight line, Hand's correlation, as will be shown later together with plait point determination, did not give a straight line. The plait points were determined as the intersection of two curves in Figures 9 and 10, and are included in the ternary diagrams, Figures 4 and 6.

In the prediction of plait point composition, straight line extrapolation of tie-line data to the intersection with the solubility curve is supposed to give the composition. However, Hand's method of tie-line correlation did not give a straight line for either case.

Since the Othmer and Tobias correlation of tie-line data gave a straight line, it might be a good assumption that the plait point composition fell on this straight line. On this assumption, a point close to the plait point composition was taken from the straight line in Figure 7. Compositions of these points were calculated and located in Figure 9. This manipulation made extrapolation of tie-line data easier and more accurate, resulting in a more accurate prediction of the plait point compositions. These points are shown on Figure 9 as black dots.

TABLE II

EQUILIBRIUM AND PHASE BOUNDARY DATA FOR THE 95% AQ. PHENOL-CETANE-1-METHYLNAPHTALENE SYSTEM AT 140° F.

Weight Fractions

Charge			Phase I Component			Phase II Component		
A	B	C	A	B	C	A	B	C
0.5806	0.4194	0.0000	0.9595	0.0405	0.0000	0.0633	0.9367	0.0000
0.5429	0.3925	0.0646	0.9004	0.0470	0.0526	0.0816	0.8532	0.0652
0.5430	0.3924	0.0646	0.9103	0.0415	0.0482	0.0781	0.8564	0.0655
0.5429	0.3925	0.0646	0.9051	0.0466	0.0489	0.0807	0.8540	0.0653
0.5099	0.3687	0.1214	0.8188	0.0695	0.1117	0.1179	0.7621	0.1200
0.4803	0.3479	0.1718	0.7534	0.0849	0.1617	0.1469	0.6833	0.1698
0.4548	0.3287	0.2165	0.6792	0.1121	0.2087	0.1680	0.6182	0.2138
0.4317	0.3116	0.2567	0.6043	0.1464	0.2493	0.2169	0.5255	0.2576
0.4326	0.3201	0.2570	0.5998	0.1451	0.2510	0.2132	0.5266	0.2555
0.4188	0.3024	0.2788	0.5632	0.1690	0.2687	0.3866	0.3429	0.2705

Component A, 95% ag. phenol.
Component B, Cetane
Component C, 1-Methylnaphthalene

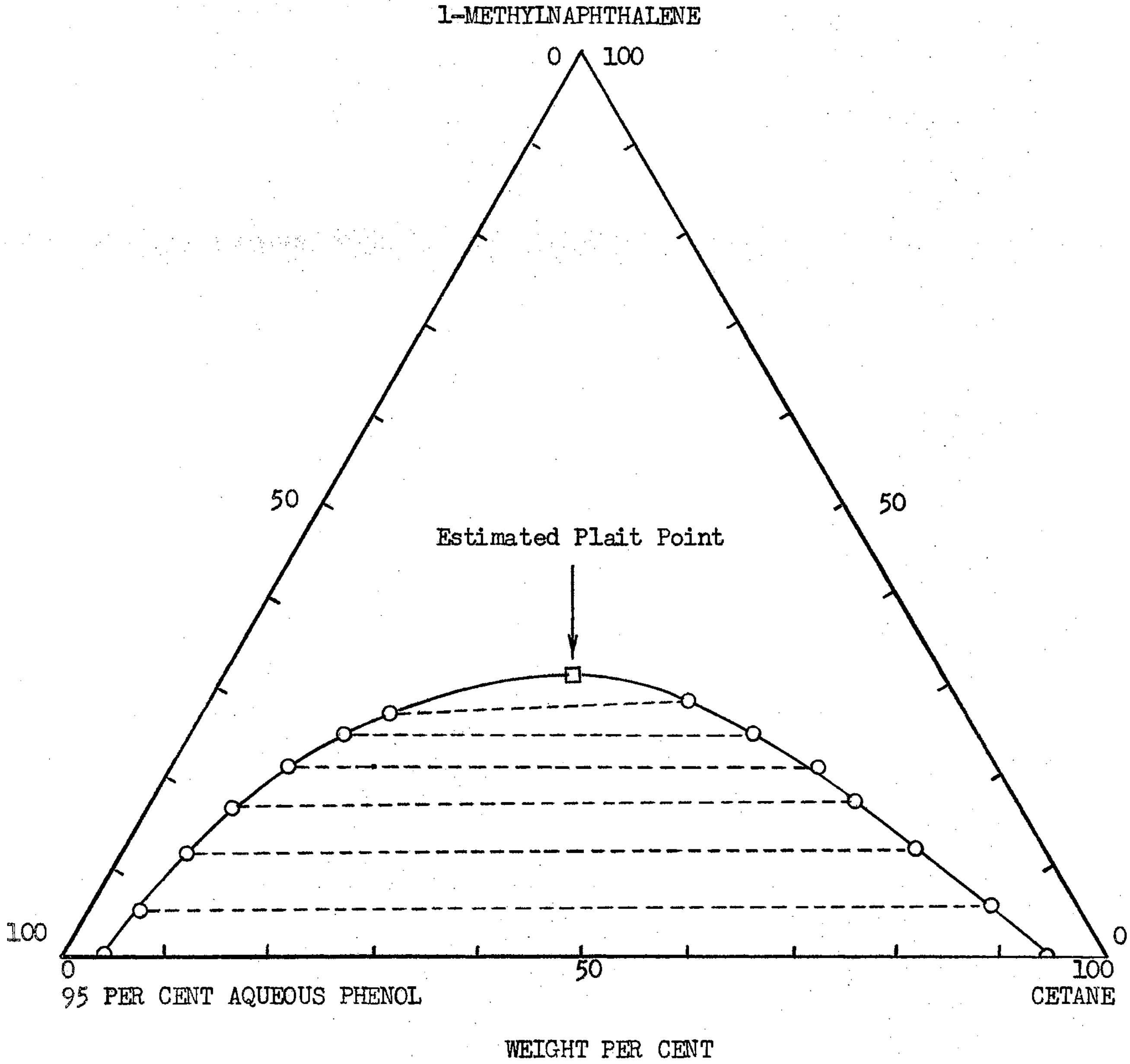


Figure 4. Ternary Diagram for the 95 Per Cent Aqueous Phenol-Cetane-1-Methylnaphthalene System at 140° F.

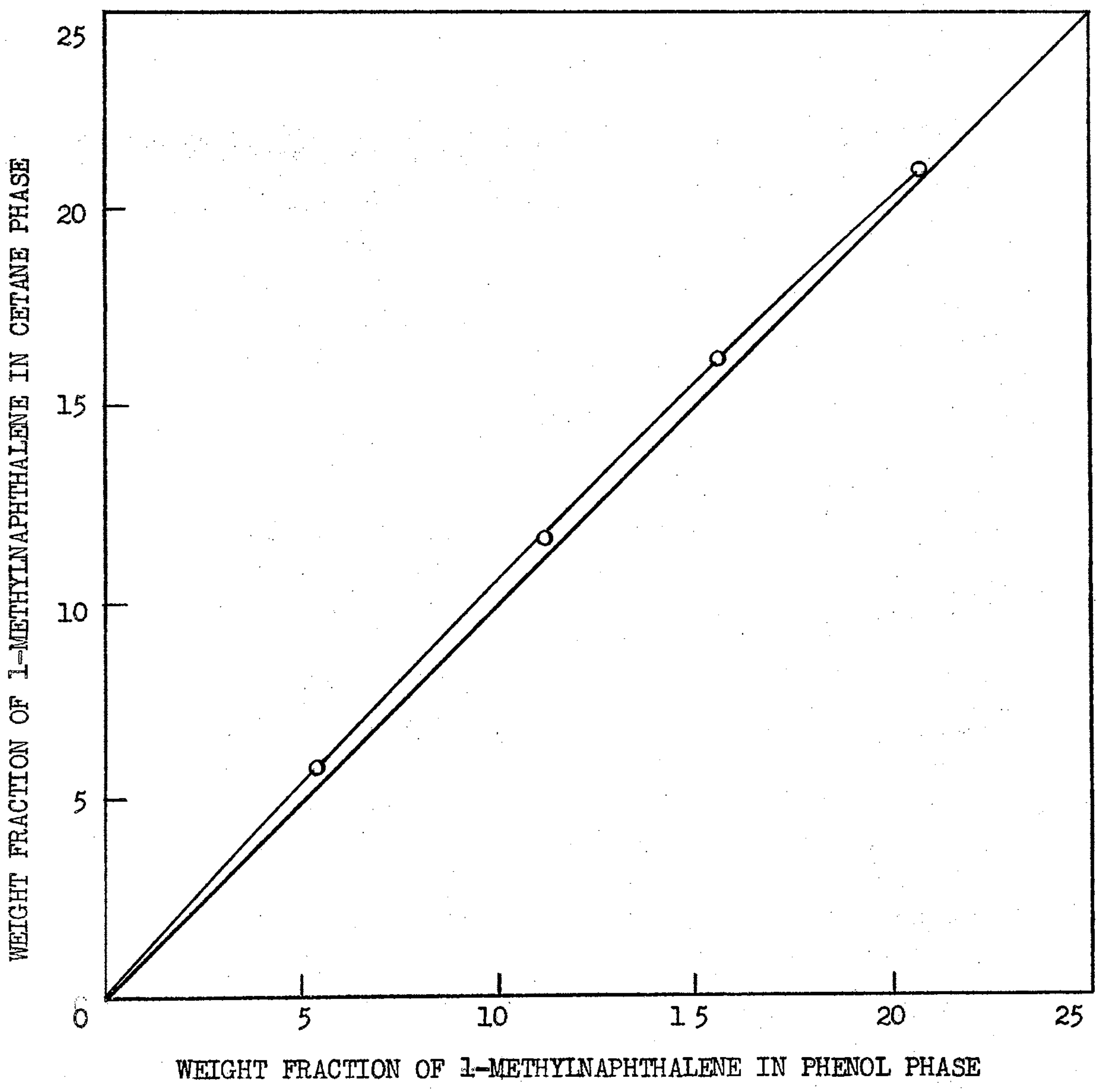


Figure 5. Distribution Data of 1-Methylnaphthalene Between Cetane and 95 Per Cent Aqueous Phenol at 140° F.

TABLE III

EQUILIBRIUM AND PHASE BOUNDARY DATA FOR THE 95% AQ. PHENOL-CETANE-1-METHYLNAPHTHALENE SYSTEM AT 160° F.

Weight Fractions

Charge			Phase I Component			Phase II Component		
A	B	C	A	B	C	A	B	C
0.5807	0.4193	0.0000	0.9447	0.0553	0.0000	0.0866	0.9134	0.0000
0.5424	0.3929	0.0647	0.8719	0.0699	0.0582	0.1121	0.8257	0.0622
0.5098	0.3688	0.1214	0.8081	0.0759	0.1160	0.1338	0.7506	0.1156
0.4797	0.3483	0.1720	0.7173	0.1210	0.1617	0.2014	0.6317	0.1669
0.4472	0.3230	0.2298	0.5950	0.1881	0.2169	0.2858	0.4892	0.2250
0.4407	0.3182	0.2411	0.5884	0.1833	0.2283	0.3679	0.3884	0.2437

Component A, 95% ag. phenol
Component B, Cetane
Component C, 1-Methylnaphthalene

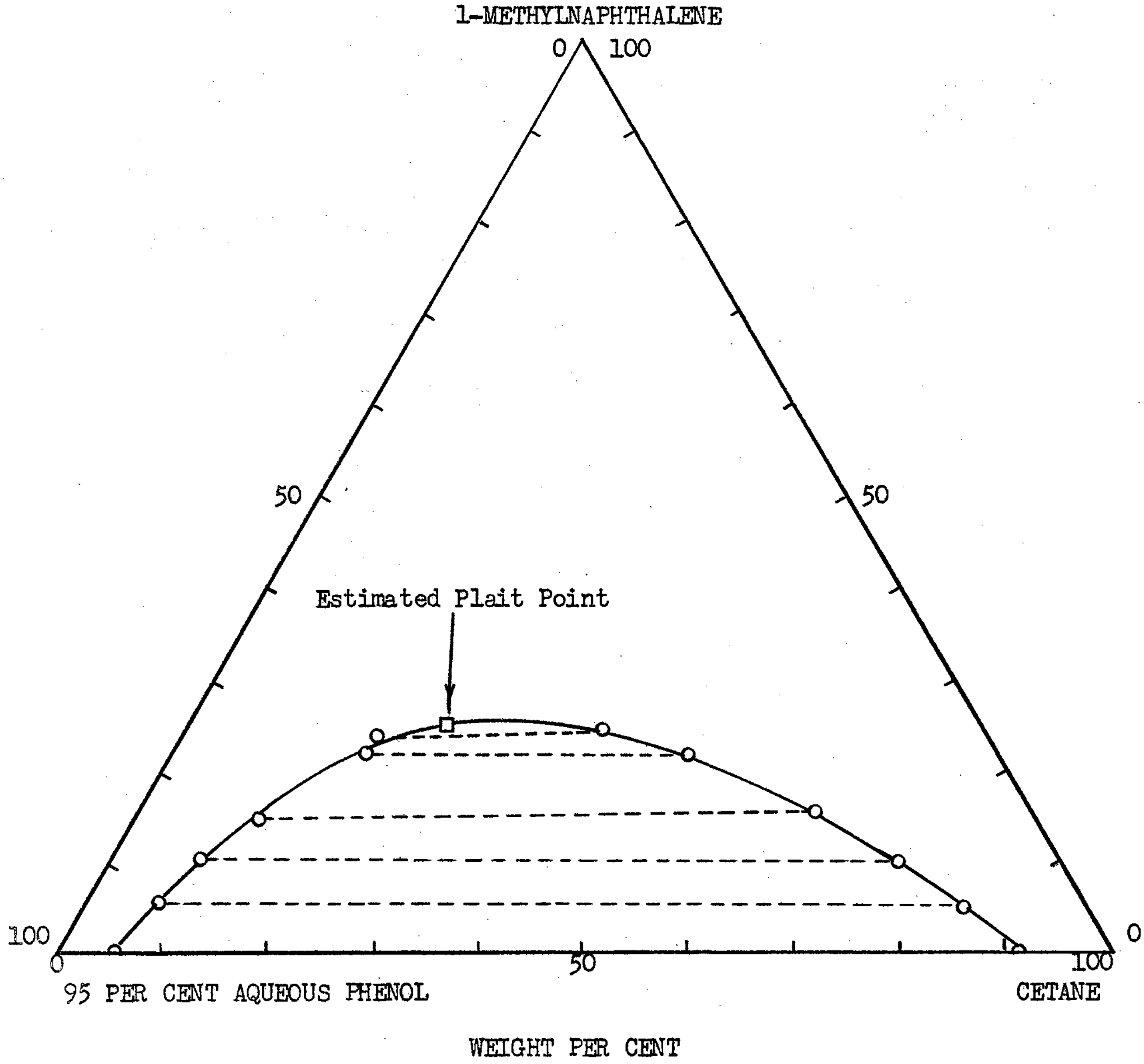


Figure 6. Ternary Diagram for the 95 Per Cent Aqueous Phenol-Cetane-1-Methylnaphthalene System at 160° F.

TABLE IV

TIE-LINE CORRELATION DATA AT 140° F.

$(1 - X_{AA})/X_{AA}$	$(1 - X_{BB})/X_{BB}$
0.0422	0.0676
0.1106	0.1721
0.2213	0.3122
0.3273	0.4635
0.4723	0.6176
0.6548	0.9029

TABLE V

TIE-LINE CORRELATION DATA AT 160° F.

$(1 - X_{AA})/X_{AA}$	$(1 - X_{BB})/X_{BB}$
0.0585	0.0948
0.1469	0.2111
0.2375	0.3323
0.3941	0.5830
0.6807	1.0442

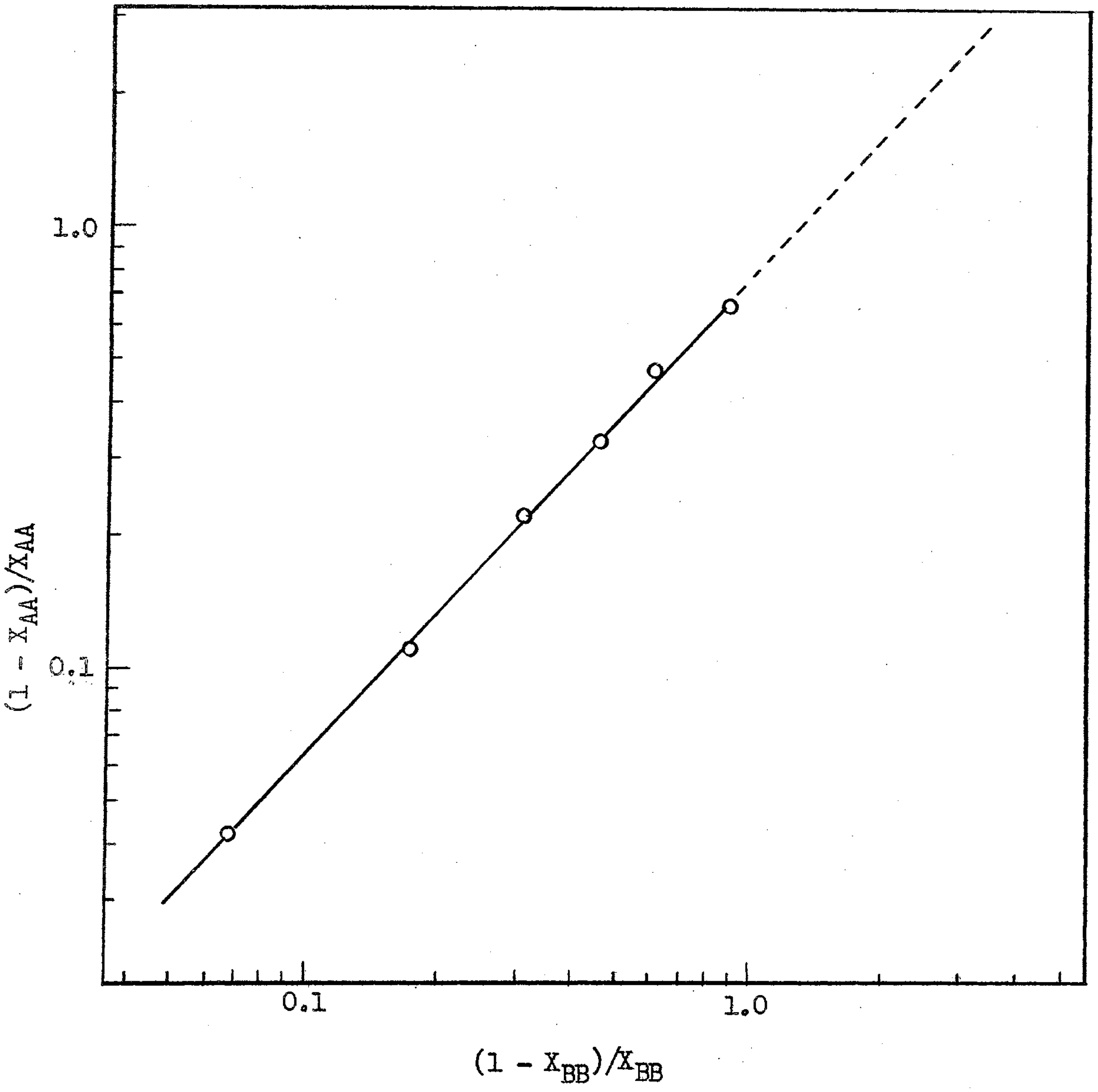


Figure 7. Othmer and Tobias Tie-Line Correlation for the 95 Per Cent Aqueous Phenol-Cetane-1-Methylnaphthalene System at 140° F.

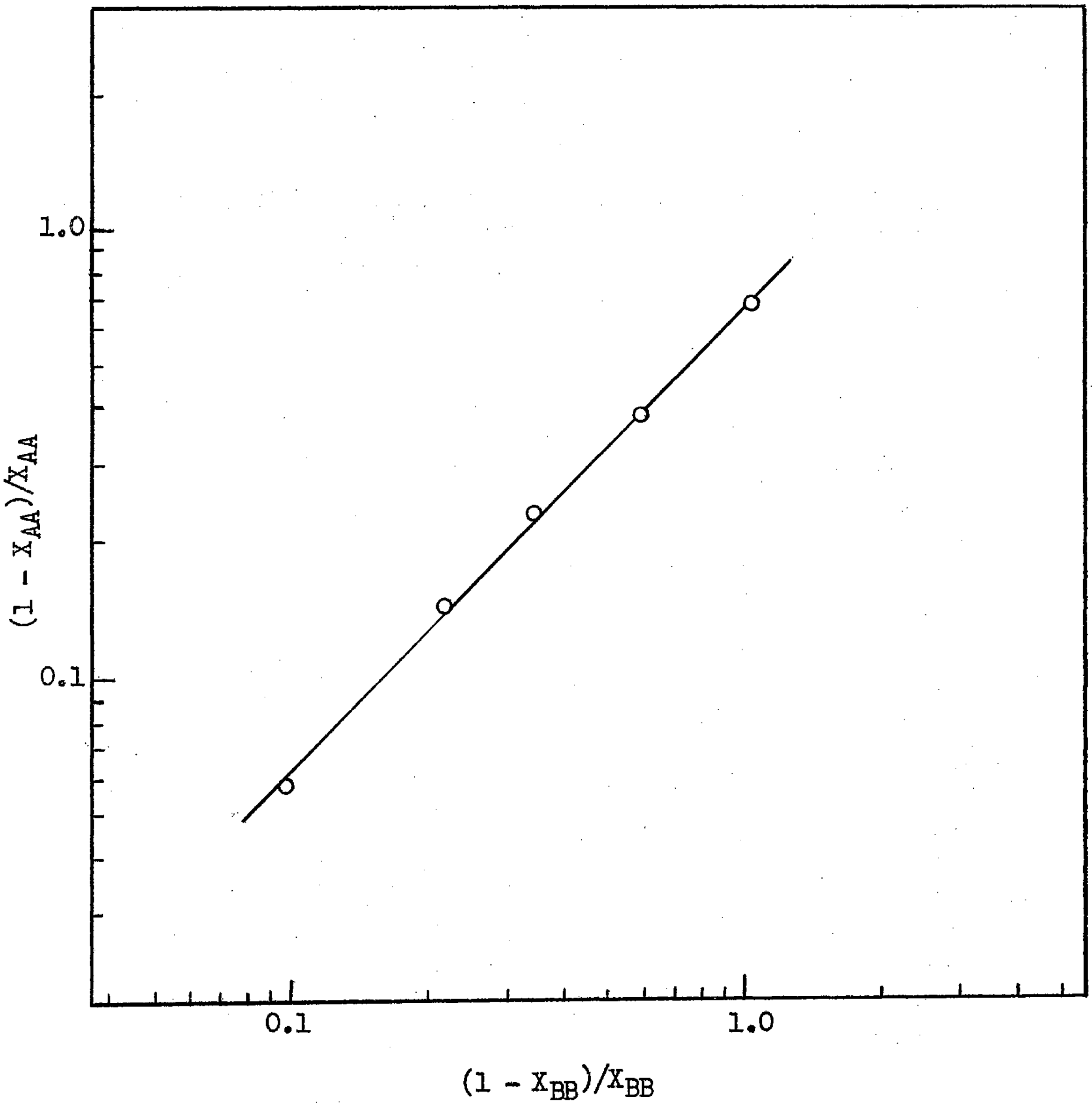


Figure 8. Othmer and Tobias Tie-Line Correlation for the 95 Per Cent Aqueous Phenol-Cetane-1-Methylnaphthalene System at 160° F.

TABLE VI

ESTIMATION OF PLAIT POINT AT 140° F.

Tie-Line Data

X_{CB}/X_{BB}	X_{CA}/X_{AA}
0.0764	0.0584
0.1575	0.1364
0.2485	0.2146
0.3458	0.3073
0.4902	0.4126

Solubility Data

X_C/X_B	X_C/X_A
1.9046	0.2146
1.8617	0.3073
1.7029	0.4125
1.5941	0.4771
0.4902	1.1876
0.3458	1.2726

Estimated Plait Point

$X_A = 0.36$

$X_B = 0.33$

$X_C = 0.31$

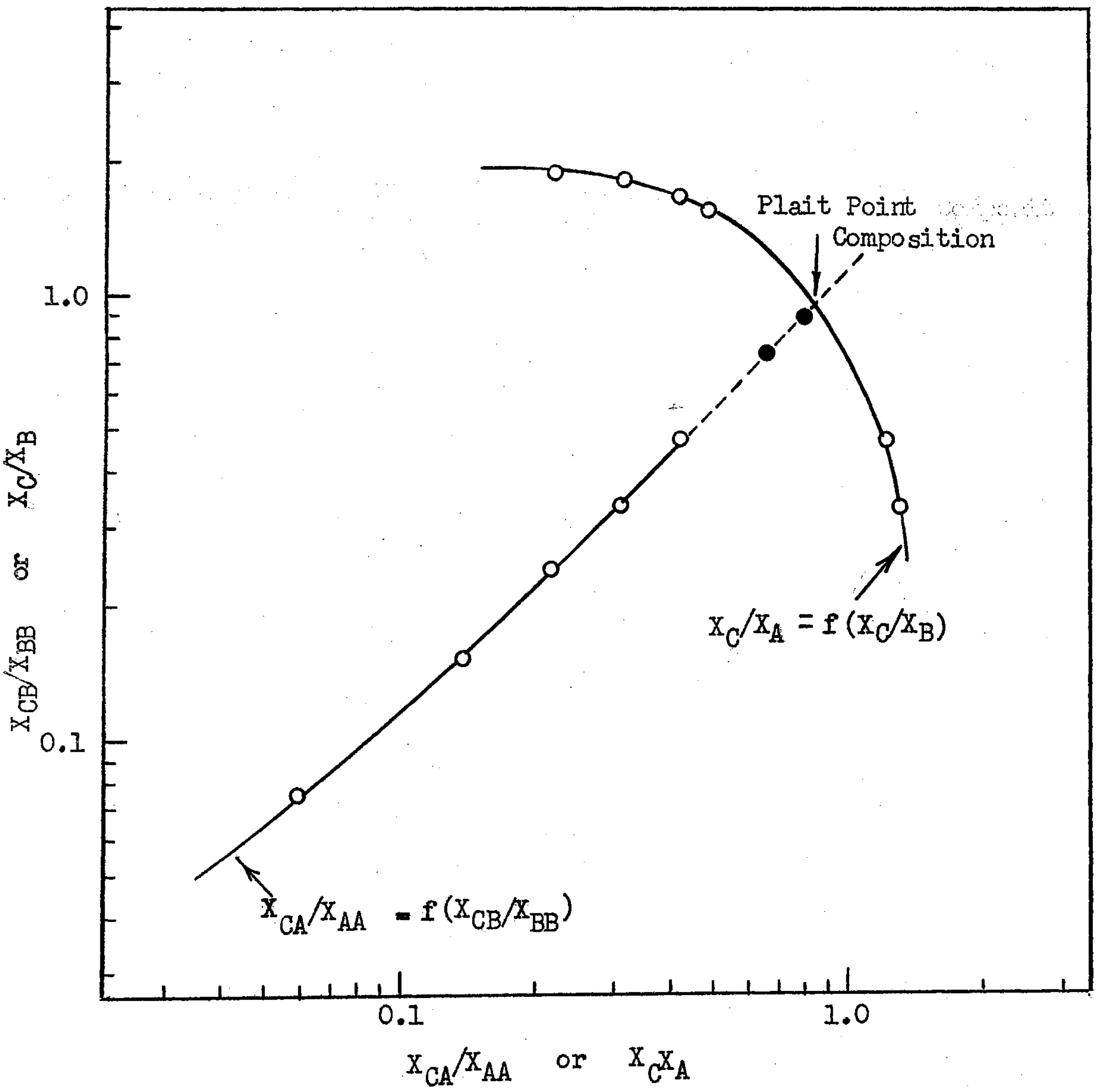


Figure 9. Tie-Line and Solubility Data for the 95 Per Cent Aqueous Phenol-Cetane-1-Methylnaphthalene System at 140° F.

TABLE VII

ESTIMATION OF PLAIT POINT

AT 160° F.

Tie-Line Data

X_{CB}/X_{BB}	X_{CA}/X_{AA}
0.0753	0.0668
0.1540	0.1435
0.2642	0.2254
0.4599	0.3326
0.6274	0.3880

Solubility Data

X_C/X_B	X_C/X_A
1.5283	0.1435
1.3364	0.2254
1.1531	0.3645
0.6274	0.6624
0.4599	0.7873
0.2624	0.8287
0.1540	0.8640

Estimated Plait Point

$X_A = 0.51$

$X_B = 0.25$

$X_C = 0.24$

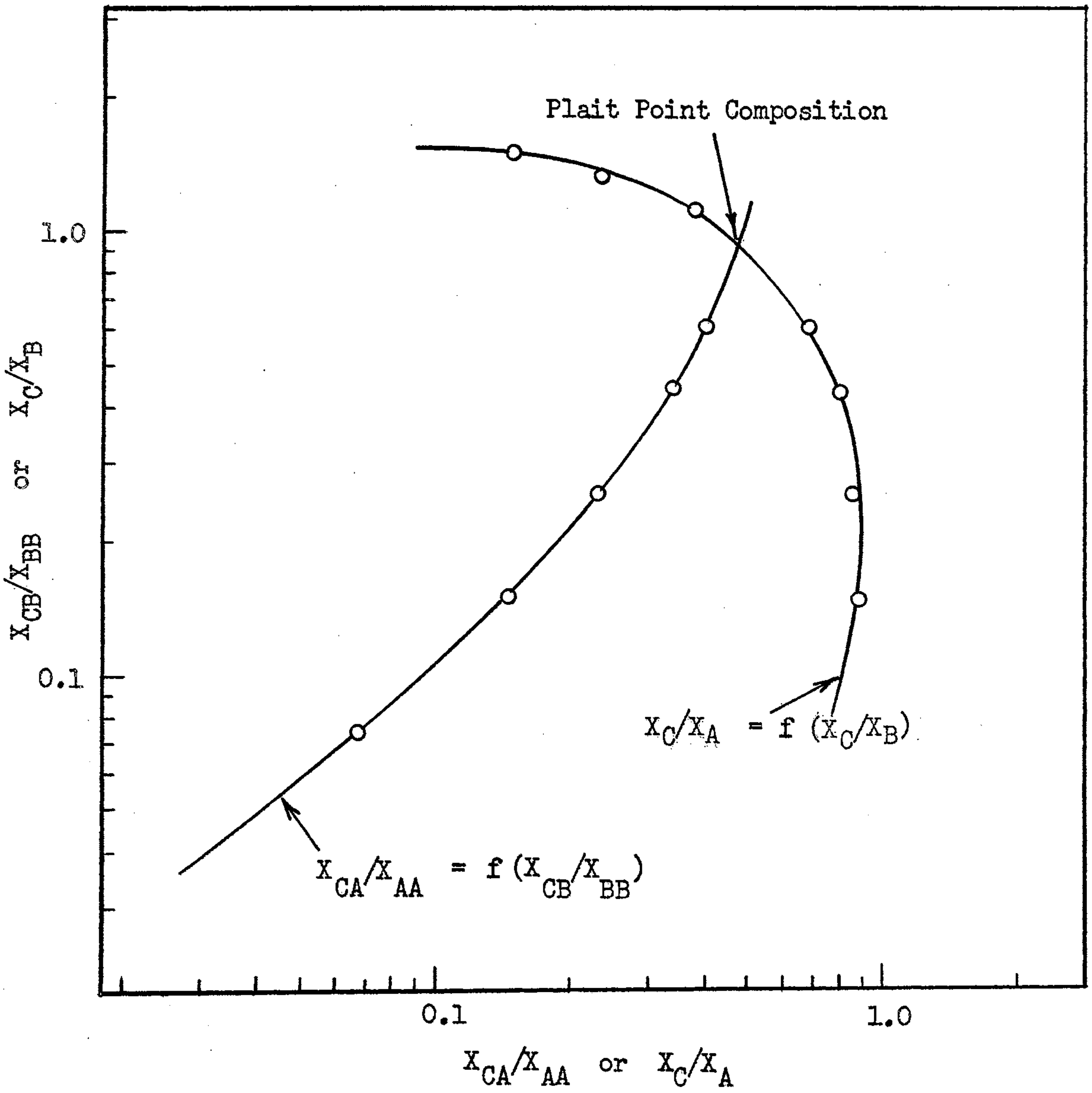


Figure 10. Tie-Line and Solubility Data for the 95 Per Cent Aqueous Phenol-Cetane-1-Methylnaphthalene System at 160° F.

Mass Transfer to and from Droplets

Estimation of Over-all Mass Transfer Coefficient, K_D.

The Number of Transfer Units, N_D, was calculated from the data in Tables XVII, XIX, XXI, XXIII, and XXV by using Equation (13). N_D was plotted as a function of the free-rise time of the drop. The over-all mass transfer coefficient for the free-rise period was obtained by multiplying the slope of these lines by d/6 as shown in Equation (14). In systems 1, 2, and 5, the distribution ratio, m, was calculated from the solubility data. Diffusivities were estimated by the method proposed by Wilke (31).

The observed and predicted over-all mass transfer coefficients had considerably different numerical values. The general tendency toward increase and decrease in the values coincided well except for systems 1 and 2 (see Table IX). For these systems, the predicted values decreased with an increase in temperature while the observed values increased. This discrepancy was possibly due to the error in the measurement of drop velocity (refer to Equations 9 and 10). At 140° F., drops took a straight line path as they rose. There was slight zigzag motion of drops at 160° F., giving low apparent drop velocity.

Comparing systems 3 and 4, it can be seen that the over-all mass transfer coefficient decreased with the increase in concentration. This does not necessarily mean a decrease in the amount of solute transferred. The driving force increases with the increase in concentration.

At the same time, it is clear from the comparison of systems 4 and 5 that the relative ease of solute transfer is largely influenced by the direction of its transfer. Transfer of solute from droplets was more rapid than the transfer of solute to droplets for the system.

End Effect

Combined end effect, E_F, was determined approximately by plotting experimental values of $-\ln(1 - E_T)$ as a function of the free-rise time, and extrapolating the curves to zero free-rise time. This procedure, though not rigorous since a linear driving potential is assumed, was adopted in this study in default of a better method. Combined end effect, E_F, is defined by the following equation (18):

$$E_F = E_{f1} + E_{f2} - E_{f1} \times E_{f2} \tag{15}$$

where E_{f1} = end effect during drop formation

E_{f2} = end effect during coalescence .

Comparing the data in Tables VIII and IX, it may be seen that the over-all efficiency, E_T, defined by the following equation:

$$E_T = \frac{C_1 - C_4}{C_1 - C^*} \tag{16}$$

where C_1 = concentration of dispersed phase at nozzle

C_4 = concentration of dispersed phase at column outlet

C^* = concentration of dispersed phase at equilibrium with the bulk phase

decreased with increase in temperature. This does not mean that the absolute amount of solute extracted decreased because the total amount of solute that could be extracted, the denominator in Equation (16), increased with temperature.

Johnson and Hamielec's method of evaluating end effects was not applicable to the systems under consideration because, as will be shown later, the correlation factor, R, varied considerably with column height.

Correlation Factor, R

Korchinski's correlation factor, R, was evaluated with the aid of Equation (8). Again, the molecular diffusivity estimated by Wilke's method was used (31). In the transfer of phenol to cetane drops at 140° F. and 160° F., R ranged from 6.7 - 12.4 and 8.8 - 14.9, respectively, showing that a circulation model close to that predicted by Handlos and Baron prevailed in droplets. In the transfer of 1-Methylnaphthalene from drops, the R values varied from 2.0 to 4.2, which included the R value ranges predicted by the Kronig-Brink model. Almost stagnant drops were formed during the transfer of 1-Methylnaphthalene into the drops with the R values ranging from 1.0 to 1.4.

According to Korchinski, drop oscillation begins at R equal approximately to 7. Therefore, during the transfer of phenol to cetane drops, drop oscillations were assumed to be present although visual confirmation was not possible.

Shape and Behavior of Droplets

In general, the droplets had a cycloidal form, having a horizontal diameter approximately three times the vertical diameter. As the column height was reduced, irregularities in drop behavior increased, possibly due to the proximity of the nozzles to the point of introduction of the continuous phase. The drops of system 4 began to vibrate horizontally, but rolling or rocking was not observed. However, at a relatively large dispersed phase flow rate, rolling or rocking of droplets was observed, possibly due to the turbulent wake left by the previous droplets.

TABLE VIII

NUMBER OF TRANSFER UNITS AND OVER-ALL EFFICIENCIES AS A FUNCTION OF THE FREE-RISE TIME

System 1. Transfer of Phenol to Cetane Droplets at 140° F.

Dispersed phase = pure cetane

Continuous phase = 95 per cent aqueous phenol saturated with cetane

Free-rise time, sec.	Number of transfer units	Over-all efficiency E_T	$1 - E_T$
2.4	1.02	0.6396	0.3604
2.6	1.03	0.6436	0.3564
2.5	1.01	0.6363	0.3637
5.8	1.59	0.7959	0.2041
5.9	1.73	0.8227	0.1773
5.8	1.75	0.8271	0.1729
8.2	2.20	0.8885	0.1115
8.0	2.22	0.8916	0.1084
8.1	2.18	0.8873	0.1127

$$\frac{\Delta N}{\Delta t} = 0.2100$$

K_D, ft/hr, observed = 0.79

K_D, ft/hr, predicted = 2.03

$E_F = 0.39$

TABLE IX

NUMBER OF TRANSFER UNITS AND OVER-ALL EFFICIENCIES AS A FUNCTION OF THE FREE-RISE TIME

System 2. Transfer of Phenol to Cetane Droplets at 160° F.

Dispersed phase = pure cetane

Continuous phase = 95 per cent aqueous phenol saturated with cetane

Free-rise time sec.	Number of transfer units	Over-all efficiency E_T	$1 - E_T$
2.7	0.70	0.5037	0.4963
2.7	0.65	0.4777	0.5223
2.6	0.67	0.4882	0.5118
6.4	1.54	0.7855	0.2145
6.5	1.50	0.7769	0.2231
6.4	1.45	0.7652	0.2348
8.6	1.97	0.8605	0.1395
8.5	2.00	0.8648	0.1352
8.6	2.10	0.8774	0.1226

$$\frac{\Delta N}{\Delta t} = 0.2438$$

K_D, ft/hr, observed = 0.84

K_D, ft/hr, predicted = 1.75

E_F = 0.10

TABLE X

NUMBER OF TRANSFER UNITS AND OVER-ALL EFFICIENCIES AS A FUNCTION OF THE FREE-RISE TIME

System 3. Transfer of 1-Methylnaphthalene from Droplets at 140° F.

Dispersed phase = cetane saturated with phenol containing 0.1015 gm. of 1-Methylnaphthalene per ml. of solution

Continuous phase = 95 per cent aqueous phenol saturated with cetane

Free-rise time sec.	Number of transfer units	Over-all efficiency E_T	$1 - E_T$
3.3	1.13	0.6769	0.3231
3.3	1.31	0.7291	0.2709
3.3	1.25	0.7134	0.2866
6.9	1.55	0.7715	0.2285
6.9	1.50	0.7532	0.2468
7.0	1.55	0.7872	0.2128
9.3	1.67	0.8050	0.1950
9.4	1.70	0.8119	0.1881
9.3	1.74	0.8247	0.1753

$$\frac{\Delta N}{\Delta t} = 0.0971$$

K_D, ft/hr, observed = 0.27

K_D, ft/hr, predicted = 0.96

E_F = 0.625

TABLE XI

NUMBER OF TRANSFER UNITS AND OVER-ALL EFFICIENCIES AS A FUNCTION OF THE FREE-RISE TIME

System 4. Transfer of 1-Methylnaphthalene from Droplets at 140° F.

Dispersed phase = cetane saturated with phenol containing 0.2030 gm. of 1-Methylnaphthalene per ml. of solution

Continuous phase = 95 per cent aqueous phenol saturated with cetane

Free-rise time sec.	Number of transfer units	Over-all efficiency E_T	$1 - E_T$
4.0	2.43	0.9188	0.0812
3.9	2.23	0.8926	0.1074
8.4	2.73	0.9344	0.0656
8.4	2.66	0.9297	0.0703
11.0	2.85	0.9420	0.0580
11.1	2.93	0.9466	0.0534

$$\frac{\Delta N}{\Delta t} = 0.0763$$

K_D, ft/hr, observed = 0.21

K_D, ft/hr. predicted = 0.88

E_F = 0.847

TABLE XII

NUMBER OF TRANSFER UNITS AND OVER-ALL EFFICIENCIES AS A FUNCTION OF THE FREE-RISE TIME

System 5. Transfer of 1-Methylnaphthalene to Droplets at 140° F.

Dispersed phase = cetane saturated with phenol

Continuous phase = 95 per cent aqueous phenol saturated with cetane containing 0.2030 gm. of 1-Methylnaphthalene per ml. of solution

Free-rise time sec.	Number of transfer units	Over-all efficiency E_T	$1 - E_T$
4.1	1.02	0.6378	0.3622
4.0	1.05	0.6476	0.3524
8.3	1.25	0.7133	0.2867
8.2	1.06	0.6521	0.3479
12.0	1.39	0.7503	0.2497
12.0	1.34	0.7367	0.2633

$$\frac{\Delta N}{\Delta t} = 0.0419$$

K_D, ft/hr, observed = 0.13

K_D, ft/hr, predicted = 0.81

E_F = 0.572

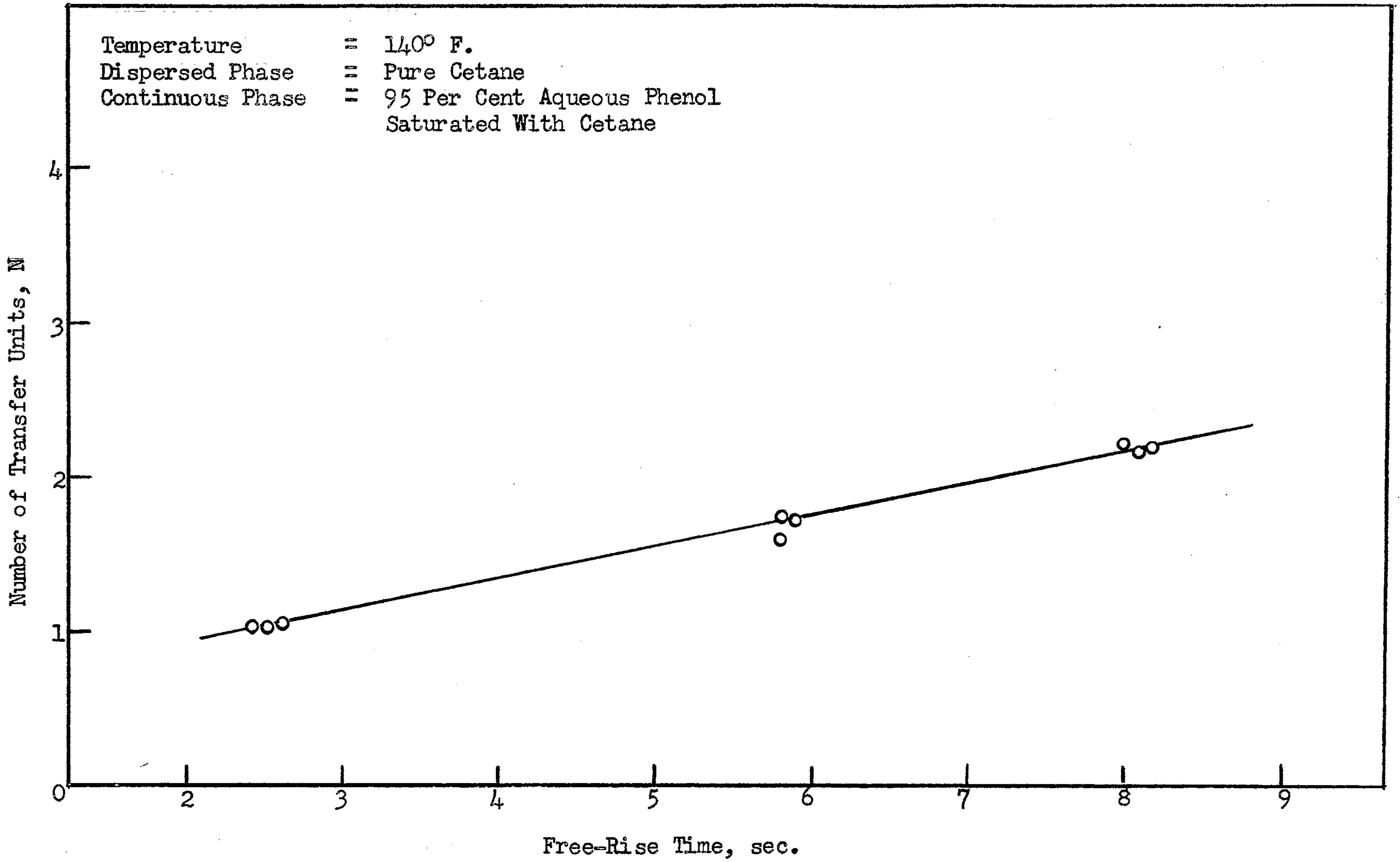


Figure 11. Number of Transfer Units as a Function of Free-Rise Time for the Transfer of Phenol to Cetane Drops

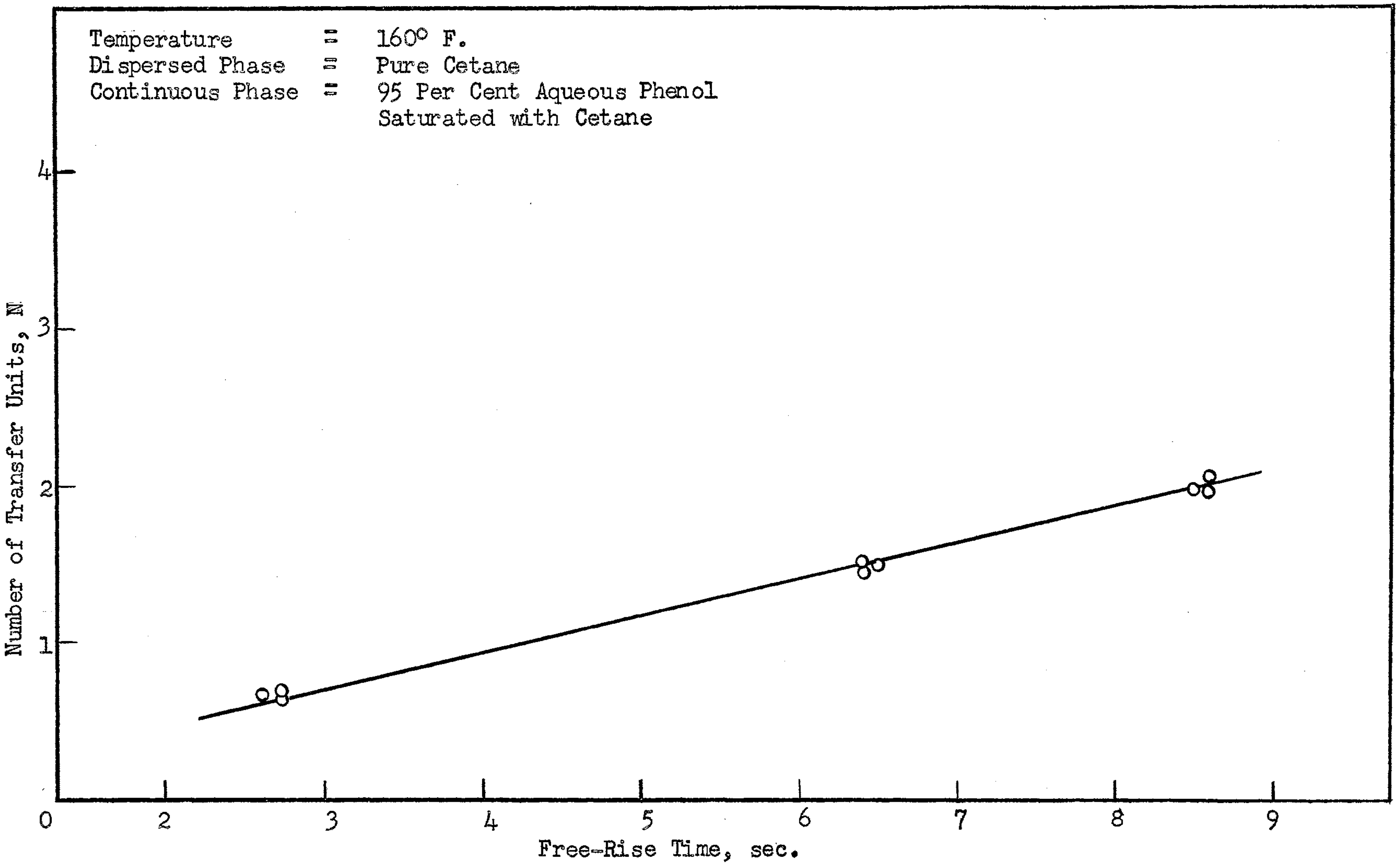


Figure 12. Number of Transfer Units as a Function of Free-Rise Time for the Transfer of Phenol to Cetane Drops

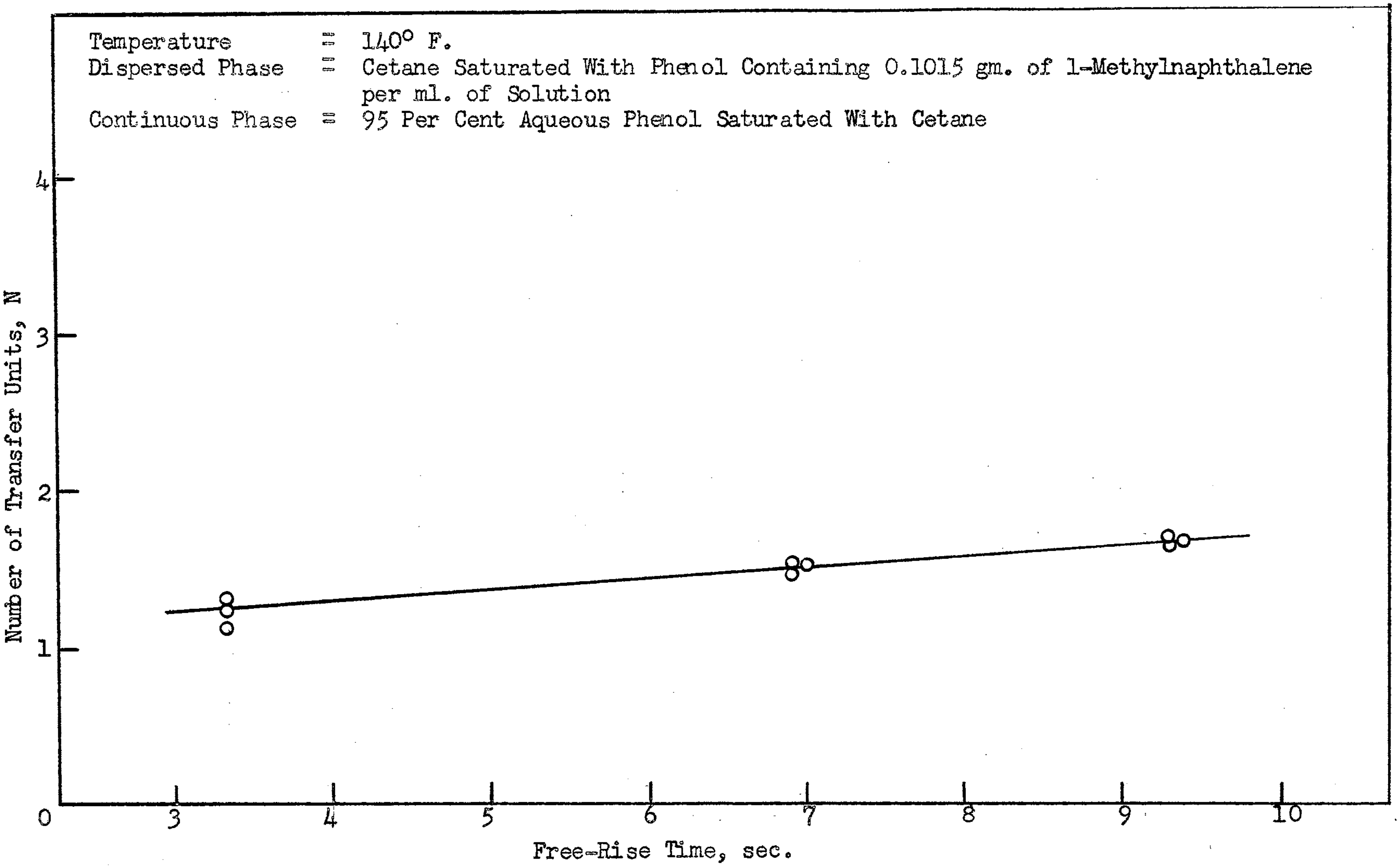
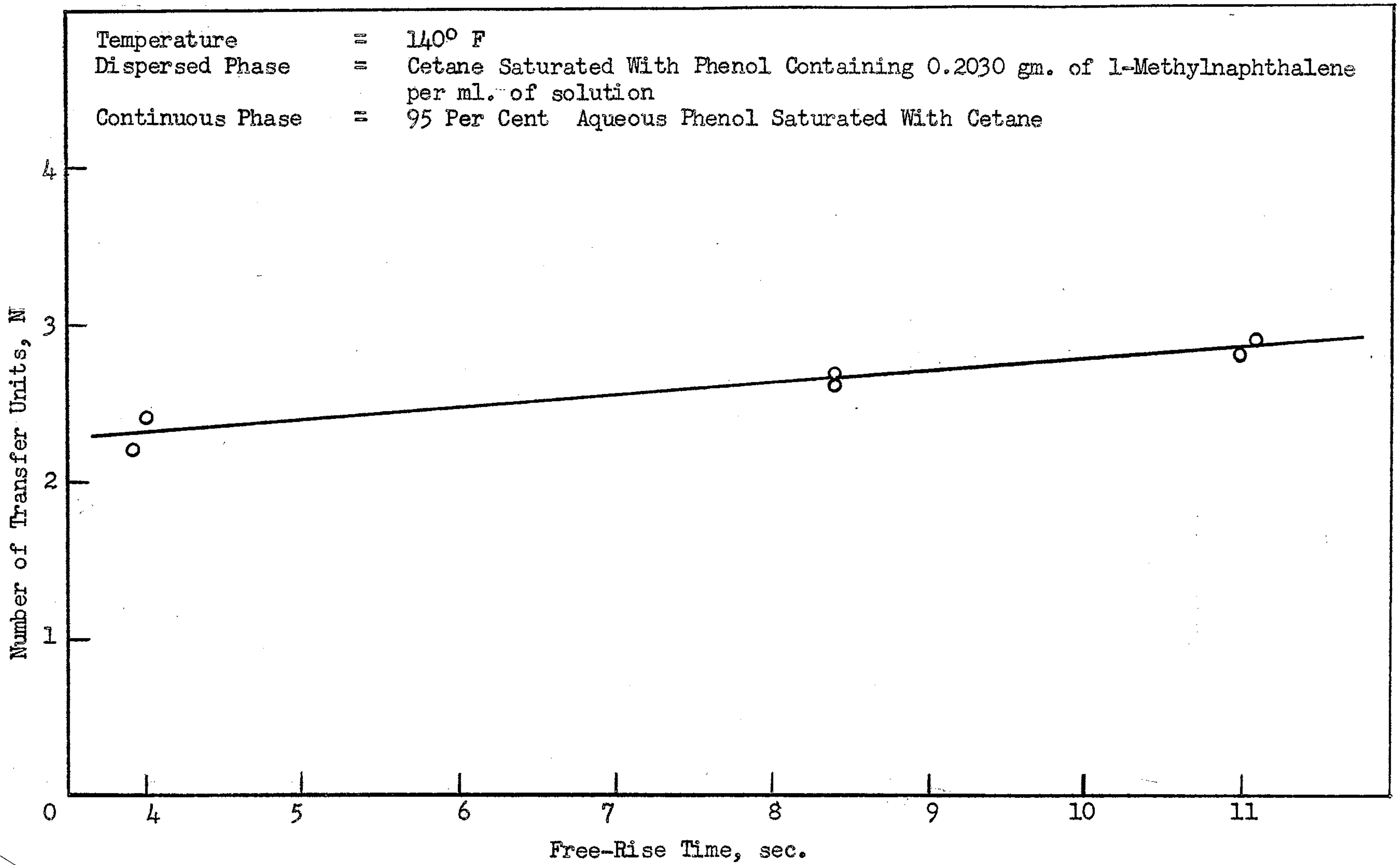


Figure 13. **Number of Transfer Units as a Function of Free-Rise Time for the Transfer of 1-Methylnaphthalene From Drops**



igure 14. Number of Transfer Units as a Function of Free-Rise Time for the Transfer of 1-Methylnaphthalene From Drops

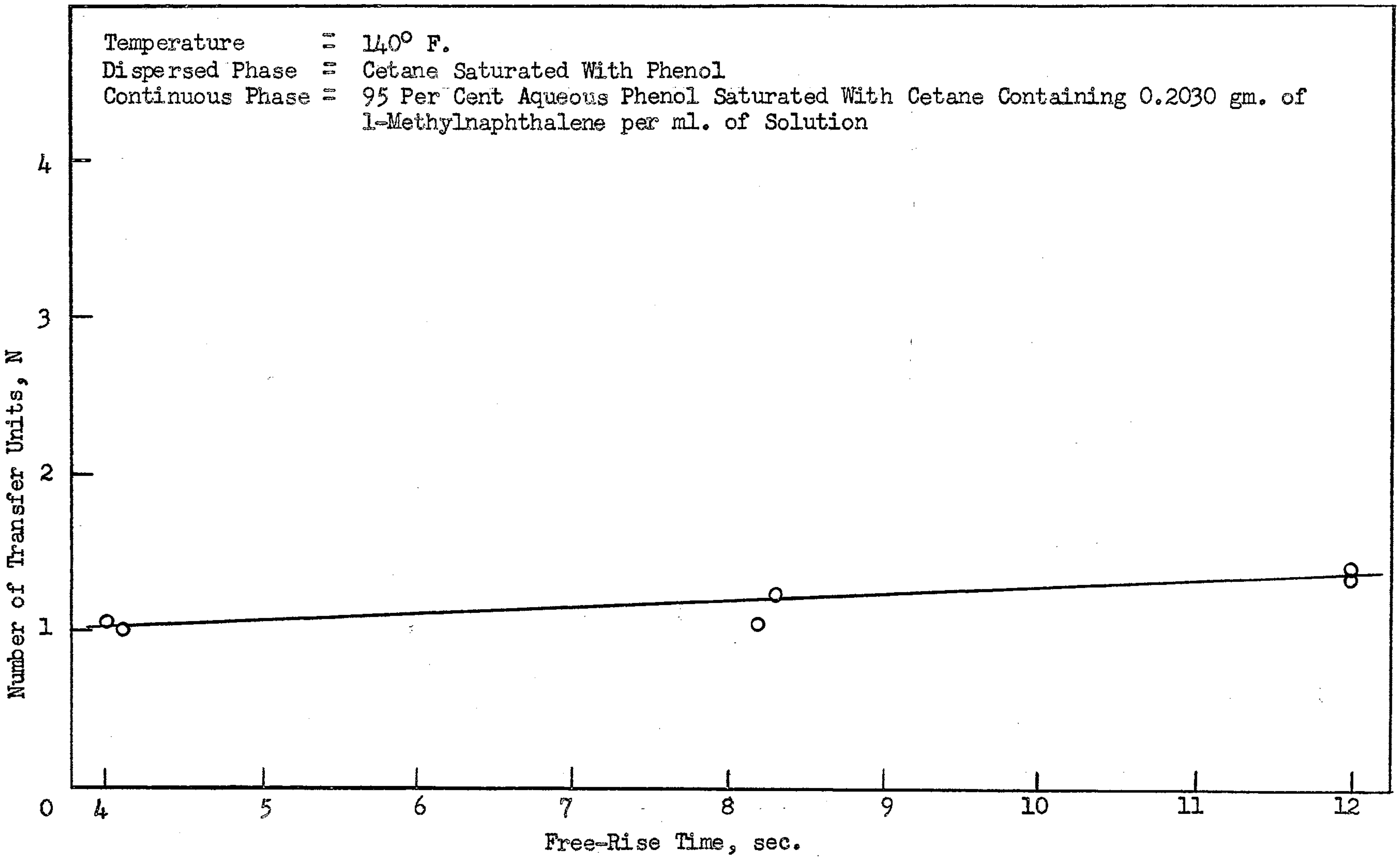


Figure 15. Number of Transfer Units as a Function of Free-Rise Time for the Transfer of 1-Methylnaphthalene to Drops

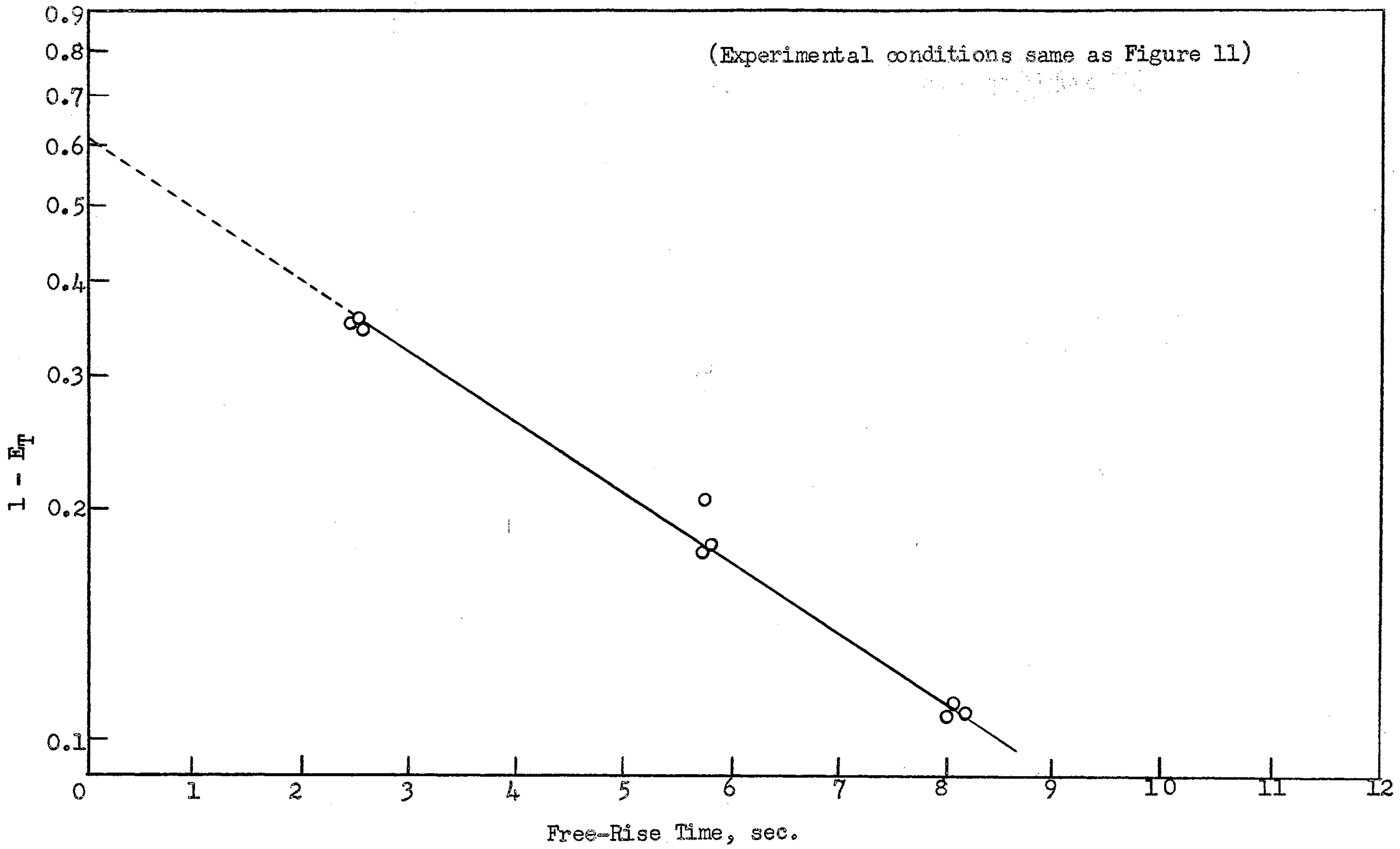


Figure 16. Amount of Solute Unextracted as a Function of Free-Rise Time for the Transfer of Phenol to Cetane Drops

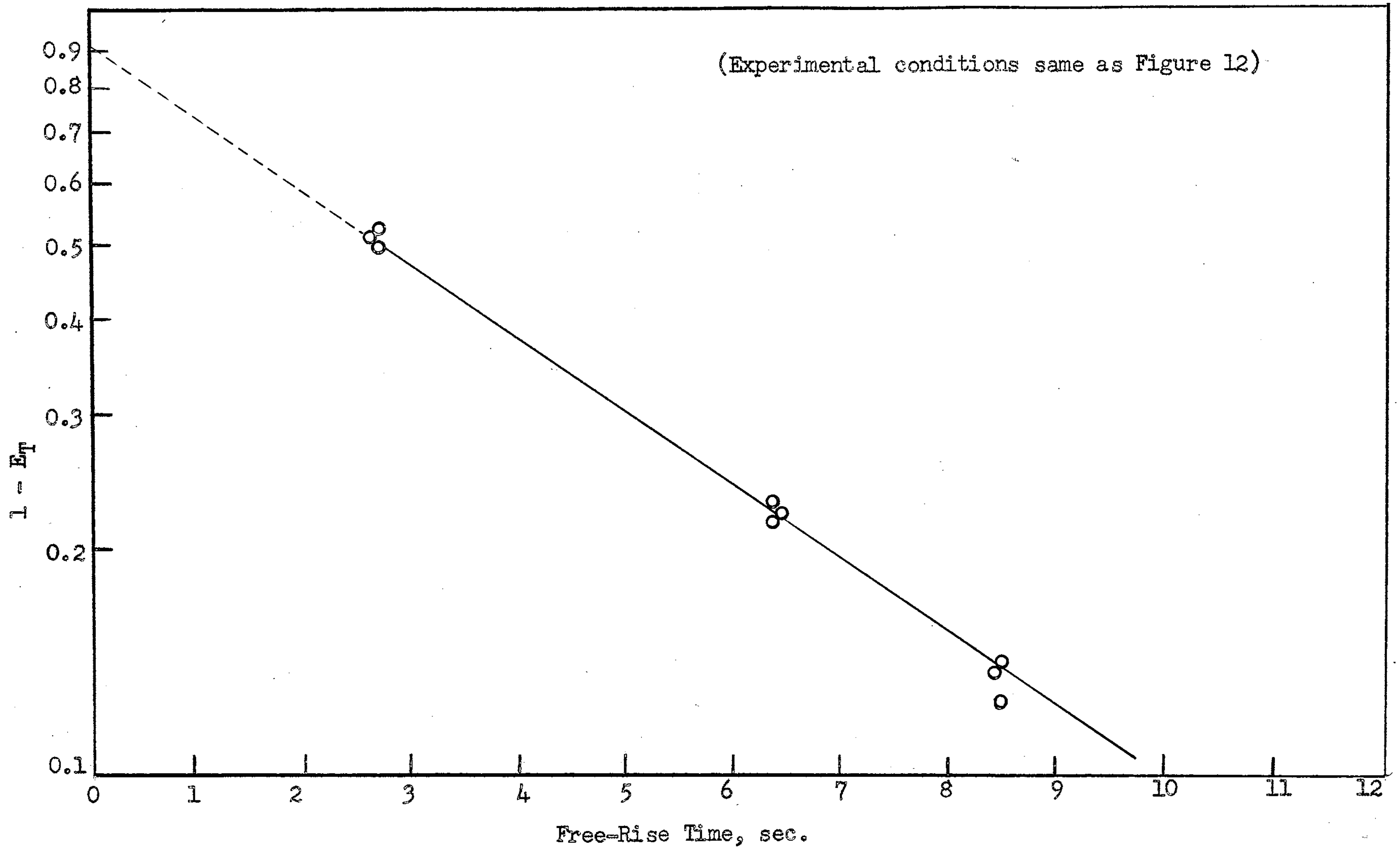


Figure 17. Amount of Solute Unextracted as a Function of Free-Rise Time for the Transfer of Phenol to Cetane Drops

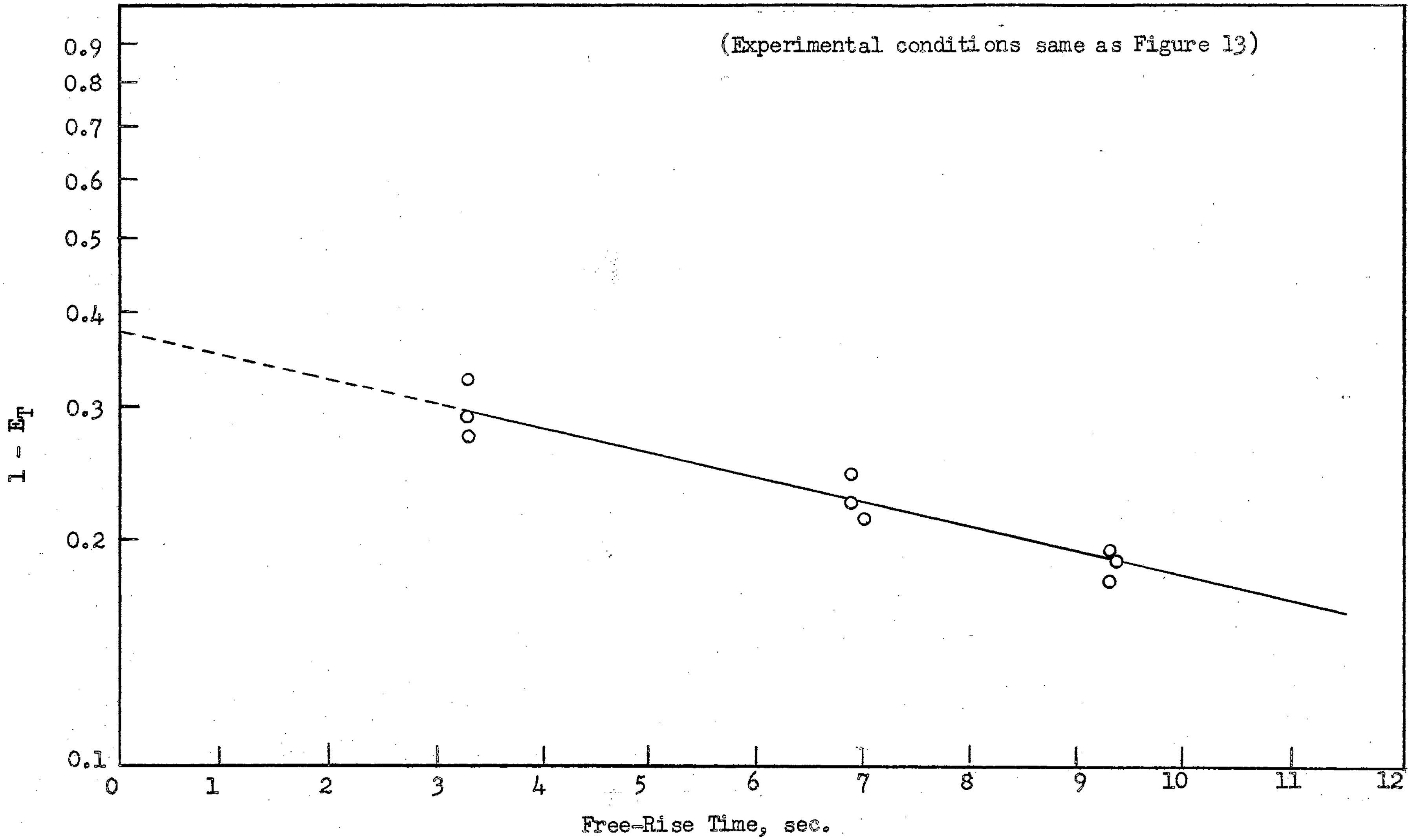


Figure 18. Amount of Solute Unextracted as a Function of Free-Rise Time for the Transfer of 1-Methylnaphthalene From Drops

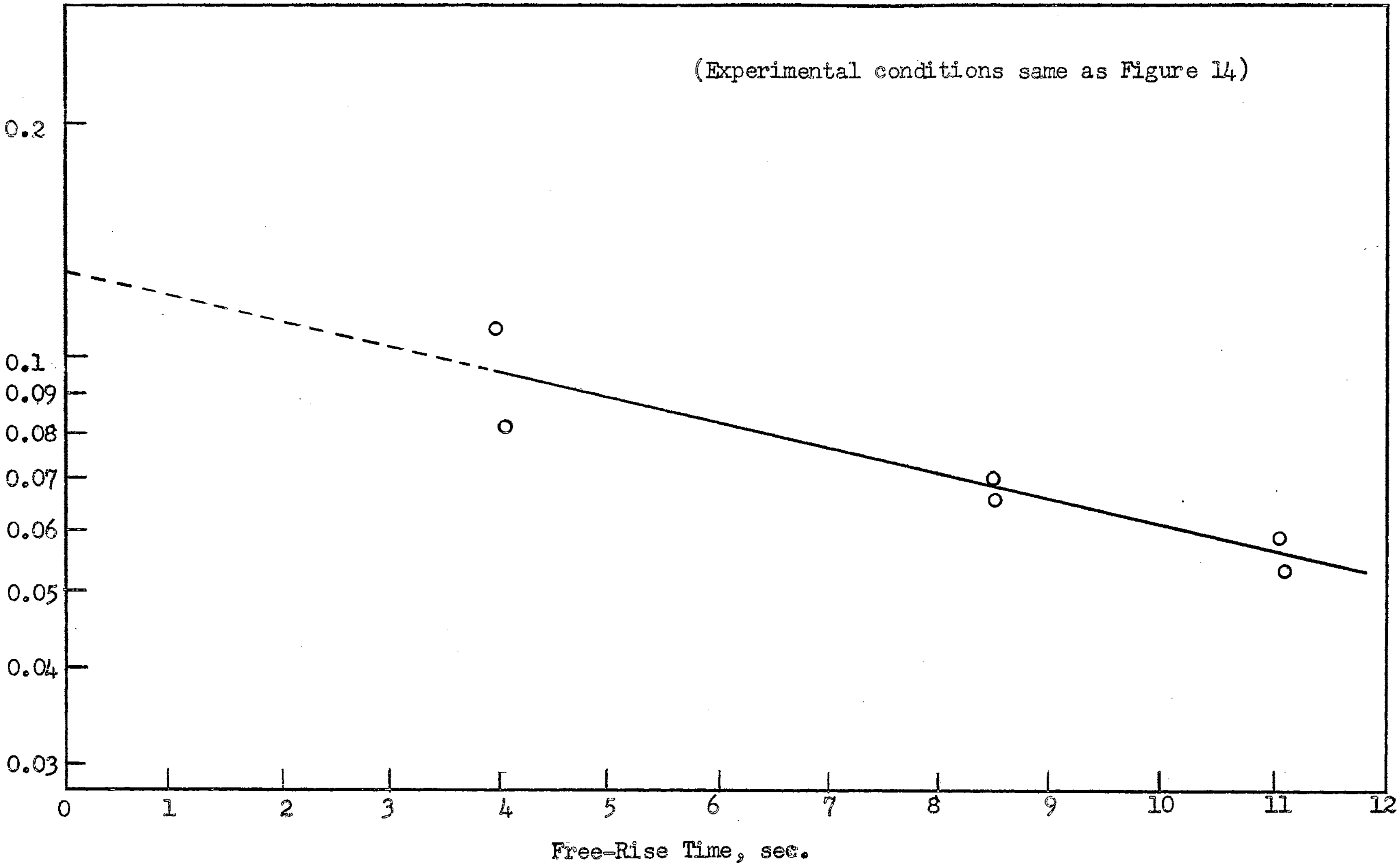


Figure 19. Amount of Solute Unextracted as a Function of Free-Rise Time for the Transfer of 1-Methylnaphthalene From Drops

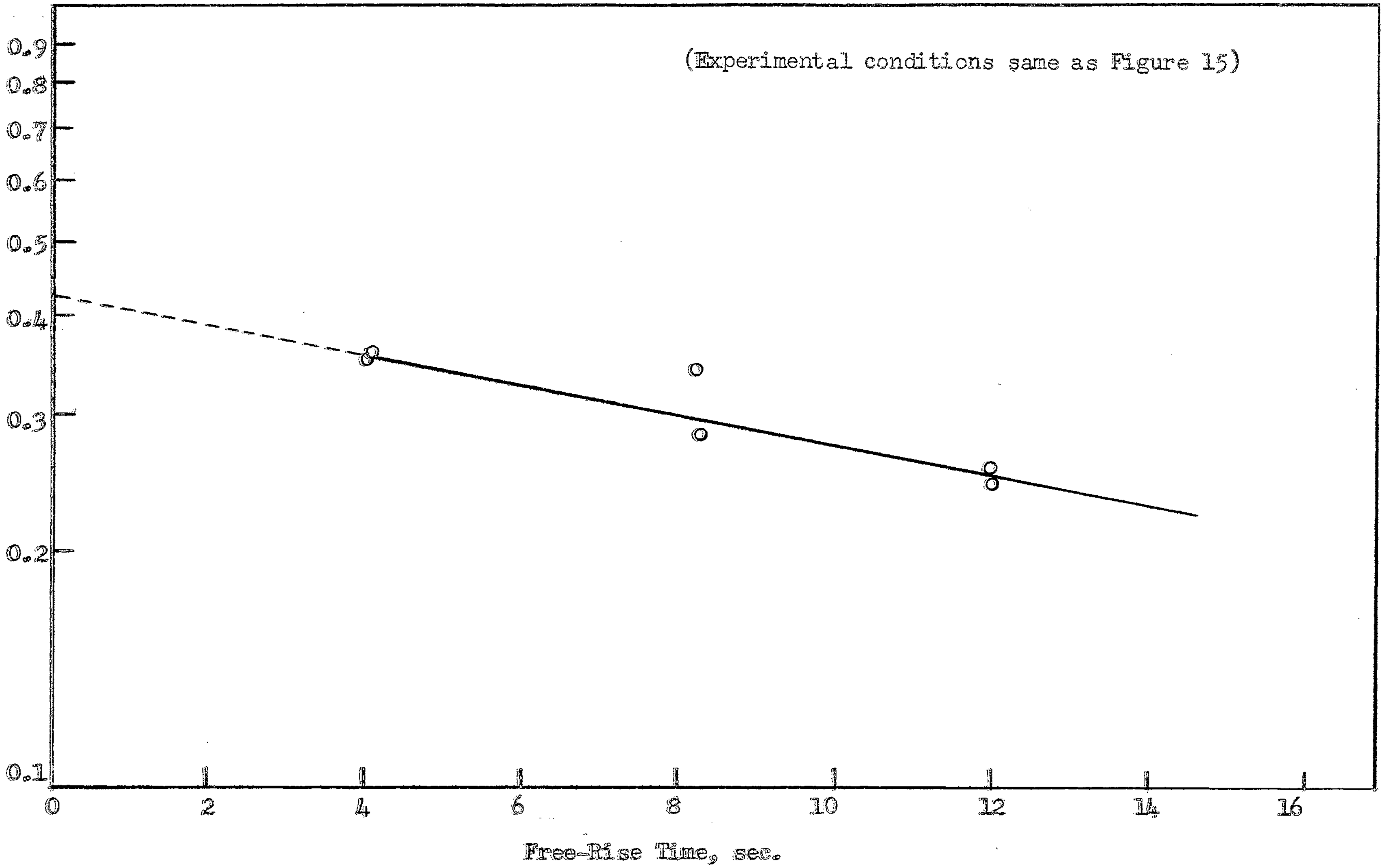


Figure 20. Amount of Solute Unextracted as a Function of Free-Rise Time for the Transfer of 1-Methylnaphthalene to Drops

TABLE XIII

CORRELATION FACTOR

System	Column height, inch	Correlation factor
Transfer of phenol to cetane drops at 140° F. (System 1)	8.5	8.8
	18.0	12.0
	24.0	14.9
Transfer of phenol to cetane drops at 160° F. (System 2)	8.5	6.7
	18.0	10.7
	24.0	12.4
Transfer of 1-Methylnaphthalene from drops at 140° F. (System 3)	8.5	2.0
	18.0	3.2
	24.0	4.2
Transfer of 1-Methylnaphthalene from drops at 140° F. (System 4)	8.5	3.3
	18.0	3.7
	24.0	4.1
Transfer of 1-Methylnaphthalene to drops at 140° F. (System 5)	8.5	1.0
	18.0	1.0
	24.0	1.4

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The following conclusions may be drawn from the investigation:

1. Tie-lines in the triangular diagram were practially horizontal at both 140° F. and 160° F. This indicates that the 95 per cent aqueous phenol does not have significant selectivity for 1-Methylnaphthalene over cetane evaluated on the weight fraction basis.
2. Tie-line data for this system was well correlated by the Othmer and Tobias method. Hand's method did not give a straight line, making extrapolation inaccurate.
3. Experimentally determined over-all mass transfer coefficients increased with an increase in temperature and with a decrease in the solute concentration.
4. The direction of the solute transfer had a significant effect on the mass transfer rate. Mass transfer rate of 1-Methylnaphthalene from droplets

was greater than mass transfer rate to droplets.

5. Handlos and Baron's mathematical model for predicting the over-all mass transfer coefficients did not give satisfactory results. However, the general tendency for an increase or a decrease in the numerical values of the over-all transfer coefficients coincided with the experimental values.
6. In general, end effects were large, and a significant proportion of the solute transferred was transferred during drop formation and coalescence.
7. Korchinski's correlation factor for mass transfer varied appreciably with the column height, suggesting that the amount of solute transferred to and from droplets had considerable effect on the internal circulation of the drop.

Recommendations

The following items are considered to be of value for future studies:

1. The Othmer and Tobias tie-line correlation gave a straight line at the lower range of solute concentration. Further study is recommended in the vicinity of plait point to confirm that a straight line extrapolation is a good approximation in that region.
2. The relationships between the structure and size of the solute molecule being transferred and the

mass transfer rate deserves further consideration.

3. The effect of changing drop diameters on the mass transfer rates.
4. Determination of the optimum drop size. As drop size becomes larger, circulation currents inside the drop become significant, increasing the extraction rate. However, stage efficiency decreases as drop size increases. This would suggest the possibility of an optimum drop size existing for a given system.
5. An increase in the flow rate of dispersed phase gives rise to the rolling and rocking of droplets, increasing the extraction rate during free-rise. But, the extraction rate during formation and coalescence will decrease. The effects of both the continuous and dispersed phase flow rates should be investigated further.

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APPENDIX A

DEFINITION OF TERMS

a - Drop radius, cm.

A_n - Constant used with Equation (6).

B_n - Constant used with Equation (1).

C_1 - Solute concentration at the nozzle, gm./ml.

C_2 - Solute concentration just before release from the nozzle, gr./ml.

C_3 - Solute concentration just before coalescence, gm./ml.

C_4 - Solute concentration at the column outlet, gm./ml.

C^* - Solute concentration of dispersed phase in equilibrium with the bulk phase.

d - Drop diameter, cm.

D - Molecular diffusivity, cm^2/sec.

E - Effective diffusivity, cm^2/sec.

E - Transfer efficiency.

E_F - Combined end effect.

E_{f1} - End effect at entry end for dispersed phase, $(C_1 - C_2)/(C_1 - C^*)$.

E_{f2} - End effect at exit end for dispersed phase, $(C_3 - C_4)/(C_3 - C^*)$.

E_m - Transfer efficiency during steady-rise period, $(C_2 - C_3)/(C_2 - C^*)$.

E_T - Over-all transfer efficiency, $(C_1 - C_4)/(C_1 - C^*)$.

k - Mass transfer coefficient, cm./sec.

K - Over-all mass transfer coefficient, cm./sec.

m - Distribution ratio.

M(0) - Mass of solute at the beginning, $t = 0$.

M(t) - Mass of solute at any time, t, in a droplet.

n - Any integer.

N - Number of transfer unit.

Nu - Nusselt number, kd/D.

Pe_i - Inside Peclet number dV/D.

Pe_i' - Modified Peclet number, $Pe_i/(1 + \mu_i/\mu_o)$.

t - Free-rise time, sec.

V - Drop velocity, cm./sec.

X - Weight fraction.

X_A - Weight fraction of A.

X_{AA} - Weight fraction of a in A-rich phase.

X_{CA} - Weight fraction of C in A-rich phase.

Greek Letters

μ - Viscosity, centipoise.

μ_n - Constant used with Equation (4).

λ_n - Eigenvalues.

Subscripts

i - Dispersed phase property.

o - Continuous phase property.

D - Based on dispersed phase concentration.

APPENDIX B

SUPPLEMENTARY DATA FOR THE DETERMINATION OF PHASE EQUILIBRIA

TABLE XIV

REFRACTIVE INDEX AS A FUNCTION OF COMPOSITION FOR THE CETANE-1-METHYLNAPHTHALENE SYSTEM AT 80° F. and 160° F.

Wt. Per Cent Cetane	Refractive Index* 80° F.	160° F.
0.00	1.6097	1.5872
7.97	1.5920	1.5693
19.26	1.5666	1.5447
28.66	1.5470	1.5254
38.61	1.5283	1.5070
47.58	1.5124	1.4911
54.98	1.4980	1.4787
68.11	1.4780	1.4577
76.02	1.4650	1.4460
86.05	1.4510	1.4316
100.0	1.4317	1.4130

*Measured by AO Spencer 1591 Refractometer.

TABLE XV

REFRACTIVE INDEX AS A FUNCTION OF COMPOSITION FOR THE CETANE-1-METHYLNAPHTHALENE SYSTEM AT 140° F.

Wt. Per Cent Cetane	Refractive Index* 140° F.
0.00	1.5930
9.98	1.5700
13.72	1.5620
23.19	1.5420
32.29	1.5240
40.08	1.5091
46.64	1.4980
54.79	1.4840
63.14	1.4701
74.58	1.4527
88.63	1.4327
100.00	1.4176

* Measured by AO Spencer 1591 Refractometer

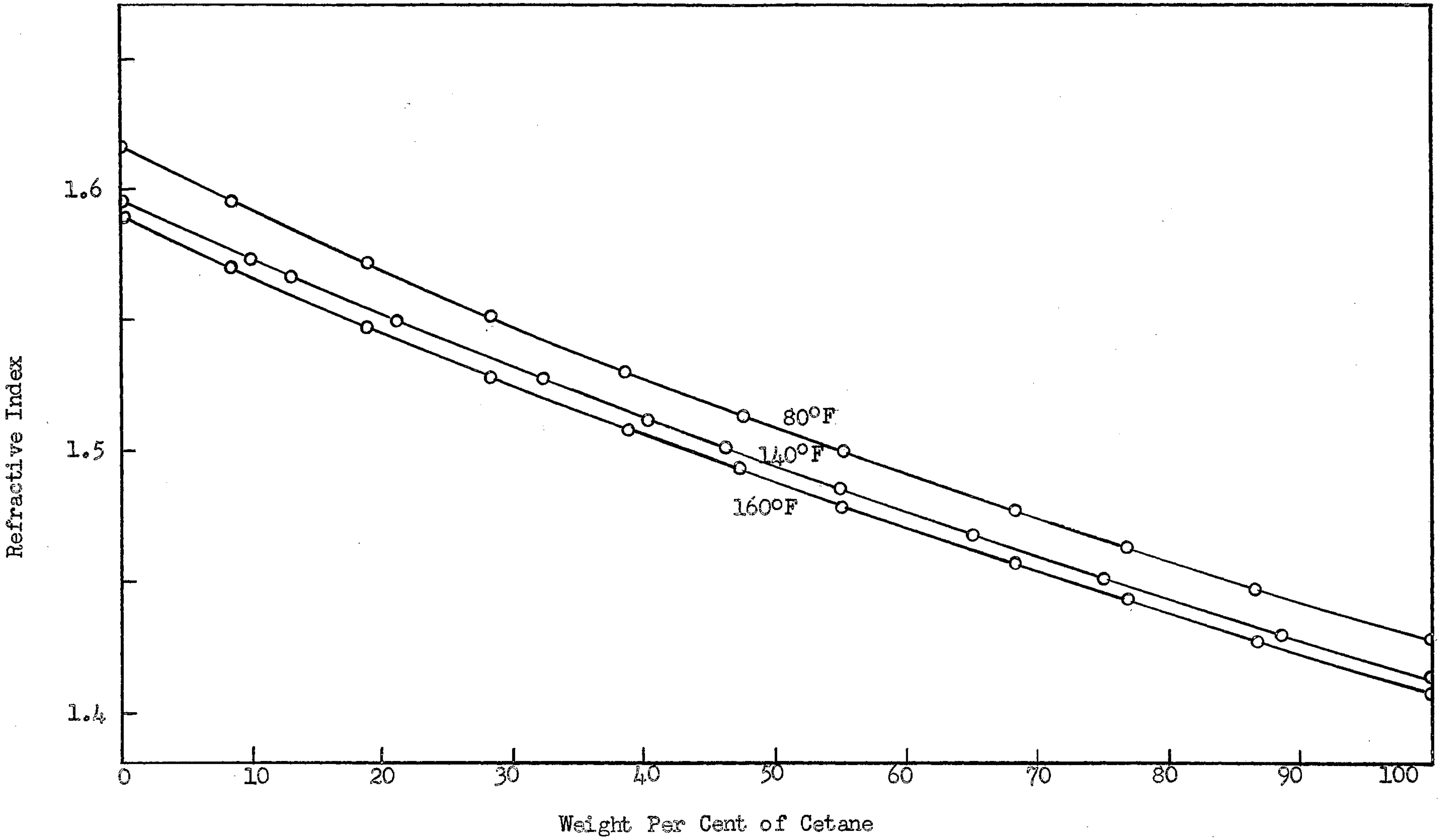

Figure 21. Refractive Index as a Function of Composition for the Cetane-1-Methylnaphthalene Mixture

TABLE XVI

DENSITY AS A FUNCTION OF COMPOSITION FOR THE CETANE-1-METHYLNAPHTHALENE SYSTEM AT 25° C.

Wt. Per Cent Cetane	Density* 25° C.
0.00	1.01525
10.31	0.98290
23.55	0.94185
32.58	0.91867
35.09	0.91266
45.01	0.88679
54.64	0.86438
63.15	0.84313
70.84	0.82679
79.47	0.80822
91.42	0.78363
100.00	0.76819

* Measured by a pycnometer.

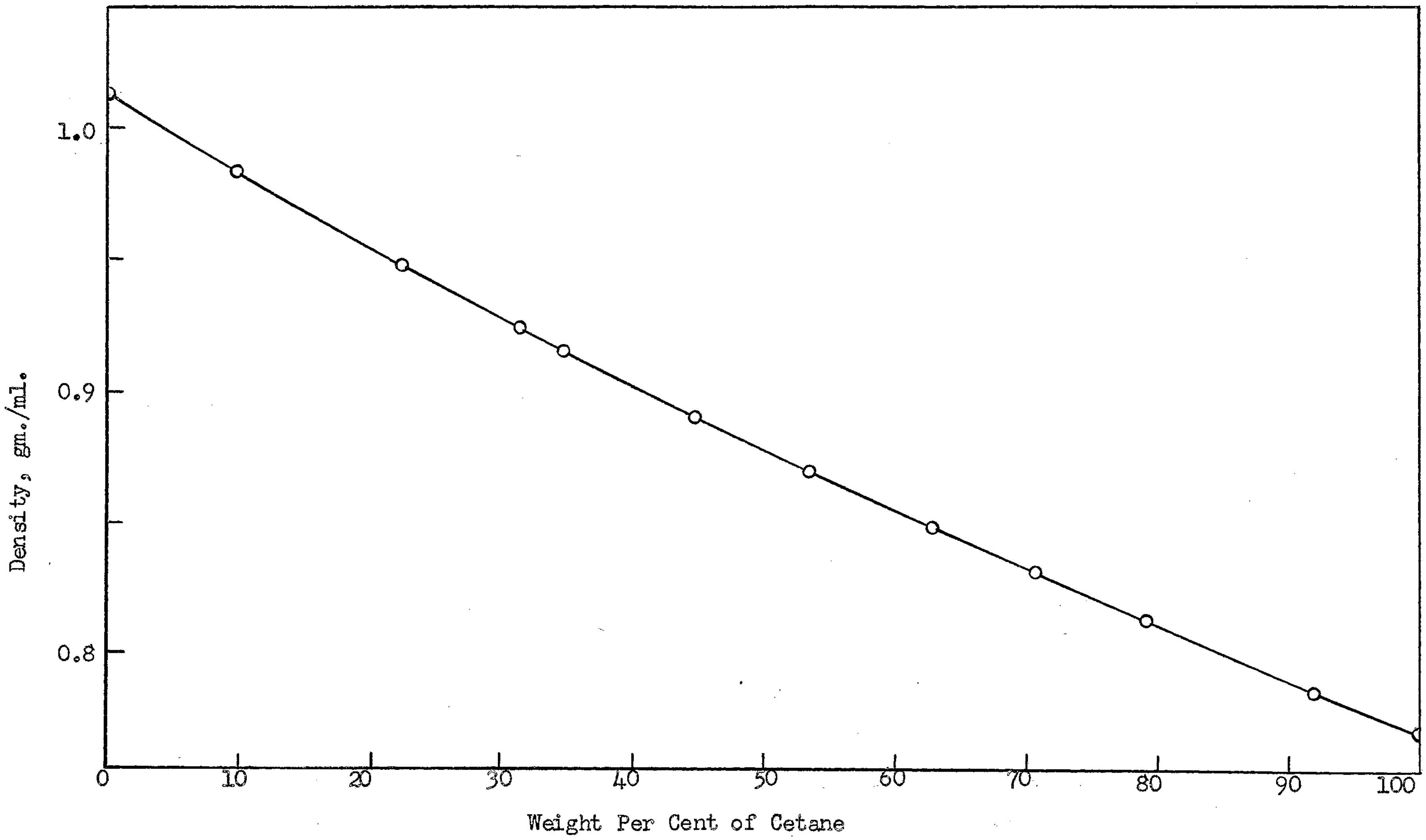

Figure 22. Density as a Function of Composition for the Cetane-1-Methylnaphthalene Mixture at 25° C.

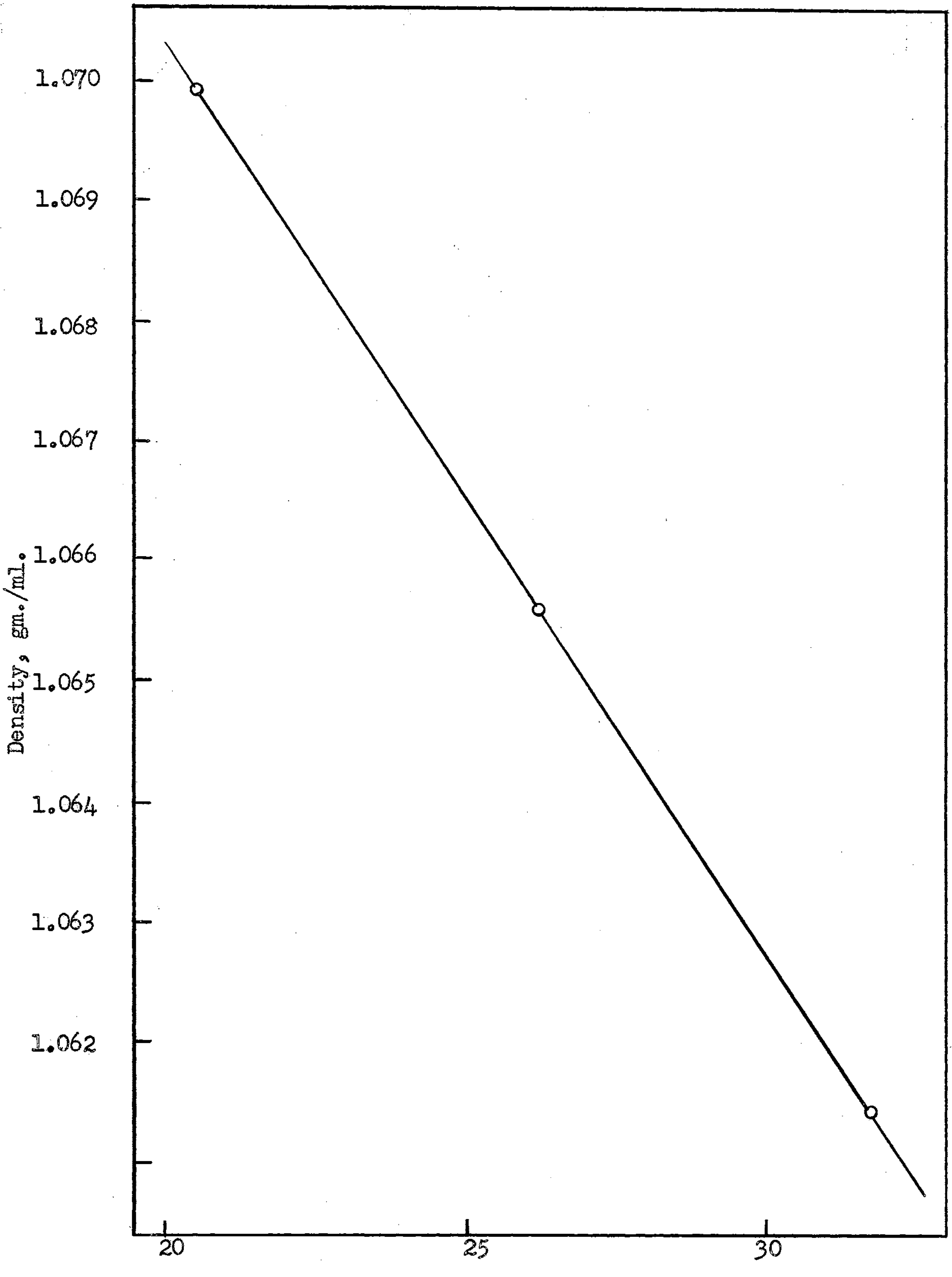

Figure 23. Density of 95 Per Cent Aqueous Phenol as a Function of Temperature

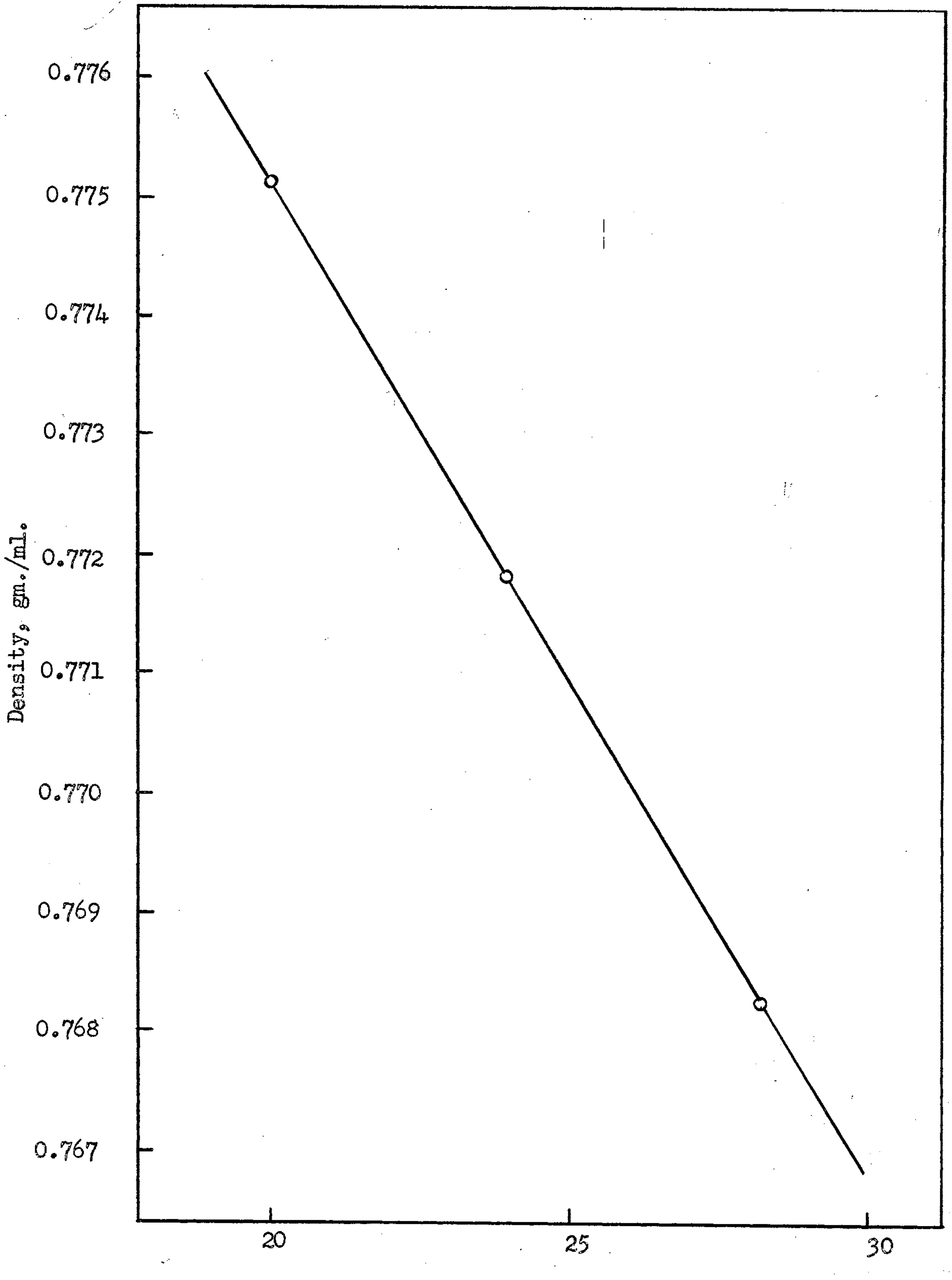

Figure 24. Density of Cetane as a Function of Temperature

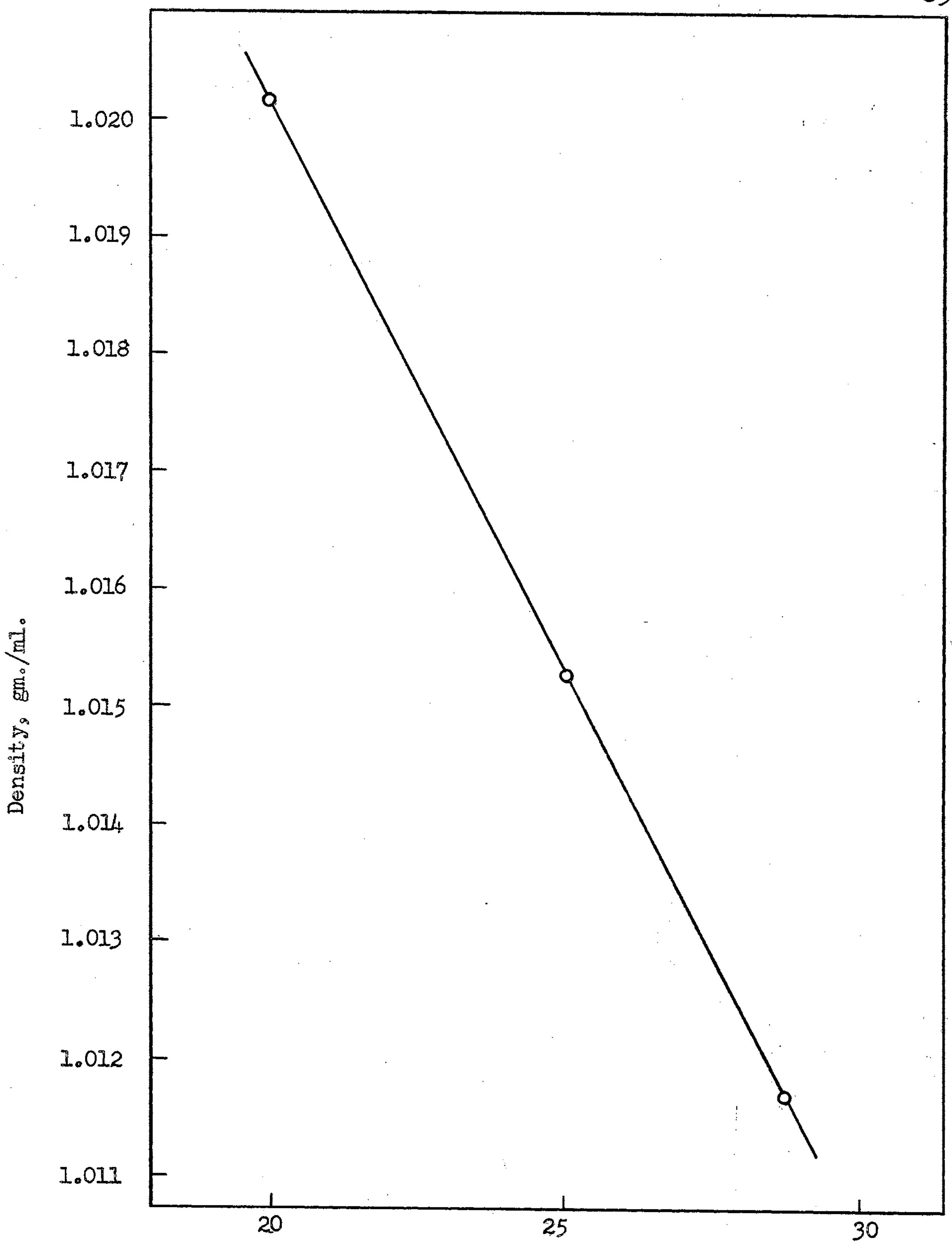

Figure 25. Density of 1-Methylnaphthalene as a Function of Temperature

SAMPLE CALCULATION OF
PHASE COMPOSITION

			Density	Units Weight	Weight Fraction
Charge:	Phenol	20 ml (25.56° C.)	1.0661 gm./ml.	21.322 gm.	0.4548
	Cetane	20 ml (")	0.7704 gm./ml.	15.408 gm.	0.3287
	1-MN	10 ml (")	1.0147 gm./ml.	10.1473 gm.	0.2165

Upper Phase:

Bottle (10) 36.4858 gm.

Bottle + Upper phase 45.0150 gm.

Net upper phase 8.5292 gm.

After NaOH extraction

Oil phase

Volume 8.66 ml

Ref. Ind. 1.4530

Composition 74.30% cetane

Density 0.8194 gm./ml.

Weight 8.66 x 0.8194 = 7.096 gm.

Cetane = 7.096 x 0.743 = 5.2723 gm.

1-MN = 7.096 x 0.257 = 1.8237 gm.

Phenol by difference

8.5292 - 7.0960 = 1.4332 gm.

Weight fractions:

Cetane = 5.2723/8.5292 = 0.6182

1-MN = 1.8237/8.5292 = 0.2138

Phenol = 1.4332/8.5292 = 0.1680

Lower Phase:

Bottle (9)	36.2910 units gm.
Bottle + Lower phase	46.3906 units gm.
Net lower phase	10.0996 units gm.

After NaOH extraction

Oil phase

Volume	3.55 ml
Ref. Ind.	1.5190
Composition	34.95% cetane
Density	0.9126 gm.

Weight = 3.55 x 0.9126 = 3.2397 gm.

Cetane = 3.2397 x 0.3495 = 1.1323 gm.

1-MN = 3.2397 x 0.6506 = 2.1074 gm.

Phenol by difference:

10.0996 - 3.2397 = 6.8599 gm.

Weight fractions:

Cetane = 1.1323/10.0996 = 0.1121

1-MN = 2.1074/10.0996 = 0.2087

Phenol = 6.8599/10.0996 = 0.6792

APPENDIX C

EXPERIMENTAL DATA AND PHYSICAL PROPERTIES FOR MASS TRANSFER STUDIES

TABLE XVII

TRANSFER OF PHENOL TO CETANE DROPS AT 140° F.

Cont. phase = 95% aq. phenol saturated with cetane

Disp. phase = pure cetane

Run No.	Column height inch	Cont. phase flow rate ml/min.	Drop formation time sec.	Free-rise time sec.	Drop velocity cm/sec.	Drop diameter cm	Dispersed phase outlet conc. gm/ml.
1	24	5.7	1.1	8.1	7.52	0.1883	0.04274
2	24	5.7	1.2	8.0	7.62	0.1880	0.04295
3	24	5.7	0.95	8.2	7.44	0.1844	0.04280
4	18	5.6	1.0	5.8	7.87	0.1920	0.03984
5	18	5.6	1.1	5.9	7.75	0.1941	0.03963
6	18	5.6	1.0	5.8	7.87	0.1959	0.03934
7	8.5	5.7	1.0	2.5	8.64	0.1952	0.03065
8	8.5	5.7	1.1	2.6	8.31	0.1953	0.03100
9	8.5	5.7	1.2	2.4	8.99	0.1969	0.03081

TABLE XVIII

PHYSICAL PROPERTIES OF PHASES AT 140° F.

	95% aq. Phenol saturated with cetane	Cetane saturated with 95% aqueous phenol
Density* gm. per ml.	1.05185	0.75637
Viscosity** centipoise	2.0285	1.3851
Surface Tension*** dynes per cm.	32.78	25.18
Interfacial Tension*** dynes per cm.	2.76	

* Measured by Fisher Westphal balance.

** Measured by Ostwald viscometer, No. 100.

*** Measured by Cenco-DuNoüy Tensiometer.

TABLE XIX

TRANSFER OF PHENOL TO CETANE DROPS AT 160° F.

Cont. phase = 95% aq. phenol saturated with cetane

Disp. phase = pure cetane

Run No.	Column height inch	Cont. phase flow rate ml/min.	Drop formation time sec.	Free-rise time sec.	Drop velocity cm/sec.	Drop diameter cm	Dispersed phase outlet conc. gm/ml.
10	8.5	6.5	0.9	2.7	8.00	0.1772	0.03282
11	8.5	6.5	0.9	2.7	8.00	0.1778	0.03113
12	8.5	6.5	0.9	2.6	8.31	0.1787	0.03181
13	18	6.3	0.9	6.4	7.14	0.1736	0.05118
14	18	6.3	1.0	6.5	7.04	0.1760	0.05062
15	18	6.3	1.0	6.4	7.14	0.1755	0.04986
16	24	6.2	1.1	8.6	7.09	0.1748	0.05607
17	24	6.2	1.0	8.5	7.16	0.1733	0.05635
18	24	6.2	1.1	8.6	7.09	0.1748	0.05717

TABLE XX

PHYSICAL PROPERTIES OF PHASES AT 160° F.

	95% aq. Phenol saturated with cetane	Cetane saturated with 95% aqueous phenol
Density* gm. per ml.	1.03242	0.75239
Viscosity** centipoise	1.5346	1.0593
Surface Tension*** dynes per cm.	32.25	24.67
Interfacial Tension*** dynes per cm.	2.59	

* Measured by Fisher Westphal balance.

** Measured by Ostwald viscometer, No. 100.

*** Measured by Cenco-DuNoüy Tensiometer.

TABLE XXI

TRANSFER OF 1-METHYLNAPHTHALENE FROM CETANE DROPS AT 140° F.

Cont. phase = 95% aq. phenol saturated with cetane

Disp. phase = cetane saturated with phenol containing 0.1015 gm. of 1-Methylnaphthalene per 1 ml. of the solution

Run No.	Column height inch	Cont. phase flow rate ml/min.	Drop formation time sec.	Free-rise time sec.	Drop velocity cm/sec.	Drop diameter cm	Dispersed phase outlet conc. gm/ml.
19	24	5.4	1.2	9.3	6.55	0.184	0.0178
20	24	5.4	1.2	9.4	6.49	0.181	0.0191
21	24	5.4	1.2	9.3	6.55	0.183	0.0198
22	18	5.3	1.1	7.0	6.53	0.185	0.0216
23	18	5.3	1.2	6.9	6.63	0.182	0.02506
24	18	5.3	1.2	6.9	6.53	0.183	0.0232
25	8.5	5.3	1.1	3.3	6.54	0.186	0.0291
26	8.5	5.3	1.1	3.3	6.54	0.185	0.0275
27	8.5	5.3	1.2	3.3	6.54	0.182	0.0328

TABLE XXII

PHYSICAL PROPERTIES OF PHASES AT 140° F.

	Continuous phase*	Dispersed phase **
Density gm. per ml.	1.05185	0.77630
Viscosity centipoise	2.0285	1.2690
Surface Tension dynes per cm.	32.78	22.50
Interfacial Tension dynes per cm.	1.48	

* 95% aqueous phenol saturated with cetane.

** cetane saturated with phenol contianing 0.1015 gm of 1-Methylnaphthalene per 1 ml. of solution.

TABLE XXIII

TRANSFER OF 1-METHYLNAPHTHALENE FROM CETANE DROPS AT 140° F.

Cont. phase = 95% aq. phenol saturated with cetane

Disp. phase = cetane saturated with phenol containing 0.2030 gm. of 1-Methylnaphthalene per 1 ml. of the solution

Run No.	Column height inch	Cont. phase flow rate ml/min.	Drop formation time sec.	Free-rise time sec.	Drop velocity cm/sec.	Drop diameter cm	Dispersed phase outlet conc. gm/ml.
28	8.5	8.1	1.1	4.0	5.40	0.140	0.01790
29	8.5	8.1	1.1	3.9	5.53	0.142	0.02180
30	18	8.0	1.0	8.4	5.44	0.142	0.01332
31	18	8.0	1.0	8.4	5.44	0.143	0.01428
32	24	8.1	1.1	11.0	5.54	0.146	0.01178
33	24	8.0	1.0	11.1	5.49	0.144	0.01085

TABLE XXIV

PHYSICAL PROPERTIES OF PHASES AT 140° F.

	Continuous phase*		Dispersed phase**
Density gm. per ml.	1.05185		0.79325
Viscosity centipoise	2.0285		1.2948
Surface Tension dynes per cm.	32.78		23.46
Interfacial Tension dynes per cm.		0.85	

* 95% aqueous phenol saturated with cetane.

** cetane saturated with phenol containing 0.2030 gm. of 1-Methylnaphthalene per 1 ml. of solution.

TABLE XXV

TRANSFER OF 1-METHYLNAPHTHALENE TO CETANE DROPS AT 140° F.

Cont. phase = 95% aq. phenol saturated with cetane containing
0.2030 gm. of 1-Methylnaphthalene per 1 ml. of solution

Disp. phase = cetane saturated with phenol

Run No.	Column height inch	Cont. phase flow rate ml/min.	Drop formation time sec.	Free-rise time sec.	Drop velocity cm/sec.	Drop diameter cm	Dispersed phase outlet conc. gm/ml.
34	24	6.0	0.9	12	5.08	0.1646	0.1133
35	24	6.0	0.9	12	5.08	0.1640	0.1154
36	18	5.9	0.8	8.2	5.56	0.1626	0.1003
37	18	5.9	0.9	8.3	5.51	0.1638	0.1097
38	8.5	6.1	0.8	4.0	5.41	0.1637	0.0997
39	8.5	6.1	0.8	4.1	5.26	0.1632	0.0981

TABLE XXVI

PHYSICAL PROPERTIES OF PHASES AT 140° F.

	Continuous phase*	Dispersed phase**
Density gm. per ml.	1.02544	0.75637
Viscosity centipoise	1.8074	1.3851
Surface Tension dynes per cm.	26.81	25.18
Interfacial Tension dynes per cm.	1.43	

* 95% aqueous phenol saturated with cetane containing 0.2030 gm. of 1-Methylnaphthalene per 1 ml. of solution.

** cetane saturated with phenol

VITA

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Master of Science

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