SOLUTE TRANSFER FROM SINGLE DROPS
IN LIQUID - LIQUID EXTRACTION

By

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PREFACE

Because liquid-liquid extraction is an effective industrial technique for the separation of materials, basic data for proper design of contacting equipment has become essential. The theory of the operation is quite inadequate because of the complexity of the hydrodynamics and chemical factors involved.

Most types of liquid-liquid contacting devices function by dispersing one liquid phase into the second liquid phase as droplets. The study of the mechanism of extraction into and from droplets may help to provide a sound theoretical basis for the unit operation.

Droplet diameter, flow rates of both phases and column height were investigated. The effect of certain chemical and physical properties, such as drop diameter, velocity of the droplet, density, viscosity and interfacial tension, on extraction rates were also studied. Attempts have been made to confirm mass transfer mechanisms that have been proposed.

I am indebted to many for their valuable guidance and assistance throughout the course of this study. Drs. J. B. West, R. N. Maddox, J. M. Marchello and the late C. L. Nickolls were particularly helpful in the literature search, equipment design, and finalization of this thesis. Messrs. E. E. McCroskey, A. L. Harris and J. Shannon were of considerable aid in construction of component parts of the extraction unit. I am indebted to the Department of Chemistry for financial assistance as a Teaching Assistant.

Most of all, I am forever indebted to my wife, Judy, for her continued interest and aid throughout the last two years of my college work.

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CHAPTER I

INTRODUCTION

Because of its effectiveness as a complement to distillation in the separation of materials, liquid-liquid extraction has assumed considerable importance as one of the unit operations of chemical engineering. Many investigations have been conducted to determine the rate of mass transfer, by liquid-liquid extraction in spray towers, (17), (21), (23), perforated plate columns (30), and pulse columns. The results have provided only empirical knowledge of these transfer rates. Therefore, investigators recognized the need to separate the mass transfer into basic studies of formation, free-rise and coalescence of the droplets.

Improvement in the design of spray-type extraction towers and their characteristics, such as column height and diameter, number and size of nozzles, flow rates, and the effect of coalescence and redispersion by perforated plates, without extensive trial and error, cannot be achieved unless the effect of physical properties of the systems on the extraction efficiencies during each of the three distinct stages of extraction is first obtained.

It has been found that the physical, chemical and hydrodynamic properties such as viscosity, density, interfacial tensions, velocities, drop diameter, diffusivity and flow rates, have a great influence on the amount of extraction during all three stages. Various mass transfer mechanisms have been proposed for each of the three stages of extraction. Higbie (16), Heertjes (17), and Johnson (19) have proposed mechanisms for extraction rates during formation and coalescence. The amount of extraction during the free-rise of the droplet is governed by convection currents around and inside the drop, which are established by physical and chemical properties of the system. Mechanisms of mass transfer for stagnant drops (11), (33), partial circulation (22), and full circulation accompanied by oscillation (15), (19), (25), have been proposed. Also, free-rise extraction rates have been correlated with various chemical, physical and hydrodynamic properties to describe the degree of circulation within the droplets (6), (15).

The objectives of this research study were reached by transferring the solute from the organic droplet to the aqueous continuous phase.

The objectives to be attained were:

1. To evaluate the experimental transfer rates and confirm any of the mass transfer mechanisms that have been proposed;
2. To correlate the rate of extraction in terms of physical and chemical properties by successive variable elimination;
3. To obtain extraction rate coefficients which will aid in the design of spray and perforated plate columns.

CHAPTER II

REVIEW OF SINGLE DROPLET EXTRACTION

The first of many investigations in liquid-liquid extraction from single droplets was that of Sherwood, Evans and Longcor (30). The next investigation was that of West, et al., (34), who tried to verify the results of Sherwood, but without success. Licht and Conway (23) then proposed the basic premise, "that in the life of each drop there must be three distinct stages and the mechanism of solute transfer in each stage must be studied separately." The motivation for this premise was the variance of their results with those of the two previous investigators. The stages proposed were:

1. Drop formation;
2. Drop rise or fall in steady state;
3. Drop coalescence of dispersed phase at the terminal end of the column.

Since the proposal by Licht and Conway, many investigators have attempted to provide mechanisms which would describe the rate of solute transfer during each stage.

End Effects

The combined end effects are usually obtained by plotting the fraction of solute extracted against column height or an equivalent, free-rise time and then extrapolating to zero column height or time. Sherwood, Evans and Longcor followed this procedure, but they assumed that the intercept at zero height was the fraction extracted during drop formation, which was erroneous. This is one reason why Licht and Conway had such difficulty in verifying Sherwood's results.

Many attempts have been made to measure end effects (4), (5), (16), (17), (19), (23), (25), (30), (34). From these investigations several mechanisms have been proposed. By assuming Higbie's (16) equation for transient diffusion into the surface of the drop as it is formed, Heertjes (17) developed the following equation for the formation efficiency:

$$E_f = \frac{20.6}{d} \sqrt{\frac{D\theta_f}{\pi}} \qquad (1)$$

Where:

E_f = transfer efficiency during formation = $C_1 - C_2/C_1 - C^*$
d = drop diameter
D = molecular diffusivity
θ_f = drop formation time.

Licht and Pansing (25) assumed unsteady state diffusion into a plane surface with an area equivalent to that of a sphere. They obtained the following expression:

$$E_f = \frac{2.90\ m}{d} \sqrt{\frac{D\theta_f}{\pi}} \qquad (2)$$

where:

m = Equilibrium distribution ratio (C_a/C_o).

Johnson and Hamielec (19) have presented a mechanism for the transfer efficiency during coalescence. In this mechanism it is assumed that, as each drop coalesces, it spreads a layer of initial uniform concentration (C_3) across the previously settled dispersed phase and that transient mass transfer occurs until the next drop arrives to cover the surface. This mechanism is given by the expression:

$$E_c = \frac{2A_i}{v} \sqrt{\frac{D\theta_f}{\pi}} \qquad (3)$$

where:

A_i = interfacial area at coalescence
v = drop volume.

Johnson and Hamielec combined their coalescence mechanism with the formation mechanism of Heertjes (17) for an expression for the combined end effects:

$$E_F = E_f + E_c - E_f \times E_c$$

$$= \left(\frac{20.6}{d} + \frac{2A_i}{v} \right) \sqrt{\frac{D\theta_f}{\pi}} - \left(\frac{41.2}{d} \; \frac{A_i}{v} \; \frac{D\theta_f}{\pi} \right) \qquad (4)$$

Free-Rise

The mechanisms proposed for the transfer efficiency during free-rise are based on the degree of circulation within the droplet and the amount of resistance in the continuous phase.

For the efficiency of the steady-rise period for a stagnant drop with continuous phase transfer resistance, Grober (11) derived the following expression:

$$E_M = 1 - 6 \sum_{n=1}^{\infty} B_n \exp. \left(\frac{-\lambda_n^2 \, D\theta_M}{r^2} \right) \qquad (5)$$

where:

$$E_M = \frac{C_2 - C_3}{C_2 - C^*}$$

For the particular case of no resistance to transfer in the continuous phase the above expression has been reduced by Grober to the following form:

$$E_M = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp. \left(- \frac{n^2 \pi D \, \theta_M^2}{r^2} \right) \qquad (6)$$

Kronig and Brink (22) proposed a mechanism in which the interior of the drop is assumed to contain streamline currents resulting from the drag of the continuous phase against the drop. The assumptions made in the mathematical solution of the differential rate equation were: That the drop was spherical and had a Reynolds number less than unity; and that the resistance in the continuous phase was negligible. With the preceding boundary conditions they obtained the following expression:

$$E_M = 1 - 3/8 \sum_{N=1}^{\infty} B_n^2 \exp.\left(\frac{-\lambda_N \, 16 \, D \, \theta_M}{r^2} \right)$$

The first two eigenvalues and coefficients have been evaluated (25) as:

$$\lambda_1 = 1.678 \qquad B_1 = 1.32$$

$$\lambda_2 = 9.83 \qquad B_2 = 0.73$$

Another type of solute transfer mechanism was originally proposed by Higbie (16) in connection with gas absorption. He attempted to show that even though a liquid film may exist around a gas bubble, the actual time of contact of the gas with the liquid at any point was so short that the film acted equivalent to an infinite medium with respect to solute transfer.

West, et al.,(34) have indicated how this theory might be applied to liquid-liquid extraction. They have assumed that in addition to the transient film in the continuous phase proposed by Higbie , a transient film is constantly being formed in certain areas on the surface of the drop. This film moves over the surface of the drop and it is enriched with solute and then disappears into the bulk of the continuous phase. Their mechanism is basically the same as the two film theory but with a more detailed picture of the films. For the particular case in which the film of the continuous phase side offers negligible resistance,

$$k_o = \infty \ , \ m = \frac{C_a}{C_o} \gg \frac{D_c}{D_o} \quad \text{and } K_o = k_i.$$

Then

$$\log (1 - E_M) = - 2.95 \sqrt{\frac{DV}{d^3}} \ f_c \ \theta_M \tag{8}$$

where:

$$f_c \leqq 1,$$

and the effective life of the films can be related to the time for the drop to travel a distance equal to its own diameter,

$$t_L = d/V \quad f_c^{\ 2} \tag{9}$$

Handlos and Baron (15) proposed a circulation model which included radial motion for their mechanism:

$$\ln (1 - E_M) = \ln 2 B_1^2 - \frac{_1\lambda \ \ 16D \ t \ \ Pe'}{d^2 \quad 2048} \tag{10}$$

they also obtained an expression for the effective diffusivity as a function of the radius of the drop.

$$E(r) = \frac{D \ Pe'}{2048} \quad (6r^2 - 8r + 3) \tag{11}$$

Thus the multiplication factor of the molecular diffusivity is directly proportional to the modified Peclet number.

$$R = \frac{Pe'}{2048} \int_o^i \quad (6r^2 - 8r + 3) \quad dr = \frac{Pe'}{2048} \tag{12}$$

$$R = \frac{dV}{D(1 + \frac{u_o}{u_a}) \ 2048} \tag{13}$$

Other correlation factors have been proposed. Kronig and Brink (22) say that under the conditions of their model a value of R should be about 3.

The latest mechanism that has been proposed is that of Johnson and Hamielec (19). For low efficiency studies, they have obtained the following empirical relationship:

$$E_M = 0.905 \sqrt{\frac{RD\pi^2 t}{r^2}} + 0.0189 \qquad (14)$$

For high efficiency studies they have combined the equation of Grober and the multiplication factor of molecular diffusivity presented by Handlos and Baron. The resulting expression is:

$$E_M = 1 - 6 \sum_{n=1}^{\infty} B_n \ \exp. \left(\frac{-\lambda_n^2 \ RDt}{r^2} \right) \qquad (15)$$

Overall Transfer Coefficient and Correlation

From the circulation model of Handlos and Baron, a correlation for the inside or dispersed phase mass transfer film coefficient was presented:

$$k_i = \frac{0.00375 \ V}{\left(1 + \frac{u_o}{u_a}\right)} \qquad (16)$$

Another proposal has been that of West, et al., in conjunction with their transient film mechanism:

$$k_i = 2 \sqrt{\frac{D \ V \ f_c^2}{d}} \qquad (17)$$

where:

$(d/V \ f_c^2)$ = the contact time of the film.

Whitman's "two-film" model can be simplified into the "one-film" model by saturating the continuous phase with the solvent of the dispersed phase and assuming that:

1. The concentration at the interface of the droplet is that of the bulk of the continuous phase;
2. The continuous phase resistance is negligible; that is, there is very little mass transfer into the droplet;
3. The ratio of the solute capacity of the continuous phase to that of the dispersed phase is large; thus the concentration of the continuous phase is approximately zero.

This has been done so that the film coefficient of the dispersed phase becomes equal to the overall transfer coefficient. This can be readily seen from the expression:

$$\frac{1}{K_o} = \frac{1}{mk_o} + \frac{1}{k_i} \qquad (18)$$

Where:

K_o = overall coefficient
k_o = outside film coefficient
k_i = inside film coefficient
m = distribution ratio, C_a/C_o.

If m is large and k_o is infinite, K_o then becomes equal to k_i.

Because many investigators felt the experimental agreement with transfer mechanisms proposed was fortuitous, they have attempted to correlate the transfer rates with physical and chemical properties of the systems. Believing that the rates of transfer were functions of viscosity, density, velocity, drop diameter, molecular diffusivity and interfacial tension, they have, by successive variable elimination, correlated the rates in terms of the Reynolds, Schmidt and Weber numbers.

Garner, et al., (6) found that for spherical drops with circulation, but no oscillation, the transfer rates should correlate with $Re^{1/2}Sc^{1/3}$ for stagnant drops and $Re^{1/2}Sc^{1/2}$ for drops with full circulation patterns.

However, for most drops an intermediate case will be obtained. Therefore, the exponent of the Schmidt number will lie between (1/2) and (1/3). For drops that exhibit oscillation, which is purely a hydrodynamic effect, the exponent of the Reynolds number will be changed due to the altered flow patterns around the drop. Garner (6), et al., obtained the following correlation:

$$Sh = -126 + 1.8\,(Re)^{.5}\,(Sc)^{.42} \tag{19}$$

SUMMARY

The study of liquid-liquid extraction in spray towers has been separated into three individual stages of extraction--drop formation, free-rise, and coalescence. Various mass transfer mechanisms for each stage have been proposed. These mechanisms attempt to describe mathematically the rates of extraction produced by various types of liquid films and the circulation patterns which they develop. Because it has not been possible to experimentally determine when circulation starts or the effect of oscillation on circulation patterns, investigators have attempted to describe the effect on the extraction rates by dimensional analysis of the system properties.

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURE

Experimental Apparatus

The experimental apparatus used in this investigation is shown in Figure 1 and Plate 1. Preceding the design of the single droplet extraction column, the literature listed in the Bibliography was reviewed, and an attempt made to incorporate the features of other studies in the construction of this column.

Column Construction

The column consisted of three rectangular glass sections, each 5.5 in. by 6.5 in. and 10.5 in. in height. The equivalent cylindrical diameter was made greater than 5.5 in. in order to eliminate excessive wall effects (32). Teflon gaskets were placed between each section in order to eliminate possible sources of contamination caused by chemical reactions of the continuous or dispersed phase with material used in column construction. The glass sections were made by cutting the bottoms out of Pyrex battery jars. The top and bottom plates of the column were made of 3/16 in. stainless steel on an 8 in. square.

Nozzles

The nozzles used were chamferred away from the opening at a 45° angle to prevent spreading of the dispersed phase onto the metal around the opening (27). In the table below listing each nozzle and its dimensions, a number has been assigned to each and all references to particular nozzles will be made by these numbers.

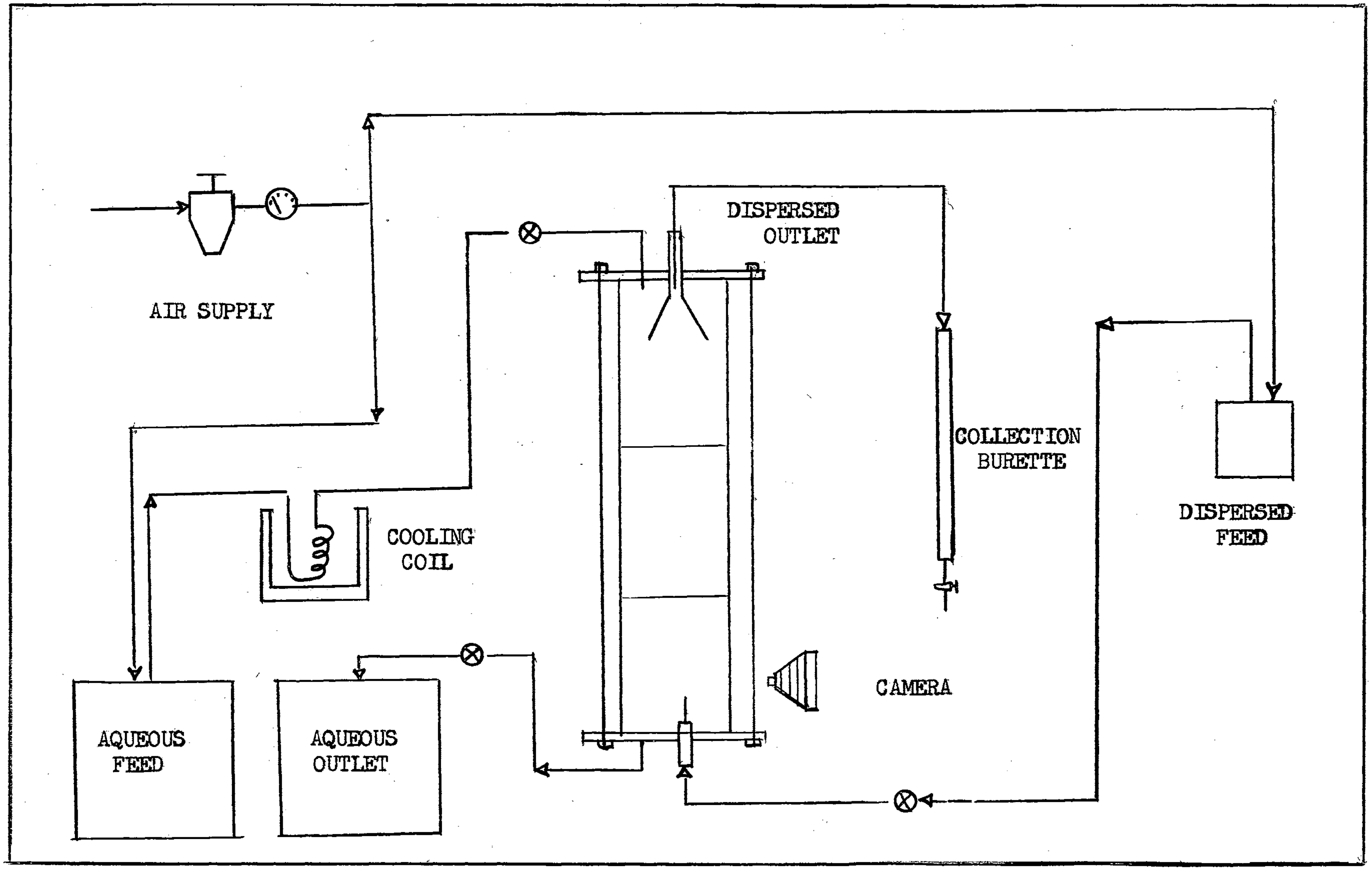


FIGURE 1, SCHEMATIC DIAGRAM OF SINGLE DROPLET EXTRACTION UNIT

PLATE I

DROPLET EXTRACTION COLUMN

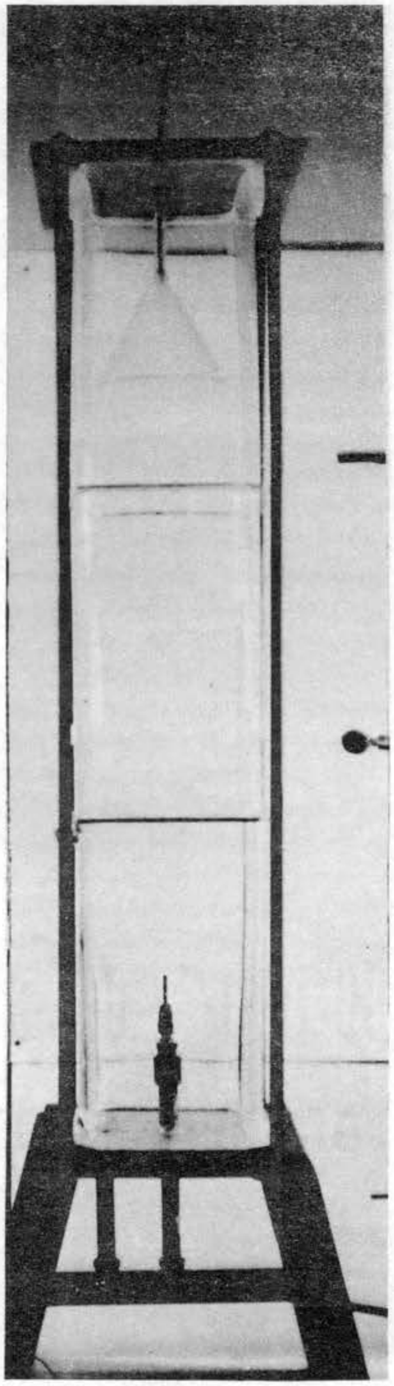


TABLE I

DESCRIPTION OF EXPERIMENTAL NOZZLES

No.	Description	O.D.	I.D.
1	Copper Cap. Tubing	0.00175	0.00121 in.
2	Brass 1/8 in. Half Union		0.125 in.
3	Copper Tubing	0.25	0.1785 in.
4	Copper Tubing	0.375	0.250 in.

Photographs of these nozzles are presented in Plates II and III.

Collection

The collection devices used for the dispersed phase are shown in Figure 2 and Figure 2A. The funnel shown in Figure 2 was 80 mm. in diameter, and a 1/8 in. copper tube was sealed in the stem of the funnel and used to siphon the dispersed phase. The other funnel differed in that the dispersed phase was collected in the stem of the funnel, and 3 mm. glass tubing was used to siphon the dispersed phase. The siphoned dispersed phase was collected in a 50 ml. burrette.

Lines and Fittings

All valves used were 1/4 in. Hoke stainless steel needle valves with Teflon gaskets. All lines were 1/4 in. copper tubing with flare type fittings with the following exceptions: Exit line for continuous phase was 3/8 in. copper tubing; line for removal of coalesced phase using funnel in Figure 2 was 1/8 in. copper tubing; when the funnel in Figure 2A was used, 1/4 in. polyethylene tubing connected to glass tubing was used.

Materials

The two systems selected for droplet extraction work were: Methyl isobutyl ketone - acetic acid - water; and toluene - acetic acid - water.

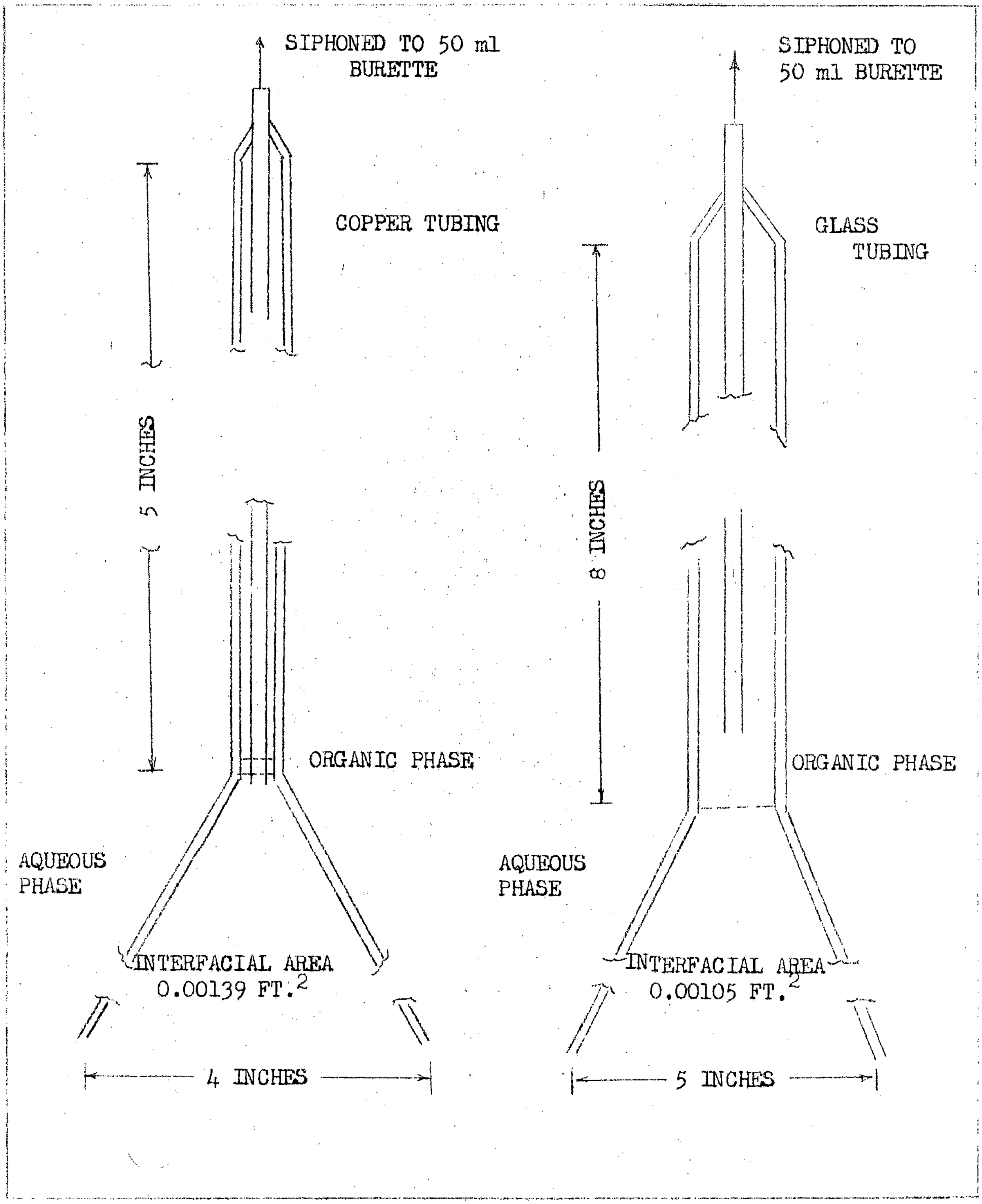
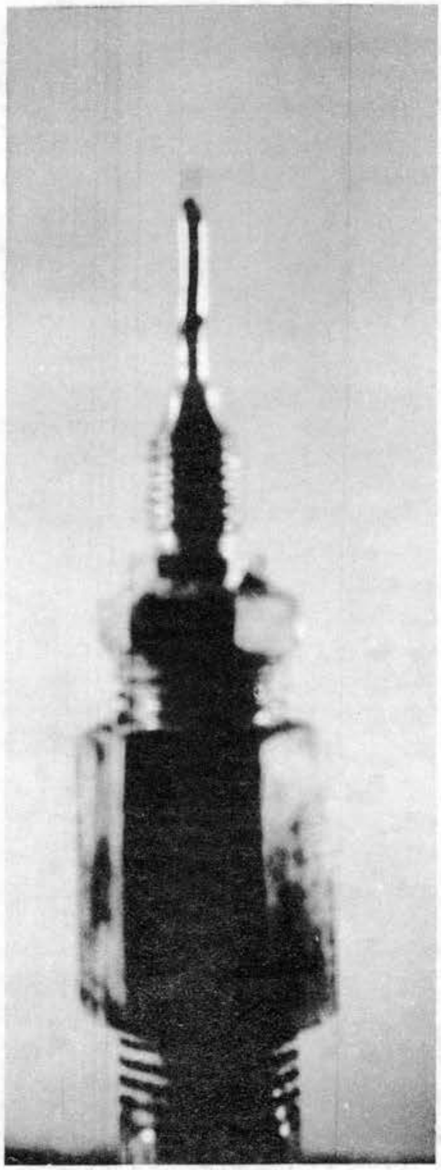


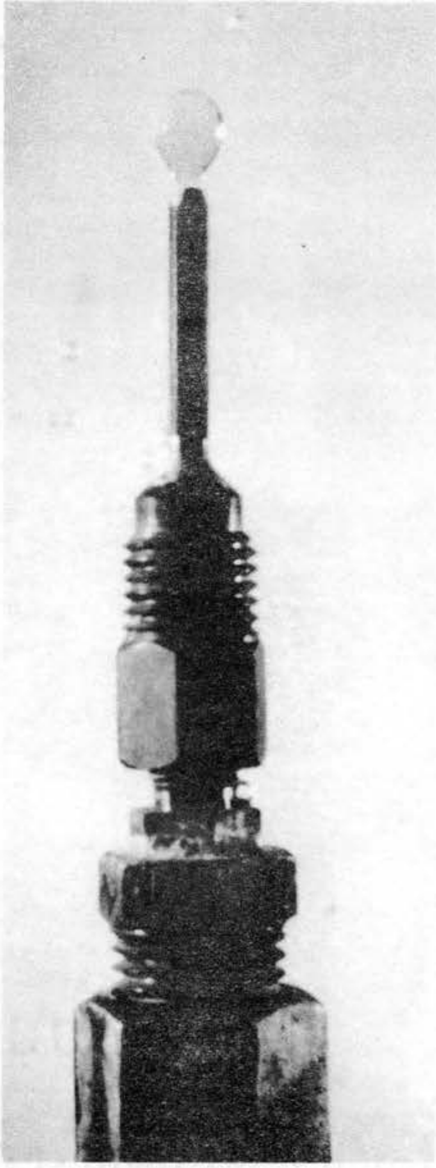
FIGURE 2, COLLECTION DEVICES FOR DISPERSED PHASE

PLATE II

NOZZLES USED FOR DISPERSING ORGANIC PHASE



NUMBER I NOZZLE
TOLUENE DISPERSED

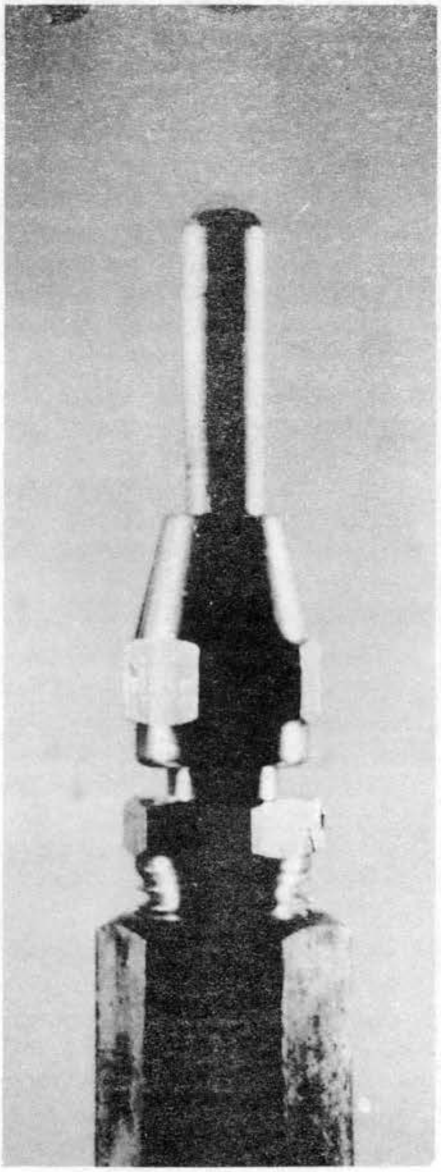


NUMBER II NOZZLE
TOLUENE DISPERSED

PLATE III

NOZZLES USED FOR DISPERSING ORGANIC PHASE

NUMBER III NOZZLE
TOLUENE DISPERSED



NUMBER IV NOZZLE
TOLUENE DISPERSED

The methyl isobutyl ketone and acetic acid were purified grade, as received from the Fisher Chemical Company. The toluene was obtained from Phillips Petroleum Company and was a technical grade. Once distilled city tap water was the other component. These two systems have been widely used for extraction studies (5), (24), (30), (20), (21).

Physical Properties

The physical properties of the two systems were obtained by the following means:

1. Density - Pychometer
2. Viscosity - Cannon-Fenske Viscometer
3. Interfacial tensions - Capillary rise method

TABLE II

PHYSICAL PROPERTIES OF EQUILIBRATED AQUEOUS AND ORGANIC PHASES*

Methyl Isobutyl Ketone - Acetic Acid - Water

	Aqueous	Organic
Density, gms./cc.	0.993	0.8025
Viscosity, cp.	0.925	0.5895
Interfacial Tension, dynes/cm.	7.35	
Acid Concentration, lb. moles/ft.^{3}	0.0	0.0108

Toluene - Acetic Acid - Water

	Aqueous	Organic
Density, gms./cc.	0.994	0.863
Viscosity, cp.	0.926	0.568
Interfacial Tension, dynes/cm.	17.1	
Acid Concentration, lb. moles/ft.^{3}	0.0	0.0103

*Data was obtained at 77° F.

Experimental Procedure

Drop Studies

Preliminary studies were conducted to determine the terminal velocities of the dispersed phase for a particular drop size. The experimental data was compared with that of previous investigators, (5), (15), (20), (21), and with that of perfect spheres, (5). This is shown in Figures 19 and 20 of Appendix D. This study was made so that the drop diameters obtained from the photographs could be used to check the velocities recorded during experimental runs. Thus, if wall effects or any abnormal effect occurred which altered the velocity, it would be noted.

The column was constructed so that photographic studies could be made from one of the flat sides. Photographs were made using a 35 mm. Agfa Karat 36 camera with a +6 enlarging lens. This enabled the author to obtain the photographs from a distance of 6 in. from the drops. The film used was Eastman Kodak Plus X. The best results were obtained at a shutter speed of 1/300 sec. and a lens opening of f/11. Flood lamps were placed perpendicular to the direction of the camera and about 6 in. from the side of the column walls. A white background provided the best contrast.

The photographs shown in Plate IV are typical of those obtained in this study. However, a small amount of iodine was added to increase the reflectivity of the drops. This was done by adding 0.005 gm. of iodine to 500 ml. of the organic phase. Then a 3 ml. sample was injected into the dispersed stream at a point 2 ft. from the nozzle outlet by means of a hypodermic syringe. No difference in the equivalent drop diameter was found in the photographs of the dispersed phase containing iodine and the photographs of the dispersed phase which did not contain iodine under the same experimental conditions. Photographs were taken at the nozzle tip and at a point 1 ft. above the nozzle. The equivalent diameter at these two points agreed within a 3 per cent deviation. Drop velocities were measured at the same time the photographs were taken.

The column contained two small beads which were adjusted in height so that they would appear in the photographs of the drops as a reference. They were the same distance from the lens of the camera as the drops. The smaller bead was 0.168 inches in diameter, and the larger bead was 0.271 inches in diameter.

Measurements obtained from the photographs made it possible to compute an equivalent spherical volume for each drop, based on an ellipsoid of revolution about the minor axis. The volume of an ellipsoid of revolution about the minor axis is given by the expression: (29)

$$V = 4/3\ (\pi\ a^2 b) \tag{20}$$

where:

a = major axis
b = minor axis.

The volume of a perfect sphere is given by the expression:

$$V = 4/3\ (\pi\ r^3) \tag{21}$$

where:

r = radius.

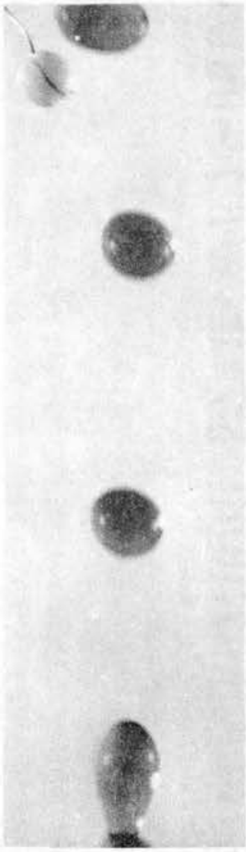
The drop volumes were also calculated from the volume of the dispersed phase collected per unit time and the number of drops per unit time. The standard error was ±7 per cent. Therefore, all diameters recorded are those values obtained from the photographs.

Temperature Control

In this study an attempt was made to keep the column temperature

PLATE IV

TYPICAL PHOTOGRAPHS OF DROPS DURING EXPERIMENTAL RUN



NUMBER III NOZZLE
TOLUENE DISPERSED

NUMBER II NOZZLE
TOLUENE DISPERSED

NUMBER III NOZZLE
TOLUENE DISPERSED

NUMBER IV NOZZLE
TOLUENE DISPERSED

at 77±0.2° F. This was done by allowing the continuous phase to pass through a cooling coil which was surrounded by water at 67° F. Before entering the cooling coil, the water was usually at 82° F., depending on the room temperature. Two thermometers were placed in the column, one about 3 in. from the bottom and the other about 5 in. from the top level of the continuous phase. By development of experimental technique, the author was able to maintain the temperature standard reported above. The thermometers were calibrated before being used in the column.

Flow Rate Control

An air pressure of 2 psig. was maintained on both the continuous and dispersed feed tanks during all experimental runs. The flow rate of the continuous phase was maintained at 4 liters per hr. For the dispersed phase, methyl isobutyl ketone, the drop rate was 120 drops per min. for 32 runs. For the dispersed phase, toluene, a drop rate of 60 drops per min. was maintained for 32 runs, and 120 drops per min. for 8 runs.

During the early part of this work it was noted that if the drop rate was above 150 drops per min., the drops had a greater deviation from a vertical rise, and a large number of the drops coalesced with the preceding drops before reaching the top of the column.

Experimental Runs

The runs in which MIBK was dispersed were made at a drop rate of 120 drops per min. Two series of runs were made with each of the four nozzles. The two series were identical except for the funnel used to collect the dispersed phase. During each series four individual runs were made, each at a separate column height.

The method used in the toluene runs was the same as that of the methyl isobutyl ketone. Two series of runs were made using the same nozzle. One funnel was used for one series and another for the other series. Four individual runs were made in each series, each at a different column height. The drop rate for the eight series of runs was 60 drops per min. Also, four series of runs were made using the #1 and #2 nozzles at a drop rate of 120 drops per min. Again the two funnels were used for the two series of runs from each nozzle.

The data recorded during each run were:

1. Drop rate, D_r
2. Drop formation time, Θ_f
3. Column height, H
4. Drop rise time, Θ_t
5. Total volume collected, V_t
6. Total operation time, Θ
7. Interfacial coalescence area, A_i
8. Continuous phase temperature, t_a

Also, photographs of the drops were taken during each run. All data recorded during experimental runs are recorded in Appendix D.

A 50 ml. sample of the dispersed phase was collected during each run. The samples were titrated with 0.1 N and 0.0483 N solutions of sodium hydroxide to determine the acid concentrations of the dispersed phase at the column outlet.

CHAPTER IV

RESULTS AND DISCUSSION

Experimental Results

Drop Behavior

It was observed that methyl isobutyl ketone drops with a diameter of less than 0.115 in. remained spherical throughout free-rise. All other methyl isobutyl ketone drops and all toluene drops exhibited oscillations during free-rise. Droplets dispersed from the same nozzle and from each of the two systems had distinct but different characteristics. The drop diameters of the toluene runs were more than twice the size of the methyl isobutyl ketone drops while using the same nozzle. This can be directly attributed to the differences in the interfacial tensions because interfacial tension of the toluene system was more than twice that of the methyl isobutyl ketone system. The toluene drops also exhibited a greater deviation from a vertical free-rise.

Physical Properties

The values obtained in the measurements of the physical properties of the two systems were in agreement with those obtained by other investigators. However, one exception did exist. Values of the interfacial tension for the methyl isobutyl ketone system found in the literature ranged from 3.0 dynes/cm. to 12.5 dynes/cm. for the same acid concentrations. The experimental value obtained was 7.33 dynes/cm.

Comparison of the experimental velocity profile with that of other investigators seemed to be quite satisfactory. This comparison is shown in Figures 19 and 20 in Appendix D. These comparisons show that there were on wall effects or abnormal flow patterns in the column.

Concentration Profiles

From the experimental outlet concentrations obtained while using the same nozzle, a plot on a semilog scale of C_{in}/C_{out} against column height yielded a straight line over the range of experimentation. The smallest column height was 4 inches; therefore, it was felt that an extrapolation to zero column height could be made without serious error. The intercept obtained at zero column height was the amount of acid which was extracted by the combined end effects. The concentration profiles for the experimental runs are shown in Figures 3 through 5 of this chapter.

The method outlined in Appendix D, Page 79, for the separation of the combined end effects, which was obtained through the use of two different coalescence areas, provided consistent results. From the experimental results, the best straight line was drawn to connect the points of: Total fraction extracted; fraction extracted by the combined end effects; and the separated end effects. The difference between the total fraction extracted and the fraction extracted by the combined end effects was the fraction extracted during free-rise. These results are shown in Figures 6 and 7 of this chapter for the toluene runs, Series B, and methyl isobutyl ketone Series A.

Evaluation of Results

End Effects

The transfer efficiency during formation ranged from 8 per cent to

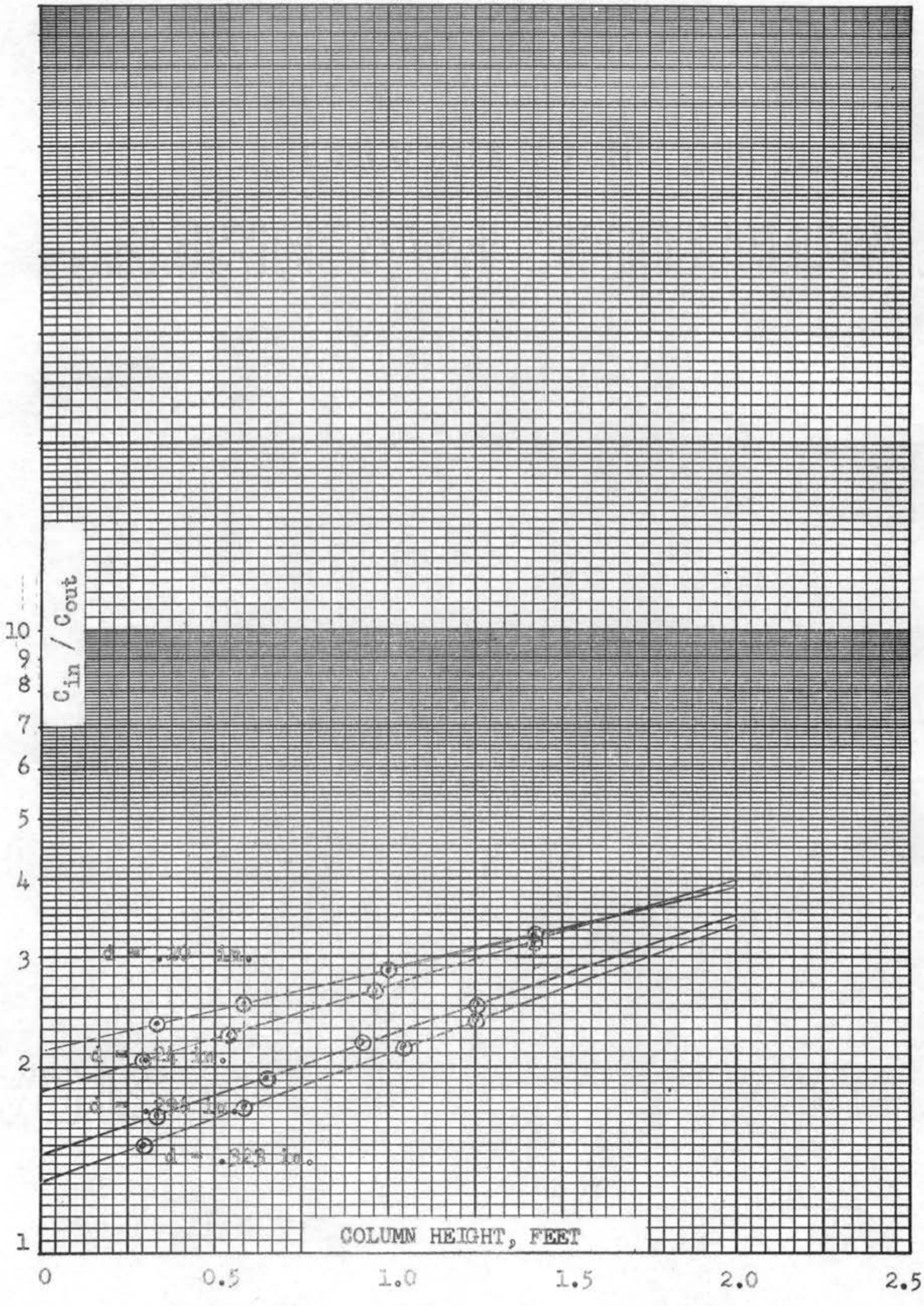


FIGURE 3, EFFECT OF COLUMN HEIGHT ON THE RECIPROCAL FRACTION OF TOLUENE UNEXTRACTED - SERIES B

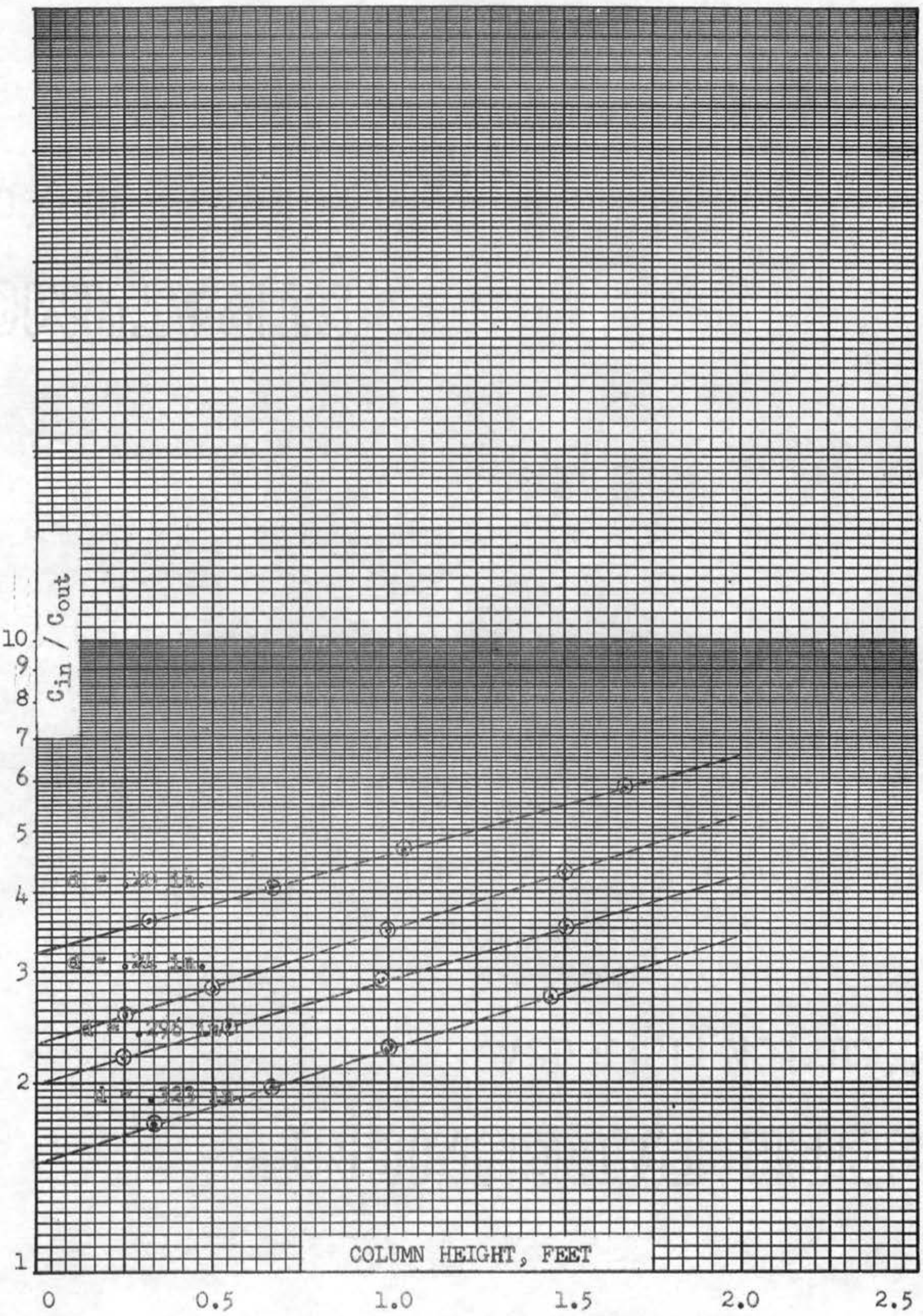


FIGURE 4, EFFECT OF COLUMN HEIGHT ON THE RECIPROCAL FRACTION OF TOLUENE UNEXTRACTED - SERIES C

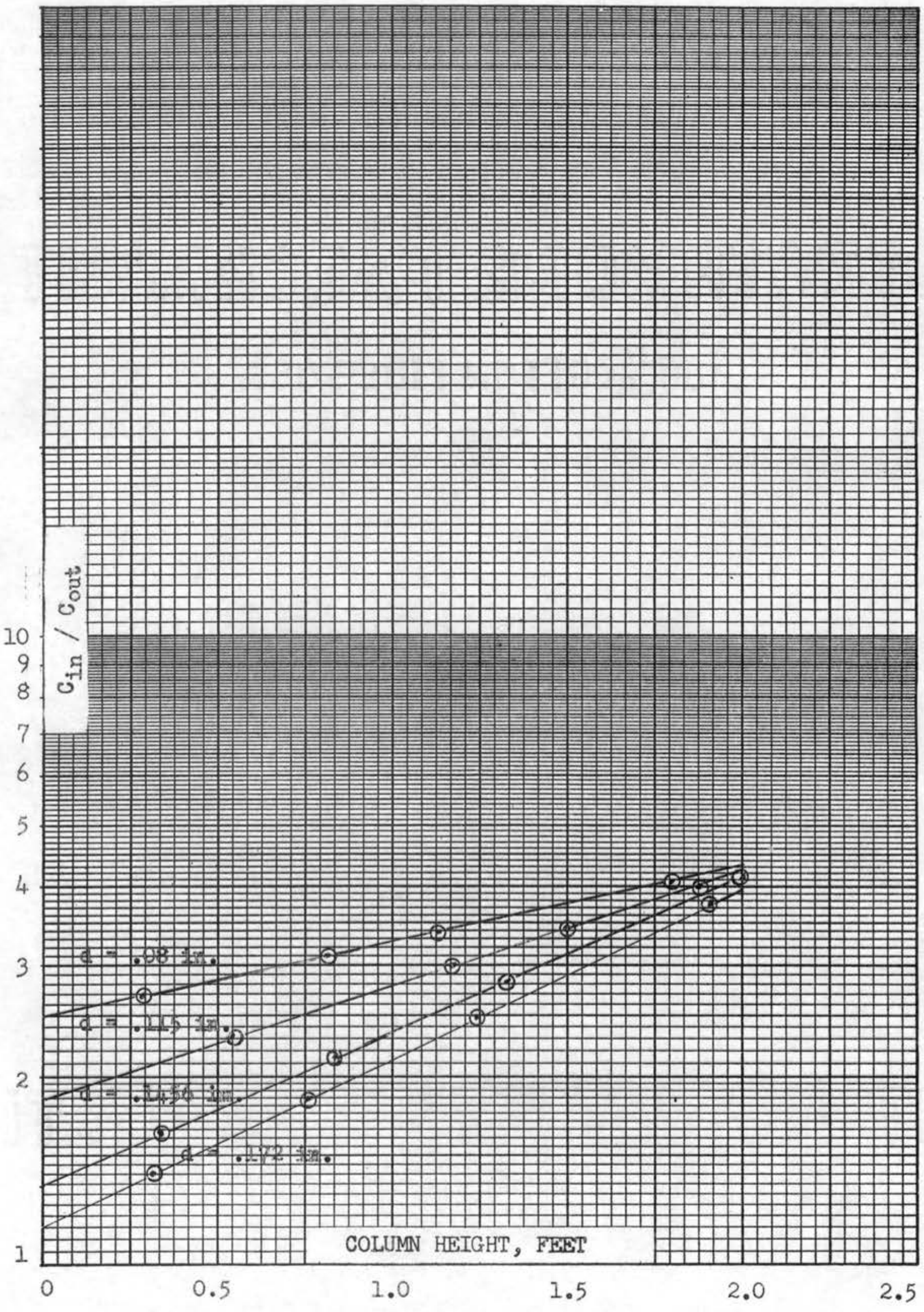


FIGURE 5, EFFECT OF COLUMN HEIGHT ON THE RECIPROCAL FRACTION OF MIBK UNEXTRACTED, SERIES A

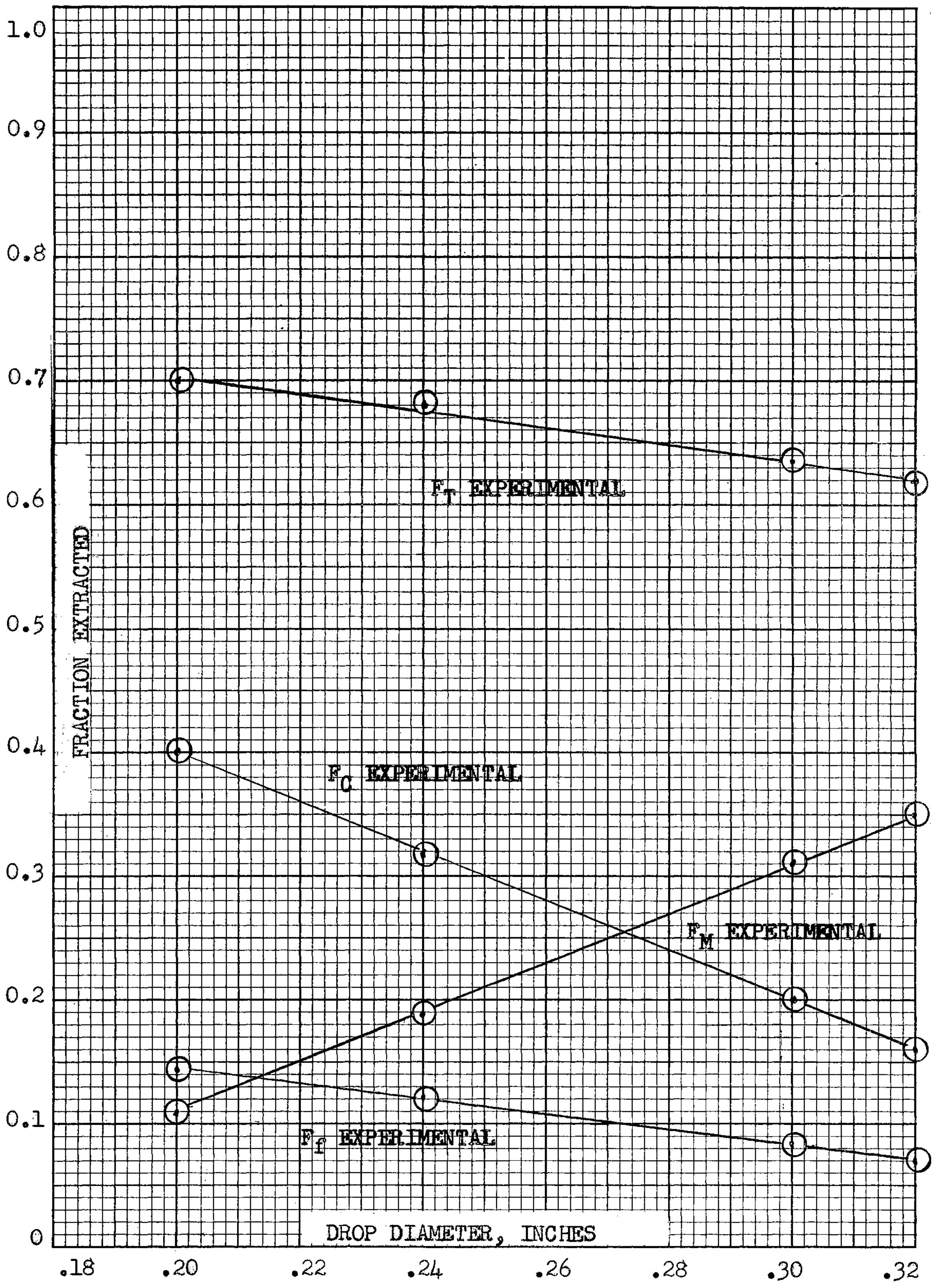


FIGURE 6, FRACTION EXTRACTED AS A FUNCTION OF DROP DIAMETER, TOLUENE DISPERSED, SERIES B

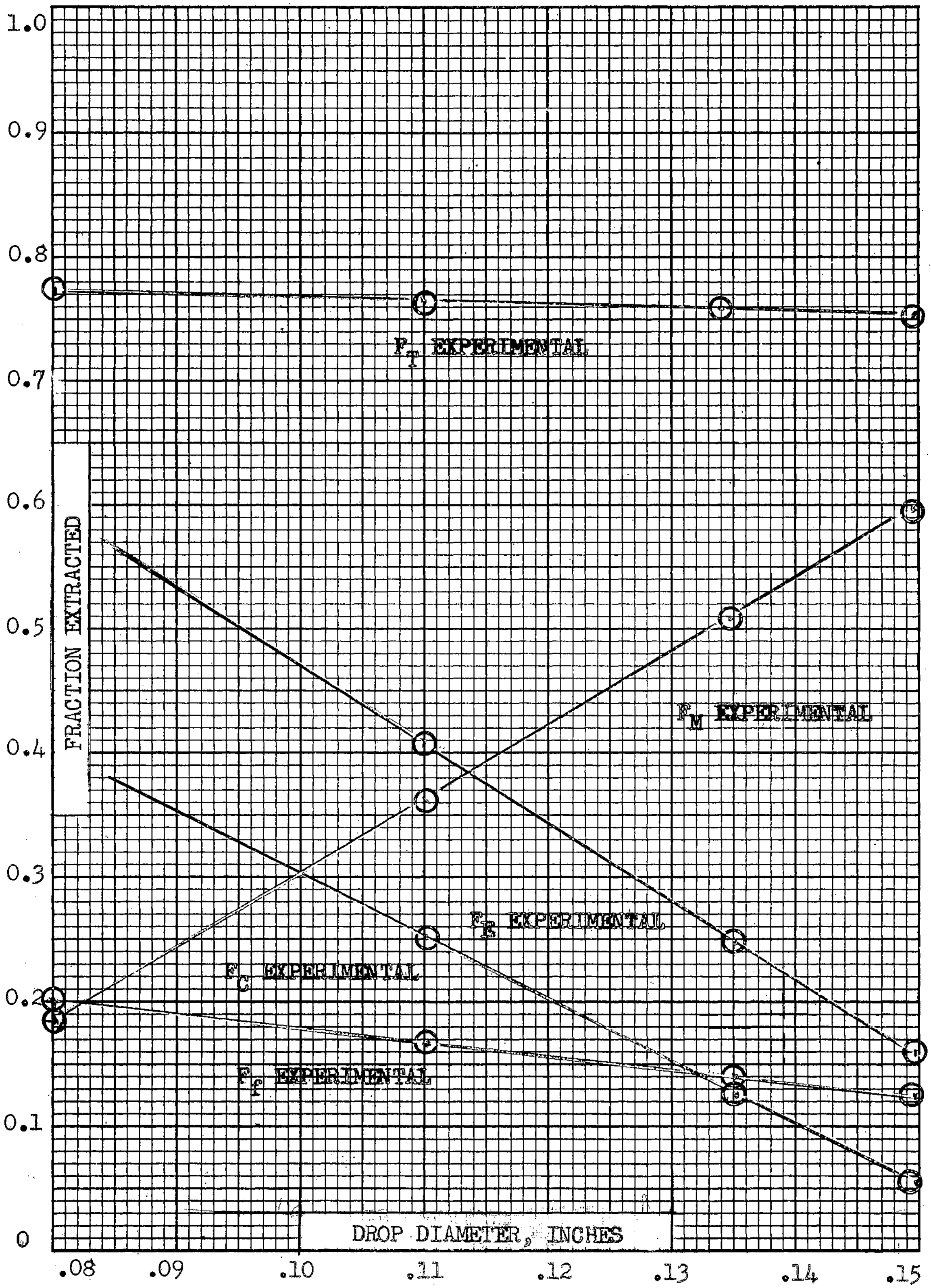


FIGURE 7, FRACTION EXTRACTED AS A FUNCTION OF DROP DIAMETER, MIBK DISPERSED

14 per cent for toluene drops with diameters of 0.323 inches through 0.20 inches. The formation transfer efficiency for methyl isobutyl ketone drops ranged from 12 per cent for 0.18 inch drops to 19 per cent for 0.08 inch drops. The only formation mechanism which was found to be applicable was that of Heertjes. The experimental value was found to be within 5 per cent of that predicted by the Heertjes equation. Licht and Pansing, using methyl isobutyl ketone droplets obtained a formation efficiency of 16.6 per cent for a 0.157 inch drop. This value obtained by Licht and Pansing was within 2 per cent of the experimental value obtained by this author.

The separation of the end effects by the method used in this work seems to be quite satisfactory by the comparison of both formation and coalescence results with those found in the literature. The only mechanism that has been presented for efficiency during coalescence has been that of Johnson. The theoretical results predicted by Johnson's equation were very unsatisfactory in comparison with the experimental results. The percentage error was 325 per cent for toluene drops and 62 per cent for methyl isobutyl ketone drops. All values obtained were larger than those predicted by Johnson's equation. The results of the toluene runs, Series b, are shown in Figure 8, and the MIBK runs, Series A, in Figure 9.

Free-Rise

Because it was possible to separate the combined end effects, the transfer efficiency during free-rise could be obtained. All of the mechanisms mentioned in Chapter II were compared with the experimental values. The circulation model of Handlos and Baron proved to be the most suddessful of those used. The multiplication factor of molecular diffusivity, R, was used for the comparison between the experimental

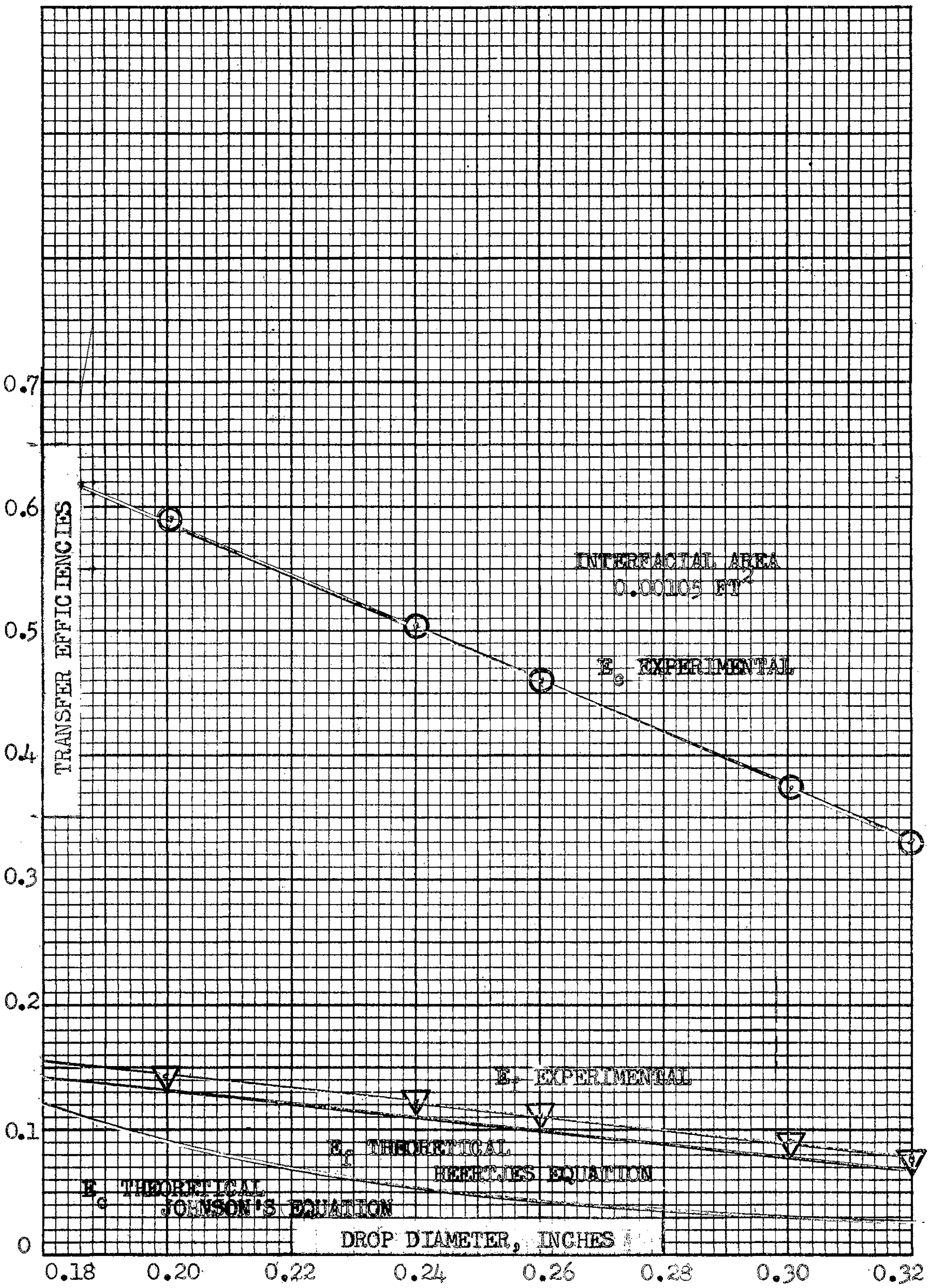


FIGURE 8, TRANSFER EFFICIENCIES AS A FUNCTION OF DROP DIAMETER, SERIES B, TOLUENE DISPERSED

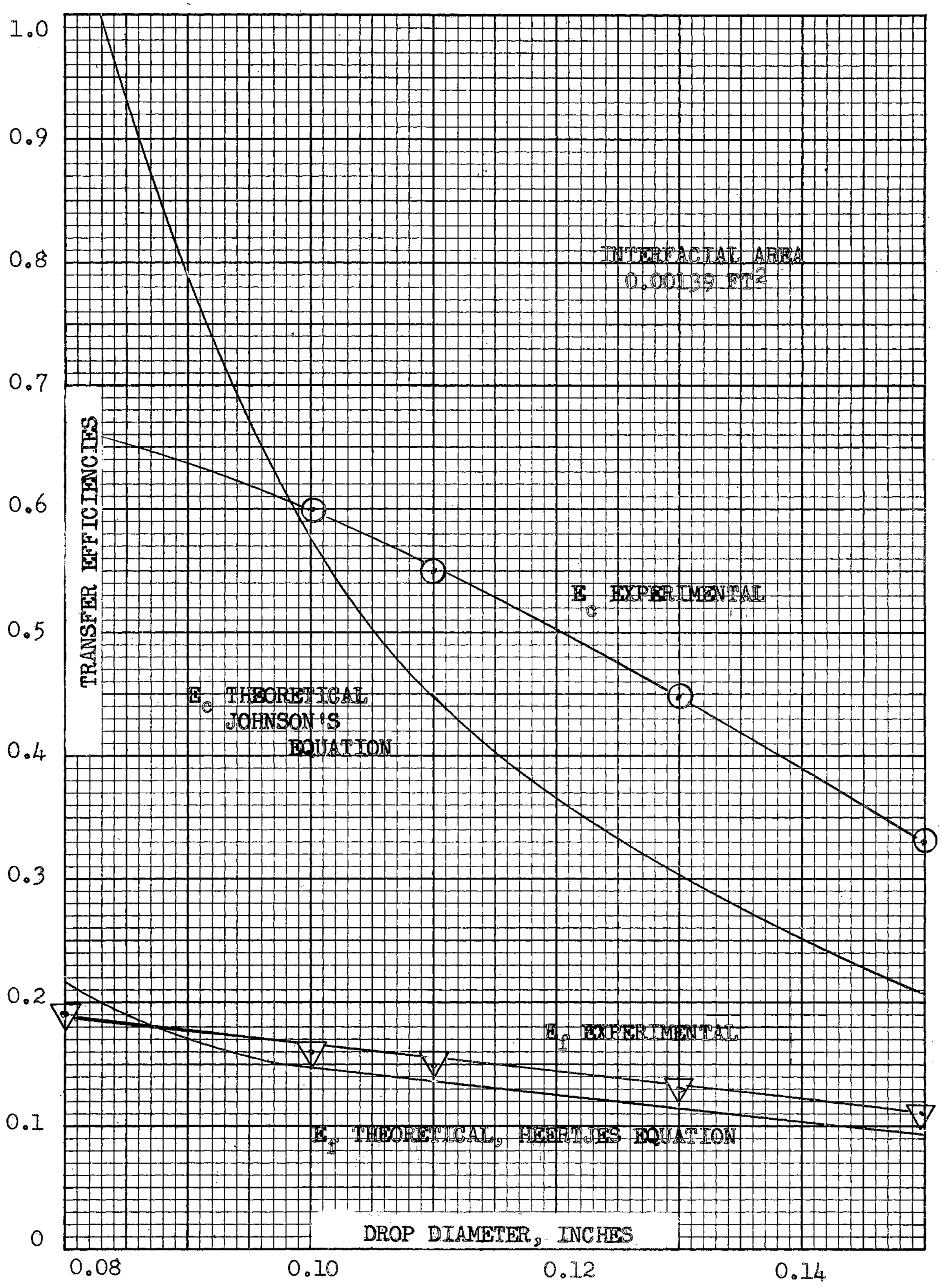


FIGURE 9, TRANSFER EFFICIENCIES AS A FUNCTION OF DROP DIAMETER, SERIES A, MIBK DISPERSED and theoretical transfer efficiencies. The experimental values of R obtained for the toluene system compared more satisfactorily with the theoretical values of R than did the methyl isobutyl ketone system. The experimental values for the toluene system were, on the average, 22 per cent below the predicted value for drops with diameters of 0.27 inches or less. The values obtained for larger toluene drops showed a sharp increase. This can be seen in Figure 10. The values obtained for the methyl isobutyl ketone system were considerably below the theoretical values of R. This is shown in Figure 11.

The multiplication factor of molecular diffusivity used to compare transfer rates obtained by other investigators with rates encountered in stagnant drops is shown in Table III. A portion of this table was abstracted from the work of Calderbank and Korchinski (3). The results presented in this table show the favorable comparison of values of R for the same Reynolds numbers. This table indicates that there could be a relationship between the Reynolds number or some other similar group with the multiplication factor. However, the amount of data is too limited for an investigation. The values of R obtained by the author follow the same pattern as that of the other investigators. The values of R presented in the table fell below the multiplication factor predicted in the Handlos and Baron model. Thus it might be said that the Handlos and Baron model represents an upper limit in the transfer rates. However, since many of the results fell below the Handlos and Baron multiplication factor, it is felt that this model does not exactly describe circulation within the droplet and results obtained from its use will be erroneous.

The experimental values of E_M, E_F, and E_T for toluene and MIBK

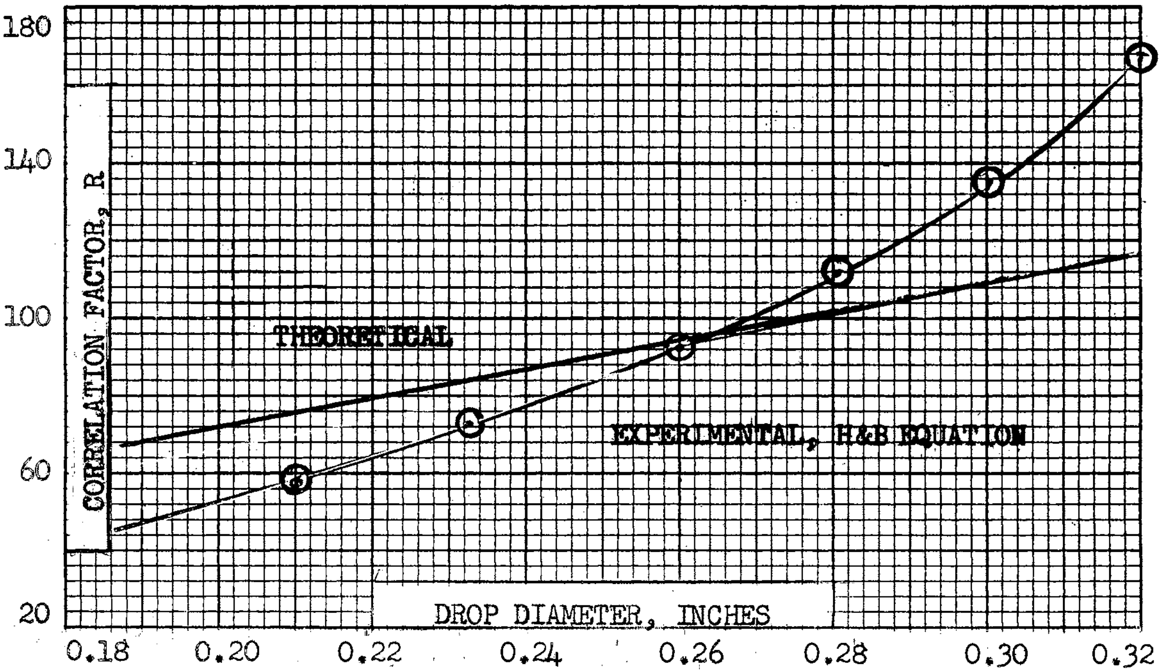


FIGURE 10, CORRELATION FACTOR AS A FUNCTION OF DROP DIAMETER, SERIES B, TOLUENE DISPERSED

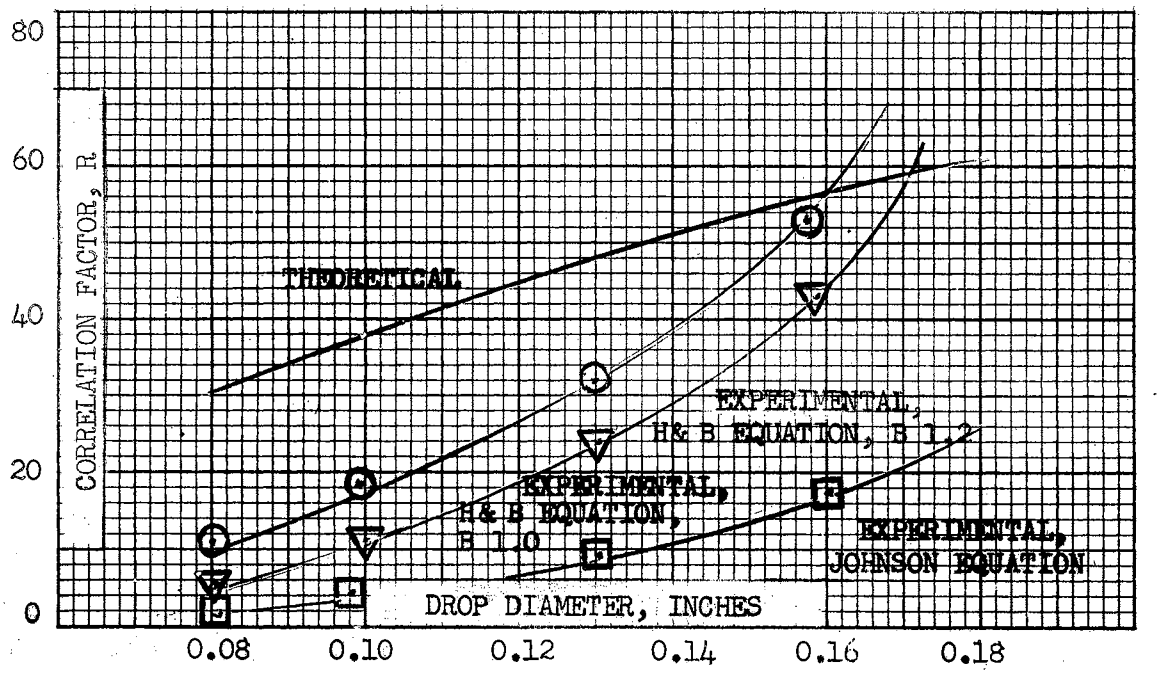


FIGURE 11, CORRELATION FACTOR AS A FUNCTION OF DROP DIAMETER, SERIES A, MIBK DISPERSED

drops are shown in Figures 12 through 14. The factors which affect these transfer efficiencies are discussed in the correlation section of this chapter.

Overall Transfer Coefficient

The overall transfer coefficient during free-rise was obtained by the evaluation of equation 7-D. The results for toluene, Series B, are shown in Figure 15. The MIBK results are shown in Figure 16. The results obtained were compared with data from spray columns. Generally the spray column data fell below that of the single droplets. This suggests that single droplet data represents an upper limit for the mass transfer in the dispersed phase. The overall coefficient has approximately the same profile as that of the velocity. The overall coefficient for both systems approached an upper limit as the drop diameters increased.

The transient film mechanism of Higbie with the f_c factor of West (Equation 16) was evaluated. For toluene drops with 0.2 inch diameters a value of $f_c = .25$ was obtained; and $f_c = .8$ was obtained for drops of 0.34 inch diameter. For methyl isobutyl ketone drops the value of f_c ranged from 0.04 for a drop diameter of 0.08 inches to 0.54 for a drop diameter of 0.18 inches. An attempt has been made to correlate the values of f_c with system properties by West et al., (34) and Licht and Pansing (25), but without success.

The mechanism of Handlos and Baron (15), (Equation 15) was also examined. The results obtained were unsatisfactory. The overall transfer coefficient profiles were approximately the same as the experimental profiles, but the theoretical values for the methyl

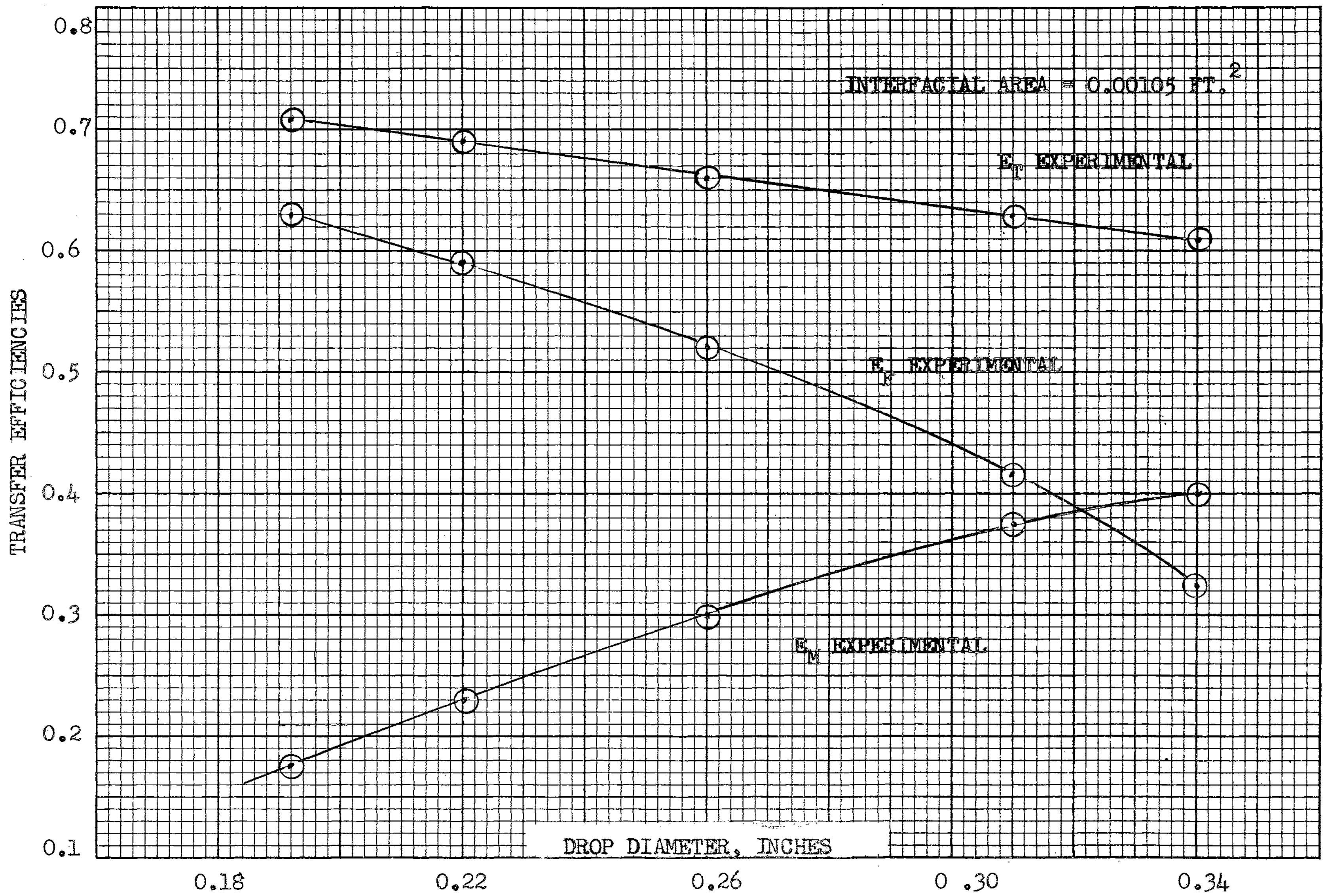


FIGURE 12, TRANSFER EFFICIENCIES AS A FUNCTION OF DROP DIAMETER, SERIES B, TOLUENE DISPERSED

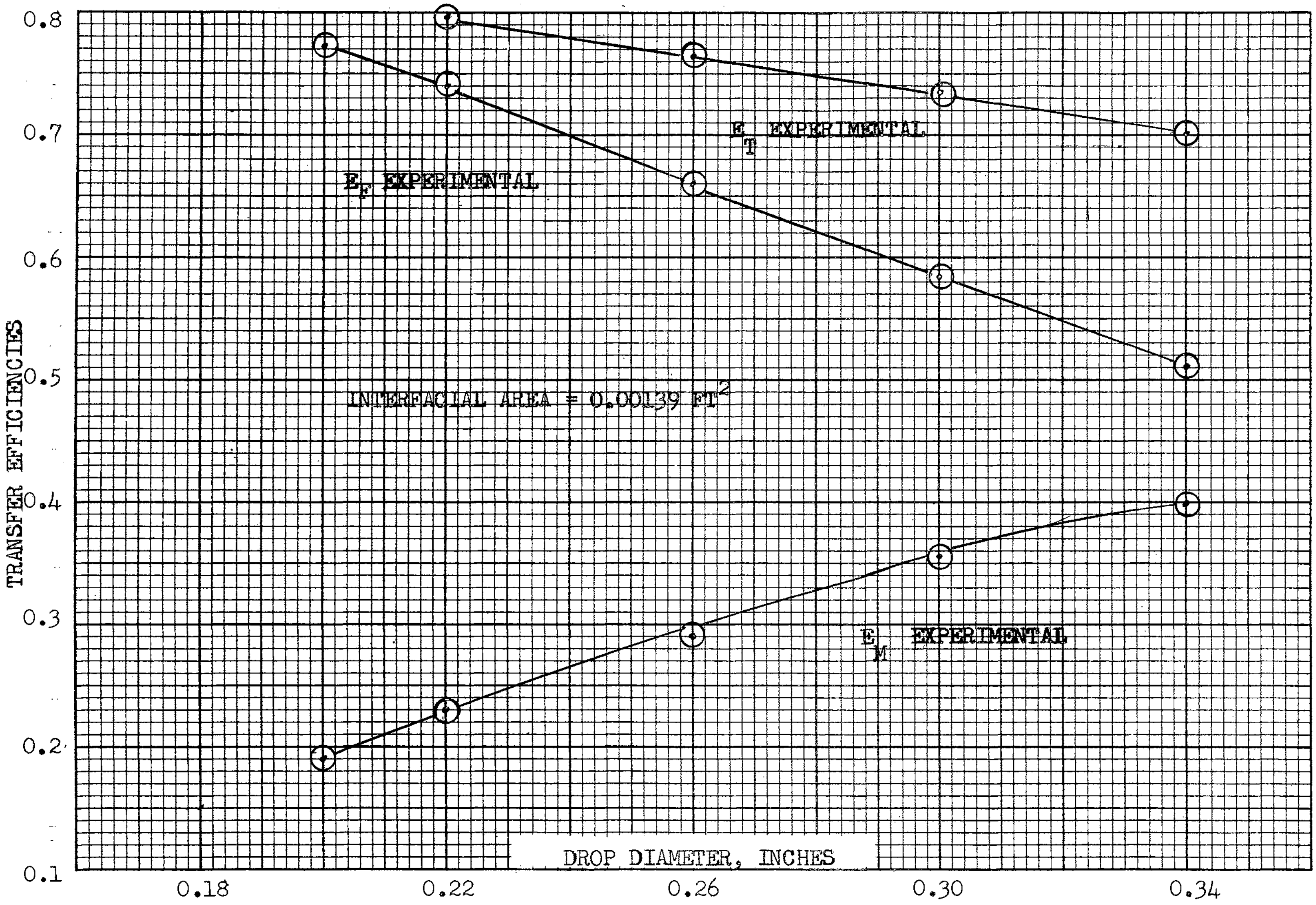


FIGURE 13, TRANSFER EFFICIENCIES AS A FUNCTION OF DROP DIAMETER, SERIES C, TOLUENE DISPERSED

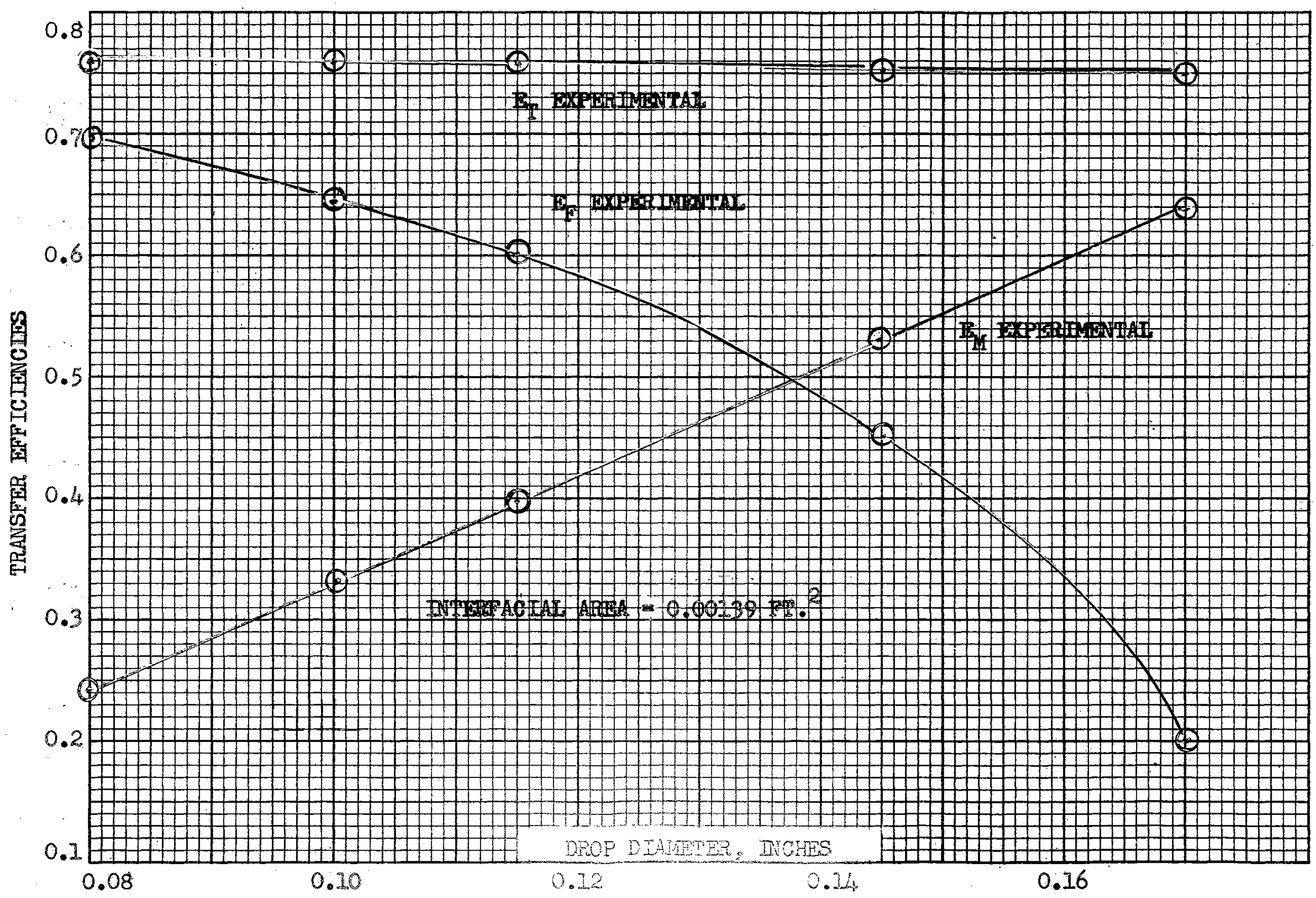


FIGURE 14, TRANSFER EFFICIENCIES AS A FUNCTION OF DROP DIAMETER, SERIES A, MIBK DISPERSED

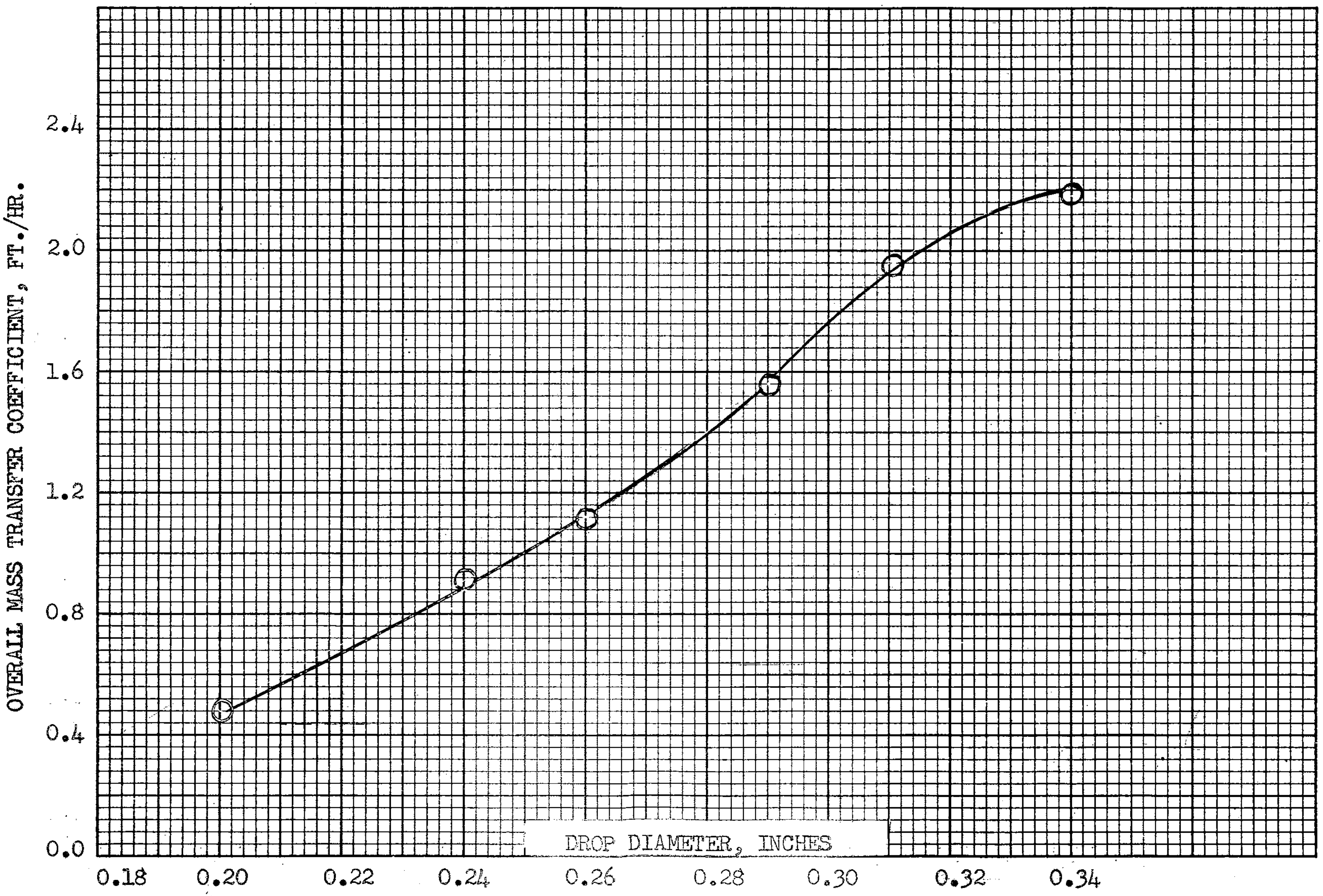


FIGURE 15, OVERALL MASS TRANSFER COEFFICIENT AS A FUNCTION OF DROP DIAMETER, TOLUENE DISPERSED

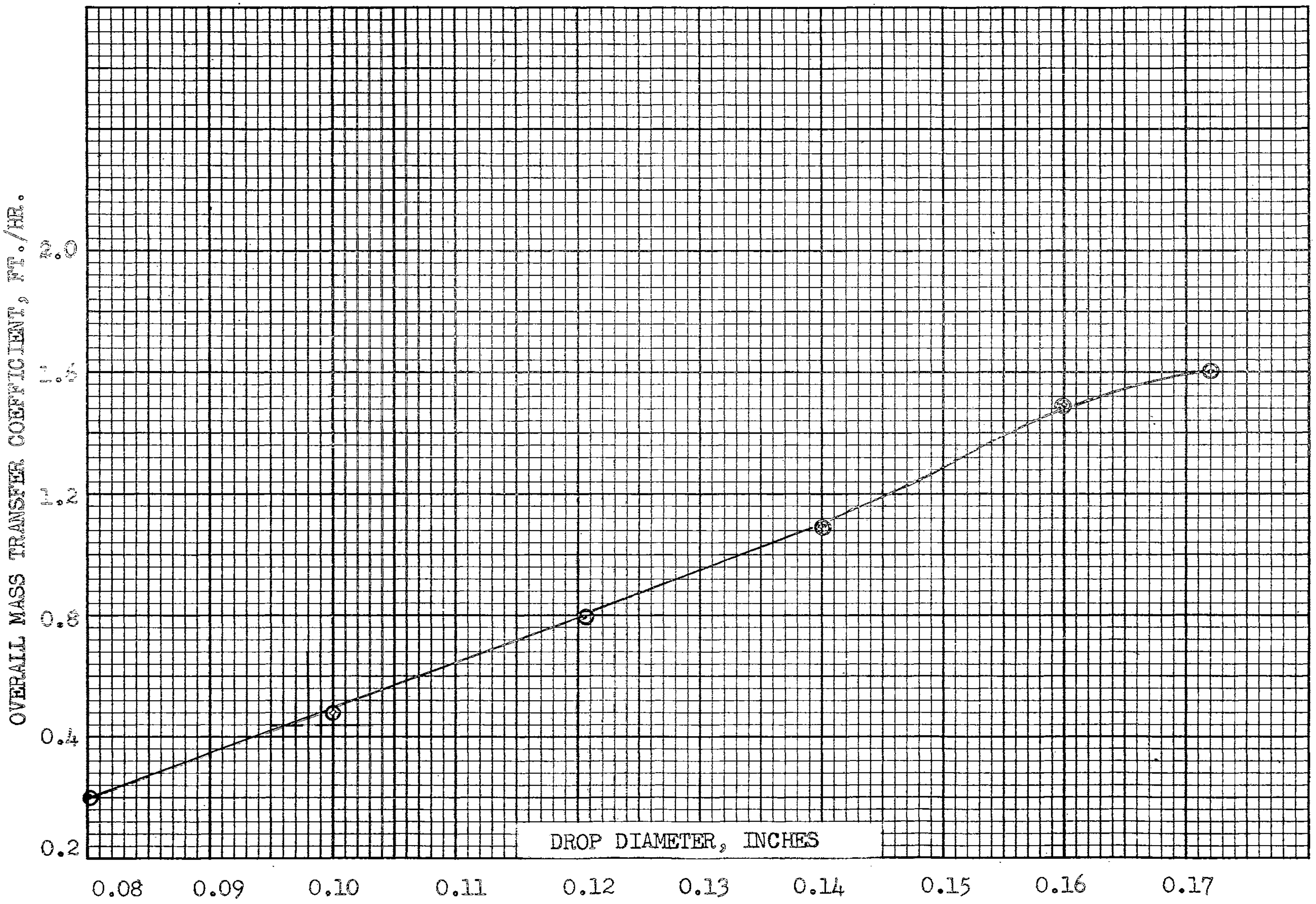


FIGURE 16, OVERALL MASS TRANSFER COEFFICIENT AS A FUNCTION OF DROP DIAMETER, MIBK DISPERSED

TABLE III

CORRELATION FACTOR OF HEAT AND MASS TRANSFER INVESTIGATIONS

SOURCE	SYSTEM	R	Re	DROP BEHAVIOR
1. Garwin and Smith	Cold benzene drops rising in hot water-heat transfer	1.72 to 2.1	1500 to 1780	No Oscillation
2. Garwin and Smith	Hot benzene drops rising in cold water-heat transfer	1.6 to 2.4	730 to 810	No Oscillation
3. McDowell & Myers	Cold xylene drops rising in hot water	2.75	2400	No Oscillation
4. Calderbank & Korchinski	Bromobenzene drops falling in hot or cold glycerol water solutions	1.8 to 3.3	10 to 120	No Oscillation
5. Heertjes	Isobutanol drops rising in water-mass transfer of water	1.9 to 2.1	20 to 200	No Oscillation
6. Calderbank & Korchinski	Bromobenzene drops falling in hot or cold glycerol water solutions	7.0 to 12	315 to 670	Oscillations of droplets
7. Hughes and Gilliland	Water drops falling through CO_2 -mass transfer of CO_2.	20	300 to 3000	Oscillation of droplets
8. Garner and Skelland	Nitrobenzene drop containing AcOH falling in water-mass transfer of acetic acid.	6.5 10 21	270 370 480	Oscillation indicated by R's
9. Pansing	Perchloroethylene containing AcOH falling in water M.T. of AcOH	23-53 40-61 50-70	375 591 700	Oscillation of droplets

TABLE III CONT'D

SOURCE		SYSTEM	R	Re	DROP BEHAVIOR
10.	Johnson	Water drops falling through cyclohexanol- M.T. of cyclohexanol	2.2 to 3.8	2.0 to 15	No Oscillation
11.	Johnson	Water drops falling through n-butanol- M.T. of n-butanol	3.0 to 33	42 to 87	No Oscillation
12.	Johnson	Water drops falling through ethyl acetate- M.T. of ethyl acetate	32 to 52	430 to 700	Oscillation but no regular circulation patterns
13.	This work	MIBK drops containing AcOH rising through water-M.T. of AcOH.	10 to 65	250 to 600	Oscillation of droplets
14.	This work	Toluene drops rising through water- M.T. of AcOH into water.	60 to 115	865 to 1400	Oscillation of droplets

isobutyl ketone were approximately 75 per cent greater than the experimental values for the same system. For the toluene system, the upper limit of the theoretical values was about 50 per cent greater than the upper limit of the experimental values.

Correlation

The rate of transfer which is used to evaluate the free-rise transfer efficiency and the overall mass transfer coefficient is affected greatly by the degree of circulation of solute within the droplets. However, no satisfactory criterion for the onset or the degree of circulation within the droplet has yet been developed. Many investigators have observed circulation within the droplet (6), (7), (8), (9), (15), (18), (23), (34).

From examination of the physical properties of the system used by the investigators, the factors which do affect circulation can be easily seen. The interfacial tension is one of the more predominant factors. If the interfacial tension is high (above 70 dynes/cm.), then a very small amount of circulation will exist, even if the drop diameter is greatly increased. Therefore, it can be said that as the interfacial tension decreases the probability of circulation increases and larger mass transfer coefficients will result. This can be directly observed in this work. For drops of the same size and approximately the same velocity and viscosity, the overall mass transfer coefficient for methyl isobutyl ketone was four times greater than that for the toluene drops. Oscillation of the droplets will certainly increase the mixing within the droplets. Oscillation of the droplets can usually be expected when the drop diameters are large or when a significant density difference exists. Also the viscosity difference has an effect.

The most promising method for preducting transfer rates seems to lie in the correlation of the system properties. The factors considered in this study were viscosity, velocity, density, drop diameter, diffusivity and interfacial tension. The most recent work in this area has been that of Garner et al., (6). They found that the degree of circulation within the droplet was a function of the exponent of the Schmidt number. They found that their correlation could not be improved by inclusion of the Weber Group. However, it must be noted that interfacial tensions of the four systems studied by Garner ranged only between 4.8 dynes/cm. and 7.0 dynes/cm. Since the system used in this investigation had distinct differences in interfacial tension, the Weber Group was included.

It was noted in Chapter III that the methyl isobutyl ketone drops with diameters of less than 0.115 inches remained spherical throughout free-rise. Therefore, the correlation of Garner could be used for comparison with the experimental values.

The correlation of Garner was:

$$Sh = -126 + 1.8\ Re^{0.5}\ Sc^{0.42}$$

The correlation obtained for the spherical methyl isobutyl ketone drops was:

$$Sh = -126 + 0.777\ Re^{0.5}\ Sc^{0.43}$$

The standard deviation of this correlation was 2.75 per cent. For toluene and methyl isobutyl ketone drops in which oscillation was observed it was found that a correlation could not be obtained by use of only the Reynolds and Schmidt Groups. However, by inclusion of the Weber Group the following correlation was obtained:

$$Sh = -610 + 0.46\ Re^{0.5}\ Sc^{0.47}\ We^{0.9}$$

The average deviation was 7.5 per cent. However, the greatest deviation occurred at the lower end of the correlation. This is shown in Figure 17. The theory proposed by Garner that the degree of circulation in spherical droplets can be represented by the exponent of the Schmidt number was not ruled invalid by this investigation although there was oscillation of the droplets encountered. However, the Weber Group must be included in the correlation developed from the present study.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Restatement of Study

A study of liquid-liquid extraction involving single droplets was conducted in order that the individual stages of extraction could be investigated. Also, it was intended to confirm any of the previously proposed transfer mechanisms. The effect of chemical and physical properties on the rate of extraction during free rise were to be correlated by succesive variable elimination.

CONCLUSIONS

The experimental velocity profiles were in agreement with those found in the literature. This indicated that there were no wall effects or any abnormal flow patterns which developed under the experimental conditions of this study. All drops observed exhibited oscillation except for methyl isobutyl ketone drops with diameters of less than 0.115 inches.

End Effects

The operating variables were held constant except for the use of two different coalescense areas, which allowed the combined end effects to be separated. The experimental transfer efficiencies during drop formation were within 5 per cent of those values predicted by the Heertjes equation.

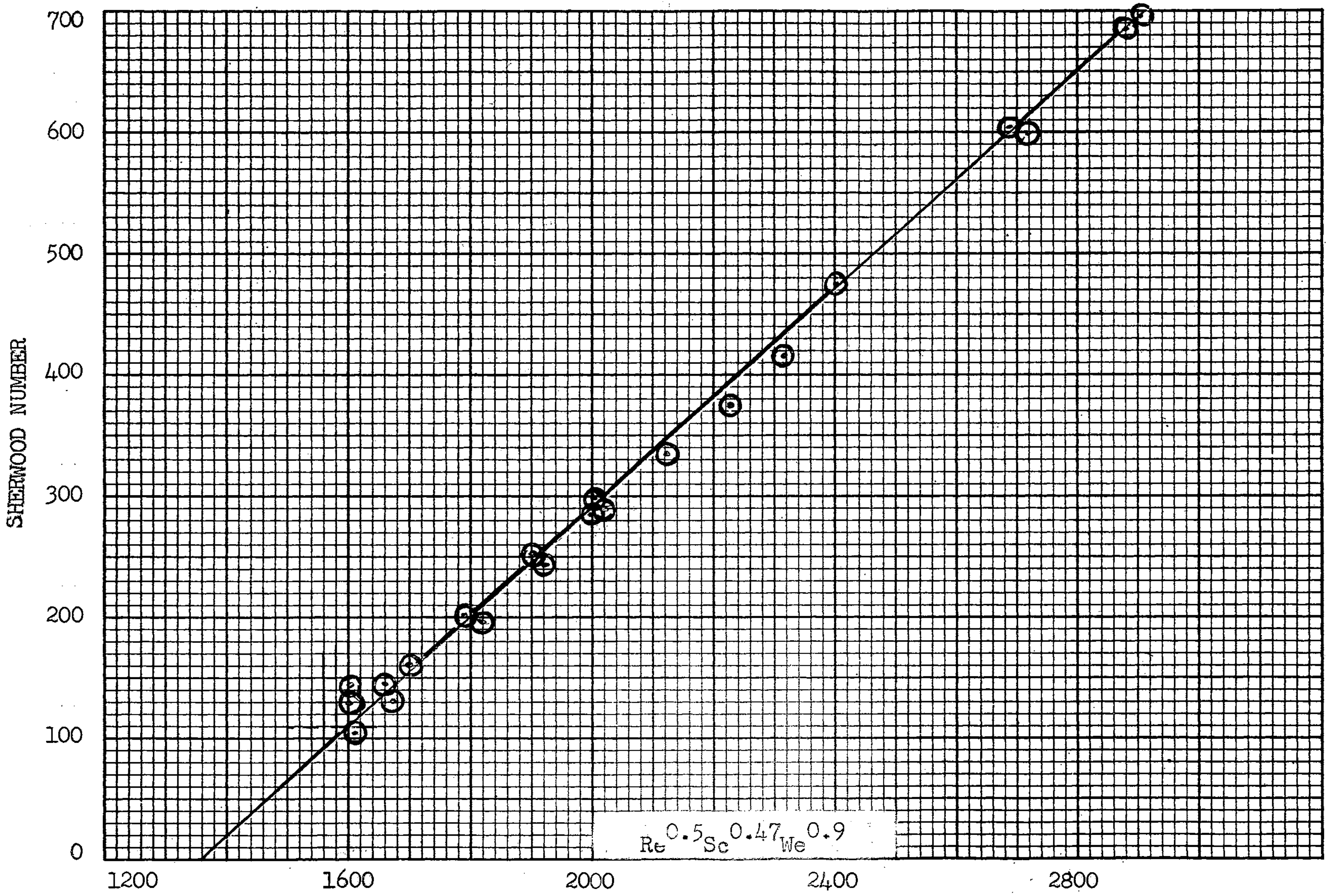


FIGURE 17, CORRELATION OF THE SHERWOOD NUMBER AS A FUNCTION OF THE REYNOLDS, SCHMIDT AND WEBER NUMBERS

The mechanism proposed by Johnson for the transfer efficiency during coalescence of the dispersed phase was very unsatisfactory in comparison with the experimental results. The mean variation was 325 per cent for the toluene drops and 62 per cent for the methyl isobutyl ketone drops. It is felt that the transfer efficiency during coalescence is a function of drop diameter, coalescence area, drop rate, concentration prior to coalescence, and molecular diffusivity. The mechanism of Johnson has been simplified too much to give an accurate picture of the coalescence effect.

Free-Rise

The multiplication factor of molecular diffusivity used to describe the actual transfer rates has been compared in Table III with the results of other investigators. The comparison of the values obtained by other investigators was favorable with the results of this work. All experimental values of the multiplication factor fell below those predicted by the Handlos and Baron model, including this work which was 20 to 50 per cent below the predicted values. The Handlos and Baron model did not provide completely acceptable results, but it was the best of the mechanisms tested which attempted to predict the transfer efficiency by means of the multiplication factor of molecular diffusivity.

Overall Transfer Coefficient

The overall mass transfer coefficients obtained in this study were higher than those found in the literature for spray towers. Both systems exhibited an upper limit of the overall transfer coefficient as the drop diameter increased. For the same size drops the overall transfer coefficient of the MIBK system was four times that of the toluene system. The system properties were almost the same except for the interfacial tension; therefore, it is felt that the greater interfacial tension of the toluene system caused a decrease in the circulation within the droplet.

Correlation

Garner et al., found that the exponent of the Schmidt number could be used to describe circulation within the spherical droplet. An exponent of 1/3 for stagnant drops and 1/2 for full circulation was proposed. It was not necessary to include any group which contained interfacial tensions in the Garner correlation because the interfacial tension of the systems used were approximately the same. Because the MIBK system had the same interfacial tension as that of the systems used by Garner, for spherical drops the following correlation was obtained:

$$Sh = -126 + 0.777\ Re^{.5}\ Sc^{.43}$$

However, for the toluene and MIBK drops which exhibited oscillation the following correlation was obtained:

$$Sh = -610 + 0.46\ Re^{.5}\ Sc^{.47} We^{.9}$$

The Weber group was included because of the wide range of interfacial tension of the two systems. The mean variation was 7.5 per cent.

RECOMMENDATIONS

Future Studies

It is recommended that future extraction studies involving single droplets be conducted. The transfer mechanism during drop coalescence, both experimentally and theoretically, should be rigorously investigated. The correlation of transfer rates with physical properties should be extended to include a wider range of values for the physical properties. Also, it is recommended that aluminum power be used as a tracer to study circulation patterns in the droplet and the effect of oscillation of the patterns. The miltiplication factor of molecular diffusivity obtained in this study fell below the values predicted by the Handlos and Baron model. Because the results of other investigations followed the same pattern as this study, it is recommended that the Handlos and Baron model be revised or a new correlation be developed after further investigation. It is also recommended that further studies be conducted to reaffirm the conclusion of this study that the Heertjes mechanism for extraction efficiency during formation is very satisfactory.

Equipment Alteration

A redesigned column should be constructed. It should include a more accurate temperature control system, stainless steel fluid lines, and collection devices which will allow the use of three or more coalescence areas. Also the number of dispersing nozzles should be increased to allow a wider and more complete range of drop sizes.

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APPENDIX A

DEFINITION OF TERMS

A_i - Interfacial area at coalescence, ft.^{2}

a - Minor axis of ellipsoid.

B - Coefficient.

b - Major axis of ellipsoid.

C - Concentration of dispersed phase, lb. moles/ft.^{3}

C' - Viscometer tube constant.

d - Drop diameter, inches.

D - Molecular diffusivity, ft.^{2}/sec.

D_r - Drop rate.

E - Transfer efficiency.

F - Fraction extracted.

g - Gravitational constant.

H - Column height, ft.

h - Height of fluid in capillary tube.

K - Overall mass transfer coefficient, ft./hr.

k - Film mass transfer coefficient, ft./hr.

$P\bar{e}$ - Modified Peclet number, $P\bar{e}/1 + \frac{\mu_i}{\mu_a}$.

R - Dimensionless correlation factor.

r - Drop or tube radius.

Re - Reynolds number, $DV\rho_i/\mu_i$.

Sc - Schmidt number, $\mu\rho/D$.

t - Time.

V - Velocity, ft./hr.

v - Drop volume, ft.^{3}

We - Weber number, $d\rho_c V^2/\gamma$.

Sh - Sherwood number, kd/D.

Greek Letters

λ - Eigenvalue.

γ - Interfacial tension, dynes/cm.

ρ - Density, lb./hr.

μ - Viscosity, lb./ft. hr.

θ - Time

Subscripts

1 - In the nozzle.

2 - Beginning of transfer mechanism during free-rise.

3 - Point at which drop strikes coalesced dispersed phase.

4 - At column outlet.

a - Aqueous or continuous phase.

c - Coalescence.

d - Dispersed.

E - Combined end effects.

F - Combined end effects.

f - Formation.

i - Interfacial.

M - Free-rise.

o - Organic phase.

APPENDIX B

PHYSICAL PROPERTIES OF THE EQUILIBRATED PHASES

This appendix is a description of the experimental methods used and the results obtained in the determination of the physical properties. Experimental data are given in Tables III through VII. Sample calculations are given at the end of this report.

MATERIALS

Samples used for these determinations were taken from each of the four gallons of the two dispersed phase systems. The continuous phase was once-distilled city tap water, saturated with the organic of the dispersed phase. The samples taken were used immediately.

DENSITIES OF THE EQUILIBRATED PHASES

Densities of the two phases in each system were determined by use of a pycnometer of 11.97 ml. capacity at 77° F. Densities in gm./cc. at 77° F. were calculated and compared with the known value of water at 77° F. The experimental data and the calculated densities are given in Table III. The calculations are shown in the sample calculations at the end of the appendix.

SURFACE AND INTERFACIAL TENSIONS OF THE EQUILIBRATED PHASES

The surface tension of the organic phase of each system was determined by the capillary rise method as described by Steinbach and King (31). The expression for calculating the surface tension is given by the following equation:

$$\gamma_o = 0.5 h_o \, r \, \rho_o \, g \qquad (1\text{-B})$$

where:

γ_o = surface tension of organic phase

h_o = height of fluid in the capillary tube, cc.

ρ_o = density of organic phase, gms./cc.

r = radius of capillary tube, cm.

g = gravitational constant, 980 cm.^{2}/sec.

The interfacial tension between the two saturated phases was obtained from the following equation:

$$\gamma_i = 0.5\ r\ (h_a \rho_a + h_o \rho_o) - \gamma_o \qquad \text{(2-B)}$$

where:

a = continuous phase

o = organic phase

The experimental data and the calculated values of γ_i and γ_o are compared in Tables V and VI.

Description of Capillary Tube

The capillary tube used in this work was made from a 0 to 400° C. thermometer cut off in the middle of the bulb and at the 400° mark. Each unit degree was equal to 0.06667 cm. The tube was mounted vertically in a 25 mm. x 200 mm. test tube.

Radius Determination

The tube radius was determined by the capillary rise of distilled water in the tube. From the known surface tension of distilled water at 77° F. (14), the tube radius was calculated by using equation (1-B). Experimental data for this method are given in Table IV. The calculations of the tube radius are presented in the sample calculations in this appendix. The tube radius used for determination of surface and interfacial tension was found to be 0.01207 cm.

VISCOSITIES OF THE EQUILIBRATED PHASES

The viscosities of the two saturated phases of each system were determined by the method described in A.S.T.M., D445-35T (1). A number 100 Cannon-Fenske Viscometer was calibrated with distilled water to determine the tube constant, C', at 77° F. The equation given for the calculation of the viscosity was:

$$\mu = \rho C' t \qquad (3\text{-}B)$$

where:

μ = absolute viscosity, centipoises
C' = tube constant
t = time interval, minutes.

The experimental data recorded are presented in Table VII.

RESULTS

A summary of the experimentally determined physical properties is given in Table II, Chapter III. The data and results of physical properties determinations are presented in the following tables.

TABLE IV

DENSITIES OF THE EQUILIBRATED PHASE AT 77° F.

Component	Weight of 11.96 cc. gms.	Average Weight gms.	Density at 77° F. gms./cc.
Distilled Water	11.9205 11.9107	11.9153	0.9971
Organic Phase MIBK - AcOH	9.6062 9.6051	9.6055	0.8025
Aqueous Phase H_2O - Sat. MIBK	11.8902 11.8805	11.8551	0.9945
Organic Phase Toluene - AcOH	10.3210 10.3105	10.3155	0.8625
Aqueous Phase H_2O - Sat. Toluene	11.8990 11.8976	11.8983	0.9957

TABLE V

CALIBRATION OF THE CAPILLARY TUBE WITH DISTILLED WATER

	Run Number		
	1	2	3
Upper Scale Reading*	183.0	183.0	183.0
Lower Scale Reading*	182.5	183.0	183.0

Average Scale Reading = 183
1° C. = .06667 cm.

Average Column Height = (183)(.06667) = 12.2 cm.

Calculated Tube Radius = .012073 cm.

*The upper and lower scale readings refer to the difference between the fluid level in the test tube and that in the capillary tube. The identical readings are accounted for by the fact that the tube was very clean.

TABLE VI

SURFACE TENSION OF THE SATURATED ORGANIC PHASES

Methyl Isobutyl Ketone

	Run Number			
	1	2	3	4
Upper Scale Reading	76.1	75.6	75.2	75.2
Lower Scale Reading	73.7	74.2	74.6	74.6

Average Reading = 74.9

Average Column Height = (74.9)(.06667) = 4.97 cm.

Calculated Surface Tension = 23.6 dynes/cm.

Toluene

	Run Number			
	1	2	3	4
Upper Scale Reading	92.4	92.4	92.3	92.3
Lower Scale Reading	92.0	92.1	92.1	92.1

Average Reading = 92.2

Average Column Height = 92.2 (.06667) = 6.13 cm.

Calculated Surface Tension = 28.9 dynes/cm.

TABLE VII

INTERFACIAL TENSION BETWEEN THE AQUEOUS AND THE ORGANIC PHASES

Methyl Isobutyl Ketone

Run	1		2		3	
	h_o	h_a	h_o	h_a	h_o	h_a
Upper Scale Reading	58.6	27.4	58.5	27.2	58.5	27.2
Lower Scale Reading	58.2	26.8	58.3	27.0	58.2	27.0

Average Organic Reading = 58.4

Average Aqueous Reading = 27.1

h_o = 58.4 (.06667) = 3.89 cm.

h_a = 27.1 (.06667) = 1.80 cm.

Calculated Interfacial Tension = 7.35 dynes/cm.

Toluene

Calculated Interfacial Tension = 17.0 dynes/cm.

TABLE VIII

VISCOSITIES OF THE SATURATED AQUEOUS AND ORGANIC PHASES AT 77° F.

Time, Minutes

	MIBK - AcOH - H_2O		Toluene - AcOH - H_2O	
Distilled Water	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase
.718	.743	.595	.744	.530
.718	.745	.590	.746	.528
.719	.745	.592	.746	.529
.716	.744	.590	.745	.530
.717	.743	.590	.744	.530
		Averages		
.718	.744	.591	.745	.530

Calculated Viscosities

MIBK - AcOH - H_2O

Aqueous Phase = .925 cp.

Organic Phase = .5895 cp.

Toluene - AcOH - H_2O

Aqueous Phase = .926 cp.

Ortanic Phase = .568 cp.

SAMPLE CALCULATION

Determination of the Capillary Tube Radius

Capillary Rise of Distilled Water

From Table IV, the average column height, h, of distilled water due to capillary rise in the tube was 12.2 cm. The density of distilled water is 0.9971 gms./cc. The surface tension of water is 71.8 dynes/cm.

$r = 2\gamma/h\rho g = 2(71.8)/12.2\ (.9971)\ 980 = .012073$ cm.

Determination of the Viscometer Tube Constant

The tube constant, C', was calculated from the following values and equation (3-B).

Viscosity of pure water at 77° F. = 0.8937 cp.

Density of pure water at 77° F. = .9971 gms./cc.

Average time of flow through tube = 0.718 min.

$C' = \mu/\rho t = .8937/(.09971)(.718)$

$C' = 1.245$

SAMPLE CALCULATION

Determination of the Saturated Phase Viscosity

MIBK - AcOH - H_2O

The viscosities of the organic and aqueous phases are calculated by using equation (3-B) and the data from Table VII.

$$\mu_a = \rho C't = (.9945)(1.245)(.744) = .925 \text{ cp.}$$

$$\mu_d = (.591)(1.245)(.8025) = .5895 \text{ cp.}$$

Toluene - AcOH - H_2O

$$\mu_a = \rho C't = .9957(1.245)(.745) = .926 \text{ cp.}$$

$$\mu_d = (.8625)(1.245)(.530) = .568 \text{ cp.}$$

SAMPLE CALCULATION

Determination of the Surface Tension and Interfacial Tension of the System Phases

MIBK - AcOH - H_2O

The surface tension was calculated from equation (1-B) and the data in Table V.

$$\gamma_o = .5h_o r \rho_o g = .5(4.95)(.01207)(.8025)(980)$$

$$\gamma_o = 23.6 \text{ dynes/cm.}$$

The interfacial tension was obtained from equation (2-B) and the data in Table VI.

$$\gamma_i = .5r\,(h_a \rho_a + h_o \rho_o)g - \gamma_o = .5(.01207)$$

$$[(1.80)(.9945) + (3.89)(.8025)]\ 980 - 236$$

$$= 30.95 - 23.6 = 7.35 \text{ dynes/cm.}$$

Toluene - AcOH - H_2O

$$\gamma_o = (.5)(6.13)(.8625)(980)(.01207) = 28.9 \text{ dynes/cm.}$$

$$\gamma_i = (.5)(.01207)(980)[(.8625)(4.63) + (3.8)(.9957)]$$

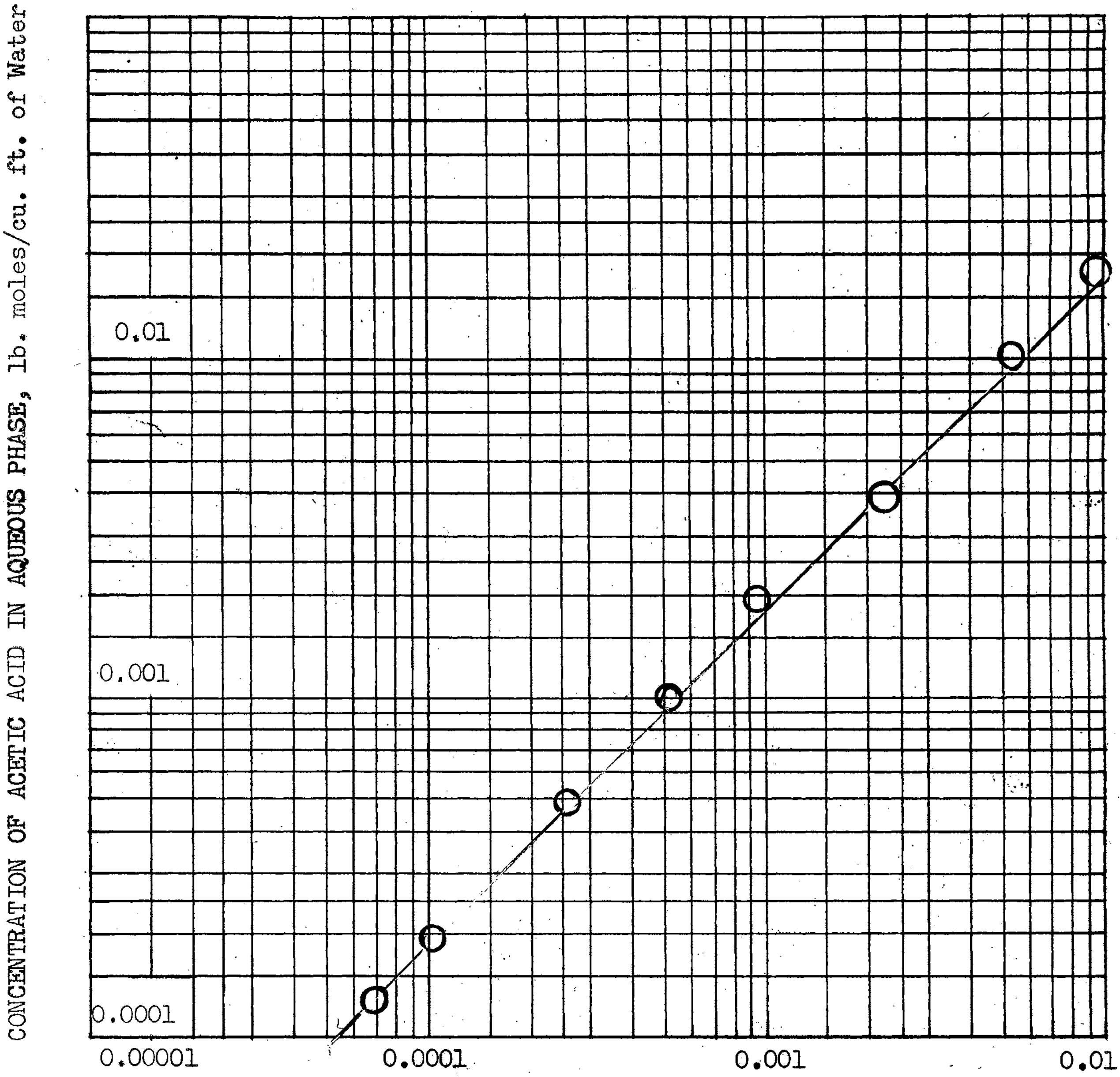
$$- 28.9 = 35.9 - 28.9 = 17 \text{ dynes/cm.}$$

APPENDIX C

EQUILIBRIUM AND DISTRIBUTION DATA FOR EXTRACTION SYSTEMS

This appendix is devoted to the equilibrium and distribution data of the extraction systems used in this experiment. The logarithmic mean driving force is employed in computing the overall mass transfer coefficients. In order to calculate the driving force, an exact knowledge of the equilibrium distribution ratio between the solvents is needed.

In evaluating transfer efficiencies, it is necessary to know the concentration in the bulk phase in equilibrium with the concentration of the solvent from which the acetic acid is being transferred. The data presented here has been abstracted from many experimental studies (5), (23), (28), (30).



CONCENTRATION OF ACETIC ACID IN ORGANIC PHASE, lb. moles / ft.^{3} of MIBK

FIGURE 18

DISTRIBUTION DIAGRAM FOR METHYL ISOBUTYL KETONE - ACETIC ACID - WATER

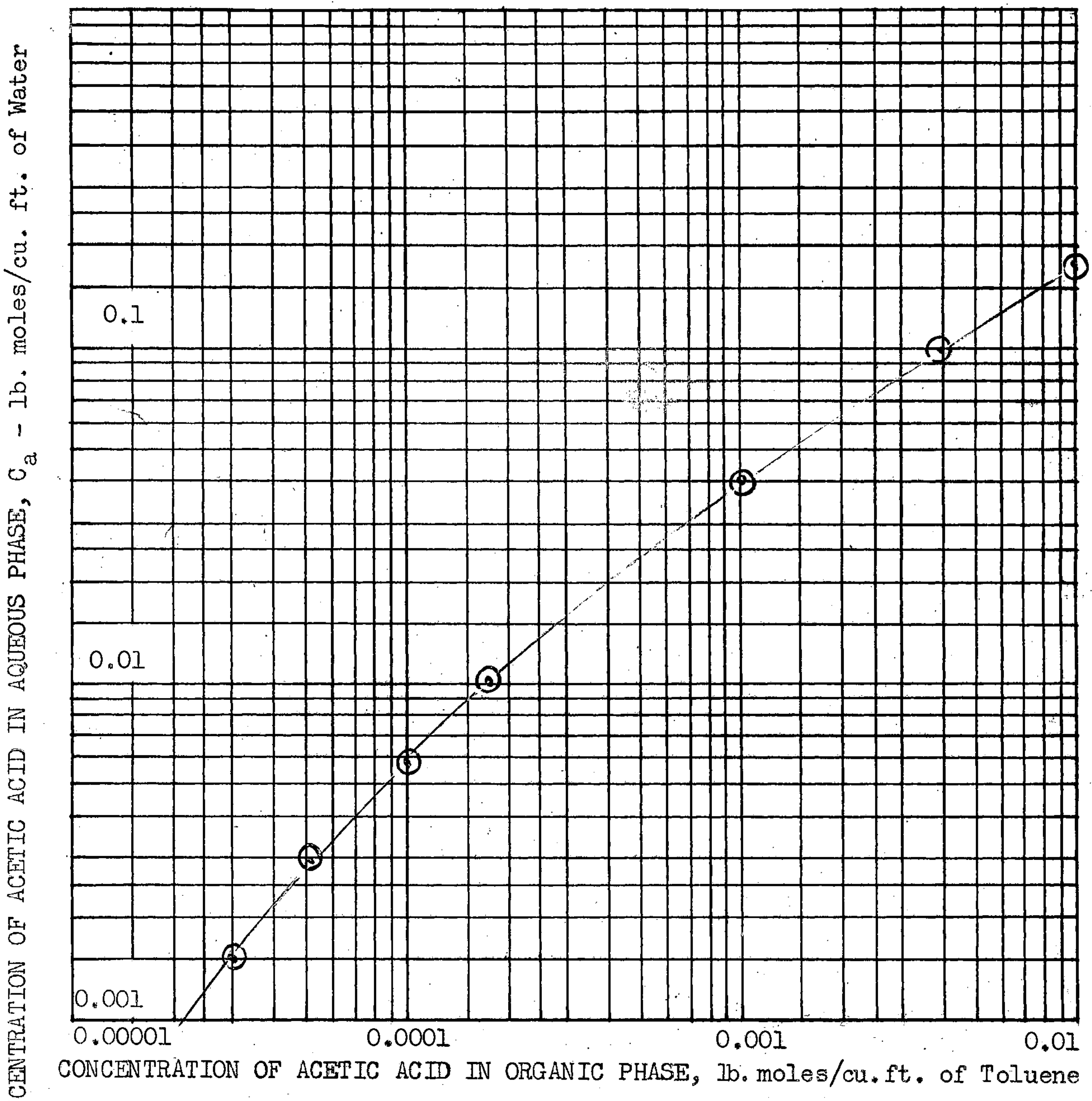


FIGURE 19, DISTRIBUTION DIAGRAM FOR TOLUENE - ACETIC ACID - WATER

APPENDIX D

EXPERIMENTAL DATA AND CALCULATIONS

The same measurements and analysis of data were made for all of the experiments. A 50 ml. sample was collected during each run and titrated to determine the outlet of acetic acid concentration. Four runs were made at various column heights using the same nozzle and the same collection funnel.

The results obtained were converted into terms which could be employed to determine the overall mass transfer coefficient during free-rise, the total end effects, and also the separation of the end effects into the transfer efficiencies.

Overall Mass Transfer Coefficient

The overall mass transfer coefficient was obtained from an expression that was based on a modified two film theory; that is, a one film theory. The rate equation for the resistance of the dispersed film can be written:

$$LdC = K_o \, (C_i - C) \, dA \qquad (1\text{-}D)$$

Setting $C_i = 0$:

$$\int_1^2 \frac{dC}{C} = \frac{K_o}{L} \int dA$$

Integrating the above expression:

$$\ln \frac{C_{in}}{D_{out}} = KA/L \qquad (2\text{-}D)$$

Rearrangement yields:

$$K_o = \frac{L \ln \frac{C_{in}}{C_{out}}}{A} \qquad (3\text{-}D)$$

Replacing L and A in terms of experimental variables:

$$L = \frac{\pi d^3 D \theta}{6} \tag{4-D}$$

$$A = D \theta_t \pi d^2 \theta \tag{5-D}$$

The resulting expression is obtained:

$$K = \frac{d \ln C_{in}/C_{out}}{6 \theta_t} \tag{6-D}$$

where:

K = overall mass transfer coefficient, ft./hr.
d = drop diameter, ft.
C = concentration, lb. moles/ft.^{3}
A = interfacial area, ft.^{2}
L = flow rate, ft.^{3}/hr.
θ = total operation time
θ_t = contact time.

The time of contact, θ_t, can also be replaced by H/V, where H is the column height and V is the velocity.

$$K = \frac{V\,d}{H\,6} \ln \left(C_{in}/C_{out}\right) \tag{7-D}$$

End Effects

The values of C_{in}/C_{out} were plotted on a semilog scale against column height. An extrapolation to zero height yielded the fraction unextracted by the combined end effects. Since there were two series of runs at the same drop rate and using the same nozzle, the fraction extracted during drop formation was assumed to be the same. The only variable involved in the fraction extracted during coalescence was the interfacial area. By means of the two funnels used, two equations could be written to express the fraction extracted during the combined end effects:

$$F_f + F_c = F_E$$

$$F_f + 1.32\, F_c = F_E$$

The coefficient (1.32) of the F_c term in the second equation is the ratio of the two interfacial areas. Thus the combined end effects could be separated.

Free-Rise

Since it was possible to separate the end effects, the fraction extracted and the transfer efficiency during free-rise could be obtained. The transfer efficiency was obtained from the following expression:

$$E_M = \frac{E_T - E_F}{1 - E_F} \tag{8-D}$$

where:

$$E_M = \frac{C_2 - C_3}{C_2} \tag{9-D}$$

$$E_T = \frac{C_1 - C_4}{C_1} \tag{10-D}$$

$$E_F = E_f + E_c - E_f \times E_c \tag{11-D}$$

$$E_f = \frac{C_1 - C_2}{C_1} \tag{12-D}$$

$$E_c = \frac{C_3 - C_4}{C_3} \tag{13-D}$$

Correlation

The overall transfer coefficient during free-rise was incorporated in the Sherwood number and correlated with the Reynolds, Schmidt and Weber numbers. The correlation was:

$$Sh = -610 + 0.46\ (Re)^{.5}\ (Sc)^{.47}\ (We)^{.9} \tag{14-D}$$

TABLE IX

EXTRACTION AS A FUNCTION OF COLUMN HEIGHT

Series A*

Methyl Isobutyl Ketone - Acetic Acid (Dispersed)

Water - Saturated With MIBK (Continuous)

Run	Nozzle Number	Velocity ft./sec.	Drop Diameter	Column Height ft.	Conc. In lb. moles/ft.^{3}	Conc. Out lb. moles/ft.^{3}	θ_f Sec.	Interfacial Area ft.^{2}
1.	I	0.312	0.08	0.30	0.0108	.00400	0.7	0.00139
2.	I	0.312	0.08	0.81	0.0108	.00346	0.7	0.00139
3.	I	0.312	0.08	1.12	0.0108	.00314	0.7	0.00139
4.	I	0.312	0.08	1.80	0.0108	.00257	0.7	0.00139
5.	II	0.364	0.115	0.54	0.0108	.00470	0.7	0.00139
6.	II	0.364	0.115	1.16	0.0108	.00360	0.7	0.00139
7.	II	0.364	0.115	1.50	0.0108	.00312	0.7	0.00139
8.	II	0.364	0.115	1.85	0.0108	.00270	0.7	0.00139
9.	III	0.343	0.145	0.33	0.0108	.00655	0.7	0.00139
10.	III	0.343	0.145	0.83	0.0108	.00491	0.7	0.00139
11.	III	0.343	0.145	1.31	0.0108	.00377	0.7	0.00139
12.	III	0.343	0.145	2.00	0.0108	.00258	0.7	0.00139
13.	IV	0.336	0.172	0.302	0.0108	.00790	0.7	0.00139
14.	IV	0.336	0.172	0.760	0.0108	.00570	0.7	0.00139
15.	IV	0.336	0.172	1.22	0.0108	.00428	0.7	0.00139
16.	IV	0.336	0.172	1.89	0.0108	.00288	0.7	0.00139

*The drop rate for both runs was 120/min., and the temperature of both phases was 77±.2° F.

TABLE X

EXTRACTION AS A FUNCTION OF COLUMN HEIGHT

Series B*

Toluene - Acetic Acid (Dispersed)

Water - Saturated Toluene (Continuous)

Run	Nozzle Number	Velocity ft./sec.	Drop Diameter	Column Height ft.	Conc. In lb. moles/ft.^{3}	Conc. Out	θ_f Sec.	Interfacial Area ft.^{2}
1.	I	0.375	0.200	0.35	0.0103	.00407	1.3	0.00105
2.	I	0.375	0.200	0.60	0.0103	.00381	1.3	0.00105
3.	I	0.375	0.200	1.00	0.0103	.00350	1.3	0.00105
4.	I	0.375	0.200	1.40	0.0103	.00319	1.3	0.00105
5.	II	0.380	0.241	0.30	0.0103	.00505	1.3	0.00105
6.	II	0.380	0.241	0.55	0.0103	.00462	1.3	0.00105
7.	II	0.380	0.241	0.95	0.0103	.00398	1.3	0.00105
8.	II	0.380	0.241	1.40	0.0103	.00339	1.3	0.00105
9.	III	0.384	0.296	0.35	0.0103	.00605	1.3	0.00105
10.	III	0.384	0.296	0.65	0.0103	.00529	1.3	0.00105
11.	III	0.384	0.296	0.90	0.0103	.00495	1.3	0.00105
12.	III	0.384	0.296	1.25	0.0103	.00412	1.3	0.00105
13.	IV	0.382	0.323	0.30	0.0103	.00660	1.3	0.00105
14.	IV	0.382	0.323	0.60	0.0103	.00589	1.3	0.00105
15.	IV	0.382	0.323	1.08	0.0103	.00494	1.3	0.00105
16.	IV	0.382	0.323	1.25	0.0103	.00438	1.3	0.00105

*The drop rate was 60/min., and the temperature of both phases was 77±.2° F.

TABLE XI

EXTRACTION AS A FUNCTION OF COLUMN HEIGHT

Series C*

Water - Saturated Toluene (Continuous)

Toluene - Acetic Acid (Dispersed)

Run	Nozzle Number	Velocity ft./sec.	Drop Diameter	Column Height ft.	Conc. In	Conc. Out	θ_f Sec.	Interfacial Area ft.^{2}
					lb. moles/ft.^{3}			
1.	I	0.375	0.200	0.33	0.0103	.00284	1.3	0.00139
2.	I	0.375	0.200	0.66	0.0103	.00252	1.3	0.00139
3.	I	0.375	0.200	1.08	0.0103	.00215	1.3	0.00139
4.	I	0.375	0.200	1.66	0.0103	.00174	1.3	0.00139
5.	II	0.380	0.241	0.25	0.0103	.00400	1.3	0.00139
6.	II	0.380	0.241	0.50	0.0103	.00360	1.3	0.00139
7.	II	0.380	0.241	1.00	0.0103	.00293	1.3	0.00139
8.	II	0.380	0.241	1.50	0.0103	.00240	1.3	0.00139
9.	III	0.384	0.296	0.25	0.0103	.00536	1.3	0.00139
10.	III	0.384	0.296	0.58	0.0103	.00455	1.3	0.00139
11.	III	0.384	0.296	0.96	0.0103	.00378	1.3	0.00139
12.	III	0.384	0.296	1.50	0.0103	.00300	1.3	0.00139
13.	IV	0.382	0.323	0.33	0.0103	.00624	1.3	0.00139
14.	IV	0.382	0.323	0.66	0.0103	.00536	1.3	0.00139
15.	IV	0.382	0.323	1.00	0.0103	.00458	1.3	0.00139
16.	IV	0.382	0.323	1.42	0.0103	.00382	1.3	0.00139

*The drop rate was 60/min. and the temperature of both phases was 77±.2° F.

TABLE XII

CALCULATED CONCENTRATIONS OF EACH STAGE OF EXTRACTION

Series A

MIBK - Acetic Acid - Water

Drop	C_1	C_2	C_3	C_4	Column	K_o
Diameter in.		lb. moles/ft.^{3}			Height ft.	ft./hr
.08	0.0108	0.00879	0.00695	0.00248	2.0	0.163
.09	0.0108	0.00886	0.00670	0.00251	2.0	0.250
.115	0.0108	0.00902	0.00535	0.00254	2.0	0.572
.12	0.0108	0.00910	0.00513	0.00256	2.0	0.642
.13	0.0108	0.00918	0.00469	0.00258	2.0	0.77
.14	0.0108	0.00926	0.00413	0.00260	2.0	0.90
.15	0.0108	0.00934	0.00373	0.00261	2.0	1.12
.16	0.0108	0.00942	0.00350	0.00263	2.0	1.42
.17	0.0108	0.00950	0.00300	0.00264	2.0	1.53
.18	0.0108	0.00958	0.00274	0.00266	2.0	1.60

TABLE XIII

CALCULATED CONCENTRATIONS OF EACH STAGE OF EXTRACTION

Series B

Toluene - Acetic Acid - Water

Drop Diameter in.	C_1	C_2 lb. moles/ft.^{3}	C_3	C_4	Column Height ft.	K ft./hr.
.20	0.0103	0.00886	0.00736	0.00310	1.5	0.51
.21	0.0103	0.00892	0.00713	0.00315	1.5	0.59
.22	0.0103	0.00896	0.00700	0.00324	1.5	0.70
.23	0.0103	0.00901	0.00685	0.00330	1.5	0.80
.24	0.0103	0.00906	0.00671	0.00337	1.5	0.90
.25	0.0103	0.00911	0.00661	0.00343	1.5	1.00
.26	0.0103	0.00917	0.00650	0.00350	1.5	1.13
.27	0.0103	0.00922	0.00636	0.00359	1.5	1.26
.28	0.0103	0.00927	0.00626	0.00365	1.5	1.36
.29	0.0103	0.00932	0.00616	0.00372	1.5	1.55
.30	0.0103	0.00937	0.00602	0.00380	1.5	1.73
.31	0.0103	0.00942	0.00594	0.00386	1.5	1.86
.32	0.0103	0.00947	0.00585	0.00393	1.5	2.00
.33	0.0103	0.00952	0.00580	0.00402	1.5	2.10

TABLE XIV

CALCULATED CONCENTRATIONS OF EACH STAGE OF EXTRACTION

Series C

Toluene - Acetic Acid - Water

Drop Diameter in.	C_1	C_2 lb. moles/ft.^{3}	C_3	C_4	Column Height ft.	K_o ft./hr
.20	0.0103	0.0085	0.00737	0.00192	1.5	0.52
.21	0.0103	0.00894	0.00715	0.00196	1.5	0.60
.22	0.0103	0.00897	0.00701	0.00207	1.5	0.70
.23	0.0103	0.00902	0.00684	0.00219	1.5	0.79
.24	0.0103	0.00907	0.00670	0.00237	1.5	0.92
.25	0.0103	0.00912	0.00661	0.00243	1.5	1.03
.27	0.0103	0.00922	0.00638	0.00271	1.5	1.25
.28	0.0103	0.00929	0.00627	0.00282	1.5	1.36
.29	0.0103	0.00933	0.00615	0.00291	1.5	1.56
.30	0.0103	0.00938	0.00601	0.00312	1.5	1.74
.31	0.0103	0.00944	0.00592	0.00328	1.5	1.85
.32	0.0103	0.00948	0.00584	0.00341	1.5	2.02
.33	0.0103	0.00953	0.00579	0.00349	1.5	2.12

TABLE XV

CALCULATED DIMENSIONLESS GROUPS

	d	Sh	Re	Sc	We
MIBK	.08	12.6	256	320	2.50
	.09	21.9	312	320	3.29
	.10	36.0	364	320	4.03
	.11	50.8	410	320	4.60
	.12	74.7	450	320	5.07
	.13	97.2	483	320	5.46
	.14	124.0	508	320	5.56
	.15	163.0	530	320	5.63
	.16	220.0	550	320	5.67
	.17	252.0	582	320	5.95
	.18	279.0	612	320	6.27
Toluene	.20	100.0	865	270	3.86
	.21	120.0	913	270	4.05
	.22	148.0	960	270	4.25
	.23	179.0	1000	270	4.45
	.24	209.0	1050	270	4.64
	.25	242.0	1110	270	4.83
	.26	287.0	1130	270	5.03
	.27	330.0	1170	270	5.22
	.28	370.0	1218	270	5.41
	.29	437.0	1270	270	5.60
	.30	505.0	1310	270	5.80
	.32	622.0	1390	270	6.18
	.34	713.0	1470	270	6.57

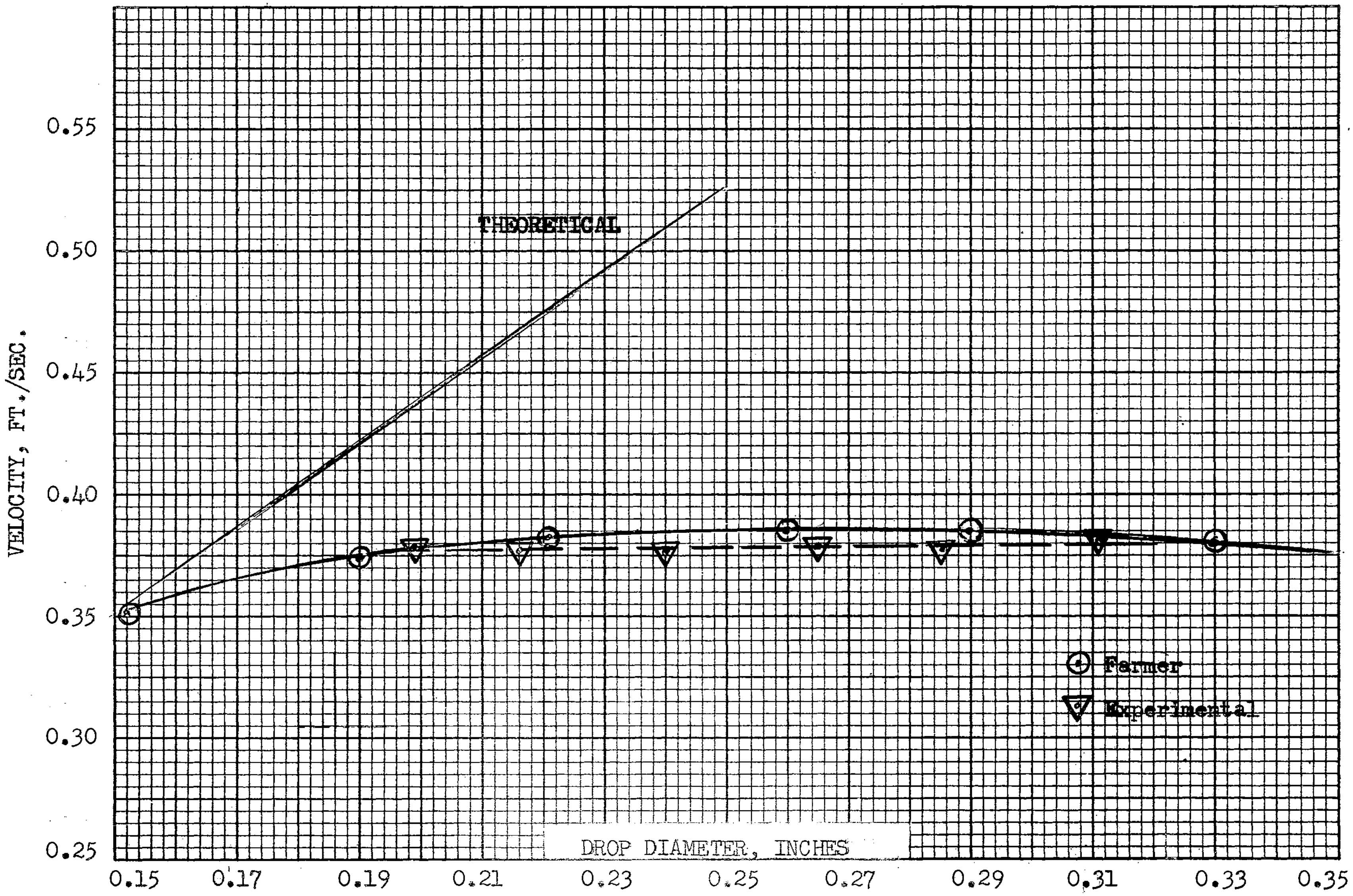


FIGURE 20, VELOCITY AS A FUNCTION OF DROP DIAMETER, TOLUENE DISPERSED

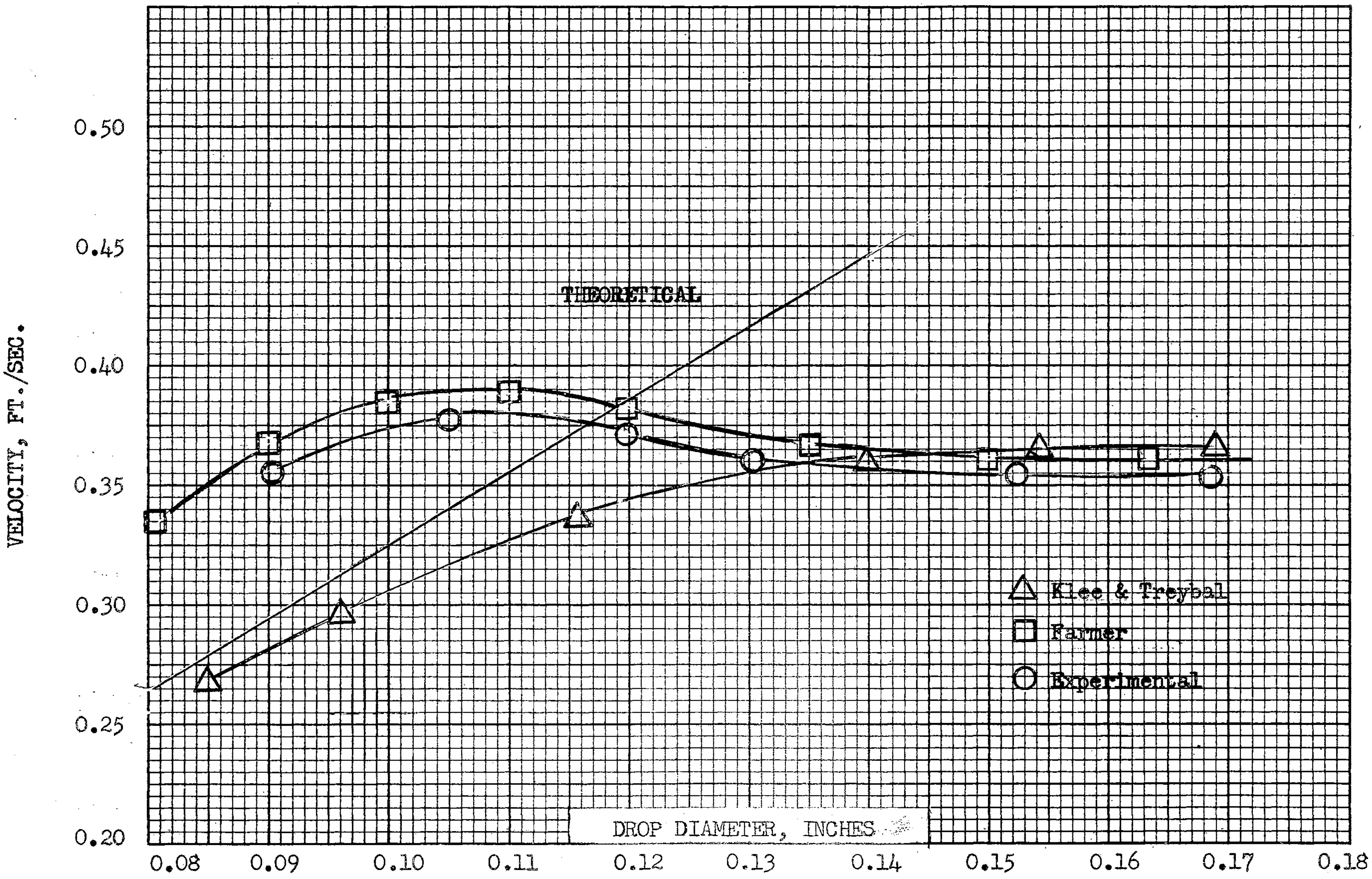


FIGURE 21, VELOCITY AS A FUNCTION OF DROP DIAMETER, MIBK DISPERSED

SAMPLE CALCULATIONS

End Effects

The calculations below will be based on the data from Tables XI and X, in which the No. II nozzle was used. This data is plotted in Figures 3 and 4 in terms of concentration in, divided by concentration out, against column height. An extrapolation to zero column height yielded the fraction unextracted by the end effects; that is, drop formation and coalescence.

No. II nozzle, d = 0.240 in.

Series B: $F_E = 1 - .55 = 0.45$

Series C: $F_E = 1 - .444 = 0.556$

Since the fraction extracted during drop formation should be the same, and since only the interfacial area during coalescence was changed, the following expression could be used:

$$F_f + (A_{i2}/A_{i1})\ F_c = F_E \qquad (1)$$

$$F_f + (A_{i1}/A_{i1})\ F_c = F_E \qquad (2)$$

$$F_f + (.00139/.00105)\ F_c = .556$$

$$F_f + (.00105/.00105)\ F_c = .450$$

Subtracting (2) from (1):

$$0.32\ F_c = 0.106$$
$$F_c = 0.332$$
$$F_f = 0.118$$

A plot of F_c, F_f, and F_E is shown in Figures 6 and 7 for all experimental runs.

Total Extraction

For all toluene runs the total fraction extracted (F_t) at a column height of 1.5 feet was obtained from Figure 3 and plotted in

Figure 6. Knowing the individual fractions of extraction, the following concentrations could be obtained.

No. II nozzle - 4 = 0.241 in.

Series B

C_1 = 0.0103 lb. moles/ft.^{3}
C_2 = 0.00906 lb. moles/ft.^{3}
C_3 = 0.00671 lb. moles/ft.^{3}
C_4 = 0.00337 lb. moles/ft.^{3}

Series C

C_1 = 0.01030 lb. moles/ft.^{3}
C_2 = 0.00907 lb. moles/ft.^{3}
C_3 = 0.00670 lb. moles/ft.^{3}
C_4 = 0.00237 lb. moles/ft.^{3}

The preceding data is presented in Tables XII and XIII.

Transfer Efficiencies

The transfer efficiencies were obtained in order to compare the experimental results with the theoretical models of Johnson (18), Handlos (14) and others.

$$E_T = \frac{C_1 - C_4}{C_1}$$

$$E_f = \frac{C_1 - C_2}{C_1}$$

$$E_c = \frac{C_3 - C_4}{C_3}$$

$$E_M = \frac{C_2 - C_3}{C_2}$$

$$E_F = E_c + E_f - E_c \times E_f$$

Series B	Series C
$E_T = 0.674$	$E_T = 0.769$
$E_f = 0.120$	$E_f = 0.120$
$E_c = 0.498$	$E_c = 0.647$
$E_F = 0.558$	$E_F = 0.689$
$E_M = 0.260$	$E_M = 0.260$

The preceding data is presented in Figures 6, 17, and 18.

Theoretical Model for End Effects

Johnson's model for end effects is given by the following expression:

$$E_f = \frac{20.6}{d} \sqrt{\frac{D\Theta_f}{\pi}}$$

$$E_c = \frac{2A_i}{v} \sqrt{\frac{D\Theta_f}{\pi}}$$

Series B	Series C
$\Theta_f = 1.3$ sec.	$\Theta_f = 1.3$ sec.
$D^* = 2.63 \times 10^{-8}$ ft.^{2}/sec.	$D^* = 2.63 \times 10^{-8}$ ft.^{2}/sec.
$d = 0.24$ in.	$d = 0.24$ in.
$A_i = 0.00105$ ft.^{2}	$A_i = 0.00139$ ft.^{2}
$E_f = 0.112$	$E_f = 0.112$
$E_c = 0.055$	$E_c = 0.0725$
$E_F = 0.161$	$E_F = 0.176$

D* = The values used for diffusivities are an average of the values abstracted from the literature, 5, 15, 23 and 24.

Theoretical Correlation Factor

The multiplication factor of molecular diffusivity proposed by Handlos and Baron (14) to be used in conjunction with the mathematical models for extraction during free-rise is given by the following equation:

$$R = dV/D \ (1 + u_d/u_a) \ 2048$$

Series B, No. II nozzle

$$R = \frac{(.241)(.35)}{12(2.63 \times 10^{-8})(1.64)(2048)}$$

$$R = 84.5$$

Experimental Correlation Factor

Using the Handlos and Baron model:

$$\ln (1-E_M) = \ln 2B_1^2 - \frac{16DtR}{d^2}$$

$$R = \frac{d^2}{16Dt} \left[\ln 2B_1^2 - \ln (1-E_M) \right]$$

$$= \frac{(.241)^2}{144(2.88)\ 16\ (2.63)\ 10^{-8}\ (4.3)} (\ln 2 - \ln .74)$$

$$= 75$$

A plot of experimental and theoretical value of R is shown in Figures 10 and 11.

Overall Transfer Coefficient

The overall transfer coefficient for free-rise is obtained by using equation (7-D).

$$K_o = \frac{Vd}{H6} \ln \frac{C_{in}}{C_{out}} = \frac{(.38)(.24)(3600}{(1.5)(12)(6)} \ln (\frac{.00906}{.00671})$$

$$= 0.9 \text{ ft./hr.}$$

Correlation

The overall transfer coefficient was incorporated in the Sherwood number and correlated with the Reynolds, Schmidt and Weber numbers.

$$Sh = -610 + 0.46 \, Re^{.5} \, Sc^{.47} \, We^{.9}$$

Series B, Toluene Dispersed

Reynolds Number

$$\frac{dV\rho_i}{\mu_i} = \frac{(.24)(.35)(.8625)(62.4)}{12\ (.568)(.00067)} = 1050$$

d = .24 in.

V = .35 ft/sec.

ρ_i = .8625 gm/cc.

μ_i = .568 cp.

Schmidt Number

$$\frac{\mu\rho_i}{D} = \frac{(.568)(.00067)(.8625)(62.4)}{2.63 \times 10^{-8}} = 270$$

$D = 2.63 \times 10^{-8}$

Weber Number

$$\frac{d\rho V^2}{\gamma} = \frac{(.24)(62.4)(.372)^2(.995)}{(12)(17)(12)(2.54)(32.2)} = 4.45 \times 10^5 = 4.64$$

d = .24 in.

ρ = .995 gm/cc.

V = .385 ft/sec.

γ = 17 dynes/cm.

Sherwood Number – Theoretical Value

$$\frac{kd}{D} = \frac{(0.98)(0.24)}{2.63 \times 10^{-8} \quad (12)\ (3600)} = 209$$

Correlation

$$Sh = .46(1050)^{.5}(270)^{.47}(4.64)^{.9} - 610$$

$$= (.46)(32.2)(13.9)(3.99) - 610 = 824 - 610$$

$$Sh = 214$$

VITA

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