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UNIVERSITY OF CINCINNATI

May 25 1949

I hereby recommend that the thesis prepared under my supervision by Joseph B. Conway

entitled Liquid-liquid Extraction: The Mechanism of Solute Transfer in Spray Towers

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

William Licht Jr.

R S Dow

E L Mongan

Form 668—G. S. and T. C.—1M—6-41

LIQUID-LIQUID EXTRACTION: THE MECHANISM OF SOLUTE TRANSFER IN SPRAY TOWERS

A dissertation submitted to the
Graduate School of Arts and Sciences
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

1949

by

Joseph B. Conway

B.Ch.E. Villanova College 1943
M.S. University of Cincinnati 1947

ACKNOWLEDGEMENTS

The author wishes to express sincerest thanks to Professor William Licht, Jr. who acted as thesis advisor during this work. His keen criticisms and timely suggestions were deeply appreciated.

Considerable thanks are due also to Dr. E. F. Farnau for his ever pleasant cooperation. As a result of many instructive consultations with Dr. Farnau the solutions of several laboratory problems were facilitated.

The author acknowledges the help of Mr. R. T. Dickerson, Jr. in the photographic portion of this research. The assistance of Mr. Paul Schwaegerle, Mr. Harry N. Perk, Mr. Elmer L. Boehm in certain phases of the laboratory work is also gratefully acknowledged. Thanks are also due to Mr. Walter Scholl for the construction of the column support used throughout the experimental work.

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ABSTRACT

This research project is concerned with liquid-liquid extraction. Specifically, it is a study of the mechanisms of solute transfer in spray towers. A theory is proposed which postulates the existence of three separate stages of solute transfer. These stages of extraction and the operating variables which seem to affect them are discussed.

The extraction of acetic acid from water is studied using the following solvents: isopropyl ether, methyl isobutyl ketone and ethyl acetate. The acetic acid-water solution (1.063 N) was the dispersed phase.

A special feed device was designed to disperse the feed solution in the continuous phase. The design of this device also enabled the volume of the drops delivered to be measured quite accurately. The reproducibility of this feed device was found to be quite satisfactory.

Two different columns were designed and employed to prove the existence of the three stages of extraction postulated in the theory. The experimental data obtained made it possible to calculate the amount of solute extracted from the dispersed phase in the different stages. Values obtained for the extraction occurring during drop formation were lower than those previously reported in the literature. The differences in this case are thought to be due to the

different directions of extraction. Two different drop sizes were studied while using isopropyl ether and methyl isobutyl ketone. Overall extraction coefficients are calculated for one of the stages of extraction and although these values vary with the different solvents, they are seen to be little affected by varying drop size.

A short section is devoted to drop behavior. The physical properties which seem to affect the drop size of the dispersed phase are discussed. A curve is included to show the effect of inlet solute concentration on drop size. The behavior of drops during fall is also commented on. Certain peculiarities regarding the falling velocities of drops are pointed out.

Methods of calculating liquid diffusivities are presented; Newman's equation as applied to extraction is discussed; the Ilkovic equation of polarography is reviewed; and finally the previous research articles concerned with spray tower operation are considered, discussed and evaluated.

INTRODUCTION

As a unit operation, solvent extraction is gradually assuming industrial importance. Since Elgin (8) first reviewed this field, rapid and encouraging advances have been made. These have catalyzed the interest in this branch of chemical engineering to the extent that its industrial applications are increasing proportionately.

Solvent extraction refers to the separation of the components of a solution by treatment with a solvent in which one or more of the components of the solution are soluble. In the case where all the substances involved are liquids the process is referred to as liquid-liquid extraction. The solvent used being immiscible with the solvent of the treated solution, a distribution of solute between the two layers ensues.

Extraction processes are usually concerned with separating the components of a binary mixture although this need not be the case. In the petroleum industry, for example, numerous applications of this unit operation have to deal with multi-component mixtures.

As a means of separation, extraction is particularly successful in the following instances:

a) when the two components of a binary mixture form an azeotrope and cannot be separated by distillation;

b) when one of the components is heat sensitive and cannot be subjected to high temperatures;

c) when both components of a binary mixture have equal volatilities and cannot be separated by distillation;

d) when the solute is present in very small concentrations and hence separation by distillation would be uneconomical;

e) as a preliminary operation prior to distillation in order to save heat (the latent heat of vaporization of most solvents is low).

In all phases of extraction work certain terms are used consistently. These must be thoroughly understood before proceeding further and must be kept in mind throughout the perusal of this dissertation. For purposes of simplification these terms will be defined from the standpoint of ternary systems, although the definitions can readily be extended, with certain obvious modifications, to more complex systems.

Equilibrium diagram - a diagram showing the solubility relationship existing between the three components. (For a detailed explanation of the equilibrium diagram see (6).

Saturation or binodal curve - a curve on the equilibrium diagram which indicates the composition of saturated phases of the three components. It forms a boundary between one-phase and two-phase areas on the equilibrium diagram.

Diluent - the solvent of the solution to be treated. The diluent originally contains the solute or material to be recovered.

Solute - the material to be recovered or removed from the diluent.

Solvent - the substance used to extract solute from the diluent.

Non-consolute pair - a pair of liquids which exhibit partial or complete immiscibility.

Consolute pair - a pair of liquids exhibiting complete miscibility.

Conjugate layers - layers of liquid solutions which are in physical and chemical equilibrium; their compositions are represented by points on the binodal curve.

Tie-line - a line on the equilibrium diagram which connects the two points representing the compositions of the conjugate layers.

Extract layer - that layer, after contacting, which is rich in solvent.

Raffinate layer - that layer, after contacting, which is rich in diluent.

The principle of extraction is based on the fact that when a solvent and a diluent, which are immiscible, are brought in contact, the solute originally present will distribute itself between these two layers. With intimate

contact and sufficient time, definite equilibrium compositions determined by the chemical nature of the compounds, the concentration and the temperature, are set up between the two layers. Hence, if a solution of this solute in the diluent is treated with the solvent in proportions which give two layers, the liquids intimately mixed, allowed to settle, separated, and the solvent then removed from each, a separation and recovery of the solute from the original solution is effected.

Extraction processes are thus seen to consist of three parts:

a) mixing of original solution and solvent;

b) separation of phases formed;

c) removal and recovery of solvent from each phase.

The mixing and separation operations constitute a unit or "extraction stage". A stage in which equilibrium between the two phases is attained is an ideal or theoretical extraction stage. The degree to which equilibrium is approached is used as a measure of the efficiency of the stage.

The mixing or contacting operation is of immediate interest to the design engineer because it affects the degree of extraction and the separation obtainable. Methods of contacting can be classified generally as either batch or continuous. These methods are listed by Sherwood (22) and more recently by Elgin (8,9,10,11).

The present study is concerned with a type of operation referred to as continuous countercurrent. In this method of operation the material to be treated is fed continuously at one end of the apparatus while the treating solvent is fed continuously at the opposite end, the two liquid streams flowing countercurrent to each other. Vertical column extractors operating in this manner usually belong to one of the following types:

a) Spray columns

b) Plate columns

c) Packed columns

d) Wetted-Wall type columns

A modification of the packed tower has been proposed by Scheibel (20,21). This apparatus consists of alternate empty (mixing) and packed (separating) sections and is provided with a central rotating shaft carrying agitating blades at each empty section and extending through the entire tower. High efficiencies are reported.

The following discussion is concerned primarily with spray tower operation and is a study of the mechanisms by which solute may be transferred from the diluent to the solvent phases.

In spray tower operation, one of the phases is dispersed (by means of spray nozzles) in the form of fine drops and these drops rise or fall through the other (continuous)

phase depending on the relative densities of the two phases. Either phase may be dispersed in this type of operation. The direction of extraction is obviously influenced by the choice of the dispersed phase. When the solvent is dispersed, extraction occurs from the continuous phase into the drops; when the diluent phase is dispersed the direction is reversed.

The advantages of spray tower operation are:

(a) high rates of flow;

(b) ease of operation;

(c) low initial cost, and low maintenance costs;

(d) ease of cleaning.

This combination of advantageous factors results in spray towers being of industrial importance. The performance of a spray tower is usually expressed in terms of an overall extraction transfer coefficient, which is somewhat analogous to an overall heat transfer coefficient. The detailed calculation of such a coefficient will be explained later, but for the moment it is sufficient to say that it is a measure of the net overall rate at which solute is transferred from the diluent phase to the solvent phase in the tower.

The mechanism of solute transfer in spray towers is still a controversial topic. Many questions concerning tower performance remain unanswered. Among the more important of these are the following:

a) what general circumstances combine to give the highest values of the extraction coefficient?

b) which phase should be dispersed for maximum efficiency?

c) what is the effect of flow rates and drop size on the extraction coefficient?

Elgin and Browning (12) studied the extraction of acetic acid from water with isopropyl ether in a spray column. Their results indicate that the capacity of a spray column is dependent upon the rates of flow of both dispersed and continuous phases, upon which phase is dispersed, and upon the direction of solute transfer. Inlet solute concentration was shown to have an appreciable effect. Graphs are presented to indicate the effect of operating variables on the transfer coefficients. The diameter of the spray nozzle (and hence drop size) also affects transfer coefficients.

Sherwood, Evans and Longcor (23) made a study of the mechanism of diffusion in spray towers employing benzene and methyl isobutyl ketone. Acetic acid was the solute and water the third component in each case. Experiments were employed to study the extraction from single drops. It was shown that the transfer coefficient varied with the diameter of the inlet drops. The transfer coefficients were shown to increase with increased solute concentration when benzene was used and to be unaffected when the ketone was used. It was shown also that 40-45 percent of the solute is extracted

before the drop leaves the nozzle. Extraction during these experiments was from the benzene and ketone to water with the former phase dispersed.

Elgin (7) in a written discussion reports that 20 to 70% of the total extraction obtained in a spray column, four feet high, may occur within an inch or so of the entrance of the dispersed liquid.

Blanding and Elgin (3) studied flooding velocities in spray and packed towers. They also pointed out the importance of end construction in the operation of a spray column. The proper end design for a column is illustrated. Graphs are presented to indicate allowable rates of flow of the continuous phase at specified rates of flow of the dispersed phase, etc.

Johnson and Bliss (18) studied liquid-liquid extraction in spray towers and employed four systems. They indicated that the extraction coefficient increases with increasing flow rates of both dispersed and continuous phases, increases slightly with increase in concentration of the entering solute and tends to decrease somewhat with increase in tower length. When the direction of extraction was from continuous to dispersed phase, the extraction coefficient was shown to be greater and drop coalescence was less than when extraction was in the opposite direction. The column end section reported by Blanding and Elgin (3)

was employed. The following proposals concerning operating techniques are deduced:

a) disperse the phase with the highest flow rate; if the flow rates are equal, disperse the phase receiving the solute as this reduces coalescence of drops, thus keeping contact area at a maximum.

b) spray towers are most efficient when operating with systems of low interfacial tension.

These few published articles concerned with spray tower operation have done much to stimulate interest in this mode of operation. The mechanism of solute transfer in these towers is still in need of investigation and clarification. J. C. Elgin in the January issue of Industrial and Engineering Chemistry continues to review this field annually and as late as 1949 has emphasized the need for more research in spray tower work.

The present work is an attempt to elucidate the mechanism of solute transfer in spray towers and to correlate the results of research work previously reported.

THEORY

Postulates:

Heterogeneous equilibrium in ternary liquid-liquid systems is described by the so-called Distribution Law. This law expresses mathematically the relationship between the concentrations of the solute in the two phases, at constant temperature. A simple algebraic statement of this law takes the form

$$\frac{C_1}{C_2} = H \qquad (1)$$

where C_1 is the concentration of solute in the first, and C_2 that in the second, liquid phase and H is a constant. Actually, this ratio of concentrations is constant only for a limited number of ternary systems. For accurate relationships the equilibrium diagram together with tie-line date is needed.

In continuous countercurrent extraction, equilibrium between the flowing phases is seldom realized but merely approached. The equilibrium distribution law then, is only of limited use. Any investigation of this type of operation must concern itself with the rate of extraction, and the factors which affect it; i.e. the kinetics rather than the thermodynamics of the process.

Theoretical considerations, based on the close physical similarity of extraction with the process of gas-absorption and supported by the few available data, justify the assumption that the same diffusional mechanism is operative in both of these processes. In the theory of liquid-liquid extraction, two liquid films in series replace the gas and liquid films in gas-absorption theory. In applying the so-called "two-film theory" it is assumed that when the immiscible liquids flow past each other there exists on either side of the interface between the two liquids, a relatively stagnant film of each liquid. Employing these concepts the present day theory of extraction has been developed.

Consider the transfer of a solute between two immiscible liquids in contact, moving counter-currently to each other, where the interface between the two liquid phases represents the boundary surface. In the moving and disturbed main portion of each liquid, solute concentration gradients will be rapidly and completely equalized, and passage of solute throughout the main body of each liquid will take place due to mixing by the turbulence of the prevailing fluid motion. In the relatively stagnant films on either side of the interface, however, passage of the solute cannot take place by means of mixing. Solute may only traverse these stagnant liquid layers by diffusion,

with the result that solute concentration gradients are set up in the stationary films adjacent to the interface. Therefore, the transfer of solute between two immiscible liquids under the above conditions must be controlled by the laws of diffusion. Furthermore, the two-film theory assumes that equilibrium exists at the interface between the phases in contact.

The postulates involved in the two-film theory of solute transfer between two immiscible phases in contact may be summarized as follows:

a) On either side of the interface between two moving immiscible liquids in contact, there exists a relatively stationary fluid film.

b) The disturbed main body of each fluid is in comparatively violent motion, and solute concentration gradients therein are rapidly equalized due to mixing by fluid motion.

c) In the stationary films passage of solute can occur only by diffusion, and in consequence, concentration gradients are set up through each stationary film.

d) Transfer of solute across the interface itself does not take place by diffusion. This transfer is so rapid that it is not a controlling factor in the process. Equilibrium is set up here and the transfer of solute involved is the result of the

prevailing equilibrium conditions.

e) The only controlling factor in the process is the rate of solute diffusion across the interfacial stationary films.

Fick's Law:

Hunter and Nash (17) have reviewed the theories of solute transfer and have developed working equations pertinent to the design of liquid-liquid contacting equipment. These workers employed the two-film theory and assumed that the transfer of solute between two immiscible liquids in contact is controlled by the law of diffusion known as Fick's Law (13). This law states that the rate of diffusion is proportional to the concentration gradient and the surface area of cross section through which diffusion is taking place. For diffusion in one direction only, the amount of solute ds which traverses a given cross-sectional area "a" of solution in a time dt is expressed by

$$ds = - D\, a\, \frac{dc}{dx}\, dt \qquad (2)$$

where the minus sign denotes that the solute diffuses in the direction of decreasing concentration. The rate of diffusion is given then by

$$\frac{ds}{dt} = - Da\, \frac{dc}{dx} \qquad (3)$$

where D is the diffusion coefficient or specific diffusivity; i.e., the amount of solute diffusing across a unit area in unit time under a unit concentration gradient if the rate is constant during that time, that is, with a uniform or stationary concentration gradient.

In applying Fick's Law due consideration must be given to the assumptions made in developing this law. These assumptions are (16):

a) all motions except that of molecular agitation are rigorously excluded.

b) linear diffusion only is considered.

c) diffusion takes place linearly upward against the force of gravity.

If Fick's Law is applied in conjunction with the two-film theory, the concentration gradient through each interfacial film represents the driving force causing transfer of solute. The mass of solute per unit time, M/θ, transferred at a constant rate through either film must be proportional to the surface of the interface A, and the concentration difference in the film. Therefore, if a solute is being extracted from phase P at a steady rate by countercurrent scrubbing with phase W (see Figure 1) the following expressions can be written:

For the P film:

$$\frac{M}{\theta} = k_p (C_p - C_i)A \qquad (4)$$

and for the W film:

$$\frac{M}{\theta} = k_w (C_I - C_w)A \qquad (5)$$

where: C_p is the solute concentration on the outside of the P film - any units of concentration;

C_i is the solute concentration on the P side of the interface - same concentration units as above;

C_I is the solute concentration on the W side of the interface - same concentration units as above;

C_w is the solute concentration on the outside of the W film - same concentration units as above;

M is the mass of solute passing across the interface during the time θ;

A is the interfacial area;

k_w and k_p are "individual film coefficients" for phases W and P respectively.

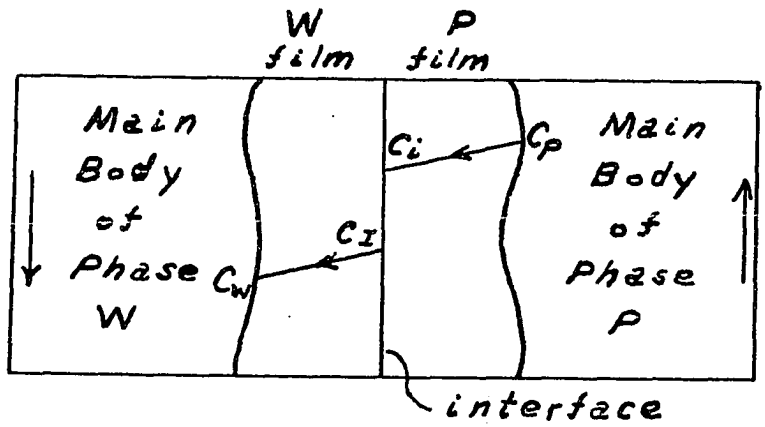


Figure 1

The term "film coefficient" introduced here is defined as follows:

$$k = \frac{D}{x} = \frac{\text{specific diffusivity}}{\text{film thickness}}$$

as may be seen by comparing equations (4) and (5) with Fick's Law, equation (3).

Writing the distribution law

$$\frac{C_P}{C_W} = H \tag{6}$$

it is seen that

$$\frac{C_i}{H} = C_I \tag{7}$$

because equilibrium conditions are assumed to exist at the interface.

Now, if a steady state is maintained, the amount of solute diffusing per unit time through each film must be the same, hence, equations (4) and (5) can be equated:

$$\frac{M}{\theta} = k_P (C_P - C_i) A = k_W (C_I - C_W) A \tag{8}$$

The concentrations at the interface, C_i and C_I are difficult if not impossible to measure. It becomes convenient therefore to employ an "overall coefficient" to be used with an "overall concentration gradient". Equation (8) then becomes

$$\frac{M}{\theta} = K_W (C'_W - C_W) A = K_P (C_P - C'_P) A \tag{9}$$

where: C_W and C_P are as previously defined;

C'_W is the W phase concentration which would be in equilibrium with the P phase concentration C_P;

C'_P is the P phase concentration which would be in equilibrium with the W phase concentration C_W;

K_W and K_P are the overall transfer coefficients for the W and P phase respectively.

The overall concentration gradient employed here is seen to be a measure of displacement from equilibrium conditions. It should be noted from equation (9) that overall transfer coefficients can only be employed in cases of isothermal extraction where the simple distribution law holds or for normal solutes present in small concentrations where the distribution law can be assumed to hold. If in equation (9), the ratio C_P/C_W is not a constant then K_W or K_P will vary with concentration (22).

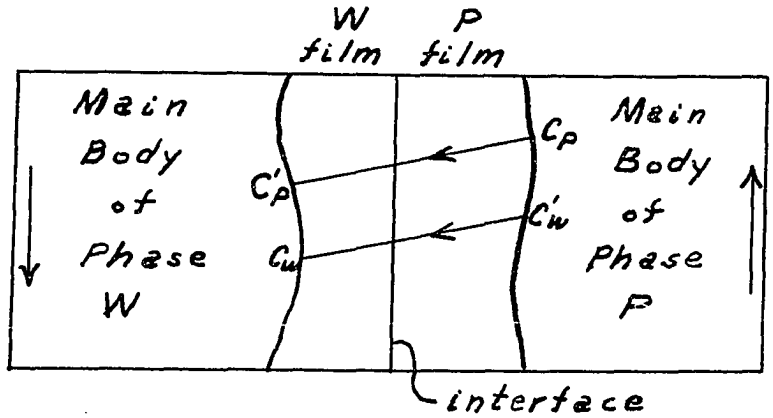


Figure 2

Application to Extraction Unit:

A counter-current extraction unit is illustrated in Figure 3. The amounts of the two solute-free liquids passing through the apparatus in unit time are P and W mols, respectively. The solute concentrations are expressed as mols of solute per mol of solute-free liquid. The P phase has inlet and exit solute concentrations of y_1 and y_o respectively. The scrubbing liquid W has inlet and exit concentrations x_o and x_1. Considering a cross-section of the tower where the concentrations are x and y, and a second cross-section a differential distance dl below the first where concentrations are x + dx and y + dy, then the amount of solute lost by one liquid is gained by the other assuming continuity of operation, so that in this section

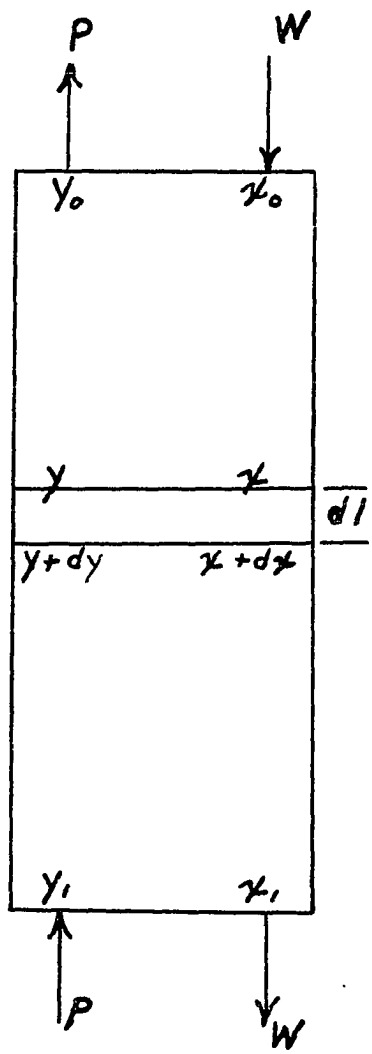


Figure 3

$$Pdy = Wdx \qquad (10)$$

With continuity of operation W and P are fixed by operating conditions, therefore, by integration

$$Py = Wx + \text{const.}$$

$$\text{or} \quad y = \frac{W}{P} x + \text{const.}$$

In other words, at any point in the system the relationship between the solute concentrations in the two liquids may be represented by a straight line plot of y versus x with a slope equal to W/P, the mol ratio of the inlet solute-free liquids, always assuming of course that the two liquids are mutually insoluble. This line determined solely by a material balance is called the "operating line" and is of the same significance as the operating line used in gas absorption theory, the slope of which is the ratio of liquid to gas flow rates.

The driving force for the calculation of the overall coefficient K_W is, from equation (9), $(C'_W - C_W)$, that is $\frac{y}{H} - x$, hence

$$\frac{dy}{H} - dx = df \qquad (12)$$

where df is the differential shift in driving force across the section dl.

Since from equation (10) $dy = \frac{W}{P} dx$

then

$$dx = \frac{df}{\left(\frac{W}{PH} - 1\right)} \qquad (13)$$

In figure 3, if "a" is the interfacial area per unit volume of the extractor, and A is the cross-section of the tower, then the total interfacial area exposed in the section dl will be (aAdl). Now Wdx must be the differential weight of solute transferred in area (aAdl) per unit time, therefore

$$- Wdx = K_W \left[\frac{y}{H} - x \right] aAdl$$

$$\text{and} \quad - \frac{Wdf}{\frac{W}{PH} - 1} = K_W f \, aAdl$$

$$\therefore \quad - \frac{df}{f} = K_W \, aAdl \left[\frac{1}{PH} - \frac{1}{W} \right] \tag{14}$$

Assuming K_W, "a", and H constant across the column (14) may be integrated to yield:

$$\ln \frac{f_1}{f_o} = K_W \, aAl \left[\frac{1}{PH} - \frac{1}{W} \right] \tag{15}$$

Now let F be a "mean concentration difference" over the total length of the extractor, then

$$F \ln \frac{f_1}{f_o} = F \, K_W \, aAl \left[\frac{1}{PH} - \frac{1}{W} \right] \tag{16}$$

when F is so defined that FK_W aAl is the total amount of solute transferred per unit time. Thus:

$$FK_W \, aAl = P \, (y_1 - y_o) \tag{17}$$

and from (11),

$$\frac{1}{W} = \frac{x_1 - x_o}{P(y_1 - y_o)} \tag{18}$$

Substituting these values in equation (16) and simplifying:

$$F \ln \frac{f_1}{f_o} = \left(\frac{y_1 - y_o}{H}\right) - (x_1 - x_o)$$

$$= \left(\frac{y_1}{H} - x_1\right) - \left(\frac{y_o}{H} - x_o\right) = f_1 - f_o$$

$$\therefore \quad F = \frac{f_1 - f_o}{\ln \frac{f_1}{f_o}} \tag{19}$$

or from the definition of f

$$F = \frac{\Delta C_1 - \Delta C_o}{\ln \frac{\Delta C_1}{\Delta C_o}} \tag{20}$$

Thus F is seen to be a "logarithmic mean driving force" for a continuous extractor operating under the conditions assumed and is used with overall transfer coefficients to calculate the total amount of solute transferred per unit time by this equation

$$\frac{M}{\theta} = K A \Delta C_{lm} \tag{21}$$

where K is the overall transfer coefficient for the film corresponding to the concentrations used. ΔC_{lm} is the

logarithmic mean driving force as given by equation (20) and A is the interfacial area.

In most types of tower operation it is impossible to calculate or measure the actual interfacial area A. Under these conditions a specific area term is employed in conjunction with the tower volume to make possible the use of overall coefficients. Equation (21) then has the form

$$\frac{M}{\theta} = Ka\ V\ \Delta\ C_{lm} \qquad (22)$$

where "a" is the specific area, ft^2 of interfacial area per unit of volume and V is the tower volume in ft^3. When this equation is employed, tower operation is reported in terms of the values of Ka. These values are considered preferable to the values of K as given by equation (21). In using values of Ka, however, certain precautions must be observed and these will be discussed below.

The theory outlined above is that which appears in the literature at this time. It is felt, however, that there are a number of objections to be raised in connection with the application of this theory to spray towers. Therefore, it was considered desirable to undertake a more detailed study of the actual mechanism by which solute is transferred in spray towers.

The Mechanism of Solute Transfer:

It is impossible to obtain a correct interpretation of spray tower performance by employing the overall coefficients as calculated by equations (21) and (22). The very nature of these coefficients prohibit this, as explained below. The present work, concerned as it is with the mechanism of solute transfer, will employ these coefficients only under certain conditions when it is felt that they are applicable.

A closer analysis of this mechanism may be had by dividing spray tower operation into three distinct parts. It is assumed that extraction or solute transfer occurs in three stages. First, extraction occurs as the drop is forming at the spray tip. Secondly, extraction occurs as the drop falls or rises through the continuous phase. This stage of extraction begins the instant the drop is detached from the tip and ends when the drop strikes the bottom or top interface. Thirdly, extraction may occur when the drop strikes the bottom or top interface or when it breaks and crosses this interface.

A graphical interpretation of the three stages of extraction as outlined above is given by the accompanying figure, which represents a spray tower in continuous operation.

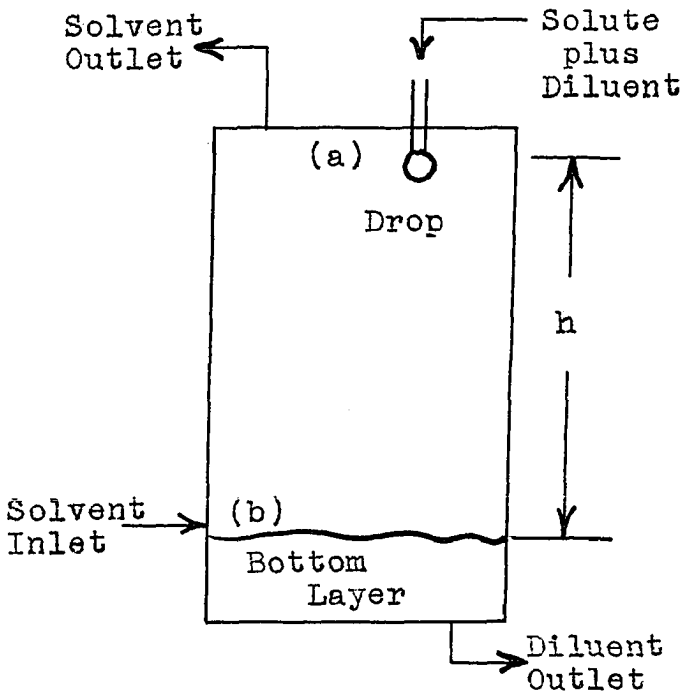


Figure 4

Stage 1 - Extraction occurs at (a) during drop formation.

Stage 2 - Extraction occurs during fall of drop; drop falls through height "h".

Stage 3 - Extraction occurs at (b); either as a result of drop striking the interface or during its breaking and subsequent crossing of the interface.

Referring to equations (21) and (22) it is seen that the term M/θ is a rate of solute transfer. Indeed, it is the total overall rate at which solute is transferred in the tower as a whole. In view of the above assumption, this overall rate can be considered as a combination of three individual rates; thus,

$$R_o = \frac{M_1 + M_2 + M_3}{\theta_1 + \theta_2 + \theta_3} \qquad (23)$$

where R_o is the overall rate of solute transfer as represented by M/θ;

M_1 is the amount of solute transferred by means of stage 1 in time θ_1;

M_2 is the amount of solute transferred by means of stage 2 in time θ_2;

M_3 is the amount of solute transferred by means of stage 3 in time θ_3.

In view of the above then, a correct interpretation of extraction phenomena is not possible unless each individual stage and the factors which affect it are considered separately. It is quite possible for instance, that the factors affecting the amount of solute lost during stage 2 may not be the same as those which affect the amount of solute lost during the other stages. The extraction mechanism and the rate in each individual stage of extraction must then be considered. If appreciable difference in the factors affecting each individual stage is found, it is obviously unsound to try to correlate all three by means of a single overall K as proposed in the theory outlined above.

Stage 1:

The mechanism of extraction during drop formation has been studied by comparatively few authors but all seem to agree that a large portion of the extraction takes place during this period. Sherwood, Evans and Longcor (23) have

shown that 40 to 45 percent of the total solute present in the drop originally is lost during the formation of the drop. Elgin (12) reported that 20 to 70 percent of the total extraction obtained in a spray column four feet high may occur within one inch or so of the entrance of the dispersed liquid.

In spray tower operation it is thought that the film within the drop is controlling. It is felt that the convection currents set up within the forming drop are responsible for the rapid extraction during this period, inasmuch as mass transfer by convection is fairly rapid.

The factors which influence extraction during drop formation are as yet not fully understood. It is desirable, therefore, to list all possible variables which might be pertinent in this stage and attempt to explain or predict the effect of each. Such a list might include: drop size, drop formation time, inlet solute concentration, direction of extraction, phase dispersed, and tip diameter.

1) Drop size - During drop formation this variable increases from zero (as also does the surface area of the drop) to a maximum at the moment of detachment. For a given drop size at detachment, however, what is the interrelation between drop size and the amount of extraction? Sherwood, Evans and Longcor (23) report that the amount of extraction during drop formation will vary with drop size. It seems quite logical to assume that the amount of extraction during drop

formation is proportional to drop size. Indeed it should be proportional to the drop volume to the two-thirds power. This, of course, must be based on equal times of drop formation in each case. Under this condition, the time rate of drop volume increase will be greater in the case of the larger drops thus:

$$\left(\frac{dV}{dt}\right)_{T,2} > \left(\frac{dV}{dt}\right)_{T,1} \qquad (24)$$

where V is drop volume

t is time

T is drop formation time

2 indicates the larger drop

1 indicates the smaller drop.

2) Drop formation time - The research work cited previously indicated very rapid extraction during the formation period. In the work by Sherwood, Evans and Longcor (23) a drop formation time of 0.5 seconds was employed. If the amount of extraction during drop formation is directly proportional to the time of drop formation, it would be advantageous to employ long periods of time for drop formation. Theoretical considerations seem to indicate that a direct proportionality exists here. In other words, doubling the drop formation time should produce a two fold increase in the amount of extraction. There is, however, no experimental data available on this point.

3) Inlet solute concentration - According to Fick's Law and to equation (21), increased inlet solute concentration should lead to an increased rate of extraction during this stage. Overall transfer coefficients, on the other hand, should be independent of this variable (see equation (21). Sherwood, Evans and Longcor (23) using overall coefficients found these to be independent of solute concentrations in the ranges studied, for the extraction of acetic acid from methyl isobutyl ketone with water with the acetic acid-ketone solution dispersed. However, in another case they found that the overall coefficient was affected by solute concentration when acetic acid was being extracted from benzene with water. The acetic acid-benzene solution was dispersed. It is interesting to note in regard to this work that the solute concentrations in the benzene were very much lower than those in the ketone.

Inasmuch as the above investigation was concerned with overall coefficients, it is not possible to apply their conclusions with respect to solute concentrations to a prediction of extraction rates for stage 1. These results, however, should be kept in mind in considering this variable.

4) Direction of Extraction - There are data available for the extraction of acetic acid from methyl isobutyl ketone, and from benzene with water but no data exist with which to compare them for extraction in the opposite direction, i.e.,

the extraction of acetic acid from water with methyl isobutyl ketone or benzene. This lack of data, therefore, prevents an accurate interpretation of the effect of this variable. It seems possible, nevertheless, that opposite directions of extraction will have a pronounced effect on both the rate and amount of extraction during drop formation.

When a drop is formed at the delivery tip, it immediately possesses surface free energy which tends to remain at a minimum. This free energy is the result of molecular attractions and is fully discussed by Adam (1). (The meaning of the term "free energy" as applied here to surfaces should not be confused with the meaning of the term free energy as used in chemical thermodynamics). Furthermore, the possession of surface free energy causes droplets to assume the smallest possible volume. It is also responsible for the fact that work must be done in extending these surfaces. This tendency of the surface free energy to remain at a minimum is also responsible for the orientation of certain molecules in the surface. This latter concept is manifested in the marked lowering of the surface tension when rather small amounts of certain solutes are placed in solution. By so concentrating themselves in the surface of a solution these molecules cause a substantial decrease in the surface tension and also cause the surface free energy

to become a minimum.

Employing this concept of surface free energy, it might be possible to anticipate the effect brought about by different directions of solute transfer. If, for instance, a solute is contained in a solvent and causes a decrease in the surface tension of this solvent, it is to be considered that this represents a condition in which the surface free energy of a drop formed of this solution is at a minimum. A loss of solute by this drop consequently would necessitate an increase in the surface free energy and since this is opposed by the tendency for this quantity to remain at a minimum it might be expected that solute transfer would be slow. If, on the other hand, however, this same solute is contained in a solvent with no appreciable reduction in surface tension being effected (and hence without a similar effect on the surface free energy) then loss of this solute by this solvent would not result in an increase in the surface free energy and would not be opposed by the tendency of the surface free energy to become a minimum. It should be expected that the solute transfer would then be faster than that of the previous case. For instance, acetic acid in water causes a reduction in the surface tension of water and consequently reduces the surface free energy. Acetic acid in methyl isobutyl ketone causes no such reduction in the surface tension of the ketone and consequently does not

reduce the surface free energy. The loss of acetic acid by the water would be accompanied by an increase in surface free energy while the surface free energy of the acetic acid-methyl isobutyl ketone solution would be unaffected by the loss of acetic acid. Therefore, under the same conditions of operation it should be easier to extract acetic acid from methyl isobutyl ketone with water than to extract acetic acid from water with methyl isobutyl ketone. This effect of different directions of extraction should show up in stage 1 of spray tower operation and possibly in other stages as well.

Further indications of the effect of direction of extraction during stage 1 may be had from a consideration of the work of Harkins (14) which may be read in Weiser (25). The work of Harkins was concerned with the spreading tendency of immiscible liquids but it is felt that some of these principles are applicable here. Harkins employed the concepts of cohesional and adhesional work. If a bar of liquid "a" of unit cross section, Figure 5, is pulled apart along the plane p, it will require the work of cohesion W_c, which is the work required to form the two new unit surfaces, that is,

$$W_c = 2 \gamma_a \text{ ergs} \qquad (25)$$

where γ_a is the free energy of surface "a", i.e., the work

required to increase its surface by 1 cm^2. Since two new surfaces of unit cross section are created, W_c is as given above.

If a bar consisting of the two liquids a and b of unit cross section is pulled apart at p, the interface ab vanishes and two new surfaces appear. The work involved, called the work of adhesion W_a, is thus:

$$W_a = \gamma_a + \gamma_b - \gamma_{ab} \qquad (26)$$

where γ_{ab} is the free energy of the interface ab and γ_b is the free energy of the surface b.

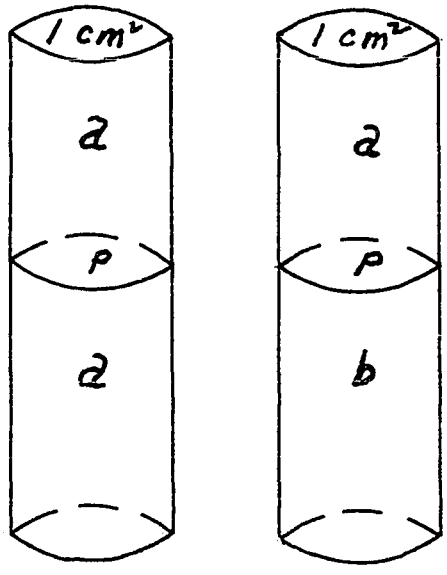


Figure 5

The presence of a polar group has the effect of increasing the work of adhesion W_a, very much more than it increases the work of cohesion W_c. The reason for this is explained diagrammatically. This figure has been reproduced below to clarify the explanation. Part 1 of Figure 6 shows the condition which exists when a bar of octyl alcohol is pulled apart. The circles represent the OH groups and the rectangles the hydrocarbon chains. At this stage, the alcohol molecules in both of the parts

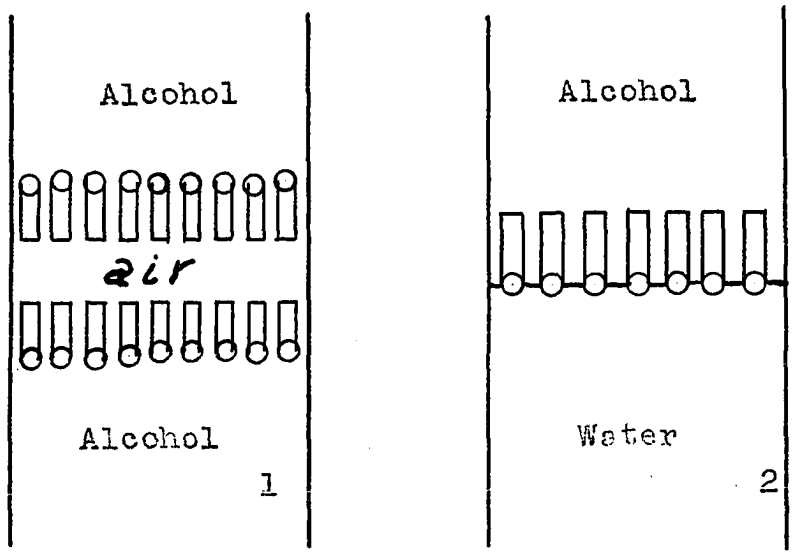


Figure 6

being separated are so oriented that their hydroxyl groups point inward. The hydrocarbon parts of these molecules, therefore, are closer to the surface. This indicates that the final work of separation will be affected chiefly by the attraction between the non-polar ends of the alcohol molecules. Harkins points out that in the first period of the separation, some of the hydroxyl groups which are to go on the upper side of the plane of separation will have to be separated from others that are to go on the lower side. One would expect, therefore, that the work of separation of the alcohol to be greater, but not much greater than that of octane. This has been verified experimentally by Harkins.

If the octyl alcohol is to be pulled away from water, Figure 6-2, the final break must come between the

polar hydroxyl groups of the alcohol and water. This is because the alcohol molecules at the interface between the alcohol and water are oriented with their hydroxyl groups pointed toward the water. Harkins shows experimentally that the work of adhesion in this case is much greater than the work of cohesion, i.e., the work needed to separate the alcohol from itself.

Now let the above considerations be applied to a definite extraction process. The extraction of acetic acid from both water and methyl isobutyl ketone will be considered to illustrate how the above principles are applied. First of all, consider the extraction of the acetic acid from water using methyl isobutyl ketone as the solvent. In the water, the acetic acid molecules are oriented in such a way that their carboxyl groups point into the water. The methyl groups, therefore, are protruding, so to speak, from the surface. When the methyl isobutyl ketone extracts the solute from the water, its dissolving influence is exerted on the methyl groups of the acetic acid molecules. When these molecules are pulled from the water, the final break must come between the carboxyl groups of the acid molecules and the OH groups of the water molecules. Since these two groups undoubtedly form hydrogen bonds between themselves, the attraction between these two groups is strong and the

extraction of the acetic acid from the water is difficult.

Now, if the extraction of the same solute from methyl isobutyl ketone with water is considered slightly different conditions exist. The solute molecules in the ketone have no special orientation or at least the orientation is not as pronounced as with acetic acid in water. When water is used to extract the solute in this case the water molecules attract solute molecules by forming hydrogen bonds between the carboxyl groups of the acetic acid molecules and the hydroxyl groups of the water molecules. This is made possible due to the random orientation of the solute molecules in the ketone. The final break in this case appears therefore to come between the methyl groups of the acid and the solvent molecules. No hydrogen bond formation is possible in this case and the attraction between these two must necessarily be weak, at least weaker than if hydrogen bond formation were possible.

In terms of the concepts proposed by Harkins (14), the adhesion between the acetic acid and water is greater than that between the acetic acid and methyl isobutyl ketone. Hence, it might be expected that the rate of extraction of acetic acid from methyl isobutyl ketone with water would be greater than the rate of extraction of acetic acid from water with methyl isobutyl ketone, all other conditions being the same.

The above considerations seem to indicate that the direction of extraction should have a significant influence on the rate of extraction during stage 1. Experimental verification of this concept must await data on the extraction of acetic acid from water with methyl isobutyl ketone. This influence may also exert its effect in other stages as well.

5) Phase dispersed - When acetic acid, for instance, is being extracted from liquid A by liquid B it is possible to disperse liquid B, the phase receiving the solute, or to disperse liquid A, the phase containing the solute. Experimental work has shown that differences in the capacity of extraction columns arise when the phase dispersed is changed. This phenomenon, however, has not been explained as yet. It might be possible to explain this in terms of the differences in convection currents set up within the drop when different phases are dispersed.

Johnson and Bliss (18) have proposed two rather simple rules to serve as guides in obtaining proper phase dispersal. These rules are cited in the introduction of this thesis. Since the work of Johnson and Bliss was concerned with overall transfer coefficients, it is not possible to employ the above rules for phase dispersal to explain or interpret solute behavior during stage 1.

6) Tip diameter - The effect of the diameter of the inlet distributor tip at which the drops are formed is important only as it affects drop diameter. The effects of drop diameter have already been discussed.

In view of the foregoing considerations several tentative conclusions may be drawn:

a) Stage 1 is characterized by rapid rates of extraction.

b) the relative amount of extraction occurring in this phase may be large.

c) the factors which affect the mechanism of extraction during stage 1 are: drop size, drop formation time, inlet solute concentration, direction of extraction and phase dispersed.

Stage 2

Stage 2 begins when the drop is detached from the tip and ends when the drop strikes the bottom (or top) interface. It is probable that the rate of extraction during this stage is slower than the rate of extraction in stage 1. The calculations connected with this phase are somewhat simpler since the transfer area remains substantially constant. Fick's Law of Diffusion therefore may be applied directly. It must be realized that this will only be an approximation due to the limitations which are imposed on Fick's Law.

When the drop is released from the tip, it has a definite volume which is dependent upon tip size, inlet solute concentration, etc. This corresponds to a certain surface area which can be assumed to remain constant during its fall through a given column height "h". This last assumption is admittedly incorrect on two counts:

a) the drop loses solute during its fall with a subsequent reduction in volume and area.

b) the drop is continually pulsating and vibrating during its fall.

The inaccuracies produced by this assumption are unavoidable. The simplification which ensues justifies its use.

As an example, let the extraction of acetic acid from water using isopropyl ether be considered. The acetic acid solution will be dispersed and falling (since its density is greater than that of isopropyl ether). The isopropyl ether is the continuous phase. Referring to Figure 4, let it be assumed that the drop has just left the tip and is starting its fall through height "h". Now if,

A_d = the surface area of the drop (assumed constant during this stage)

C_{wd} = the solute concentration in the drop at any time during stage 2 - lb moles acetic acid/ft^3 of solution

C_s = the solvent concentration, lb moles of acetic acid/ft^3 of solution

C_w^* = the solute concentration of water in equilibrium with solvent concentration C_s - lb moles of acetic acid/ft^3 of solution

then the rate at any time during stage 2 will be given by (see equation (9),

$$R_2 = K_w \ A_d \ (C_{wd} - C_w^*) \qquad (25)$$

where K_w = the extraction coefficient. The rate, R_2, during stage 2 may not necessarily remain constant since C_{wd}, C_w^*, A_d, and probably K_w change throughout the height "h".

An equation similar to (21) can be written for stage 2 by employing logarithmic mean concentration gradients as employed in ordinary extraction calculations (see Theory).

$$R_2 \text{ (overall)} = K_w \ A_d \ (\triangle C)_{lm} \qquad (26)$$

where K_w = overall extraction coefficient for stage 2.

$\triangle C_{lm}$ = logarithmic mean concentration gradient across the terminal conditions of height "h".

If it is assumed that the concentration of acetic acid in isopropyl ether is zero, as it approximately is, a simplification is possible. This assumption makes the concentration gradient equal to the instantaneous solute concentration in the falling drop. Equation (26) then becomes

$$R_2 \text{ (overall)} = K_w A_d (\Delta C)_{lm} \qquad (27)$$

where $(\Delta C)_{lm}$ is now the logarithmic mean of C_{w_o} and C_{w_f}; C_{w_o} is the drop concentration at the instant of detachment and C_{w_f} is the solute concentration of the drop when it hits the bottom interface, i.e., at the end of stage 2.

Since the rate of extraction during the falling period (stage 2) has not been studied as a separate entity it is not possible to describe accurately the effects of certain operating variables on this quantity. It is possible, however, to consider each of the supposedly important variables individually and predict tentatively the effects of each by applying the fundamental laws of diffusion. The fundamental law of diffusion, Fick's Law, may be directly applied to this stage of operation inasmuch as the transfer area remains substantially constant. However, even this assumption must be viewed with some suspicion. First of all, the drops are continuously vibrating and pulsating during this phase leading to a certain amount of agitation both within and external to the drop. Secondly, the drops are moving with a substantial velocity such that turbulent flow is present. This latter condition should certainly lead to an enhanced value of the diffusivity of the solute. The usual values of the solute diffusivity are those as given by Fick's Law, the assumptions underlying which have already been discussed.

The factors which seem to be important in stage 2 are drop size, drop formation time, inlet solute concentration, direction of extraction, phase dispersed, tip diameter, continuous phase flow rate, and dispersed phase flow rate.

1) Drop size - For a given dispersed phase rate, decreased drop size increases both total surface and total time of contact. Under these conditions, decreased drop size should result in an increase in the amount of solute extracted during this stage. The transfer coefficients, however, should be unaffected by this variable inasmuch as they are based on unit area.

On the other hand, decreased drop size results in a decrease in the pulsations occurring within the drop which decreases the internal convection and probably offsets the above factors.

2) Drop formation time - This variable would seem to have no effect on stage 2 except as it affects the concentration at the start of this stage. The concentration of the drop at the end of stage 1 is equal to its concentration at the start of stage 2, hence if drop formation time affects the concentration of the drop at the end of stage 1, its effect will show up in stage 2. Drop formation time is affected by the dispersed phase rate which is discussed below.

3) Inlet solute concentration - Increased inlet solute concentrations probably leads to higher drop concentrations at the start of stage 2. Applying the laws of diffusion to this phase it might be expected then, that the increased driving forces so produced would lead to higher rates of extraction. Since the rates of extraction during this falling period have not been studied as such it is impossible to predict the effect of this variable. The affect of inlet solute concentration on the overall transfer coefficient as studied by Sherwood, Evans and Longcor (23) has already been discussed (page 30).

Furthermore, in the work of Johnson and Bliss (18), in which overall transfer coefficients were calculated by equation 22, these coefficients were found to increase slightly with an increase in inlet solute concentration but the effect was found to be only slight. For instance, in the extraction of acetic acid from water with methyl isobutyl ketone, the water phase being dispersed, the inlet solute concentration in the water phase was increased by 50%. At constant values of the contacting phases this resulted in an increase in the overall transfer coefficient of only 10%. A similar situation was produced when the methyl isobutyl ketone was dispersed.

4) Direction of extraction - The rate of extraction during stage 2 is probably affected by the direction of extraction

in the same way as is the rate in stage 1. It is expected therefore that the same principles apply here as were discussed under this variable in stage 1. The differences in adhesions of the solute for the two liquids is probably the important factor.

5) Phase dispersed - It is difficult to see how this variable would have any effect on the rate of extraction during stage 2 under similar conditions of operation. For instance, consider the extraction of acetic acid from water with methyl isobutyl ketone. If the water phase is dispersed the solute transfer is from the drops to the continuous phase (methyl isobutyl ketone). However, if the methyl isobutyl ketone is dispersed, the solute transfer is from the continuous phase (acetic acid water solution) into the drops of methyl isobutyl ketone. Now, if the drop size is the same in both cases, there seems to be no reason why the transfer mechanism should be different in the two cases. The rate of extraction as well as the total amount of solute extracted during this stage should be the same for the two different methods of operation. Johnson and Bliss (18) however, found that a difference actually exists when the above experiment is carried out. Their results indicate that the phase receiving the solute should be dispersed as this leads to higher values of the overall transfer coefficient as calculated by

equation (22). This conclusion was based on the fact that when the phase receiving the solute was dispersed, drop coalescence in the tower was less and hence the transfer area remained at its maximum value.

This behavior might be explained in terms of the differences in convection currents set up within the drops (see page 38).

6) Tip diameter - This variable again affects only drop size, the effects of which have already been discussed.

7) Continuous phase flow rate - This variable varies the time of rise or fall of the dispersed drops and thus affects the contact time. The velocity of the dispersed phase, however, relative to the continuous phase remains fixed, and hence the film thickness and the film transfer coefficient remain constant with this variable.

8) Dispersed phase rate - The rate at which the dispersed phase is delivered into the column is also of some importance. This variable has no effect on drop fall or drop rise time; it merely affects the number of drops in the column at a given time. This increase in transfer area, however, does not affect the overall transfer coefficient which is per unit area.

The above variables seem to be the more important factors which affect the rate of extraction during stage 2. If other factors are operative in this respect, and this is

quite possible, these will have to be established experimentally.

Stage 3

Heretofore, the existence of this stage has not been recognized. At least, if it has been recognized (and there is no record of this) it has been assigned but little importance and the rate during this stage has been assumed negligible. It must, however, be considered as a separate stage of extraction and its mechanism studied individually.

The instant a drop strikes the bottom or top interface, depending on whether it is falling or rising, stage 2 ends. The drop then begins the process of crossing the interface with which it has just come into contact. Usually, the drops do not hesitate very long but break and cross the interface almost instantaneously. It is not possible to apply the same theory to this stage of extraction as applied to stage 2. As a matter of fact it appears impossible to develop any type of theory which would be applicable to this stage. The variables which affect the rate of extraction during this stage are not obvious and a detailed discussion of this stage cannot be presented at the present time.

The existence of stage 3 is no assumption. Its presence is as real and definite as that of the other stages

just discussed. The importance of this stage, however, has never been evaluated; the magnitude of the rate of extraction has never been considered nor determined. Until this is done any assumptions regarding its importance are to be questioned.

The above discussion has postulated that the extraction in spray tower operation occurs in three distinct stages. The differences in each stage have been indicated and the effects of certain operating variables on the rate of extraction during each stage have been considered. The above discussions show the reasons why overall transfer coefficients must be used with caution. Strictly speaking, stage 2 is the only stage of the extraction process to which these coefficients are directly applicable. In stages 1 and 3 the transfer areas are not constant and are not readily discernible. In the calculation of overall transfer coefficients, as presented in the literature, using equation (21), the transfer area of stage 2 is assumed to apply to the other two stages as well. The errors in this assumption are obvious. The use of overall transfer coefficients as calculated by equation (22) is also subject to criticism. The use of Ka values (equation 22) is objectionable since these have a tendency to misrepresent if not conceal the effect of the operating variables. For instance, an increase in the dispersed phase rate increases the number of drops in the

tower at a given time and hence increases the specific area term "a". Values of Ka, therefore, increase with increase in dispersed phase rate. However, a correct representation of the effect of the dispersed phase rate on the extraction mechanism is not given since the increase in Ka may or may not be due entirely to the increase in "a". The effect on K, therefore, is concealed.

The above criticisms do not imply that Fick's Law may not be applied to each of the three stages of extraction. If Fick's Law is applied, however, it is quite likely that each stage would have a different value of the individual transfer coefficient, k, since such things as film thickness, diffusivities, etc. would probably be affected differently in each stage. The use of overall coefficients therefore is still objectionable.

The present work is directed toward an investigation of the three stages of extraction just postulated. Experimental work was performed to study the rates during each of these stages as well as certain of the variables which may affect these rates.

EXPERIMENTAL WORK

Preliminary Experiments

Having postulated the existence of three separate and distinct stages of extraction in spray tower operation, the primary purpose of the experimental part of the present research was to investigate the mechanism of extraction in each of the above stages and to determine the relative importance of each stage. Such an investigation was found to be not devoid of experimental difficulties.

At the outset it was considered desirable to carry out certain preliminary experiments to exploit the work to be done. In all, twenty preliminary experiments were performed in an attempt to familiarize the writer with some of the intricacies of spray tower operation. Although the results of these experiments were entirely qualitative, this plan was quite successful in enabling the author to appreciate a little more fully the difficulties to be encountered later on in the experimental work and to plan the work more efficiently. It is not implied that all of the preliminary experiments that were performed eventually proved to be of some value. Actually many of these experiments turned out to be worthless.

The preliminary experiments which were found to be of considerable value are described below. Together with these are included the important observations made during

the performance of each of these experiments.

In all of the preliminary experiments, unless otherwise specified in the descriptions which follow, the phase to be dispersed was placed in a 250 cc. separatory funnel. To the delivery end of this funnel the distributor tip was attached. This distributor tip was simply a 6 inch length of ordinary soft glass tubing (6 mm). One end of this tubing was rotated in the flame of a bunsen burner until the glass melted enough to cause the inside diameter to be reduced to approximately 1/16". The end of the 6 inch tube with the small diameter was always used thereafter as the delivery end. The other end of this 6 inch length of glass tubing was then attached to the delivery end of the 250 cc. separatory funnel by means of a short length of rubber tubing. In actual operation the distributor tip was placed in the continuous phase; the material to be dispersed was then placed in the separatory funnel which was then supported firmly. The stopcock of the separatory funnel was opened slightly to allow the material in the separatory funnel to flow down by gravity through the distributor tip and to be delivered into the continuous phase in the form of small drops. The drops, of course, formed on the end of the 6 inch glass tube and then when they reached a certain size they were detached from the tip and then fell to the bottom of the

continuous phase (assuming here that the dispersed phase has a higher density than the continuous phase). The rate at which the dispersed phase was delivered into the continuous phase was controlled by manipulating the stop-cock on the separatory funnel.

In all the experiments which are to be described below, the continuous phase was contained in a pyrex glass column of 45 mm. inside diameter. The height of the column was varied to suit the needs of the experiment and will be mentioned in the following discussions.

Preliminary Experiment #1

System: The ternary system: ethyl ether-acetic acid-water

Continuous phase: A solution of acetic acid in ether, 4% by weight

Dispersed phase: Water with methyl orange indicator in it; falling

Column: 8" pyrex glass column; 45 mm. inside diameter

Procedure:

The 8 inch length of pyrex glass tubing was closed at one end with a rubber stopper. The column was supported vertically and filled with the continuous phase. The dispersed phase was placed in the separatory funnel. This funnel was then supported in such a way that the delivery end of the 6" distributor tip was inside the glass column and below the top interface of the continuous phase. By opening the stopcock on the separatory funnel the dispersed phase was delivered dropwise into the continuous phase.

Observations:

1) The feed solution was yellow. When the drops of this solution formed in the continuous phase, they turned pink (the acid color of methyl orange) immediately showing a very rapid pick-up of acetic acid. This pick-up was so rapid that no yellow color could be seen in the drop during any stage of its formation. However, as the drop detached

itself from the tip a yellow core could be seen.

2) About 1-1/2 inches down from the tip the drops deviated shraply from their vertical descent. This apparently agitated the drop as complete color change of the indicator seemed to coincide with this point.

Preliminary Experiment #2

System: The ternary system: ethyl ether- acetic acid-water

Continuous phase: A solution of acetic acid in ether, 4% by weight

Dispersed phase: Water with methyl orange indicator in it; falling

Column: 8" pyrex glass column; 45 mm. inside diameter

Procedure:

The column was set up exactly as that in Experiment #1. However, the separatory funnel with attached distributor tip was not used. Instead the feed solution (dispersed phase) was introduced above the top of the continuous phase by means of an eye-dropper. The drops were formed just above the continuous phase and upon being released from the tip of the dropper they fell onto and through the continuous phase.

Observations:

The drops changed color immediately showing that extraction does not necessarily occur as a result of the formation of the drop.

Preliminary Experiment #3

System: The binary system: n-butanol-water

Continuous phase: Water

Dispersed phase: n-butanol; rising

Column: 26" pyrex glass column; 45 mm. inside diameter

Procedure:

The 26 inch pyrex glass column was supported vertically. In the bottom of this column a one-hole rubber stopper was placed. The 6 inch distributor tip was then placed in the hole in the rubber stopper so that the end of the glass tube having the small inside diameter pointed upward. The other end of the 6 inch distributor tip was then external to the 26 inch column. This end was then attached to the delivery end of the separatory funnel by means of a three foot length of rubber tubing. The column was filled with water to within one inch of the top. The butanol was placed in the separatory funnel which was then supported so that the level of the butanol was above that of the water in the column. This was necessary in order for the n-butanol to flow by gravity into the bottom of the column now filled with water.

Observations:

1) The drops formed at the tip in the bottom of the column and rose through the water.

2) The drops formed at the tip seemed to be much smaller than those obtained with ethyl ether.

3) The drops became considerably smaller, rising through the water, due no doubt to the solubility of n-butanol in water.

4) A little tail could be seen on each drop, again probably due to n-butanol leaving the drop. This tail seemed to extend quite a distance below the drops, perhaps 4".

Preliminary Experiment #4

System: Same as #3

Continuous phase: Same as #3

Dispersed phase: Same as #3

Column: Same as #3

Procedure:

For this experiment another hole was drilled in the rubber stopper which was used in the bottom of the column in Experiment #3. A piece of glass tubing was placed in this hole so that water could be drawn from the bottom of the column. A stopcock was attached to this water outlet so that the rate of water withdrawal could be controlled. Then arrangement was made in a similar manner for introducing water at the top of the column. In this way the continuous phase (water) could be made to move through the column. The experiment was then run as in Experiment #3.

Observations:

The rise of the drops occurred smoothly. Their paths did not seem to be affected by the motion of the continuous phase until within 6" of the distributor of the continuous phase. The continuous phase was made to move through the column at the rate of 120 cc./minute.

Preliminary Experiment #5

System: The binary system: n-propanol-water

Continuous phase: n-propanol

Dispersed phase: Water; falling

Column: 8" pyrex glass column; 45 mm. inside diameter

Procedure:

The column was arranged in the same way as in Experiment #1. The water was placed in the separatory funnel and this was fastened in place. The column was filled with propanol.

Observations:

With the delivery tip out of the propanol, drops were formed and detached at a rate of 10 drops per minute but when the tip was placed in the propanol, a steady stream came out of the tip. Droplets could not be made to form.

Preliminary Experiment #6

Systems: The binary systems:

diethyl ether-water
benzene-water
n-butanol-water

Continuous phase: Water in all cases

Dispersed phases: Diethyl ether, benzene and n-butanol

Column: 8" pyrex glass column; 45 mm. inside diameter

Procedure:

The column was arranged as in Experiment #1. This was an attempt to study the relationship between drop size and interfacial tension. The column was filled with water; diethyl ether was placed in the separatory funnel. This was fastened in place above the column in such a way that the delivery end of the tip was below the surface of the water. The stopcock was opened slightly and the size of the drops delivered by the tip was observed. The column was then emptied and made ready for another run. The above procedure was repeated for benzene and n-butanol using water as the continuous phase in each case.

Observations:

The drops were largest in the case of benzene and smallest with the n-butanol. The interfacial tensions are:

Benzene-water	33.6 dynes/cm
Diethyl Ether-water	10.7 dynes/cm
n-butanol-water	4.04 dynes/cm

Hence, high interfacial tension leads to large drops and low interfacial tension leads to smaller drops.

Although other factors undoubtedly affect drop size, the effect of interfacial tension is thought to be more important in this case.

Preliminary Experiment #7

System: The binary system: benzene-water

Continuous phase: Water

Dispersed phase: Benzene; rising

Column: 26" pyrex glass column; 45 mm. inside diameter

Procedure:

This experiment was designed to measure the velocity of the rising drops. The set up was the same as that described in Experiment #3, with the column filled with water. The benzene was placed in the separatory funnel which was placed so that the benzene liquid level was above the water level in the column. This allowed gravity flow of the benzene into the bottom of the column filled with water.

Observations:

1) The time of rise of the benzene drops was 4.4 seconds for a height of 25 inches or a rate of 5.7 inches per second.

2) The rising drops after arriving at the top of the continuous phase paused there for several seconds before crossing the interface into the layer of benzene which accumulated above the water.

Preliminary Experiment #8

System: The ternary system: benzene-acetic acid-water

Continuous phase: Water

Dispersed phase: A solution of acetic acid in benzene, 4% by weight.

Column: 26" pyrex glass column; 45 mm. inside diameter

Procedure:

The same procedure was used as in Experiment #7. The column was filled with water and the acetic acid-benzene solution was placed in the separatory funnel. The drops formed in the bottom of the column were drops of the acetic acid-benzene solution. The time of rise of these drops was measured.

Observations:

1) The drops appeared to be exactly the same size as those obtained in Experiment #7.

2) The time of rise was 4.7 seconds for a height of 25 inches, or a rate of 5.3 inches per second.

3) The drops again paused before crossing the top interface just as in the previous experiment.

The slowing down of the drop is attributed to the presence of the solute in the drop. The water and benzene exerting attractive forces on the acetic acid act to slow down the drop by creating a drag effect.

Preliminary Experiment #9

System: The ternary system: diethyl ether-acetic acid-water

Continuous phase: Water

Dispersed phase: A solution of acetic acid in ether, 3% by weight; rising

Column: 26" pyrex glass column; 45 mm. inside diameter

Procedure:

The column was arranged in the same way as in Experiment #3. The column was filled with water. The acetic acid-ether solution was placed in the separatory funnel. When the stopcock on the separatory funnel was opened slightly, the acetic acid-ether solution was delivered into the bottom of the column in the form of drops. These drops, upon being detached from the delivery tip, rose through the continuous phase (water).

Observations:

1) As the drops were forming diffusion currents could be seen within the drop. These seemed to come to the surface of the drop and create a very thin layer around the drop. As the drop left the tip, this outer layer was shed by the drop about 3/4" off the tip and this layer then faded into the continuous phase and was no longer visible.

2) The dispersed phase (acetic acid-ether solution) rate was increased by opening the stopcock on the separatory funnel. The drops then came out of the tip faster. A point was finally reached at which the drops no longer formed at the tip. The acetic acid-ether solution came out of the tip in a fine continuous stream. This stream then broke up into drops about 1-1/2" away from the tip.

Preliminary Experiment #10

Systems: The ternary systems:

mercury-water-n-heptane
aniline-water-n-heptane

Continuous phase: Water and n-heptane

Dispersed phase: Mercury and aniline

Column: 8" pyrex glass column; 45 mm. inside diameter

Procedure:

This experiment was an attempt to investigate the conditions at an interface. The column was set up as in Experiment #1. The column was filled half-way with water. Then n-heptane was placed on top of this. These liquids are immiscible so there were two layers in the column, the n-heptane being on top. First of all, mercury was placed in the separatory funnel. This was then placed so that the delivery end of the tip was beneath the heptane. The stop-cock was opened slightly and drops of mercury were formed at the tip in the heptane.

Secondly, the mercury was removed from the separatory funnel and aniline used in its place. Aniline, water and n-heptane are mutually immiscible. Now the aniline was allowed to be delivered into the n-heptane in the form of drops.

Observations:

1) With mercury dispersed, the drops of mercury formed in the n-heptane and upon being detached from the tip fell through the heptane, crossed the interface between the water and heptane and fell through the water to the bottom of the column. When the drops crossed the interface between the water and heptane, they did not break but remained intact.

2) With the aniline dispersed, the drops of aniline formed in the n-heptane and then fell through the latter to the interface. In crossing this interface between the water and heptane, the drops were broken. The aniline continued to fall to the bottom of the column but not in the form of the original drops. When the drops of aniline arrived at the heptane-water interface, they broke and formed a thin layer at this interface. More drops of aniline arriving at this interface added to this layer. After a certain point was reached, "globs" of aniline, much larger than the original aniline drops, formed and fell to the bottom of the water layer.

3) Aniline was also dispersed in water during this experiment by allowing the delivery tip to be submerged in water. The drops formed in this case were quite large and fell through the water very slowly. This, of course, is

probably due to the very small density difference in this case. This suggests a very good binary system, aniline-water, to study experimentally in an attempt to apply Stoke's Law to falling drops. The velocity of fall is so low that viscous conditions probably prevail.

The experiments just described did much toward projecting the experimental work into its advanced stages.

While approaching the more important phase of this experimental work, several problems were anticipated. All of these problems were concerned, directly or indirectly, with operational procedures and it was felt that the success of the present research was dependent on the correct solution of these problems. Specifically, these problems were as follows:

1) the selection of the ternary systems to be studied
2) the selection of the direction of extraction
3) the selection of the phase to disperse
4) the proper concentration of solute in diluent to use
5) the design and construction of the necessary extraction columns. Specially designed columns were necessary in order to obtain the proper experimental data
6) the design of an adequate feed device. This device had to possess a distributor tip capable of delivering drops of constant size and also a means of measuring the drop size
7) the proper methods of sampling and analysis to employ.

Ternary Systems Employed

The extraction of acetic acid from water is of industrial importance. It was decided, therefore, to study the mechanism of this extraction. Acetic acid and water therefore are two of the components in all the three ternary systems studied. Furthermore, in all the experimental work to be reported the acetic acid was always extracted from the water. It was also decided to operate at all times with the acetic acid water solution as the dispersed phase. The preliminary experiments indicated that a 6% (by weight) solution of acetic acid in water would be satisfactory. This corresponds approximately to a one normal solution.

The solvents used in the present work for the extraction of acetic acid from water were chosen after a consideration of toxicity, availability, relative industrial importance, and other factors. The design of the feed device, as will be discussed later, made it necessary that these solvents be the continuous phase in all experimental runs. The design of the feed device also made it necessary for the dispersed phase, the acetic acid-water solution, to fall through the continuous phase. This, of course, imposed another restriction on the selection of the solvents. It made it necessary that their densities be less than the density of the acetic acid-water solution. (In the

concentration used this density was substantially that of water).

The solvents finally selected were Isopropyl Ether, Ethyl Acetate and Methyl Isobutyl Ketone. These solvents seemed to satisfy all the requirements previously set forth. Isopropyl Ether and Ethyl Acetate are actually two of the solvents used industrially for this extraction. Methyl Isobutyl Ketone is not, however, used in industry for this extraction, mainly because it forms an azeotrope with acetic acid making eventual recovery of the solute from this solvent rather difficult. This solvent was chosen because it is rather a good solvent for this extraction, at least from equilibrium considerations. The value of the distribution coefficient of acetic acid between methyl isobutyl ketone and water is approximately unity indicating favorable conditions for extraction.

It should be noted at this point that the above selection of solvents presents three instances in which the distribution coefficient of acetic acid between water and solvent is approximately unity. Equilibrium relationships indicate, therefore, that these three solvents should be quite satisfactory for the extraction of acetic acid from water.

It should be noted further that this selection of solvents presents three ternary systems with different interfacial tensions. The values of the interfacial tensions for these systems have not been determined experimentally but approximate methods for estimating this property indicate that the isopropyl ether system has the highest value and the ethyl acetate system the lowest interfacial tension value. The effect of interfacial tension on spray tower operation is not at present understood but Johnson and Bliss (18) have postulated that spray towers give better performance characteristics when operated with systems of low interfacial tension.

The ternary systems, therefore, chosen for experimental study in this research were:

1) Isopropyl Ether-Acetic Acid-Water
2) Ethyl Acetate-Acetic Acid-Water
3) Methyl Isobutyl Ketone-Acetic Acid-Water

These considerations represent the solutions to the first four problems discussed previously on page 70. Furthermore, problem number seven was hereby partially solved inasmuch as the analysis for acetic acid is quite simple by titrating with sodium hydroxide using phenolphthalein as indicator.

Materials

The materials used in performing the preliminary experiments are not important inasmuch as the results were only qualitative. Specifications for these chemicals will not be discussed here.

The chemicals employed in the major portion of the research were as follows:

Acetic Acid - Glacial Acetic Acid, C.P. Reagent; E. I. Du Pont de Nemours and Co., Inc.

Water - Laboratory distilled water

Isopropyl Ether - Technical grade; Carbide and Carbon Chemicals Corporation

Methyl Isobutyl Ketone - Technical grade; Carbide and Carbon Chemicals Corporation

Ethyl Acetate - C.P. Reagent, 99.5% Ethyl Acetate; Coleman and Bell Co.

Manufacturers' specifications on these solvents indicated an acidity less than 0.01% as acetic acid. It was found necessary to use the C.P., 99.5% grade of Ethyl Acetate as the cheaper grade made operation impossible. The cheaper grade is 85% Ethyl Acetate and contains 15% Ethyl Alcohol. The conditions produced when using the lower grade of Ethyl Acetate will be discussed later.

Column Design

Experimental verification of the theories presented in this thesis necessitated the design of special extraction columns. The column designs employed by previous researchers in spray tower work were inadequate for the purpose at hand.

The necessary features to be incorporated in the design of the columns were dictated by the ultimate aims set forth in the theory. Three separate objectives were indicated as being the most important. First of all, it was necessary to determine the amount of extraction occurring during drop formation. Secondly, it was necessary to study the extraction which takes place while the drop is falling through the continuous phase. Thirdly, it was necessary to devise a means for determining the amount of extraction which occurs while the drop crosses the bottom interface.

It was decided, first of all, to carry out the extraction in a batchwise rather than continuous manner. By this is meant, filling a column with a definite quantity of solvent which remains stationary, and then allowing a fixed number of drops of solution to fall through the solvent. If the concentration of the feed solution is known, the amount of extraction taking place may be determined by analyzing the drops after falling a certain distance through the solvent. This batchwise method of operation, although of no industrial importance, makes the experimental

work much simpler. This was one of the main reasons why this method of operation was chosen. It was felt that accurate conclusions in regard to the three stages of extraction could be drawn using either method of operation. If the results obtained using the batchwise method of operation were encouraging, i.e. indicated the existence of three separate stages of extraction, it was the intention to carry out future work using the continuous method of operation.

In order to identify the amount of extraction occurring in each of the three stages separately, the following procedure was adopted. Two series of experiments involving two different spray columns were used. In column #1, the drops form in the continuous phase, detach themselves and fall a certain height through the continuous phase, strike the bottom interface, break and cross this interface and go into the water layer which is placed in the bottom of the column before the remainder of the column is filled with solvent. A definite number of drops fall through the column height being studied. Now, if the bottom water layer is drained from the bottom of the column and analyzed, the total amount of solute lost during all three stages can be calculated. The above procedure is repeated for various column heights using the same number of drops

in each case. With this data a plot is made of total amount of solute extracted versus column height. This curve is then extrapolated back to zero column height. The value obtained at zero column height is the sum of the amount of solute extracted during drop formation (stage 1) and the amount of solute extracted during the process of the drop breaking and crossing the bottom interface (stage 3).

In column #2, the drops form in the continuous phase, detach themselves and fall through a certain height. After falling a given height, the drops are analyzed for solute content. The amount of solute lost is then calculated. In this case, however, the solute is lost in only two stages: drop formation (stage 1) and drop fall (stage 2). The above procedure is repeated for various column heights again using the same number of drops in each case. A plot of the amount of solute extracted versus column height is made and extrapolated to zero column height. This value of the intercept is the amount of solute extracted only during drop formation (stage 1). The value of the intercept obtained from the plot made from the data obtained using column #1 should be greater than the value of this intercept. Indeed, it should be greater by an amount equal to the amount of solute extracted during the process of drop breaking and

crossing the bottom interface (stage 3).

The above concepts are illustrated in Figure 6A. The ordinate intercept "a", at zero column height, represents the amount of solute extracted during stages 1 and 3. The intercept "b" represents the amount of solute extracted during stage 1 only. The difference between "a" and "b" represents the amount of solute extracted during stage 3.

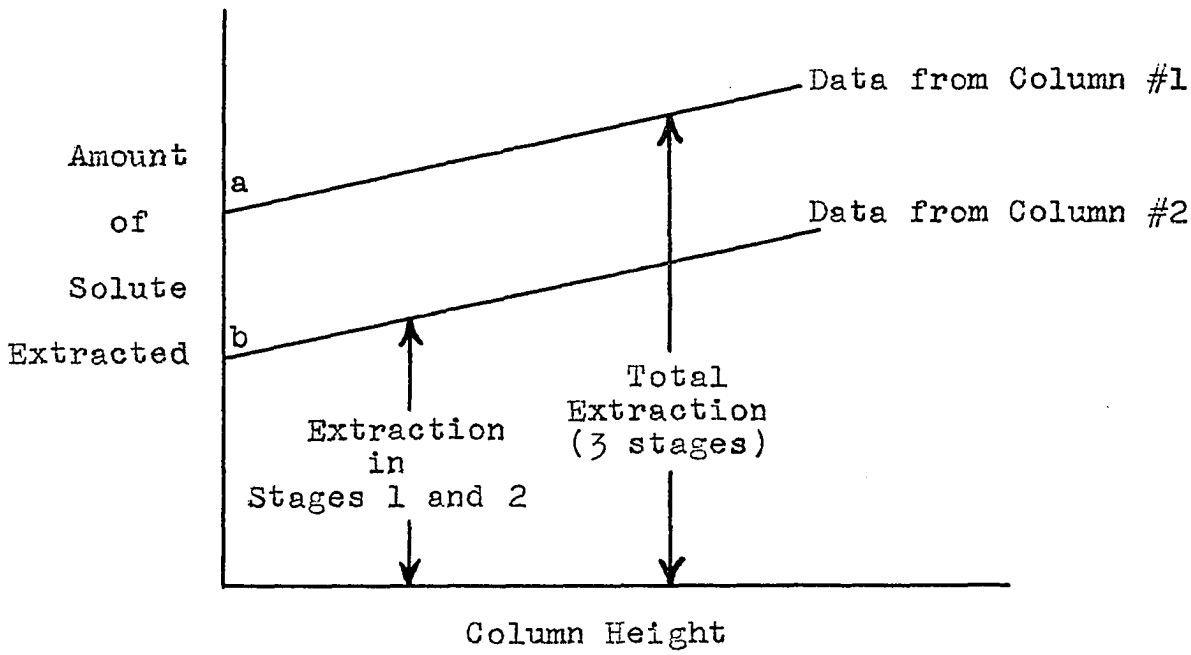


Figure 6A

The use of two separate columns completely justifies itself in the fact that two unknowns are evaluated. The ordinate intercept of the plot of data of column #2 evaluates

the amount of solute extracted during drop formation; the intercept of the plot of data of column #1 minus the intercept of the plot of data of column #2 evaluates the amount of solute extracted during the process of drop breaking and crossing the bottom interface (stage 3).

The procedure employed in the operation of column #2 for analyzing the solute content of the drops after they have fallen a given height will be discussed below in the section devoted to the design of column #2.

Design of Column #1

Obviously, the design of this column had to satisfy certain requirements. It was necessary to be able to vary the column height; it was necessary to be able to introduce a small amount (about 50 cc.) of water into the bottom of the column before the column was filled with solvent; it was necessary to make some arrangement for draining the water layer from the bottom of the tower after the drops had fallen through the solvent and crossed the interface into this water layer. This latter requirement was necessary for purposes of analysis.

The column was constructed of pyrex glass tubing 47 mm. inside diameter. The choice of this type of glass was based on its availability from the stockroom. It was necessary to choose glass tubing of sufficient inside

diameter in order to prevent the drops from hitting the walls of the tubing during their fall and in order to avoid wall effects. The 47 mm. tubing was considered large enough to avoid these difficulties.

The fact that it was necessary to introduce a water layer (50 cc.) into the bottom of the column before each experimental run required that the column, when greater than 3 inches in height, be made of two sections of pyrex glass tubing. For instance, if a 20 inch column was being employed, it would be very difficult, if not impossible, to introduce the water layer into the bottom of this column without having the water adhere to the sides of the column. Column #1, therefore, consisted of two lengths of glass tubing whenever the column height exceeded 3 inches.

Of the two lengths of tubing in column #1, the piece which was to serve as the bottom portion of the column was considered to be the more important since this section of glass tubing had to contain some means by which the water layer in the bottom of the column could be withdrawn after each experimental run.

The first lower section to be constructed consisted of an eight inch length of pyrex glass tubing 47 mm. inside diameter. The bottom of this section was fitted with a one-holed rubber stopper containing a stopcock. The space between the walls of the column and the

stopper was filled with paraffin to allow for complete drainage of the column contents when the stopcock was opened. This design proved unsatisfactory since the acetic acid attacked the wax.

The second design of the lower portion of column #1 was found to be quite satisfactory and was the one used throughout the experimental work. This column section was made from a separatory funnel whose length was much greater than its diameter. The body of this separatory funnel was cylindrical and by chance its internal and external diameters corresponded very closely with those of the pyrex glass tubing previously mentioned. The top portion of this glass stoppered separatory funnel was cut off by means of a hot wire. The resulting glass section then served as the bottom portion of column #1. Furthermore, at the lower end of this glass section its diameter gradually decreased in usual separatory funnel manner and its delivery end was fitted with a stopcock. This all-glass section thus served the purpose quite satisfactorily. The water layer could be drained quite completely with no danger of the acetic acid causing any damage to the parts of this section. The extent of drainage was determined and it was found that by careful manipulation of the stopcock on this bottom section a minimum of 99.6% of the water layer could be drained from

the column.

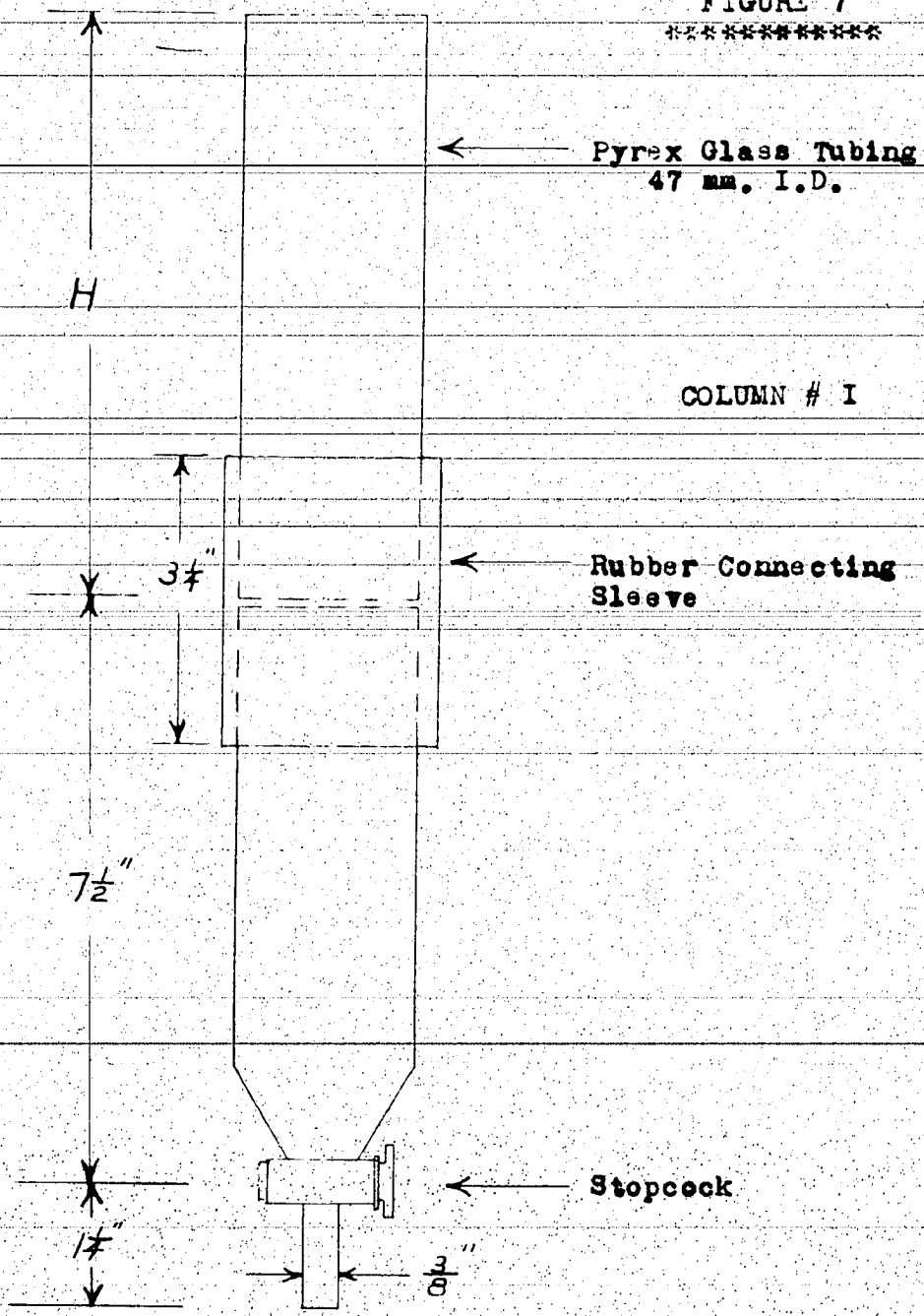
The bottom section so constructed served as the bottom portion of all columns of whatever height employed in the experimental runs. In making runs with increased column height, it was only necessary to attach a piece of pyrex glass tubing of desired length to the lower portion and make the run. The upper section of the column was attached to the lower portion with a large piece of rubber tubing, of inside diameter slightly less than the external diameter of the section to be attached. The fit of the rubber tubing used was not as good as could be desired but leaks were prevented as long as the column height was less than 30 inches. If column heights greater than this are to be studied in the future, it will be necessary to obtain a piece of tubing which fits much more snugly. The upper sections employed were pieces of pyrex glass tubing of the following lengths: 6", 11", 17", 24", 36".

A sketch of column #1 is given in Figure 7.

Design of Column #2

The design of column #2 had to satisfy the following requirements. It was necessary to be able to vary the column height and it was necessary to be able to analyze

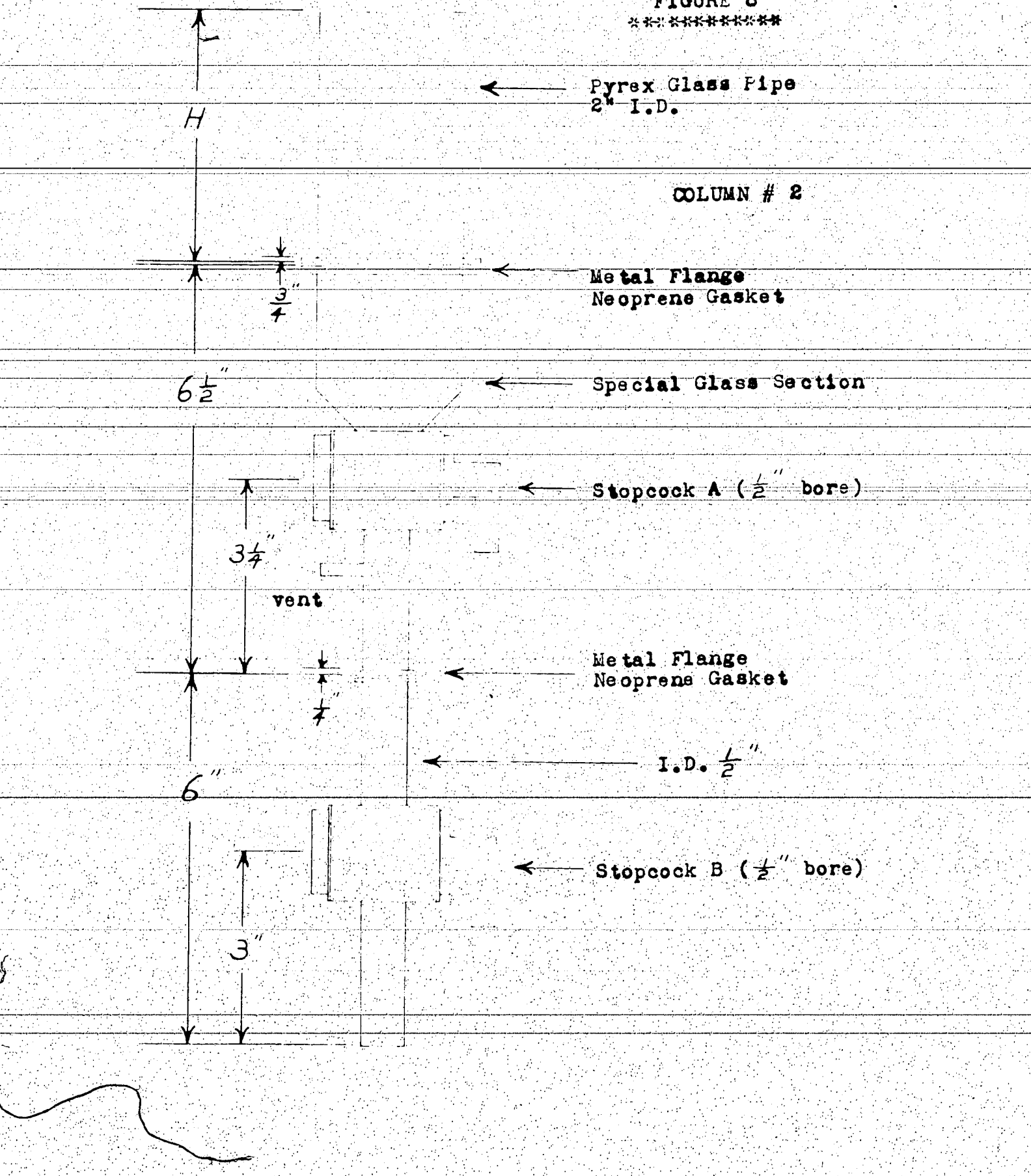
FIGURE 7



the drops for solute content after they had fallen a certain distance without being allowed to break across an interface within the column height being studied.

The design finally adopted to accomplish this was that shown in Figure 8. In making a run with this column, stopcock B is closed and stopcock A is opened. The column is filled with solvent. A fixed number of drops is allowed to fall through the continuous phase. These drops fall through the column and pass through the open stopcock A without being broken or even deformed. (The bore of this stopcock and also stopcock B is 1/2" as seen from Figure 8. The drops are much smaller in diameter and hence can pass through the stopcock without being disturbed). The drops fall to stopcock B where they accumulate. When the last drop has reached stopcock B, stopcock A is closed. Stopcock B is then opened and the entire section between the two stopcocks is drained and analyzed. (The vent allows this section to be drained even though stopcock A is closed). The results of the analysis allow the concentration of the drops to be calculated just after passing stopcock A. In other words, this procedure makes it possible to calculate the solute content of the drop after it has fallen a certain height, the height being measured from the delivery tip down to stopcock A. The drop continues to lose a small amount of solute

FIGURE 8



after it passes stopcock A but since this entire section between the two stopcocks is drained and analyzed the value obtained is truly indicative of the solute content of the drop just after passing stopcock A.

As was previously pointed out the solute lost in this column is lost in two stages: drop formation (stage 1) and drop fall (stage 2). Therefore, data obtained with this column relating the amount of solute extracted to column height is useful in making the required plot for determining the amount of extraction occurring during drop formation alone. Column height was varied by employing sections with different values of H in Figure 8.

The sections for this column were purchased from the Fischer and Porter Company of Hatboro, Pennsylvania. All the parts are standard parts with the exception of the section containing stopcock A. This section was specially designed here in the department and fabricated by the above manufacturers. Although all parts of column #2 are made of pyrex glass, all the joints are formed with metal flanges with neoprene gaskets. Referring to Figure 8, sections were obtained with "H" values of 6", 12", 18", 24" and 36".

Design of Feed Device

Any study of the extraction from liquid drops

demands that the exact size of these drops be known in order to be able to calculate the area of transfer. The first requirement then, of a feed device is that it be able to measure drop size, either drop diameter or drop volume. Furthermore, the drop size and delivery rate must be constant during the period of operation which means that the device must operate at a constant head. Finally, the device must give reproducible results. In other words, under similar operating conditions the drop size delivered by the feed device must not vary too greatly from day to day.

The glass delivery nozzles used in the feed device in the present research were obtained from the Fischer and Porter Company. These nozzles were actually lengths of precision bore, capillary glass tubing, 6 inches long, with an outside diameter of 1/4 inch and an inside diameter of 0.020 inches, running the entire length of the tubes. Furthermore, the delivery ends of these capillary tubes were slightly beveled.

The procedure to be employed in making an experimental run made it necessary that the design of the feed device be given special consideration. In the discussion concerned with column design, it was pointed out that as far as the feed solution was concerned both columns were to be operated in the same manner. In other words, in both

cases, drops of the feed solution were to be formed in the continuous phase and upon detachment from the delivery tip they were to fall through the continuous phase. Furthermore, it was indicated that a definite number of drops were to be employed in each run. Therefore, the method of operation of the feed device was clearly outlined. In every experimental run it would be necessary to count the drops of feed solution as they formed and detached themselves from the tip and when the required number of drops had been delivered it would be necessary to stop the flow of the inlet feed solution. The drop size would then have to be measured.

The first feed device tested was that described by Sherwood, Evans, and Longcor (23). A side tube was connected to the glass delivery nozzle. The feed rate was controlled by dropping from an analytical burette into the side tube attached to the glass nozzle. The level in this side tube was maintained constant by close observation and regulation of the burette cock. Thus, the feed rate was maintained constant and also the amount of feed introduced into the column was measured. This device was found to be entirely unsuitable for the purpose at hand. It was impossible for one person to both count the drops forming at the delivery nozzle and to maintain the liquid level in

the side tube by manipulation of the burette stopcock. Furthermore, the level in the burette would have to be read while the liquid was moving which, of course, leads to inaccuracies.

The feed device finally employed was very simple but proved to be sufficiently accurate. The 6 inch length of capillary glass tubing was attached to the tip of a 50 ml. graduated glass stoppered burette by means of a piece of rubber tubing in such a way that the tip of the burette was in contact with the face of the capillary tubing. When the stopcock was opened wide, the rate of flow was controlled by the pressure drop across the capillary length of glass tubing, and the height of the liquid in the burette. It was necessary to determine a height in the burette which would lead to a satisfactory discharge rate. Furthermore, it was found that the discharge rate at a given liquid height in the burette (the liquid in the burette was the same solution in all cases) was also altered when different solvents were used as the continuous phase. This, of course, was understandable inasmuch as the densities, viscosities, and surface tensions of these solvents differed and drop size and hence drop delivery rate is probably affected by these physical properties.

In all the discussions to follow when mention is made of the feed device, it will refer to the assembly just mentioned: a 50 ml. graduated glass stoppered burette with the 6 inch capillary tube attached to its tip by means of a piece of rubber tubing.

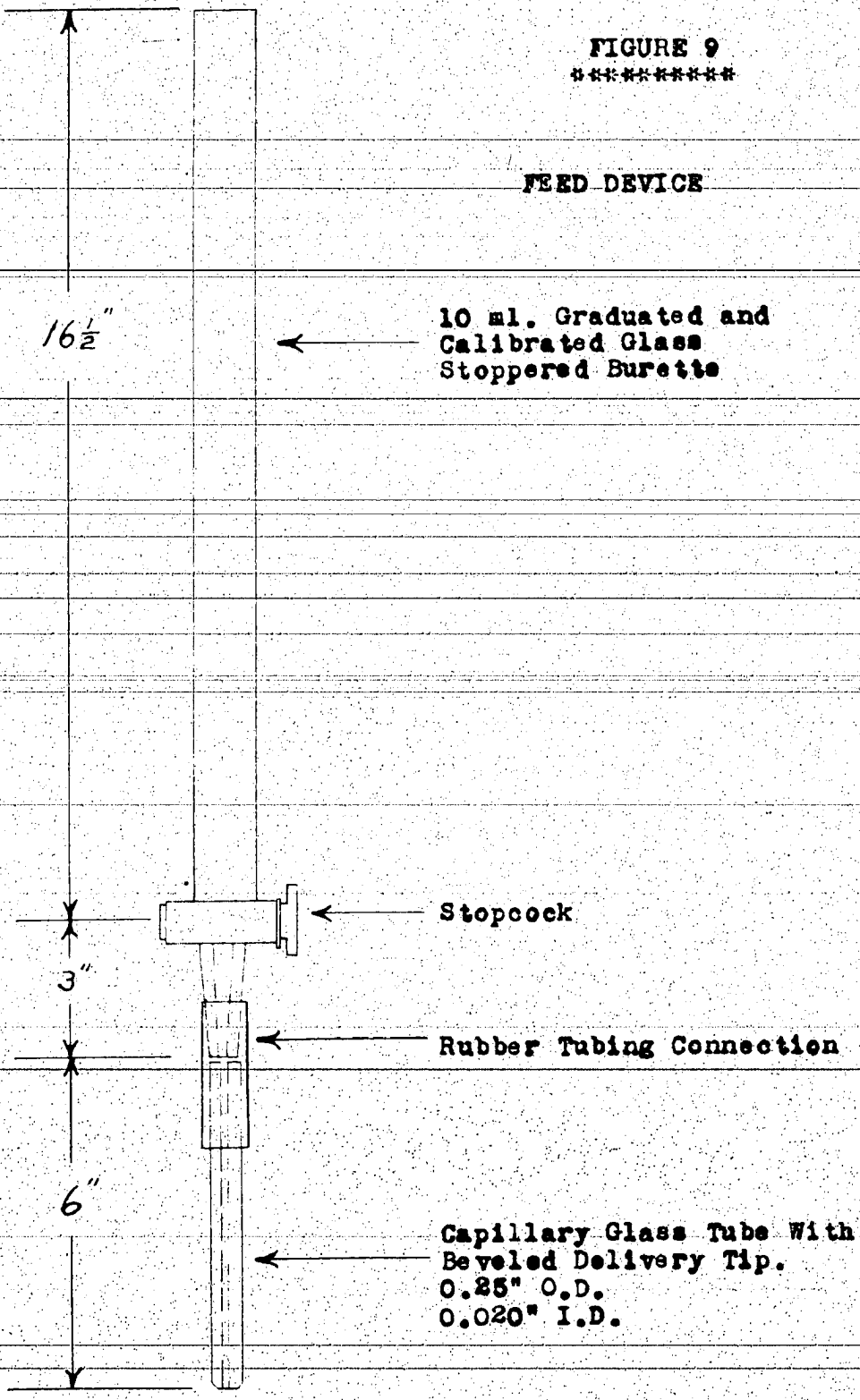
This design of the feed device obviously sacrifices the principle of constant head but it was felt that the resulting inaccuracies would not be serious. Indeed, it was shown that the small decrease in head taking place during an experimental run affects drop size and drop formation time only slightly. The sketch of the feed device is shown in Figure 9. Note that the discharge end of the delivery tip is beveled.

Calibration of Feed Device

The feed device was filled with 1.063 N acetic acid-water solution (the feed solution to be used in the experimental runs to be described later). This device was supported above column #1 in such a manner that the delivery end of the tip was below the surface of the isopropyl ether contained in the column. The burette stopcock was opened. The feed solution flowed down through the capillary tube and was delivered into the continuous phase (isopropyl ether). At first, when the liquid level was high in the burette, the

FIGURE 9

FEED DEVICE



delivery rate was very high; as a matter of fact, a stream of liquid was discharged from the capillary tip and broke up into drops about 1-1/2 inches below the tip. As the liquid level in the burette fell the discharge rate was gradually decreased until drops formed and detached individually at the tip. However, at first, each drop was followed by a secondary drop much smaller in diameter. When the liquid level had fallen a little further in the burette, these secondary drops disappeared. The feed solution was then delivered into the continuous phase in the form of individual drops. These drops formed in approximately 1 second and after reaching a certain size broke away from the tip and fell through the continuous phase. These drops were not followed by secondary drops. Finally when the liquid level had fallen still further in the burette, the formation of secondary drops was observed again. It was thought advisable to operate in the complete absence of these secondary drops. Hence, the operating range of the feed device was limited to those liquid levels in the burette which produced only individual drops. This range of liquid levels was determined by the above experiment.

The feed device was then calibrated in this range of liquid levels as follows: Column #1 was filled with

isopropyl ether. The level of the feed solution in the burette was allowed to fall until it was just within the range which produced individual drops. When the liquid level had fallen to the desired point, the stopcock was closed coincidentally with the detachment of a drop from the tip. The reading of the liquid level in the burette was then taken. The feed device was lowered carefully until the delivery tip was below the surface of the isopropyl ether. The stopcock was then opened wide and fifty drops were allowed to be delivered into the continuous phase. The stopcock was closed coincidentally with the detachment of the fiftieth drop from the delivery tip. The burette reading was again taken and thus the total volume of 50 drops was obtained. From this the volume per drop and drop diameter could be calculated by assuming each drop to be a sphere of the same size. The drop formation time was about 1 second so that the counting of the drops was in no way difficult. The time of formation of an individual drop was measured with a stop-watch. The total volume of fifty drops in this case was found to be equal to 2.40 ml.

As mentioned previously, the discharge rate at a given liquid height in the burette is affected by the physical properties of the continuous phase. The above procedure, therefore, was repeated for the other two solvents,

methyl isobutyl ketone and ethyl acetate. The same general observations were made when these solvents were used as were made when the isopropyl ether was used. However, the phenomena occurred at different liquid heights in the burette. Consequently, the range of operation of the feed device (leading to the formation of individual drops, i.e., no secondary drops) differed for each solvent. These ranges were, nevertheless, determined for each solvent and used subsequently in the calibration of the feed device for each of the remaining solvents.

The calibration of the feed device using methyl isobutyl ketone and ethyl acetate was carried out in the same manner as that employed for isopropyl ether. The ranges of liquid levels in the burette necessary for the formation of individual drops in each case being duly observed. The time of drop formation was also determined in each case, drop volumes being determined as before.

When it was observed that the total volume of 50 drops was in the neighborhood of 2.0 ml. in each case, it became obvious that the 50 ml. burette would not be sufficiently accurate for measuring this volume. Accordingly, the 50 ml. burette was replaced by a 10 ml. graduated burette which could be read accurately to the nearest one hundredth of a milliliter. Further accuracy was assured by

calibrating this burette in the ranges to be used in operation.

The feed device finally accepted for operation consisted of a 10 ml. graduated, calibrated glass stoppered burette in place of the aforementioned 50 ml. burette. The procedure for feed device calibration was again repeated for the three solvents in order to determine the operating ranges of liquid levels in the burette such that the formation of individual drops was obtained.

Reproducibility of Feed Device

As mentioned previously, one of the main requirements of a feed device is that it give reproducible results. The size of the drops delivered by this device, under similar operating conditions should not vary too greatly from day to day. At first, such was not found to be the case with the feed device just described. The calibration of the feed device on one day would differ substantially from that obtained a day later. The volume of the drops delivered was found to differ appreciably from day to day. This behavior was ascribed to the fact that the tip was dirty. The tip was continually immersed in dichromate cleaning solution. Every 24 hours the tip was removed from the cleaning solution, washed with distilled water, attached to the 10 ml. burette and a calibration was made. This procedure was continued for a week. At the end of this

period it was found that the cleanliness of the tip was such that reproducible results were obtained. The volume of the drops delivered by the feed device was the same from day to day. The calibration was periodically checked and it was shown conclusively that the feed device would deliver drops of the same volume at all times, provided the delivery tip was kept scrupulously clean.

After the feed device was used and it was necessary to suspend operation until the next day, the capillary tip was removed from the burette and washed with distilled water. The delivery end of the tube was allowed to stand in distilled water until the next run was made. In continuing operation after such a layover (even though it be only one day) the delivery end of the capillary tube was allowed to stand in warm (60°C) cleaning solution for five minutes prior to use. At the end of the five minutes, the tip was washed with distilled water and attached to the tip of the 10 ml. burette. With this procedure for the care of the capillary tip, the results of the feed device were quite satisfactory. Reproducibility was well within acceptable limits. A variation in drop volume of more than 10% was considered objectionable.

Using this capillary tip the calibrations of the feed device led to the following results with the different solvents:

Solvent	Volume	Initial Burette Reading
Isopropyl Ether	50 drops = 2.40 ml.	3.80 ml.
Methyl Isobutyl Ketone	50 drops = 1.75 ml.	7.05 ml.
Ethyl Acetate	50 drops = 1.80 ml.	7.25 ml.

The initial burette readings listed above for isopropyl ether, methyl isobutyl ketone and ethyl acetate correspond to liquid heights above the delivery end of the capillary tip equal to 18-1/2", 14-1/2", and 14-1/4" respectively. The capillary tip, of course, is 6" in length.

The capillary tip used above was called tip #1. Another delivery tip (tip #2) was used on the feed device in order to obtain smaller drops than those delivered by tip #1. Tip #2 was also obtained from the Fischer and Porter Company and had the same dimensions as tip #1, i.e., 6 inches long, 1/4 inch outside diameter and 0.020 inches inside diameter. In order to obtain small drops, however, it was found necessary to reduce the outside diameter of the delivery end of this tip. This was done on the wet grinder in the metallography laboratory in this department. The outside diameter of the delivery end of this tip was thus reduced to one-half its original size. All other dimensions remained the same. Using this tip (tip #2) the feed device was calibrated in the same manner as used for tip #1. The

following results were obtained for this tip using the different solvents:

Solvent	Volume	Initial Burette Reading
Isopropyl Ether	80 drops = 2.40 ml.	3.80 ml.
Methyl Isobutyl Ketone	90 drops = 1.95 ml.	7.05 ml.
Ethyl Acetate	not calibrated	--

Several other capillary tips were used with the feed device but calibration data were obtained only for those two mentioned above. Tip #3 was used when photographs were taken of the drops (see section on photography). This tip was 2-1/2 inches long, had an outside diameter of 1/4 inch, an inside diameter of 0.020 inches and its delivery end was beveled. Another tip was used in the photography section of this thesis. No number was assigned to this tip but its dimensions were the same as those of tip #3. However, its delivery end was flat rather than beveled. The photographs presented later show the effect of the shape of the delivery end of the tip on the shape of the drop.

Photography

The earliest work with drop formation indicated the desirability for permanently recording certain observations.

Visual studies of drop formation using a magnifying device made it possible to see diffusion currents leaving the drops during their formation. Actually, these diffusion currents, caused by the solute leaving the drops, can be seen with the naked eye. These observations seemed to indicate that these diffusion currents were more intense at the moment of drop detachment. It was felt that this observation could be verified only by photography.

Photography was employed for three reasons:

1) to record the shape of a drop during various stages of its formation;
2) to attempt to show the diffusion currents leaving the drop during its formation, thereby determining when the drops lose the solute;
3) to study the effect of the shape of the delivery tip on the shape of the drop.

The drops were photographed first, using diffused transmitted light. The light source was a reflector type photo-flood lamp behind a sheet of ground glass. The results obtained by this method were fairly satisfactory but the

light rays were too diffuse to allow the diffusion currents to be recorded on a photographic film. This light source was therefore discarded. The drops were then photographed by specular transmitted light. This light source consisted of a lantern slide projector lamp and condenser system, arranged so that the focus of light from the condenser fell upon the camera lens.

In taking photographs of the drops, the continuous phase was placed in a rectangular battery jar. The feed device, as described in a previous section, was used in delivering the dispersed phase into the continuous phase. The specular light source was set up directly behind the rectangular battery jar with the camera in front so that the center of the light source, the drop and the axis of the camera lens were in line. With the light source directed toward the camera the effective illumination was very intense so that it was possible to use a shutter speed of 1/400 seconds and effective aperture of f:64 or smaller and produce a properly exposed negative using Kodak Super Panchro Press Type B sheet film. The camera was a 4 x 5" Crown Graphic equipped with Kodak 127 mm. f 4.7 Ektar lens in supermatic shutter. Using the above procedure and equipment the photographs presented below were taken.

Photographs "a" through "j" indicate the shape of the drop during different stages of its formation. These

photographs represent a sequence of drop shapes during formation and detachment. The 1.063 N acetic acid solution was the dispersed phase using tip #1 on the feed device. The continuous phase was isopropyl ether. The temperature of both phases was 25°C.

Photographs "k" through "n" indicate the effect of the shape of the delivery tip on the shape of the drop. Photographs "k" and "l" were taken with the 1.063 N acetic acid solution dispersed in benzene. The tip used on the feed device was 2-1/2 inches long, 1/4 inches in outside diameter, and 0.020 inches inside diameter. Its delivery end was beveled. The liquid level in the burette was at a reading of about 3 ml.

In photographs "m" and "n" the 1.063 N acetic acid solution was again dispersed in benzene. A different tip was used however. This tip was 2-1/2 inches long, 5/16 inches outside diameter and 0.020 inches inside diameter. Its delivery surface was not beveled but was flat.

It was found impossible to show, by the photographic technique employed, the diffusion currents leaving the forming drops. It was felt that even the light rays from the specular light source employed were diffuse enough to prevent this. If these currents are to be photographed, and it is quite possible that they may be, a more intricate lighting system must be employed.

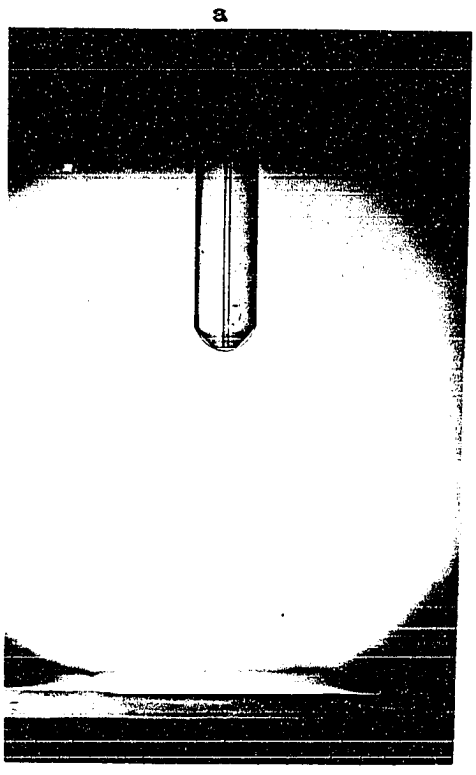
The series of photographs showing the shape of the drop during different stages of its formation reveals some very interesting points. Starting in photograph "a" where the drop is just beginning to form, the next few photographs show the drop increasing in size ("a" to "d"). In "e" the drop has gotten quite long and a "neck" forms between the main body of the drop and the tip. In "f" the drop has gotten longer and the "neck" has become narrower. Photograph "g" is quite unusual. The "neck" has become very narrow. Detachment has taken place and the photograph was taken just at the instant of detachment. The neck of liquid has narrowed down to a point at the point of separation. At this instant the drop is slightly ellipsoidal with its long axis vertical. In photograph "h" the narrow neck of liquid is in the process of springing back to the tip, being in an extreme state of tension at the moment of detachment. The detached drop is seen to flatten out somewhat just after detachment. This again was caused by the drop being in a slight tension owing to its attachment to the "neck" of liquid. In photograph "i" the neck of liquid has returned almost completely to the face of the tip. The detached drop has fallen a little further and has flattened out considerably. Note that the horizontal axis is much greater than the vertical axis at this point. As a matter of fact, the drop has assumed a disk-like shape. Finally,

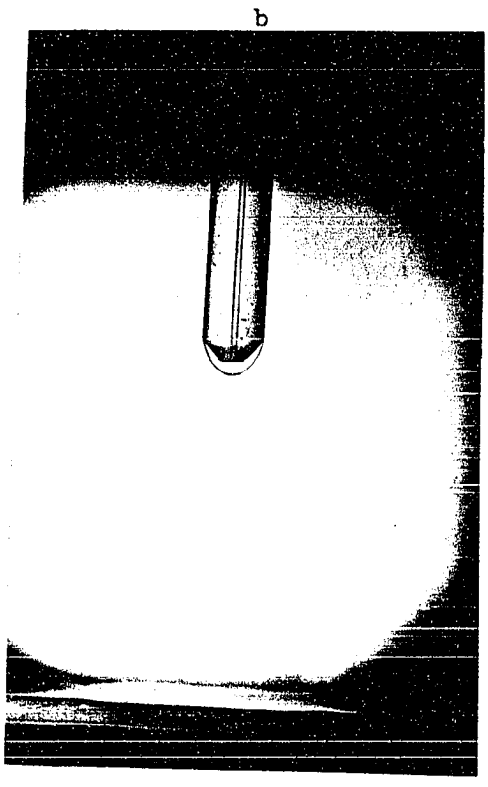
in photograph "j" a new drop is beginning to form on the tip and the detached drop has fallen still further through the continuous phase. The drop has changed shape somewhat. Its vertical axis is starting to increase and its shape is becoming more spherical.

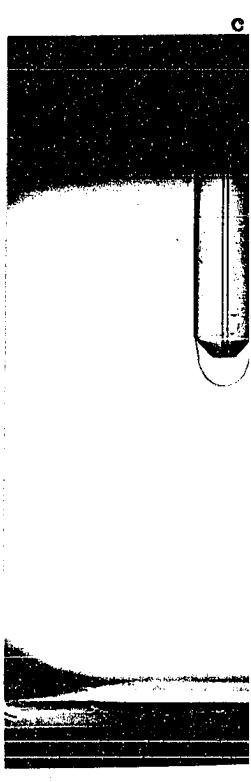
Photographs "k" and "l" show the drops forming in benzene. In "l" the flattening in the top of the drop just after detachment is clearly illustrated. This is a general effect caused by the tension in this portion of the drop due to its attachment to the "neck" of liquid. This behavior has been observed also for liquid drops forming in air (15). In "k" a drop is seen resting on the bottom water-benzene interface. Drops were found to hesitate for about one second here before crossing into the water phase.

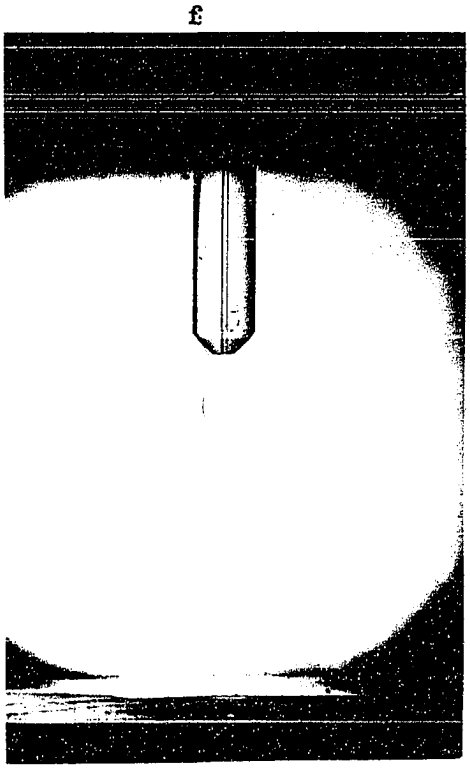
Photographs "m" and "n" indicate the effect of tip diameter on drop size, these drops being somewhat larger than those in photographs "k" and "l". Drop size was found to be substantially unaffected by the amount of bevel in the face of the delivery tip as long as the internal and external diameters were equal.

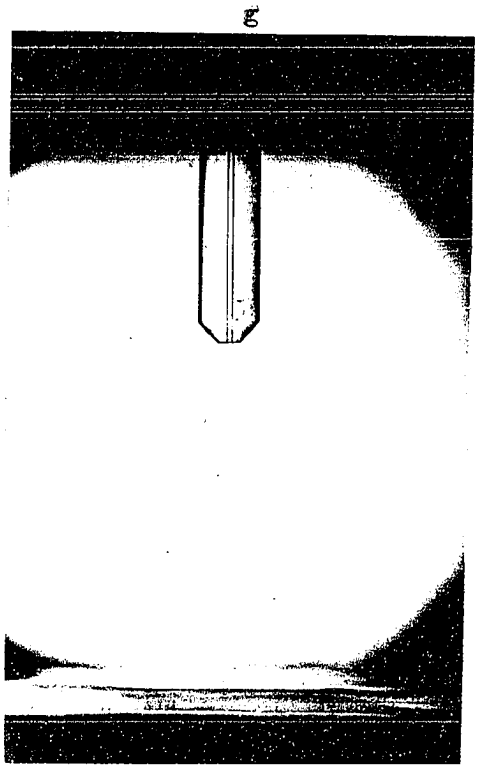
In all the photographs presented the bright streaks at the bottom are the solvent-water interface.

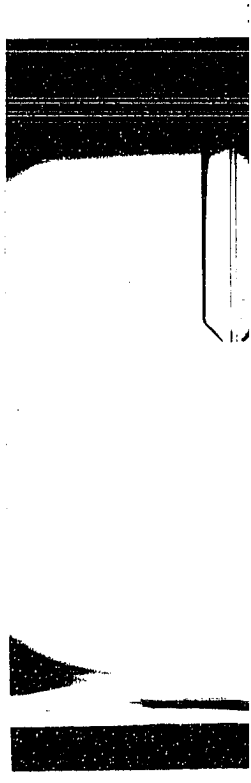


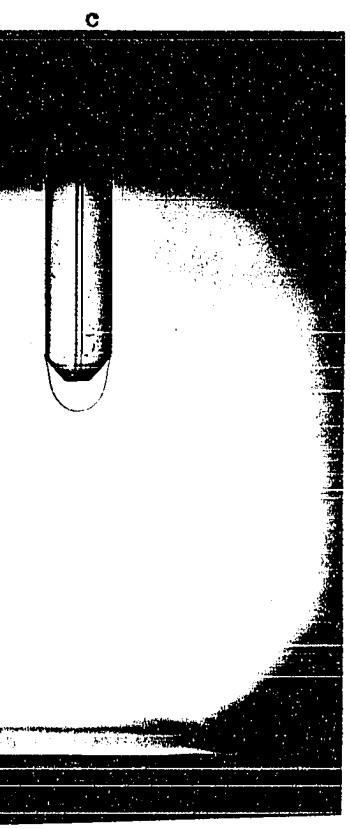


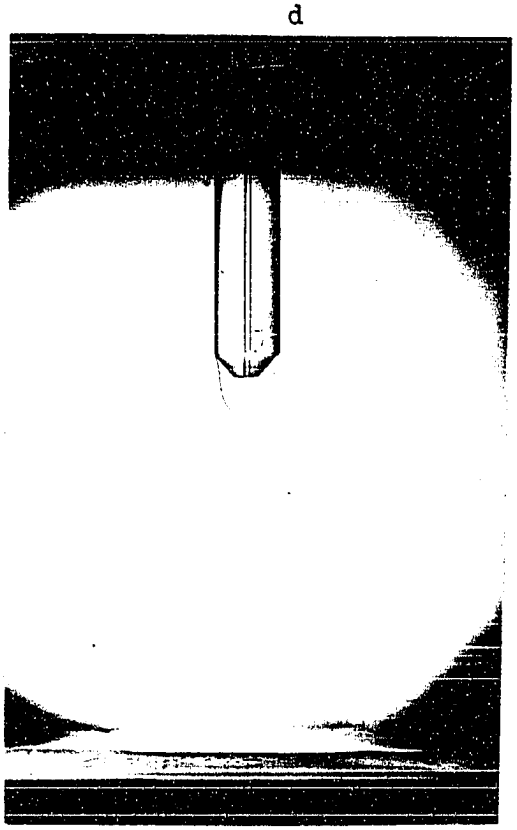


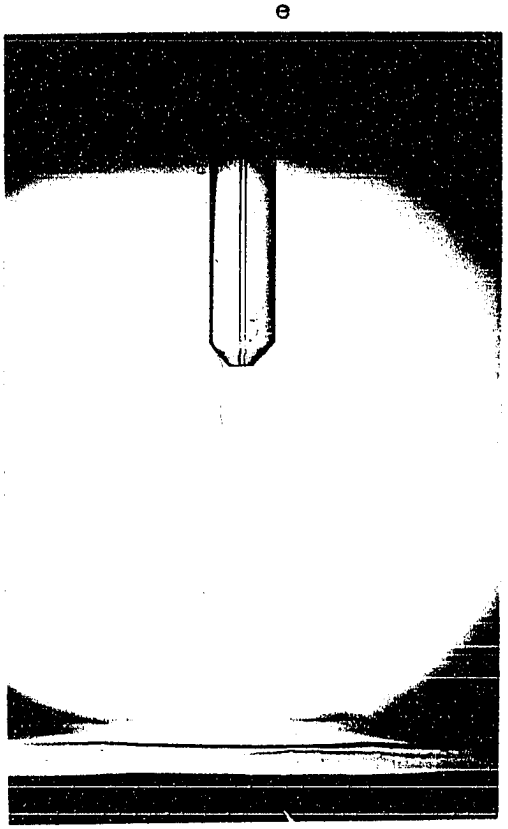


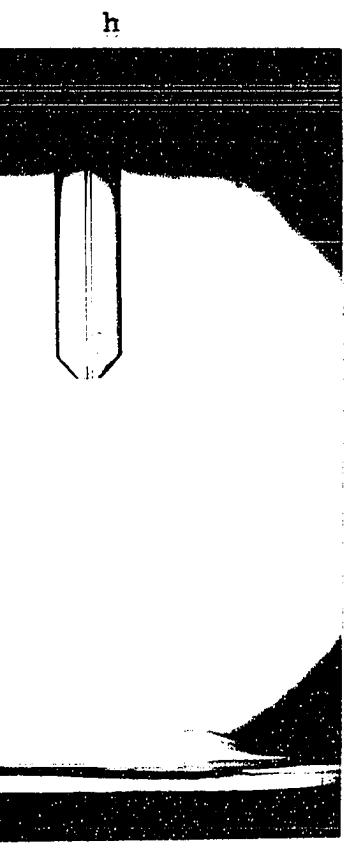


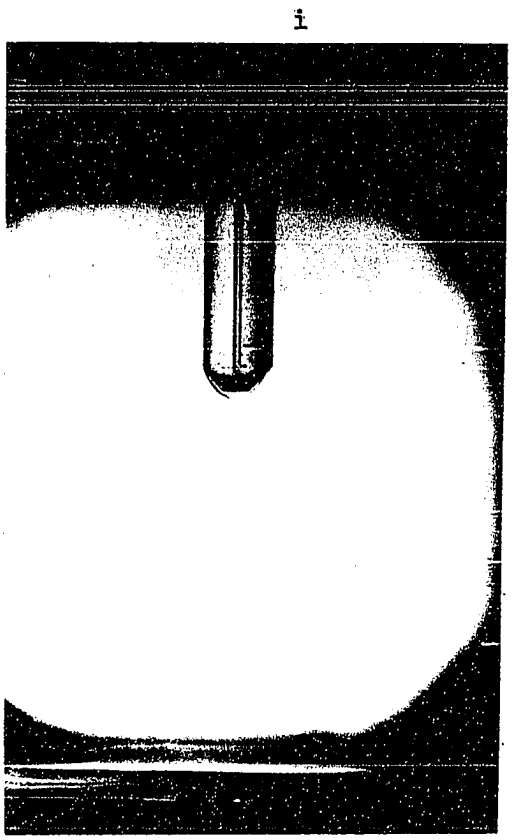


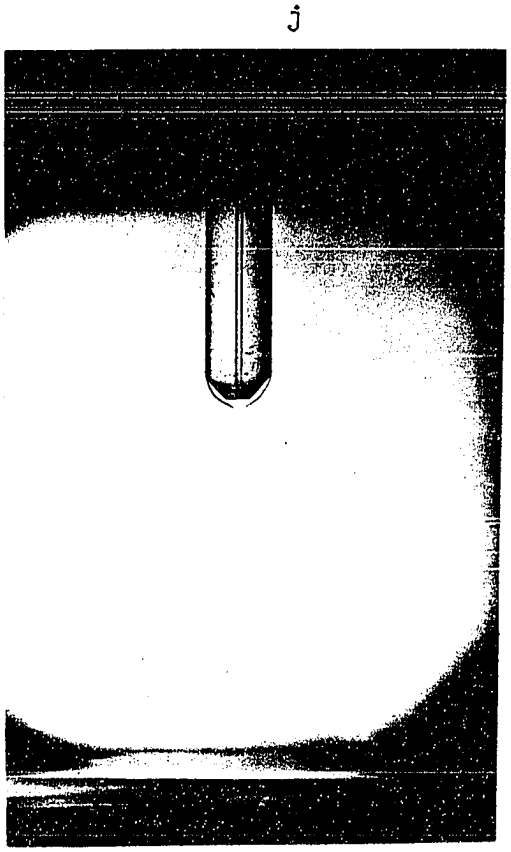




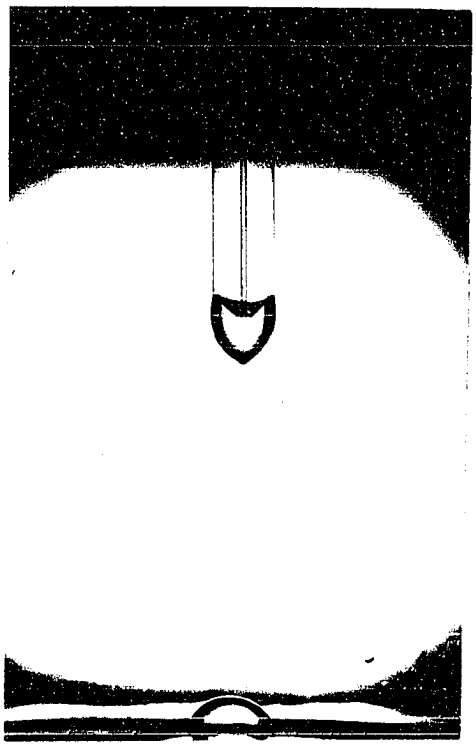




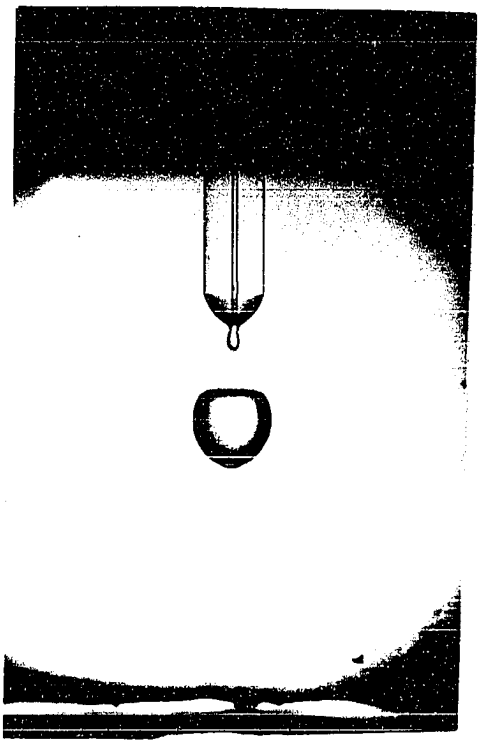




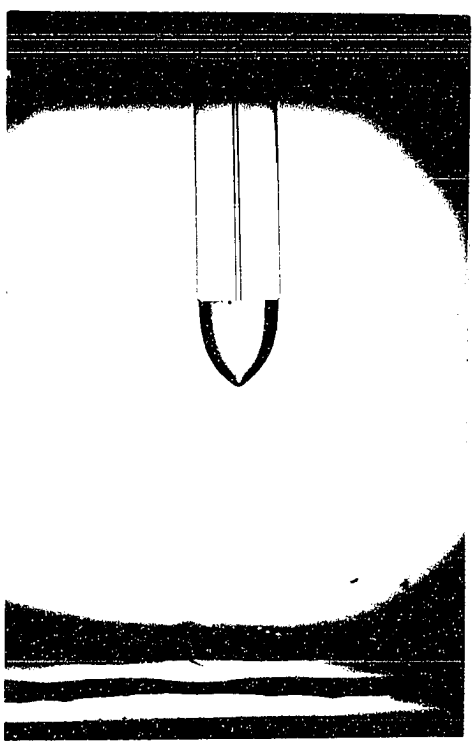
k



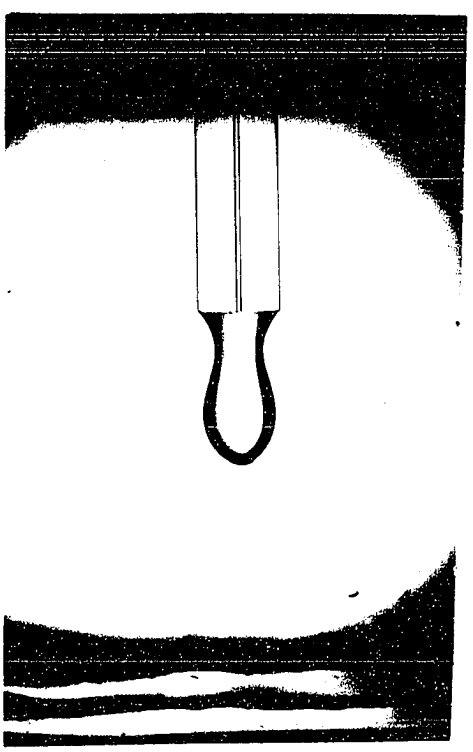
l



m



n



Procedure for Experimental Runs

Columns #1 and #2, described above, were supported, during a run, by a special column support designed and built in the department. This support was made of 1-1/8 inch angle-iron and its frame was 9 feet high and 22 inches across. Three 1/2 inch steel rods ran vertically the height of the frame. These rods made it possible to secure the extraction columns and the feed-device to this support by means of ordinary laboratory clamps. Two clamps were found sufficient to hold extraction column #1 firmly in position during a run. This made the procedure quite simple. Thus, in order to make a run at an increased column height, the securing clamps holding the column were loosened, the column in use removed, the lower clamp was slid to a lower position on the vertical rod, the column with the increased column height was placed in position, the clamps tightened and the run made.

As mentioned previously, the present study was concerned with the extraction of acetic acid from water using different solvents. The acetic acid-water solution was dispersed and the drops of this solution fell through the continuous, solvent phase, extraction taking place from the water into the solvents. The concentration of the acetic acid-water solution was 1.063 N (about 6% by weight).

A sufficient quantity of this solution was made up at the start so that the feed concentration would be the same for all the experimental runs to be made. This feed solution was stored in a cork-stoppered two gallon bottle.

Before runs were made on any given day the temperatures of the feed and solvent were taken. If these temperatures differed from 25°C by more than 1°C, runs were not made on that day. This situation was very unusual as long as runs were not attempted in July and August. During these months the laboratory temperature is high enough to raise the temperatures of these liquids much above 25°C. All runs, therefore, were made at 25°C $\pm$ 1°C.

Procedure for Column #1

Experimental runs using column #1 were the first to be undertaken. The first solvent employed was isopropyl ether.

After cleaning the tip as previously described, the tip was washed off with distilled water and attached to the 10 ml. burette. The burette was filled with feed solution and the stopcock was opened. The feed was allowed to run through the tip to make sure that the feed solution was not being diluted by the water which remained in the capillary tip after cleaning and washing. Approximately 20 ml.

of feed solution was allowed to run through the capillary tip. The feed device was then considered to be ready for use.

The first runs were made using the bottom portion of column #1 (see Figure 7). When using the bottom portion only, the rubber connecting sleeve shown in Figure 7 was not used. The bottom stopcock on this bottom portion was closed. By means of a transfer pipette 50 ml. of water was accurately measured and carefully placed in the bottom of this portion of the column. This column was then attached to the column support by means of the clamps used for this purpose. Isopropyl ether was then carefully added to the column and the column was filled to within 1/4 inch of the top.

The level in the feed device was then allowed to fall to the proper level. (The initial reading to be used with each solvent has already been indicated on pages 97 and 98). When the level had fallen to this value the stopcock on the feed device was closed coincidentally with the detachment of a drop from the tip. Allowing time for draining the burette reading was taken. Then, the clamps holding the feed device were loosened and the feed device was moved down very carefully until the delivery tip was submerged in the continuous phase until its delivery end

was 1-1/4 inches below the surface of the solvent. The clamps were tightened on the feed device and its stopcock opened. Fifty drops were allowed to form and fall through the continuous phase. Coincidentally, with the detachment of the fiftieth drop from the delivery tip, the stopcock on the feed device was closed. Time was allowed for drainage and the burette reading again was taken.

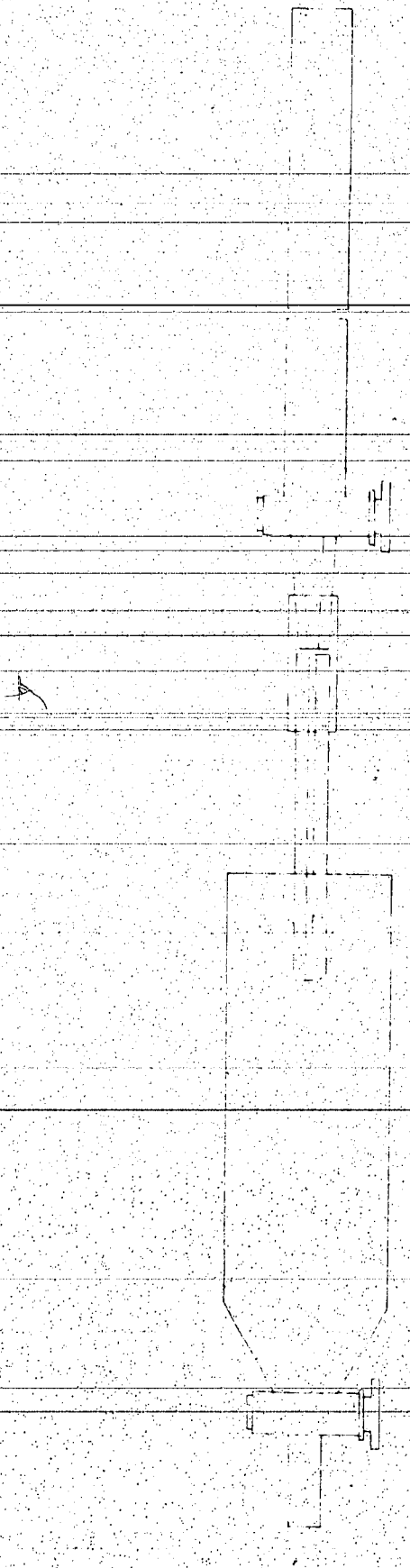
The assembly shown in Figure 10 indicates the position of the feed device relative to the column.

After all the drops had fallen through the continuous phase and passed into the bottom water layer, the latter was drained and analyzed. (See section below on sampling and analysis).

During all runs, the time of drop formation and the time of fall was measured. Furthermore, the height through which the drops had fallen was measured as from the delivery end of the tip to the bottom interface. This distance is the column height and the time of drop fall also measured during the run corresponds to this height, the time of drop fall being taken from the instant the drop detaches itself from the tip until it strikes the bottom interface. When using this bottom portion of column #1, the column height was approximately 3 inches. This was the smallest column height studied in this research.

FIGURE 10

ASSEMBLY



The next run was made at a column height made by by attaching a 6 inch length of glass tubing to the bottom portion of the column. In making such a run the rubber connecting sleeve was first attached to the bottom portion of the column. Then 50 ml. of distilled water was placed in the bottom of this portion of the column. The 6 inch length of glass tubing was then carefully worked into the other end of the rubber connecting sleeve until the glass sections were almost touching. This assembly was then fastened to the column support by means of the clamps already discussed. The column was then carefully filled with solvent until within 1/4 inch of the top. In filling the column with solvent, the latter was poured down the sides of the column very slowly to prevent splashing any of the water up onto the side walls of the column.

The feed device with its liquid level properly adjusted and read was lowered very carefully so that the delivery end of the tip was submerged in the solvent. Again, the delivery end of the tip was placed so that it was about 1-1/4 inches below the surface of the solvent. The run was then made as described before with the lower column height. Drop formation time, drop fall time and column height were again measured as previously described. After all the drops had fallen through the continuous phase and passed into the

water layer the latter was drained and analyzed.*

The above procedure was repeated for column heights obtained by attaching the following lengths to the bottom portion of the column: 11", 17", 24", 36". Thus, "H" in Figure 7 could be given values of 6", 17", 24", or 36". The rubber connecting sleeve did not form a good fit when the 36" length was attached and hence this joint leaked considerably. The use of this length therefore was abandoned except in a very few cases.

The runs at all the column heights were made in either duplicate or triplicate. In doing this the following procedure was observed. After the liquid layer had been drained for analysis and after all the necessary measurements had been made, the feed device was raised so that the delivery tip was no longer inside the column. The column in use, whether it was the bottom portion itself or the assembly of the bottom portion and an additional length, was removed from the column support. The solvent was poured from the column and the column was washed and dried. The run was then repeated using the usual procedure.

The above procedures made it possible to obtain data on the amount of solute extracted from the drops as a function of column height, i.e., the distance through which the drops fall. Furthermore, since the time of drop fall

* See Addendum, Page 205.

was also measured, it was further possible to calculate the amount of solute extracted from the drops as a function of their time of fall.

The experimental runs as just described for the solvent isopropyl ether were also made using methyl isobutyl ketone and ethyl acetate. Procedures employed were exactly the same as those described above. In using the different solvents, however, the liquid level in the feed device to be employed for each solvent was different. The liquid levels to be used in connection with the different solvents have already been discussed.

In the case of isopropyl ether and methyl isobutyl ketone the above procedures were employed for two different drop sizes. With ethyl acetate, however, only one drop size was used, the reason for which will be given later. The data obtained with the different solvents is given in a subsequent section. Although fifty drops were used when the large drop size was studied, this was not the case with the smaller drop size. The number of drops used in each set of experimental runs will be indicated in the data to be presented later.

In making experimental runs in duplicate and triplicate considerable amounts of solvent were required. After a solvent had been used once, the acidity was found

to be negligible. Thus it was possible to employ a solvent twice before it needed treatment to reduce its acidity. However, after the solvents had been used twice, the acidity was above 0.04%. Although this is very small, it was decided not to use any solvent the acidity of which was greater than 0.04%. When the acidity of a batch of solvent had risen above 0.04%, i.e., after the solvent had been used twice, steps were taken to reduce their acidity. (See section on washing of solvents).

Sampling and Analysis: Column #1

It is evident from the descriptions of column #1 and column #2 that different sampling techniques must be employed dependent upon the column in use. In the procedure pertaining to column #1, after the fifty drops had fallen through the solvents and crossed the bottom interface, sampling was begun.

The stopcock on the bottom portion of the column was opened and the water layer was drained very carefully. This sample was very close to 50 ml. since, by careful manipulation of the stopcock, almost all the bottom layer could be drained off without removing any of the solvent phase with it. A 25 ml. portion was removed by means of a 25 ml. transfer pipette and this sample was titrated with 0.1 N NaOH using phenolphthalein as the indicator. It was

thus possible to calculate the total acetic acid content of the water layer by knowing how much acetic acid was contained in the 25 ml. sample. The volume of the water layer used in this calculation was taken as the 50 ml. placed in the bottom of the column originally plus the volume of acetic acid-water solution equal to 50 drops. This is an assumption which infers that the volume of the drops at the bottom of the column is the same as that read from the burette. In other words, the loss of solute by the drop does not cause a reduction in its volume. The errors introduced by this assumption are small and will not affect, very greatly, the accuracy of this calculation.

The sampling procedure described above was quite lengthy inasmuch as after the sample was taken a further aliquot portion had to be removed for titration. Calculations were then necessary to determine the total acidity of the water layer. About halfway through the experimental work a more convenient sampling procedure was employed which saved considerable laboratory time. The design of the bottom portion of the column made it possible by careful manipulation of the stopcock, to remove in excess of 99.6% of the water layer without removing any of the solvent phase. When sampling was done in this manner, the entire sample was titrated and the acidity so obtained was assumed

to be the total acidity of the water layer. Of course, this method of sampling and analysis is slightly in error because to be strictly correct the acidity so obtained should be divided by 0.996. However, the error produced by this assumption is small enough to be tolerated especially since it saves considerable time. As a matter of fact, identical runs were made wherein the two different methods of sampling were employed. The results were found to be in satisfactory agreement. The use then of the simpler method of sampling is quite justified. Great emphasis must, however, be placed on the sampling when this shorter method is employed. Careful manipulation of the stopcock must be exercised to make certain that almost all the water layer is drained without removing any solvent.

When the water layer is being drained from the column during the sampling operation, the solvent layer in the column falls correspondingly. It was found that if the top solvent interface fell below the delivery end of the tip the portion of the drop clinging to this tip would be knocked off and would fall to the bottom. This is undesirable since this portion of the drop would be removed with the sample and be titrated to give incorrect results. This difficulty could be avoided by making certain that the delivery end of the tip was 1-1/4 inches below the surface

of the solvent before a run was begun. Thus when the bottom liquid layer is removed in sampling the top solvent interface does not fall below the delivery end of the tip.

The 0.1 N NaOH used for the titrations was prepared carbonate free and standardized with potassium acid phthalate.

When the samples required less than 10 ml. of titrant, a graduated and calibrated 10 ml. burette was used for greater accuracy.

Procedure for Column #2

In using column #2, the special glass section (see Figure 8) was never used alone. Another section of glass pipe was always joined to this section in making an experimental run.

The first runs were made at the lowest column height. The six inch length of glass pipe was joined to the special glass section. A piece of rubber tubing about 2 inches long was placed on the vent arm on the special section and its end was closed with a pinch clamp. This assembly was then attached to the column support. In attaching the assemblies of column #2 to the column support, three clamps were used, one around each stopcock and another half way up the top section. Stopcock B was closed and stopcock A opened; the column was then filled

with solvent until within 1/4 inch of the top of the column.

The capillary tip to be used in the feed device was cleaned in the same way as described in the procedure for column #1. The feed device was also used in exactly the same way as that previously described. The liquid levels in the feed device were the same as those already indicated. At the start of the run the feed device was lowered in the same way as already described until the delivery end of the tip was about 1-1/4 inches below the surface of the solvent. As a matter of fact, the entire procedure as far as the feed device is concerned is identical for both columns.

Fifty drops were allowed to fall through the continuous phase. These drops fell through the column and passed through stopcock A and collected just above the closed stopcock B. The drops in falling did not always pass through the open stopcock A without touching the sides of the special glass section. In many cases the falling drops actually hit on the sides of the special section where these sides taper down to meet stopcock A. It must be emphasized that these drops did not break here nor did they even cling to the sides after striking them. Their contact with the sides of this section was very short-lived.

The drops actually bounced off these sides after striking them and then continued down through stopcock A. The breaking of a drop as a result of its collision with these sides was never observed.

When the last of the drops had passed stopcock A, this was closed. Then stopcock B was opened and the chamber between the two stopcocks was drained. This sample was then analyzed for its acetic acid content.

The above procedure was repeated for different column heights. The column height was varied by attaching different lengths of glass pipe to the special glass section.. The column height was measured from the delivery end of the capillary tip down to the lower side of stopcock A. This is necessary because the solvent in the bore of stopcock A remains there when this stopcock is closed. This liquid is not drained when stopcock B is opened. (This point will be made a little clearer in the section on sampling which follows).

During the course of a run the column height and drop formation time were measured but the time of drop fall was not measured. The time taken by a drop in falling a given height may be determined by reference to the data obtained with column #1.

The procedure described above was used for all the different solvents and in the case of isopropyl ether and methyl isobutyl ketone two different drop sizes were studied. Runs were again made in duplicate or triplicate.

The solvents were used twice, just as described in the section concerned with column #1. When the acidity became greater than 0.04% by weight, the solvents were treated for acid removal.

When column #2 was first used, a leak was detected in stopcock A. The solvents would leak out around the barrel of this stopcock when operating at the higher column heights. It was felt that this was due to the fact that the surfaces of this stopcock were not in intimate contact. This stopcock was dismantled and some carborundum was mixed with silicone stopcock grease to form a paste. This paste was placed between the contacting surfaces of the stopcock and the barrel was carefully worked between the open and close positions for each quadrant of the stopcock. This apparently removed the rough spots and thereafter satisfactory operation was obtained. Silicone stopcock grease was used in both stopcocks on this column. This stopcock grease is attacked by the solvents used but the action is not very rapid.

Sampling and Analysis: Column #2

After all the drops had fallen past stopcock A,

the latter was closed. Stopcock B was opened and the chamber between the two stopcocks was drained. The pinch clamp on the rubber tubing on the vent line was opened and by means of a wash bottle with a 6 inch capillary delivery tube the chamber was washed out with water. The delivery tube of the wash bottle was a piece of glass tubing that had been drawn out considerably and cut to the proper size. This delivery tube could be inserted into the vent arm and its diameter was such that it extended almost into the chamber to be washed. The chamber was thus washed completely, the washings being caught in the same sampling flask as the contents of the chamber just previously drained. These samples were then analyzed by titration with 0.1 N NaOH. This gives the amount of acetic acid in the drops just after passing stopcock A. It is true that the drops continue to lose acetic acid to the solvent in passing from stopcock A to the point where they collect at the top of stopcock B but this acetic acid is detected in the titration since the entire contents of this chamber are drained for analysis. The solvent contained in the bore of stopcock A is not drained since when stopcock A is closed the solvent is still contained in the bore of the latter. The drops, however, in passing through the bore of this stopcock lost solute to the solvent therein. This is the reason why the column height

is measured from the delivery end of the capillary tip down to the bottom side of stopcock A. The titration then gives the amount of acetic acid contained in the drops just after passing stopcock A.

It is obvious that the samples obtained in the above procedure contained the fifty drops of acetic acid-water solution, (which have lost some acetic acid) the solvent which was contained in the chamber between the two stop-cocks and the washings. The titration then was made in the presence of two layers. This, however, does not affect the accuracy of the titration as was shown by analyzing known samples. The indicator was added and the end-point was taken as the first appearance of pink in the water layer after considerable shaking.

Special Data on Analysis of Ethyl Acetate Solutions:

In making the runs with ethyl acetate as the solvent, a very unfortunate observation was made. It was found impossible to titrate, accurately, the amount of acetic acid contained in the samples. Since the samples obtained using column #2 always contained appreciable amounts of the solvent as described above, it was impossible to determine the correct acetic acid content in the presence of ethyl acetate. When the samples were titrated, the ethyl acetate itself was hydrolyzed to acetic acid and ethyl alcohol. This reaction

was catalyzed by the NaOH used as titrant and probably auto-catalyzed by the acetic acid. The results, of course, of this titration are incorrect. In an attempt to remedy the situation ethyl alcohol was added to the samples before titrating them but even this procedure failed. In running known samples, even when ethyl alcohol was added to suppress the hydrolysis, the amounts of sodium hydroxide required to reach the end point were in excess of those required for the known acetic acid content of the samples.

This unfortunate circumstance was not anticipated and it was discovered too late in the research to select another solvent in place of ethyl acetate. The results reported in the runs for ethyl acetate are approximate, however, since certain corrections were made. In the first place, it is felt that the runs made with column #1 are correct since the titrations were made in the absence of this solvent. The results of column #2 were corrected by running known samples. The sodium hydroxide required in excess of the known acetic acid content of these known samples was calculated. The known samples were so chosen as to approximate the samples obtained in the experimental runs. In analyzing the samples made in the actual experimental runs then, the titrations were corrected by subtracting the appropriate amounts of sodium hydroxide as obtained in

the analyses of the known samples. The results are not accurate, however, but it is felt that this procedure enables the results to be looked upon as fairly approximate.

The circumstance just discussed is the reason why the ethyl acetate system was not studied in more than one drop size as were the other solvents.

Washing the Solvents

As already mentioned the solvent employed in making experimental runs was used twice. At this time the acidity, as acetic acid, was over 0.04% by weight. When this situation existed the batch of solvent was treated to reduce its acidity.

This was done by washing the solvents with approximately 0.5 N sodium hydroxide. This washing was carried out batch-wise in a 2 gallon cork-stoppered bottle. This bottle was half filled with the sodium hydroxide solution and then about 3 liters of the solvent was placed in the bottle. After vigorous shaking the contents were allowed to settle which required about 3 minutes. Then about 2 liters of solvent were poured out of the bottle and replaced by 2 liters of the solvent to be treated. This procedure was repeated until the batch of solvent had been washed. The final separation of the contents of the washing bottle was made by means of a 2 liter separatory funnel.

Then, the solvent which had been washed with 0.5 N

sodium hydroxide was next washed with distilled water using the same procedure as described above. The product of this washing was then allowed to stand over calcium chloride for 48 hours to dry it. The solvent was then filtered through cotton and was ready for reuse. The acidity as acetic acid was less than 0.02% in all cases.

The above washing procedure could not be used for the ethyl acetate due to the hydrolysis which would take place. The treatment of this solvent for acetic acid removal was never necessary, however, because the original batch of 5 gallons was sufficient for all the runs performed using this solvent. However, at the end of the experimental work this solvent was treated for acetic acid removal prior to returning it to storage. It was washed batchwise with 1.5 N Na_2CO_3 and then with water and dried over Drierite.

Experimental Results and Calculations

The data obtained with columns #1 and #2, tips #1 and #2, using the procedures just described are presented in tabular form in the appendix.

The main objective of the present research was the determination of the relationship between the amount of solute extracted and column height. The results of the experimental work represent such a relationship and are presented in the following tables.

These results are presented to indicate the amount of solute extracted at certain column heights with the different solvents employed. The results are presented in such a way as to include all the pertinent information in each table. This pertinent information is presented at the top of each table.

Table 1 contains the results obtained with column #1, tip #1 using the three solvents. Percentages of extraction are listed with the corresponding column heights.

Table 2 contains the results obtained with column #2, tip #1 using the various solvents. Percentages of extraction are listed with the corresponding column heights.

Table 3 contains the results obtained with column #1, tip #2 using isopropyl ether and methyl isobutyl ketone. Percentages of extraction are listed with the corresponding column heights.

Table 4 contains the results obtained with column #2, tip #2 using isopropyl ether and methyl isobutyl ketone. Percentages of extraction are listed with the corresponding column heights.

Tables 5 and 6 contain the results obtained with isopropyl ether and methyl isobutyl ketone using different tips. Runs were made at a definite column height but the drop formation time was varied (see appendix). These results may be interpreted by referring to the information at the top of each of these tables.

The results presented in Tables 1, 2, 3, 4, 5, 6 are plotted in Figures 11, 12, 13, 14, 15, 16, 17, 18, 19. Figure 20 was plotted from the data contained in the appendix and represents the relation between drop fall time and column height for the different systems and drop sizes. (The dispersed phase was always 1.063 N acetic acid solution).

Figures 21 through 23 represent the relation between the amount of acetic acid extracted and the time of drop fall.

Sample Calculation: Table 1, Run #1

Volume of feed = 6.22 - 3.82 = 2.40 ml.

Initial acetic acid = 2.40 x 1.060 = 2.54 milli-equivalents

Final acetic acid = 22.40 x 0.0974

= 2.18 milliequivalents

Acetic Acid lost = 2.54 - 2.18 = 0.36 milliequivalents

$$\text{Percent Extracted} = \frac{0.36}{2.54} \times 100 = 14.2\%$$

The calculations can also be made in terms of acetic acid lost per drop but the percent extracted, of course, is the same.

TABLE 1 - Column #1; Tip #1; Temperature = 25°C ± 1°C
50 drops of acetic acid solution used.

Isopropyl Ether			Methyl Isobutyl Ketone			Ethyl Acetate		
Run No.	Column Height (in.)	Percent Extracted	Run No.	Column Height (in.)	Percent Extracted	Run No.	Column Height (in.)	Percent Extracted
1	3 1/4	14.2	29	3 1/4	26.4	54	3 1/4	36.5
2	3 3/8	14.6	30	3 1/8	27.3	55	3 1/4	37.9
3	3 1/4	13.3	31	3 1/4	29.4	56	3 1/4	38.5
4	3 1/4	13.6	32	9 1/4	42.5	57	3 1/2	37.9
5	9 1/2	20.1	33	9 1/4	41.0	58	3 1/4	37.0
6	9 3/4	19.2	34	9 3/8	42.5	59	9 1/2	54.1
7	20 1/4	29.6	35	14	50.8	60	9 1/2	53.2
8	20	28.9	36	14 1/4	50.0	61	9 1/2	48.7
9	20	28.5	37	20	58.4	62	14 1/2	63.3
10	20	29.4	38	20	58.8	63	14 1/2	63.5
11	27 1/4	36.5	39	27 1/4	67.3	64	20 1/2	75.1
12	27 1/2	35.8	40	27 3/8	67.8	65	20 1/4	75.3
			41	27 1/2	68.2	66	27 1/2	82.1

TABLE 2 - Column #2; Tip #1; Temperature = 25°C ± 1°C
50 drops of acetic acid solution used.

Isopropyl Ether			Methyl Isobutyl Ketone			Ethyl Acetate		
Run No.	Column Height (in.)	Percent Extracted	Run No.	Column Height (in.)	Percent Extracted	Run No.	Column Height (in.)	Percent Extracted
13	8	10.9	42	8	24.7	67	8 1/4	33.5
14	8	11.7	43	8	25.1	68	8 1/4	38.6
15	8	12.5	44	8	23.9	69	8	37.0
16	8	12.2	45	13 1/2	36.2	70	8	37.2
17	13 1/2	17.6	46	13 3/4	35.5	71	8 1/4	38.1
18	14	17.9	47	13 3/4	35.3	72	13 3/4	53.4
19	14	17.8	48	20 1/4	46.8	73	13 3/4	53.4
20	20	23.8	49	20	46.3	74	13 3/4	53.0
21	20	23.6	50	20 1/4	47.1	75	20 1/4	65.5
22	20	23.9	51	25 3/4	53.8	76	20	64.5
23	26	27.4	52	25 3/4	53.1	77	20	65.6
24	26	27.0	53	25 3/4	53.7	78	25 3/4	73.0
25	26	28.0				79	25 3/4	73.0
26	25 1/2	28.2				80	25 3/4	72.0
27	25	27.6						
28	25 1/2	27.9						

TABLE 3 - Column #1; Tip #2; Temperature = 25°C ± 1°C

Isopropyl Ether (80 drops of acetic acid solution used)			Methyl Isobutyl Ketone (90 drops of acetic acid solution used)		
Run No.	Column Height (in.)	Percent Extracted	Run No.	Column Height (in.)	Percent Extracted
81	3	13.6	100	3 1/8	28.2
82	3 1/8	15.5	101	3 1/8	28.0
83	3 1/4	15.6	102	3 1/4	27.4
84	3 1/8	13.6	103	9 3/8	43.2
85	9 1/4	22.4	104	9 1/2	44.2
86	9 1/4	22.5	105	9 3/4	44.0
87	20	32.4	106	14 1/2	53.5
88	20	33.3	107	14 3/8	54.1
89	26 3/4	39.3	108	14 1/2	53.2
90	26 3/4	39.1	109	19 7/8	63.4
			110	19 7/8	61.8

TABLE 4 - Column #2; Tip #2; Temperature = 25°C ± 1°C

Isopropyl Ether (80 drops of acetic acid solution used)			Methyl Isobutyl Ketone (90 drops of acetic acid solution used)		
Run No.	Column Height (in.)	Percent Extracted	Run No.	Column Height (in.)	Percent Extracted
91	8 1/4	13.8	111	8	24.8
92	8 1/4	12.7	112	7 3/4	29.1
93	8 1/2	15.1	113	8	24.0
94	8 1/2	14.8	114	8 1/4	26.9
95	14 1/2	20.3	115	8 1/2	27.1
96	14	20.5	116	8 3/4	27.3
97	26	32.8	117	14	37.5
98	26 1/4	32.9	118	13 3/4	38.0
99	26 1/4	32.7	119	14	37.5
			120	13 1/2	38.3
			121	13 1/2	39.9
			122	13 1/4	38.1
			123	25 1/4	58.4
			124	25 3/4	58.0
			125	25 3/4	57.7

TABLE 5 - Column #1; Column Height = 3 inches (approximately)
Temperature = 25°C ± 1°C

Isopropyl Ether (Tip #1; 50 drops of acetic acid solution used)			Methyl Isobutyl Ketone (Tip #2; 85 drops of acetic acid solution used)		
Run No.	Drop Formation Time (sec.)	Percent Extracted	Run No.	Drop Formation Time (sec.)	Percent Extracted
126	1.3	14.3	147	0.7	28.0
127	1.3	14.7	148	0.8	28.2
128	1.3	13.4	149	0.8	29.4
129	1.4	13.6	150	0.8	26.7
130	2.0	12.0	151	1.5	29.5
131	3.5	11.6	152	3.0	34.2
132	3.0	14.9	153	3.0	29.4
133	2.0	13.2			
134	4.4	14.2			
135	3.9	13.0			
136	1.3	14.8			
137	1.3	13.0			

TABLE 6 - Column #2; Column Height = 8 inches (approximately)
Temperature = 25°C ± 1°C

Isopropyl Ether (Tip #1; 50 drops of acetic acid solution used)			Methyl Isobutyl Ketone (Tip #2; 90 drops of acetic acid solution used)		
Run No.	Drop Formation Time (sec.)	Percent Extracted	Run No.	Drop Formation Time (sec.)	Percent Extracted
138	1.2	11.7	154	0.8	26.9
139	1.2	12.5	155	0.8	27.1
140	1.2	12.2	156	0.8	27.3
141	1.6	11.7	157	1.9	27.3
142	1.9	12.0	158	1.6	26.9
143	2.9	12.9	159	1.9	27.6
144	4.5	13.5			
145	4.3	12.7			
146	1.2	10.9			

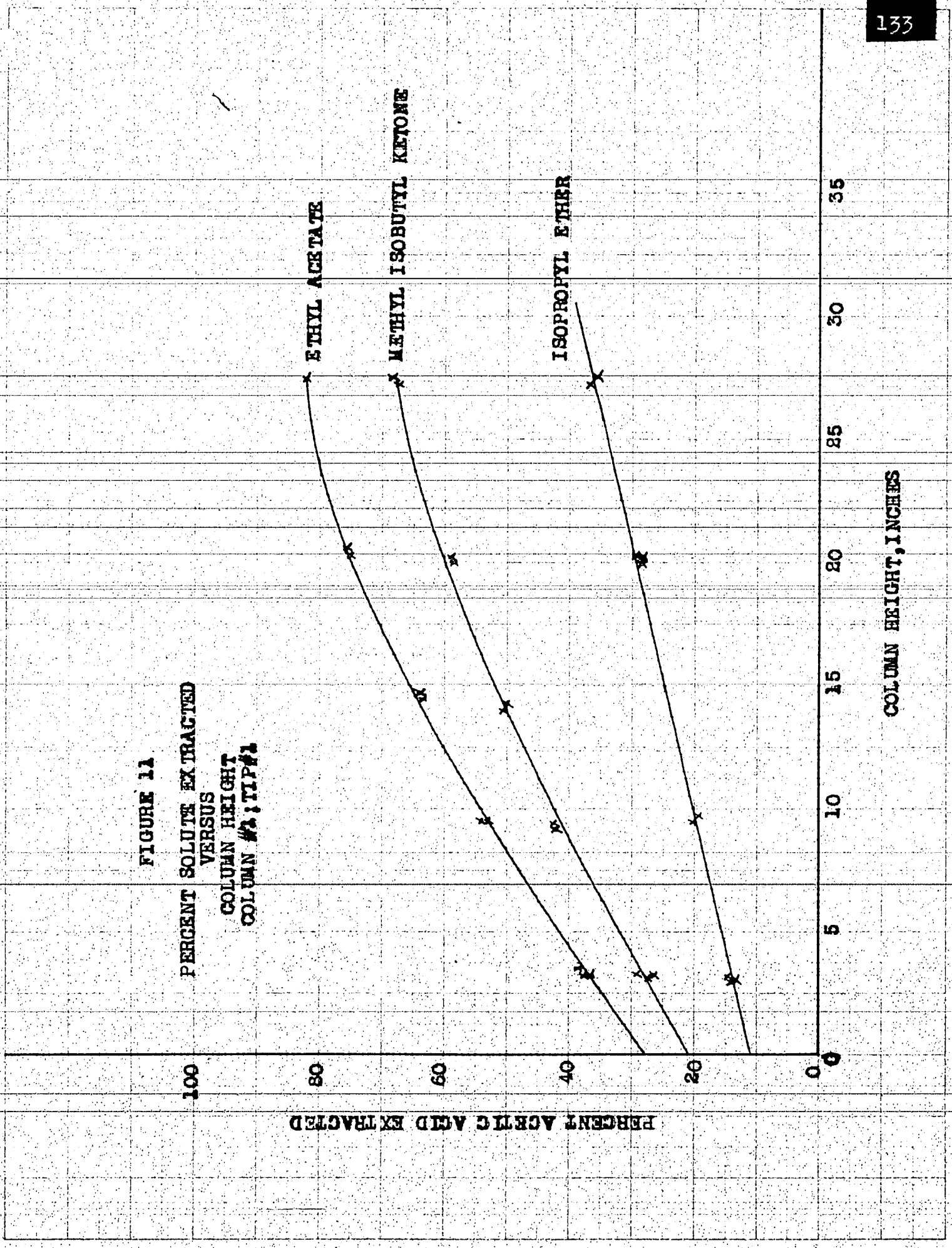
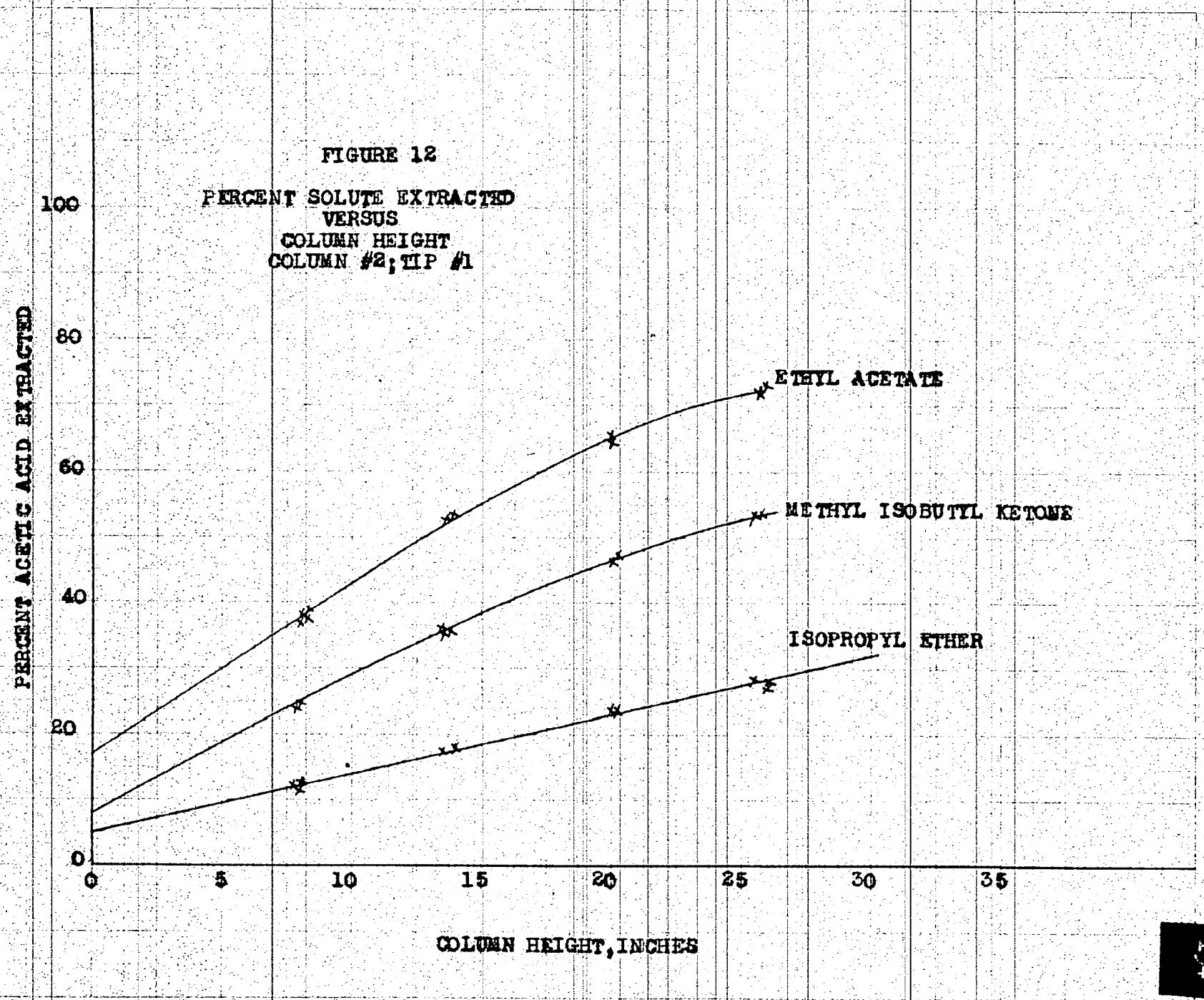


FIGURE 11

PERCENT SOLUTE EXTRACTED
VERSUS
COLUMN HEIGHT
COLUMN #1, TIP #1

FIGURE 12

PERCENT SOLUTE EXTRACTED
VERSUS
COLUMN HEIGHT
COLUMN #2; TIP #1



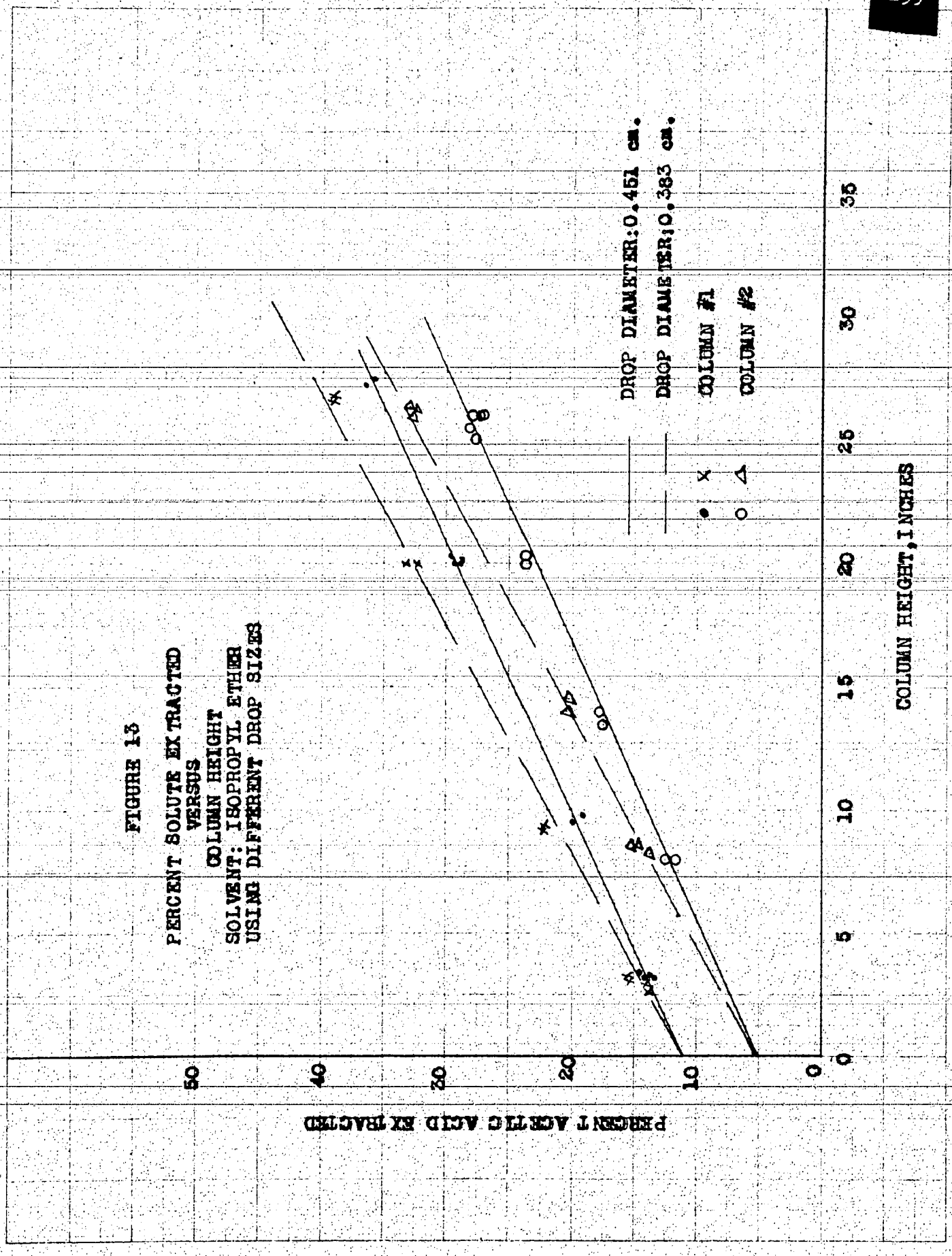
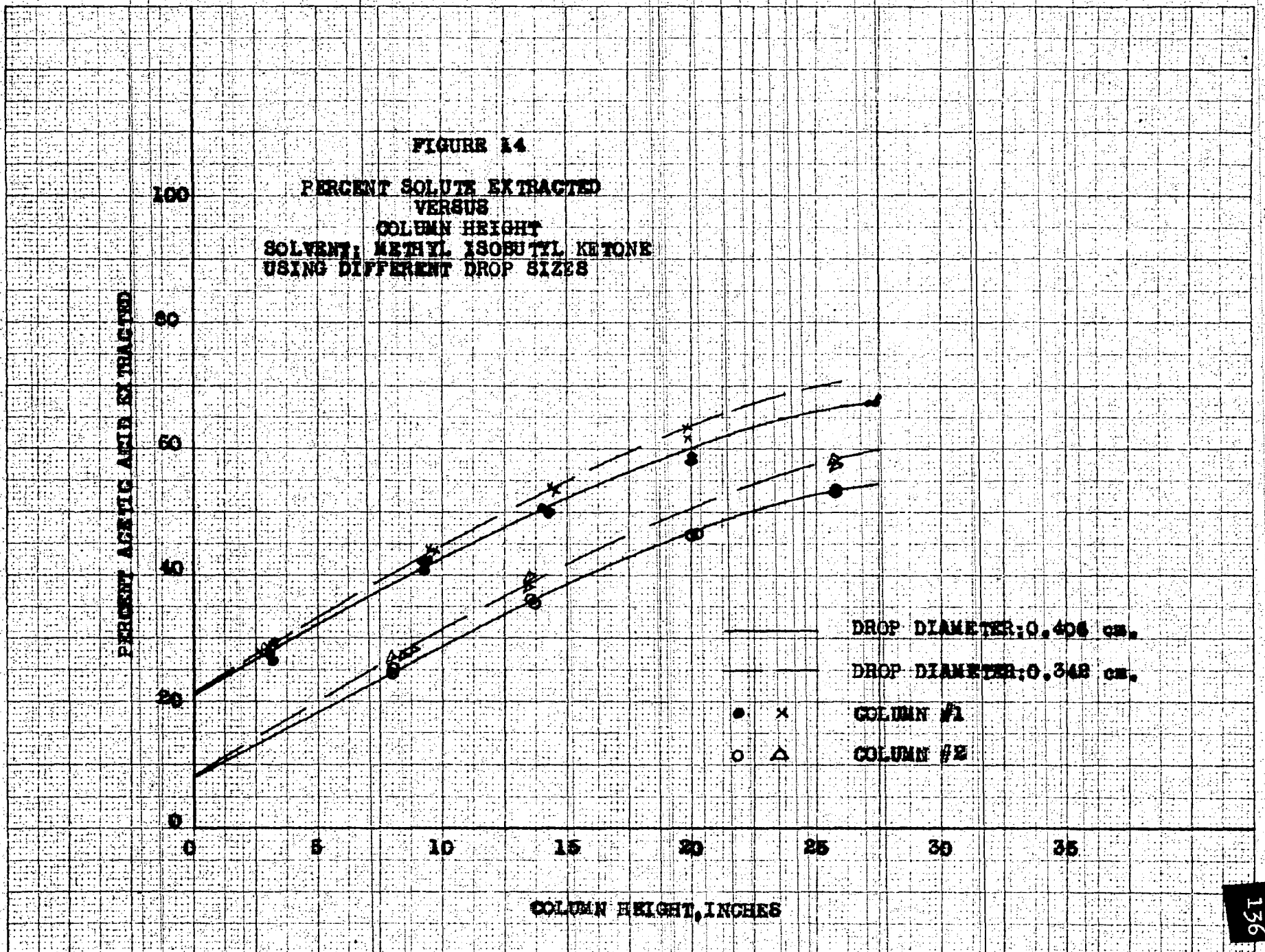


FIGURE 13

PERCENT SOLUTE EXTRACTED VERSUS COLUMN HEIGHT
SOLVENT: ISOPROPYL ETHER
USING DIFFERENT DROP SIZES



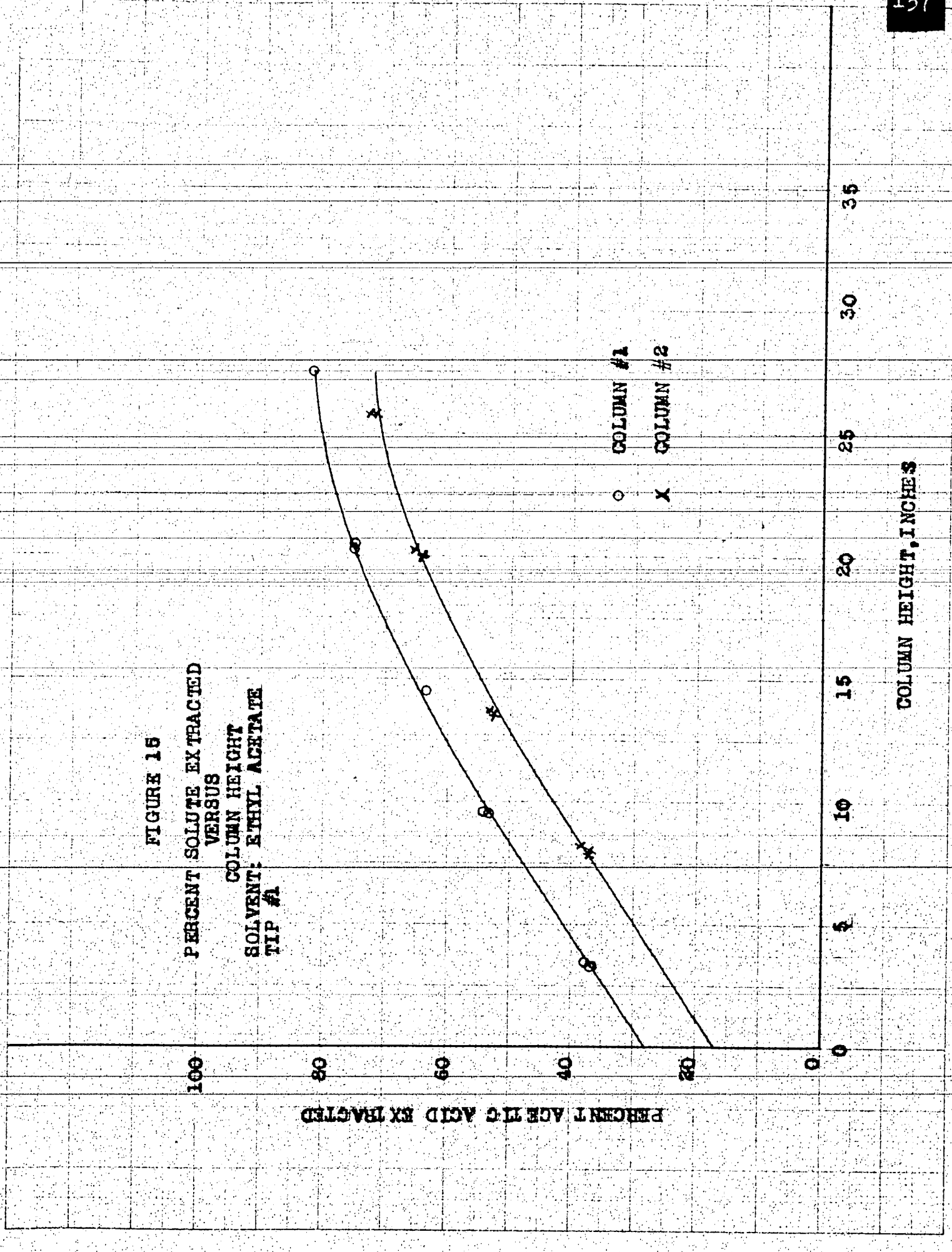


FIGURE 16
PERCENT SOLUTE EXTRACTED
VERSUS
COLUMN HEIGHT
SOLVENT: ETHYL ACETATE
TIP #1

FIGURE 16

PERCENT SOLUTE EXTRACTED
VERSUS
DROP FORMATION TIME
SOLVENT: ISOPROPYL ETHER
COLUMN #1, TP#4
COLUMN HEIGHT: 3 INCHES
DROP DIAMETER: 0.451 cm.

PERCENT ACETIC ACID EXTRACTED

100
80
60
40
20
0

0 2 4 6

DROP FORMATION TIME, SECONDS

FIGURE 18

PERCENT SOLUTE EXTRACTED
VERSUS
DROP FORMATION TIME
SOLVENT: METHYL ISOBUTYL KETONE
COLUMN #1, PIP #2
COLUMN HEIGHT: 3 INCHES
DROP DIAMETER: 0.342 cm.

PERCENT ACETIC ACID EXTRACTED

100
80
60
40
20
0

0
2
4
6

DROP FORMATION TIME, SECONDS

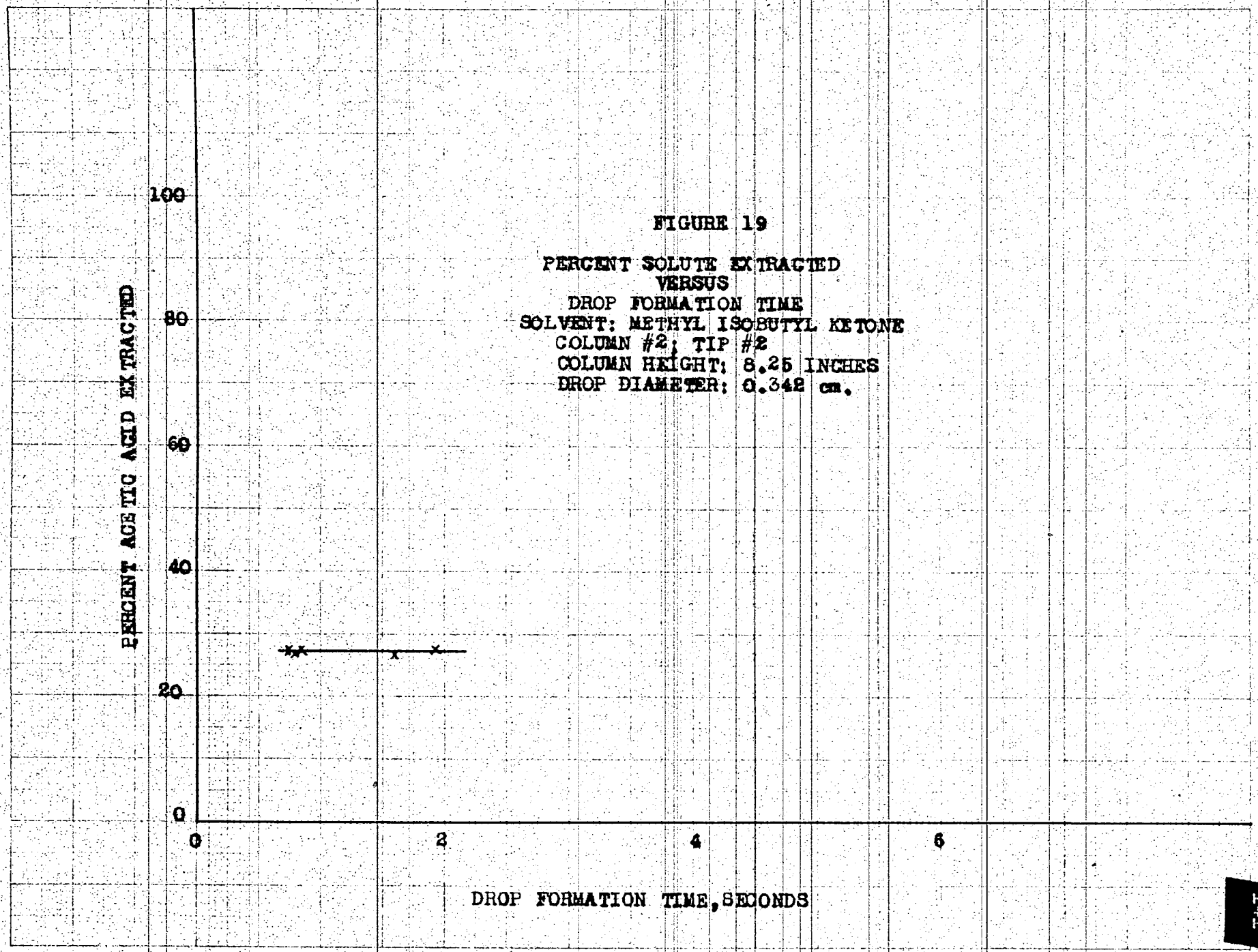


FIGURE 19

PERCENT SOLUTE EXTRACTED
VERSUS
DROP FORMATION TIME
SOLVENT: METHYL ISOBUTYL KETONE
COLUMN #2; TIP #2
COLUMN HEIGHT: 8.25 INCHES
DROP DIAMETER: 0.342 cm.

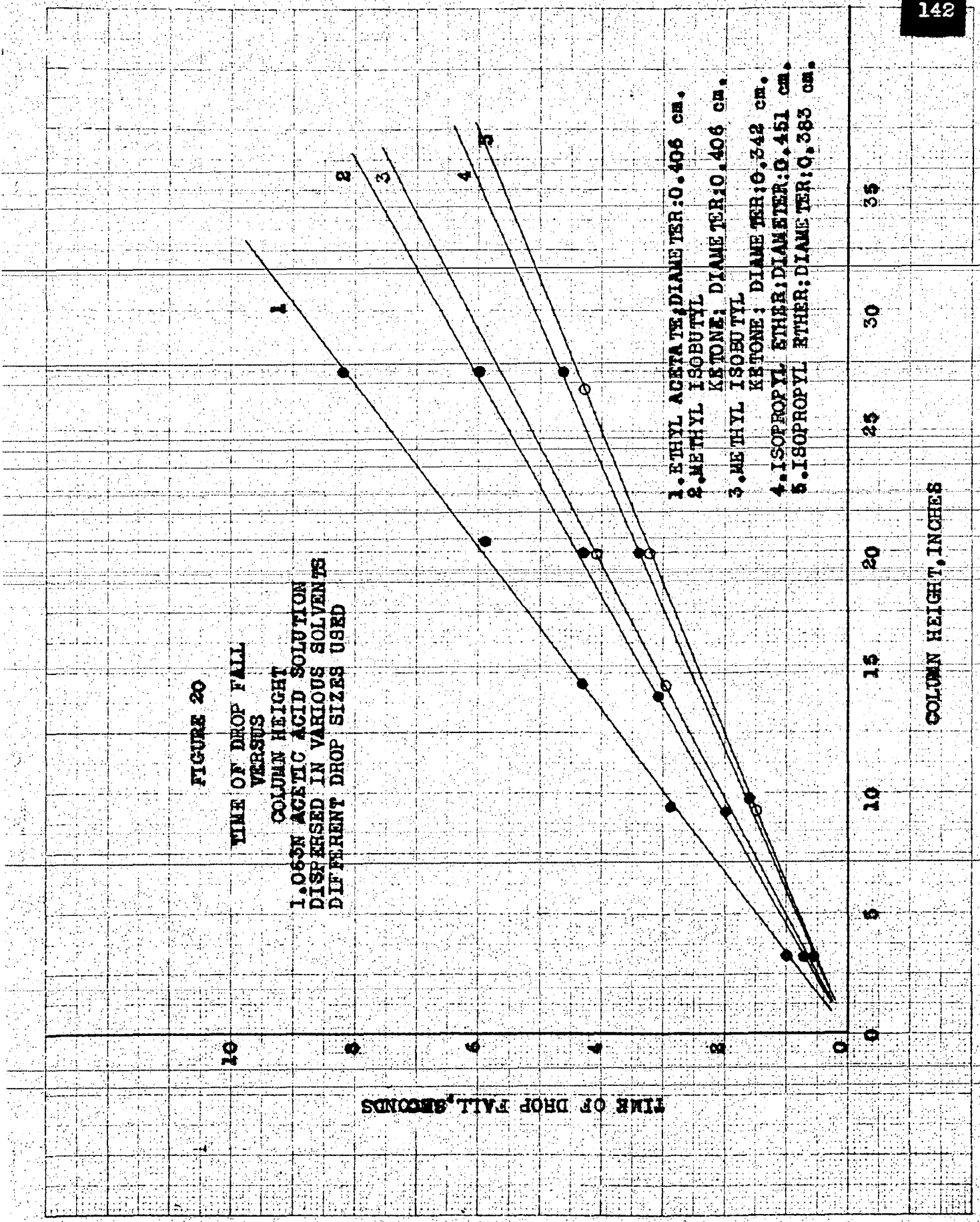


FIGURE 20

TIME OF DROP FALL
VERSUS
COLUMN HEIGHT
1.06 N ACETIC ACID SOLUTION
DISPERSED IN VARIOUS SOLVENTS
DIFFERENT DROP SIZES USED

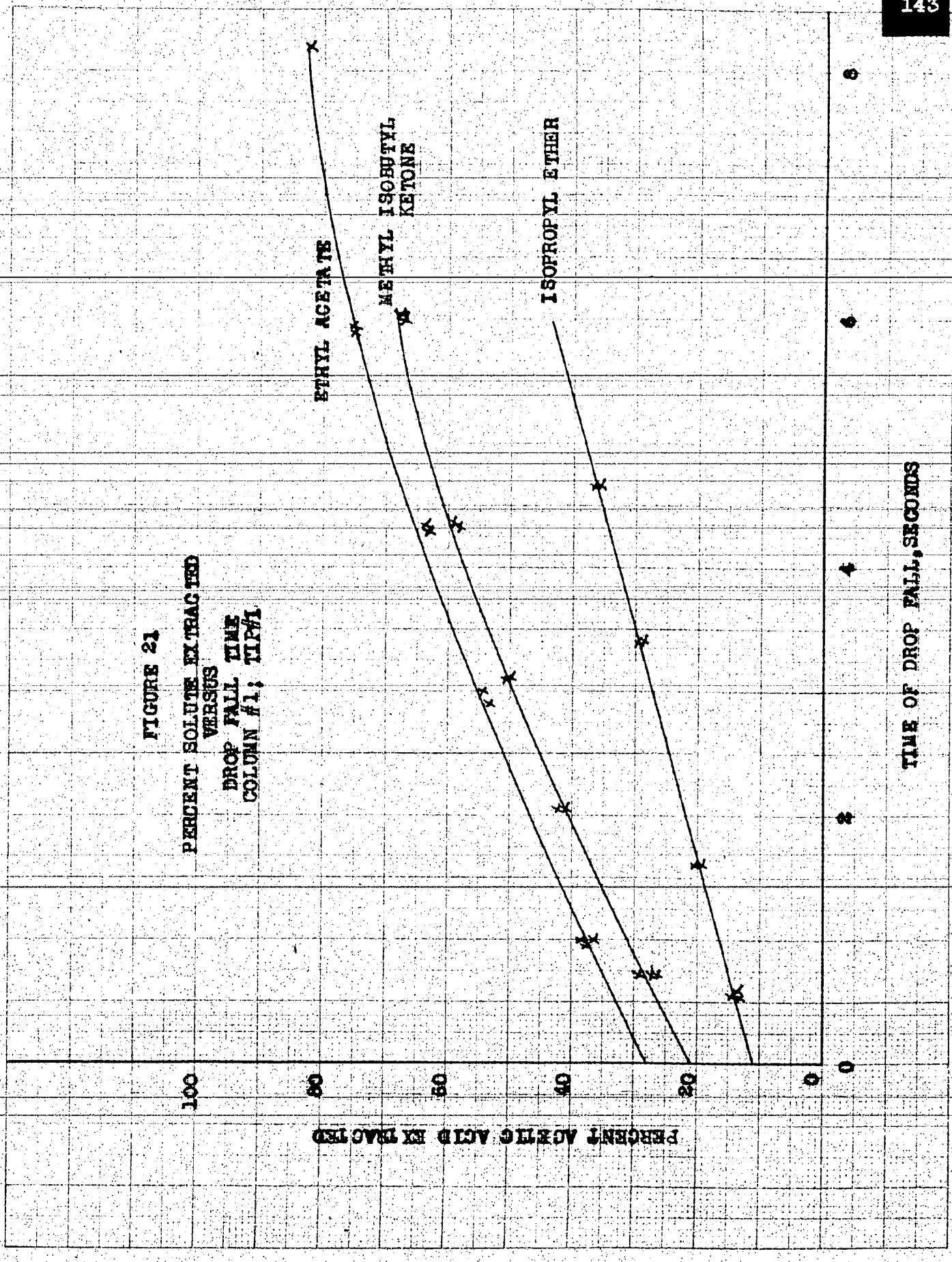


FIGURE 21

PERCENT SOLUTE EXTRACTED VERSUS DROP FALL TIME COLUMN #1; TIP#1

FIGURE 22

PERCENT SOLUTE EXTRACTED
VERSUS
DROP FALL TIME
COLUMN #2; TIP #1

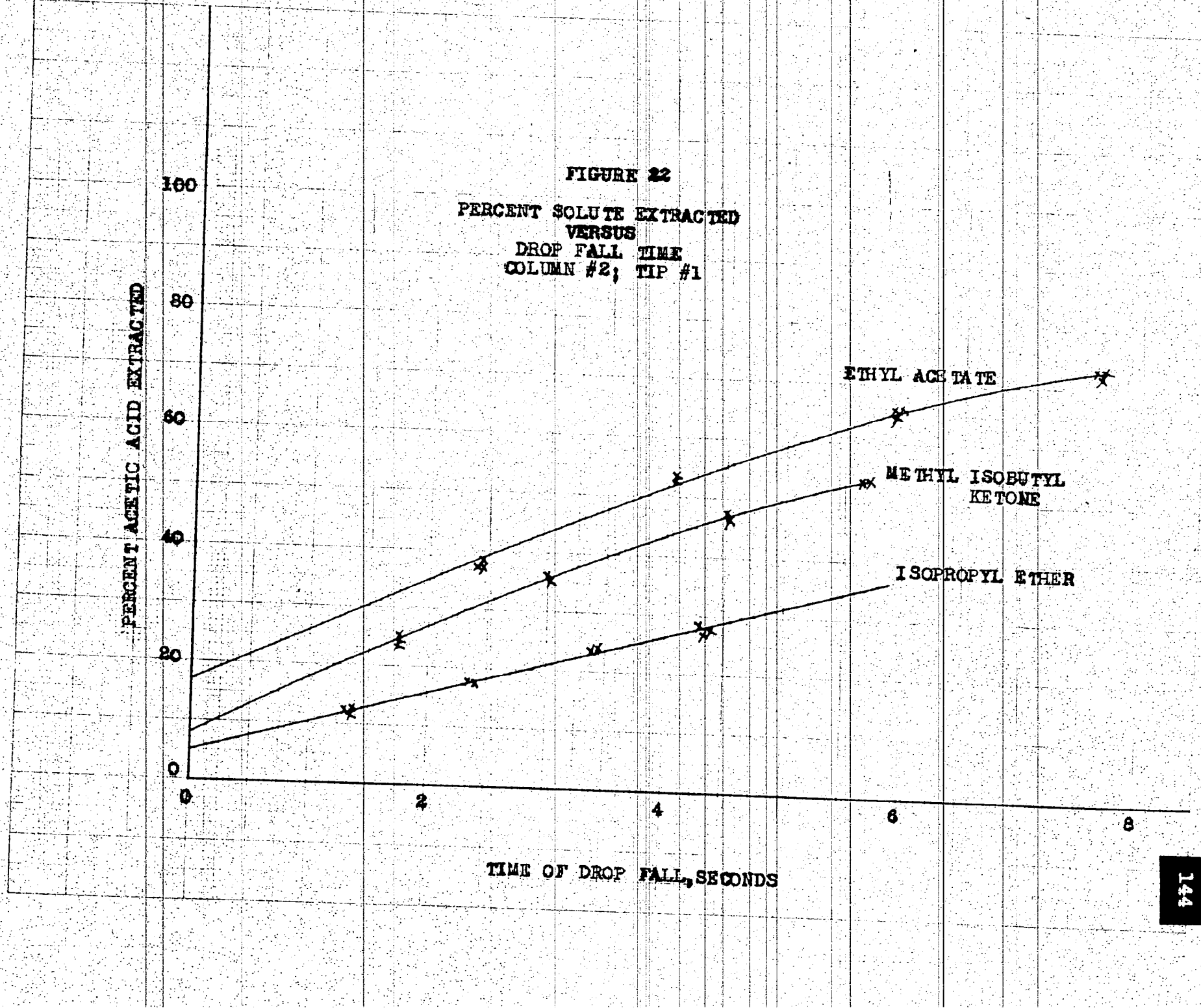
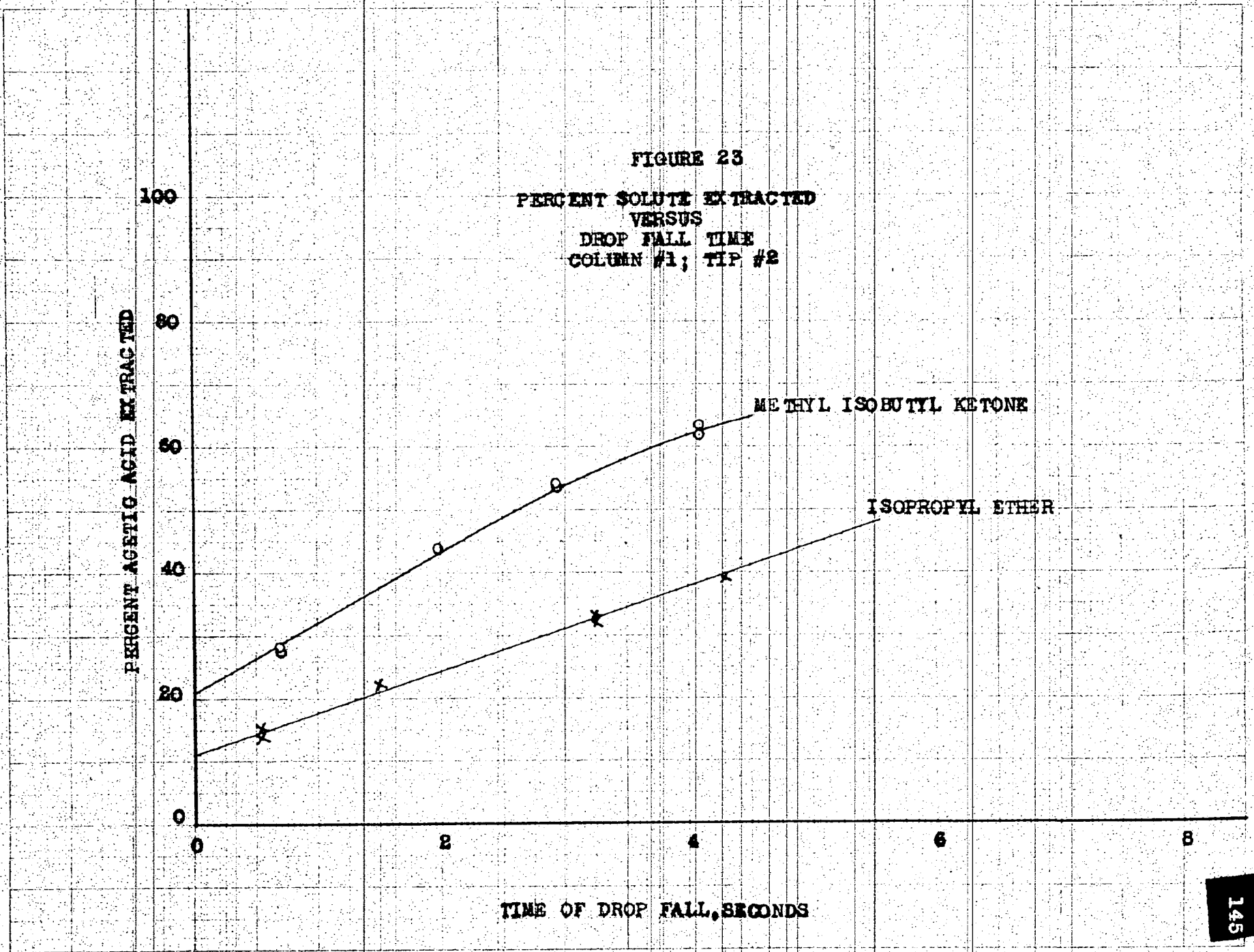


FIGURE 23

PERCENT SOLUTE EXTRACTED
VERSUS
DROP FALL TIME
COLUMN #1; TIP #2



RESULTS AND DISCUSSION

The ultimate results of the present research depend on an interpretation of the calculated results presented in the previous section. The calculations made with the experimental data (see appendix) have been presented graphically in the preceding figures. It is the interpretation and discussion of these graphs which constitutes the main object of the present section.

The curves presented in Figures 11, 12, 13, 14 and 15 have been extrapolated to zero column height. The intercepts so obtained represent the amount of solute extracted during drop formation and breaking or during drop formation only depending on the column used. It will be recalled that in the extrapolation to zero column height of the results obtained using column #1, the intercept represents the amount of solute extracted during drop formation plus drop breaking. On the other hand, the intercept obtained by extrapolating the results obtained with column #2 represents the amount of solute lost during drop formation only. The reasons why these extrapolations lead to two separate results have been presented in the discussions concerned with column design.

The intercepts obtained in Figure 12 represent the amount of solute extracted during drop formation only with each of the solvents, i.e. the amount of solute transferred

in stage 1. The intercepts of Figure 11 represent the amount of extraction which occurred in stage 1 plus stage 3, i.e., during drop formation and during drop breaking. By subtracting the value of the intercept in Figure 12 from that of the corresponding intercept in Figure 11 the amount of extraction occurring during stage 3 only is obtained.

Using the above method of interpretation the following values for the amount of solute lost during stage 1 and stage 3 were obtained. The amount of solute extracted is obtained as the percent of the total solute content of the original drop.

		Percent Acetic Acid Extracted		
Solvent	Drop Diameter	Stage 1	Stage 1 plus Stage 3	Stage 3
Isopropyl Ether	0.451 cm	5%	11%	6%
	0.383 cm	5%	11%	6%
Methyl Isobutyl Ketone	0.406 cm	8%	21%	13%
	0.342 cm	8%	21%	13%
Ethyl Acetate	0.406 cm	17%	28%	11%

These values indicate that for the two different drop sizes studied with isopropyl ether and methyl isobutyl ketone the percent of total solute, per drop, extracted during drop formation is the same in each case. Of course, the actual amount in moles is different but the percentages of the total are equal. It is difficult to explain this

observation until more is known of the mechanism of drop formation. It seems advisable to determine, first of all, when the solute is actually lost during drop formation. With this information, then, some insight into this mechanism may be obtained. For instance, if the solute is lost as a result of the "neck" of liquid springing back to the tip (see page 155) then the amount of solute lost during stage 1 may be some function of the size of this "neck" of liquid and this may account for the above observation. The same applies to the percent of solute extracted during stage 3. This behavior may be due to the fact that the same volume of feed solution was used in both cases, i.e., in the study of the two different drop sizes, the volume of feed solution delivered into the continuous phase was the same in each case although the number of drops differed in order to obtain this situation. It is felt that a definite quantity of solute is adsorbed at the bottom interface and since the volume of the feed solution employed in each case was the same the percent of the total solute lost during stage 3 would be expected to be the same despite the difference in drop size.

The percentage of the solute lost during drop formation using isopropyl ether, methyl isobutyl ketone and ethyl acetate is 5%, 8% and 17% respectively. These values are much less than the values reported by Sherwood, Evans and Longcor (23) for the extraction of acetic acid from

methyl isobutyl ketone with water with the former phase dispersed. The difference here is undoubtedly due to the difference in the direction of extraction. It is expected that it is more difficult to extract acetic acid from water with methyl isobutyl ketone than to extract acetic acid from the ketone with water. No contradiction exists here; the differences are due almost entirely to the differences in the directions of extraction. More specifically, they are due to the differences in adhesional force as discussed previously. When adhesional force was discussed, the above observation was actually predicted.

The amount of solute extracted during stage 2 is obtained from Figure 11. The intercept in this case represents the amount of solute extracted during stage 1 plus stage 3. The curves for the different solvents represent values of total solute extracted in the three stages versus column height. In determining the amount of solute transferred during stage 2 then these curves are referred to at a given column height. The reading of the ordinate is the total amount extracted. The intercept of the respective curve is substracted from the ordinate reading obtained which thus gives the amount of solute transferred during stage 2 alone. Again, this amount is given as a percent of the total solute present in the drop originally. The actual number of moles of solute transferred may be calculated using

the value for the acetic acid present initially.

The effect of drop size on the amount of solute extracted is indicated in Figures 13 and 14. Two solvents were employed, isopropyl ether and methyl isobutyl ketone. The curves obtained for both drop sizes studied are plotted on the same graph to illustrate the effect of drop size. In both these figures the extrapolation to zero column height yields the same intercept for a given solvent despite the variation in drop size. In these Figures the curves for the smaller drop size lie above those for the larger drop size. This indicates that for a given column height a greater percentage of the total solute content is extracted when using the smaller drop size. This is not unexpected and is due to the increase in transfer area. The tables of data (see appendix) indicate that when different drop sizes were studied the volume of feed solution used was approximately the same in each case. Of course, more drops had to be used when the smaller drop sizes were studied. This also is indicated in the tables of data. For a given volume of feed solution, therefore, more transfer area is made available by using a smaller drop size. This, then, accounts for the fact that the curves for the smaller drop size lie above those for the larger drop size.

A further analysis of Figures 11 through 15 leads to some rather interesting observations. In the first place,

the curves in Figures 13 through 15, for a given system and drop size, plotted from the results obtained with columns #1 and #2 are parallel. This implies that the percent of the total acetic acid lost during stage 3 is independent of column height. This is again probably due to the adsorption which occurs at the interface as discussed on page 149. In the second place, the curvature of the curves in these Figures is instructive. The curves for the isopropyl ether system are linear which indicates that the amount of solute transferred per unit increase in column height is constant up to a column height of 30 inches. This occurs despite the fact that the concentration driving force decreases as the column height increases. This, however, is not the case with the other systems studied. The amount of solute transferred per unit increase in column height gradually decreases after a certain column height is reached. This is thought to be due to the decrease in driving force caused by loss of solute from the drops.

Figures 11 through 15 may be used to compare the three solvents as far as their ability to extract acetic acid from water is concerned. Theoretically, such a comparison should be made only when all the systems are studied using the same drop size. A strict comparison here is therefore not possible since it was not convenient to

bring about such a condition. An approximate comparison can be made, however, inasmuch as the drop sizes employed in the methyl isobutyl ketone and ethyl acetate systems are almost identical. Furthermore, the smaller drop size used in the isopropyl ether system is not very much different than the larger drop sizes used in the other two solvent systems. An approximate comparison of these three solvents is therefore possible. Referring to Figures 11 through 15, it is seen that the solvents arranged in a decreasing order of effectiveness are as follows: ethyl acetate, methyl isobutyl ketone, isopropyl ether. This order is also maintained when the amounts of solute extracted during drop formation are compared, although it does not seem to hold for stage 3. Furthermore the slopes of the curves in these figures indicate that column height has a greater effect on the amount of solute extracted when methyl isobutyl ketone and ethyl acetate are used than when isopropyl ether is used.

A comparison of the amounts of solute lost during stage 3 cannot be made due to the fact that the curve in Figure 12 for ethyl acetate is questionable. The reason for this has already been discussed and was seen to be due to the inability to titrate for acetic acid in the presence of ethyl acetate. This inability was due to the hydrolysis of the ethyl acetate. The titration values actually observed in obtaining the data for this series of runs were corrected

to take care of the hydrolysis. This has been discussed in the appendix. Despite the use of the corrected values, in the case of the ethyl acetate, it is felt that the results are not more than 2% off. These results then, can be and are, used only to serve as approximations. In the comparison made above, the results of Figure 11 using ethyl acetate were used since these were not affected by the presence of ethyl acetate.

The above comparison of the three solvents is quite interesting and is also in accord with a statement made by Johnson and Bliss (18), that a spray tower gives better results with a system of low interfacial tension than with a high interfacial tension system. Approximate methods for estimating interfacial tension indicate that the values for the ethyl acetate and methyl isobutyl ketone systems are higher than that for the isopropyl ether system. This order is the same as that given above when the three solvents were compared and seems to corroborate the work of the above authors.

Figures 16 through 19 indicate the effect of drop formation time on the amount of solute extracted. The data in these figures were all obtained at a given column height. The results of this data imply that the amount of extraction obtained at a definite column height is independent of drop formation time in the ranges studied. In other words,

increasing the drop formation time does not result in proportionate increases in the amount of solute extracted at any one column height. This result is quite unexpected and suggests keeping the drop formation time at a minimum. This method of operation would obviously increase the capacity or throughput of the spray tower without a proportionate decrease in the total amount of solute extracted.

The above results seem to indicate that the solute is lost as the drop detaches itself from the tip. If this is true, then the amount of solute lost during drop formation would be independent of the drop formation time. This explanation seems to be in line with the observation that the diffusion currents leaving the drop were more intense just after the drop detached itself from the tip. This observation was discussed in the section devoted to photography. The photographs presented show the stem of liquid just at detachment. This elongated section of liquid was also shown to spring back to the face of the tip. The solute may quite possibly be lost as a result of the collision of this stem of liquid with the face of the tip. The impact of this collision may well cause ejection of the solute. As previously mentioned the photographs of drop formation failed to indicate the diffusion currents around the drop during this period. Final verification of the exact time at which the drop loses its solute must await more delicate photographic techniques.

Figure 20 represents a plot of drop fall time versus column height. The data for all the systems and drop sizes studied lead to straight lines on this chart. This, of course, infers that the drops fall with a constant velocity. Since the lowest column height studied was 3 inches, it must be concluded that the falling drops attain their terminal or maximum falling velocity within the first three inches after detachment from the tip.

It is interesting to note in Figure 20 that the smaller drops of the dispersed phase (1.063 N acetic acid solution) fall through a given solvent with a higher velocity than the larger drops. This is true in the case of isopropyl ether and methyl isobutyl ketone. Since all other conditions were the same this represents an unexpected occurrence. It was expected that smaller drops of the feed solution would fall through a given solvent with a slower velocity as is the case with solid spheres. The explanation of this phenomenon is discussed in the section concerned with a study of drop behavior.

The results plotted in Figures 11 through 15 with the aid of Figure 20 are replotted in Figures 21 through 23. These Figures represent the relation between the amount of solute extracted and the time of drop fall. It was felt that a proper comparison of the different solvents used should not

be made at constant values of column height but rather at constant values of the time of drop fall. This latter quantity represents the time of contact, hence a comparison made in terms of this variable gives some insight into the rates of extraction. Figures 21 through 23 have been extrapolated to zero time of drop fall. The intercepts obtained are the same as those previously obtained in Figures 11 through 15. These intercepts also represent the same quantities as the intercepts of Figures 11 through 15 inasmuch as a zero time of drop fall corresponds also to a zero column height.

The slope of the curves in Figures 21 through 23 indicates the amount of solute extracted per second of contact time. A comparison of the solvents based on these Figures leads to the same results as previously noted, i.e. the solvents arranged in a decreasing order of their effectiveness are as follows: ethyl acetate, methyl isobutyl ketone, isopropyl ether.

The Calculation of Overall Transfer Coefficients*

The data obtained during the experimental runs made it possible to calculate values of overall transfer coefficients. The coefficients calculated below are for the falling period only, i.e., stage 2, since this is the only stage of extraction for which the transfer area is known. Even in stage 2

* See Addendum, Page 205, for the calculation of overall transfer coefficients for stage 1.

several approximations are made which allow the transfer area to be calculated. These are that the drops are spherical and that their surface area is not reduced due to the loss of solute.

The values of the overall transfer coefficients for stage 2 were calculated using equation 21. These calculations were made using the curves of Figures 11 through 15 and were applied to single drops. In making these calculations it was necessary to select a representative drop volume. The tables of data (see Appendix) indicate that the drop volumes for a given system varied slightly throughout each series of runs. It was necessary, therefore, to select an average or representative drop volume for each system. The curves then in Figures 11 through 15 were assumed to apply to this representative drop volume chosen for each system. The drop area was then calculated for each drop volume selected and values of the overall transfer coefficient for stage 2 were then calculated based on a single drop. These calculations were based on the water phase and were made for different column heights. The values obtained are listed below; the tabulated calculations are given in the Appendix.

In the calculations presented below the following procedure was employed in obtaining values for the overall

transfer coefficients for stage 2: the initial amount of acetic acid per drop was obtained by multiplying the representative drop volume by the normality of the feed; the acetic acid lost per drop during drop formation was obtained by multiplying the initial acetic acid per drop by the proper intercept of Figure 12; the amount of acetic acid lost per drop during drop breaking was obtained in a similar manner; the total amount of acetic acid lost per drop for a given column height was obtained by multiplying the initial amount of acetic acid per drop by the ordinate on the proper curve in Figure 11 corresponding to that column height; the amount of acetic acid lost per drop during stage 2 was obtained by substracting that lost in stage 1 plus stage 3 from the total amount of acetic acid lost per drop; the amount of acetic acid per drop at detachment was obtained by subtracting the amount of acetic acid lost per drop during stage 1 from the initial amount of acetic acid per drop; the amount of acetic acid per drop at the end of stage 2 was obtained by subtracting the amount of acetic acid lost per drop during fall from the amount of acetic acid per drop at detachment; the drop concentration at detachment was obtained by applying a conversion factor to the values for the amount of acetic acid per drop at detachment in milliequivalents; the drop concentration at the end of stage 2

was obtained in a similar manner; the drop fall time was obtained from Figure 20; the pound moles per hour per drop transferred during stage 2 was obtained by applying a conversion factor to the values for the milliequivalents of acetic acid lost per drop during stage 2; the concentration driving force was obtained by assuming the concentration in the continuous phase to be zero, as it very nearly was; the driving forces then at the top and at the end of stage 2 were taken as being equal to the drop concentrations at those points; the overall driving force used in the calculation of overall coefficients was taken as the arithmetic mean of the driving forces at the top and bottom of stage 2; when the ratio of these driving forces was greater than two, the logarithmic mean was used; values of K_W were then calculated by dividing the value of the pound moles of solute transferred per hour by the product of the drop area in sq. ft. and the overall driving force in pound moles per cu. ft.

Sample Calculations

Table 22 (appendix); 20" column height

Representative drop volume = 0.048 milliliters

Drop area = 0.686×10^{-3} ft^2

Concentration of feed solution = 1.060 N

Initial Acetic acid per drop = $1.060 \times .048 = .0509$ milliequivalents

Acetic acid lost per drop during stage 1 = $.0509 \times .05 = .00254$ milliequivalents

Acetic Acid lost per drop during stage 3
= .0509 x .06 = .00305 milliequivalents

Total acetic acid lost per drop
= .0509 x .295 = .0150 milliequivalents

(29.5% was obtained from Figure 11 for Isopropyl Ether at a 20 inch column height)

Acetic Acid per drop lost during stage 2
= .0150 - .00305 - .00254 = 0.0094 milliequivalents

Acetic Acid per drop at detachment
= .0509 - .0025 = 0.0484 milliequivalents

Acetic Acid per drop at end of stage 2
= .0484 - .0094 = .0390 milliequivalents

Drop concentration at top of stage 2

$$= .0484 \times \frac{62.4}{.048 \times 1000} = 0.0629 \quad \frac{\text{lb. moles}}{\text{ft}^3}$$

Drop concentration at end of stage 2

$$= 0.0390 \times \frac{62.4}{0.048 \times 1000} = 0.0507 \quad \frac{\text{lb. moles}}{\text{ft}^3}$$

Fall time = 3.4 seconds (Figure 20)

W/θ lb. moles per hour of solute transferred

$$= 0.00793 \times \frac{0.0094}{3.4} = 2.19 \times 10^{-5} \text{ lb. moles per hour}$$

$$\Delta C = \frac{(0.0629 - 0) + (0.0507 - 0)}{2}$$

$$= 0.0568 \quad \frac{\text{lb. moles}}{\text{ft}^3}$$

$$K_W \text{ for stage 2} = \frac{W/\theta}{A \times \Delta C} = \frac{2.19 \times 10^{-5}}{0.686 \times 10^{-3} \times 0.0568}$$

$$= 0.563 \text{ lb. moles/hr. ft}^2 \text{ lb. moles/ft}^3$$

The values of the overall transfer coefficients for stage 2 calculated at various column heights are listed below in Table 7. (See Appendix for calculations).

These values are plotted as a function of column height in Figure 24. In the isopropyl ether system the coefficients increase slightly with column height. This is true for both drop sizes. Table 22 for this system indicates that the pound moles transferred per hour remains approximately constant for the different column heights. Since the transfer area also remains substantially constant, the effect must be due to the concentration driving force. The fact that the overall transfer coefficient increases is due to the fact that the overall concentration driving force decreases with column height (see Figures 25 and 26).

The values of the overall transfer coefficient are seen to be only slightly affected by varying drop size.

The values obtained in the methyl isobutyl ketone system seem to be in agreement with those reported by Sherwood, Evans and Longcor (23). (See section on Analysis of Previous Research Articles). The difference between the value presently obtained and that reported by the above authors is due to the differences in the direction of extraction and also due to the fact that these authors report the value for the ketone system as K_k instead of K_w.

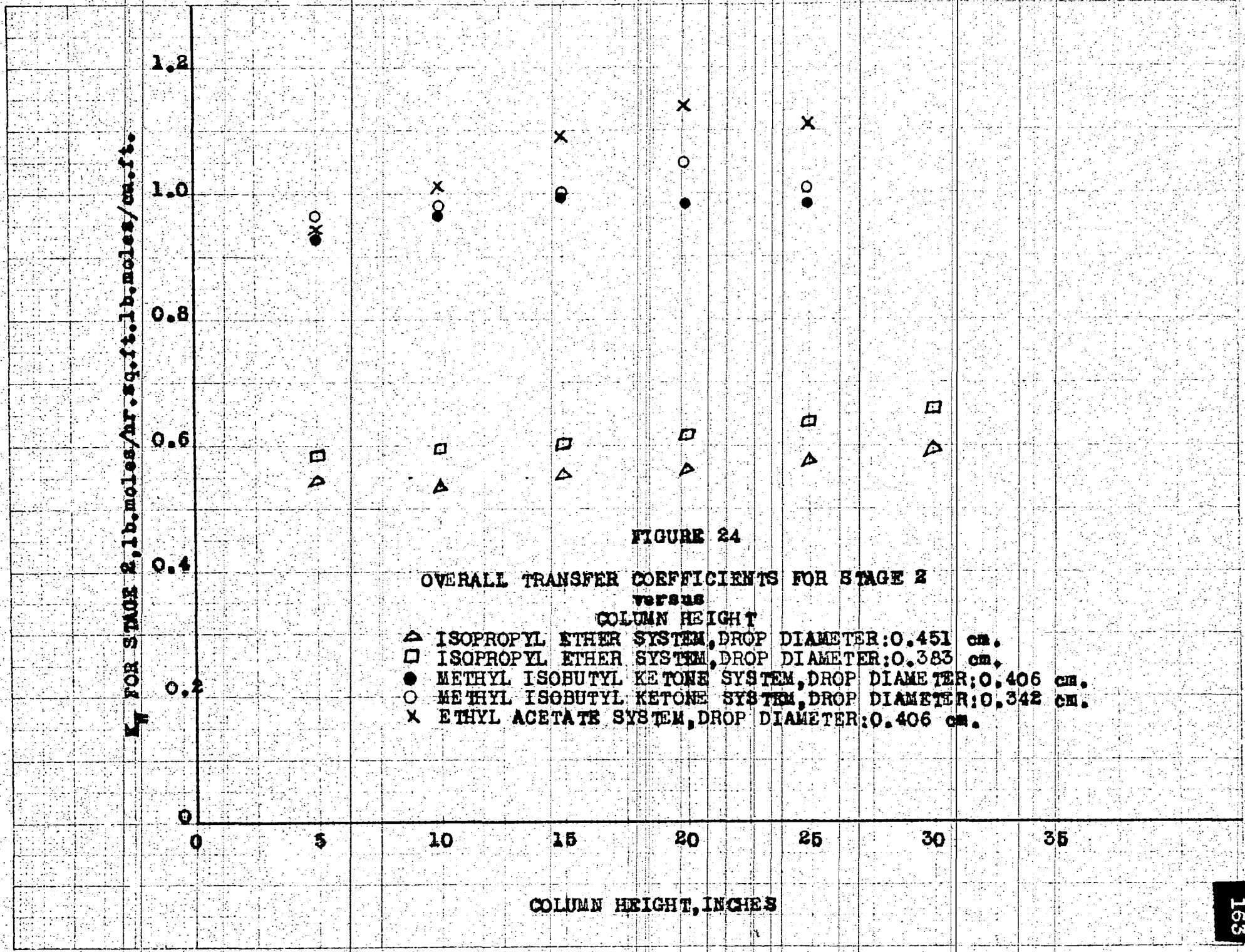


FIGURE 24

OVERALL TRANSFER COEFFICIENTS FOR STAGE 2
versus
COLUMN HEIGHT

△ ISOPROPYL ETHER SYSTEM, DROP DIAMETER: 0.451 cm.
□ ISOPROPYL ETHER SYSTEM, DROP DIAMETER: 0.383 cm.
● METHYL ISOBUTYL KETONE SYSTEM, DROP DIAMETER: 0.406 cm.
○ METHYL ISOBUTYL KETONE SYSTEM, DROP DIAMETER: 0.342 cm.
× ETHYL ACETATE SYSTEM, DROP DIAMETER: 0.406 cm.

These values, of course, are interrelated by the distribution coefficient.

The K_W values for the ethyl acetate system are questionable due to the fact that the results of Figure 12 were used in their calculation.

Figures 25 and 26 show the acetic acid concentration of the drops during stage 2. These plots were made from the calculations concerned with the overall transfer coefficients of stage 2. The drop concentration is seen to decrease with increasing column height. The horizontal line on each graph represents the drop concentration at the start of stage 2, i.e., just after it has been detached from the tip.

Note: See Addendum, Page 205, for the calculation of overall transfer coefficients for stage 1.

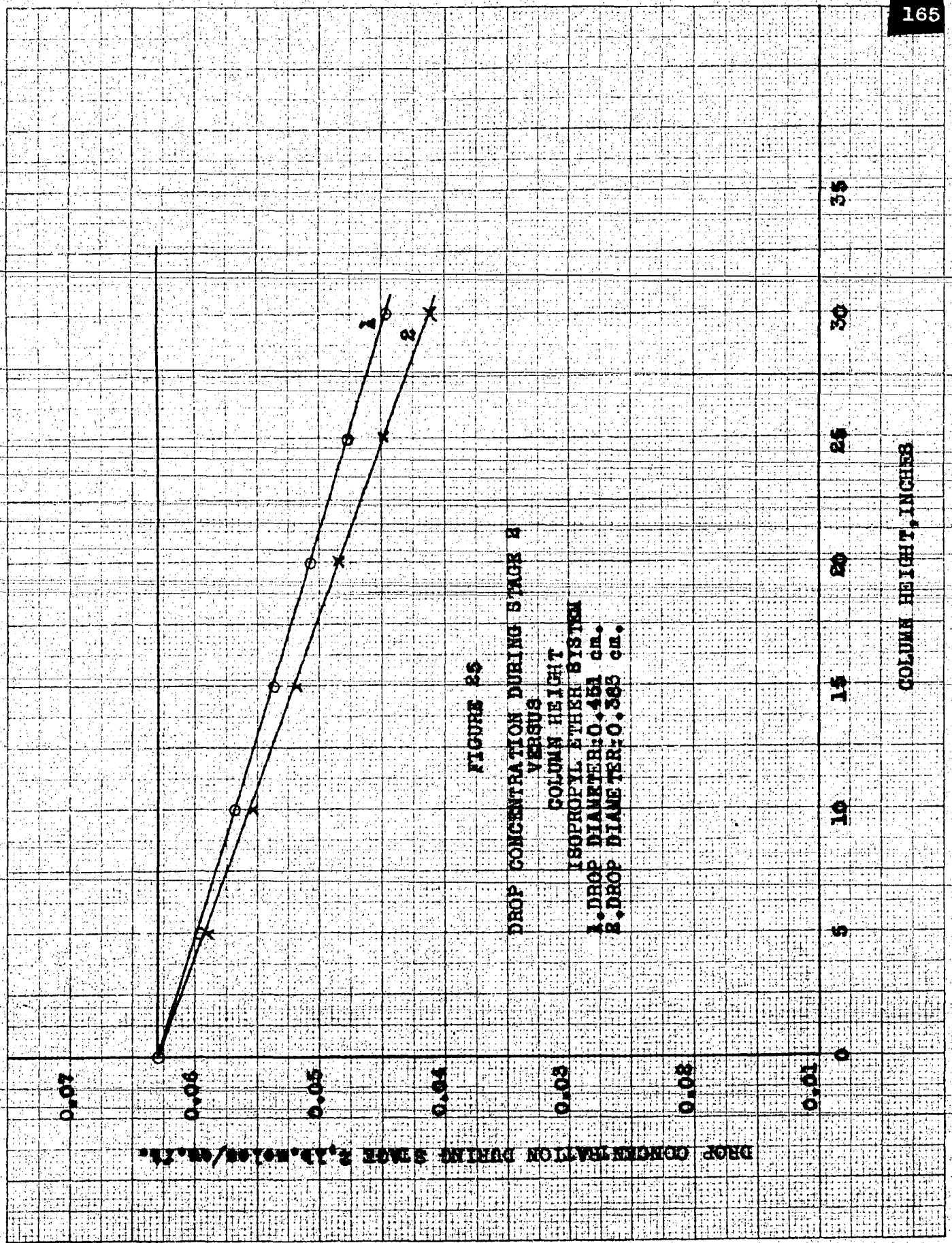


FIGURE 25

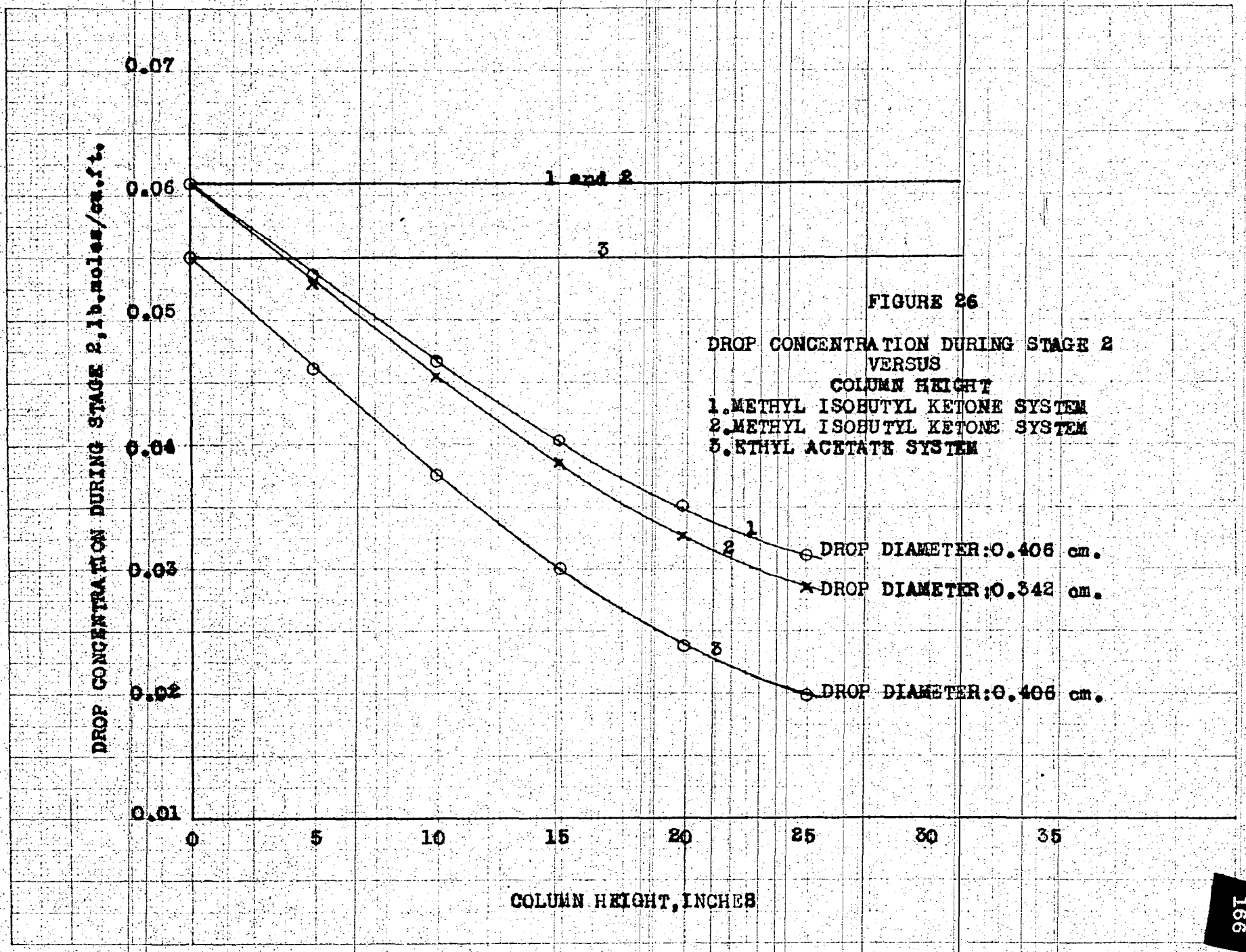


TABLE 7- Calculated Values of Overall Transfer Coefficients For Stage 2 At Various Column Heights

	Column Height, Inches					
	5	10	15	20	25	30
	Isopropyl Ether System; Representative Drop Volume = 0.048 ml.					
K_W	0.545	0.537	0.555	0.563	0.578	0.594
	Isopropyl Ether System; Representative Drop Volume = 0.0295 ml.					
K_W	0.583	0.593	0.602	0.617	0.638	0.659
	Methyl Isobutyl Ketone System; Representative Drop Volume = 0.035 ml.					
K_W	0.928	0.965	0.995	0.983	0.983	----
	Methyl Isobutyl Ketone System; Representative Drop Volume = 0.0210 ml.					
K_W	0.965	0.980	1.01	1.05	1.01	----
	Ethyl Acetate System; Representative Drop Volume = 0.0352 ml.					
K_W	0.941	1.01	1.09	1.14	1.11	----

ANALYSIS OF PREVIOUS RESEARCH ARTICLES

The experimental work with spray towers reported by other authors has been concerned primarily with the calculation of overall transfer coefficients expressed either as K_w or $K_w a$. These coefficients were calculated using equations similar to equations 21 and 22. This, of course, is the standard, present day practice in reporting the performance of extraction columns. The coefficients calculated by these authors have actually been overall-column, overall extraction coefficients inasmuch as the existence of three separate stages of extraction was not taken into account. The calculations of these coefficients were based on the inlet and exit column streams. Furthermore, the calculation of values for K_w required the use of an area term which was undoubtedly wrong. The area employed was that of the drops falling or rising through the tower. Such an area is incorrect on two counts. First of all because the transfer area during drop formation is variable and secondly, the area during stage 3 is unknown. The calculation of values of $K_w a$ is equally objectionable inasmuch as a specific area coefficient "a" is employed. These latter coefficients have the further disadvantage that the effect of operating variables on the K_w and on the "a" term is not indicated or distinguished.

It seems desirable, therefore, to review certain of the important research articles concerned with spray tower operation and attempt to analyze the results reported therein. Three such articles have been selected and will be discussed below.

1) Elgin and Browning (12).

A study of the extraction of acetic acid from water with isopropyl ether and of acetic acid from isopropyl ether with water.

These authors present a curve showing the effect of the dispersed phase flow rate on $K_w a$. The value of $K_w a$ is shown to increase with increase in the dispersed phase flow rate. Of course, a great deal of this increase in $K_w a$ is brought about by the increase in the specific area coefficient "a" which is produced. The effect then of the dispersed phase flow rate on K_w is obscured. The curves presented in this article also show that $K_w a$ is higher, for a given direction of extraction, when the phase receiving the solute is dispersed.

The effect of the inlet acetic acid concentration on $K_w a$ was also studied with the isopropyl ether dispersed. When the acetic acid was being extracted from the ether the values of $K_w a$ were found to be almost unaffected by variations in inlet acid concentration. However, when the

acetic acid was being extracted from the water the values of $K_w a$ increased with increase in inlet solute concentration. The different effects in this case are probably caused by the variations in the specific area coefficient "a". When the acetic acid concentration in the water is increased, the dispersed drops are smaller and hence for a given dispersed phase rate the value of "a" is increased. When the acetic acid is in the isopropyl ether, however, this condition does not exist and "a" is not changed by changes in the inlet solute concentration (see section entitled "A Study of Drop Behavior").

2) Sherwood, Evans and Longcor (23).

A study of the extraction of acetic acid from benzene and methyl isobutyl ketone with water. The benzene and ketone phases were dispersed and rose through the water phase.

Values of K_K (transfer coefficient based on ketone phase) and K_B (transfer coefficient based on benzene phase) were calculated as a function of drop diameter and inlet solute concentration. It was found that the values of K increased with increasing drop size and also that for a given drop size K_K was greater than K_B. Furthermore it was found that variations in acid content of the inlet ketone had no effect on K_K, but that K_B for a given drop size increased

with increase in inlet solute concentration.

The value of K_k for a drop size having a diameter of 0.405 cm. was found to be 2.2 lb. moles/hr. (sq. ft.) (lb. moles/cu. ft.).

This study also was concerned with the amount of extraction occurring during drop formation. Their results indicated that 40% of the solute present in the drop originally was lost during drop formation. This was found to be the case for both systems studied. Drop formation time was about 0.4 seconds. The solute concentration in the benzene was 0.00374 lb. moles/cu. ft. and that in the ketone was 0.0603 lb. moles/cu. ft. Drop diameters were 0.39 cm and 0.29 cm. in the benzene and ketone systems respectively.

3) Johnson and Bliss (18).

A study of the extraction of acetic acid from water with methyl isobutyl ketone and from methyl isobutyl ketone with water.

Their results show that K_ka (the overall transfer coefficient based on the ketone phase) increases with increasing dispersed phase rates. This again is probably largely due to the increased value of "a". The effect of the dispersed phase flow rate on K_k is obscured.

This article also confirms the work of Elgin and Browning (12) regarding the effect of inlet solute concentration.

Values of $K_k a$ increase with increasing inlet solute concentration in the water phase. This effect has already been explained and is probably due to the increase in "a".

The experimental results have led the authors to propose certain rules regarding the proper phase to disperse for most efficient operation. Whenever one flow rate is considerably in excess of the other, the phase with the higher flow rate should be dispersed because such dispersal results in a greater interfacial area. When the flow rates are very nearly equal, disperse the phase receiving the solute. This is based on the fact that when extraction is from the continuous phase to the dispersed phase coalescence was small, thus keeping the interfacial area at a maximum.

SPECIAL RELATED TOPICS

The Calculation of Liquid Diffusivities

It is often necessary to interpret diffusion processes in terms of diffusion coefficients. The experimental determination of these values is tedious and hence several empirical methods of calculation have been proposed. These methods are employed below to calculate the diffusion coefficients pertinent to the present research.

The diffusion coefficient of liquid solutes in liquid solvents may be estimated by the following equation proposed by Arnold (2):

$$D = \frac{B\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{A_1 A_2 Z_2^{1/2} S^2}$$

where

D = the diffusion coefficient of solute 1 in solvent 2 in $cm^2/sec.$

B = a constant equal to 0.0100 at 20°C and 0.00918 at 15°C.

M_1 = molecular weight of solute

M_2 = molecular weight of solvent

Z_2 = viscosity of solvent in centipoises

S = the sum of the cube roots of the molecular volumes thus, $S = (V_{m1})^{1/3} + (V_{m2})^{1/3}$

The units of molecular volume are cc/gram mole

A_1, A_2 = abnormality factors for the solute and solvent respectively, no units.

Acetic Acid in Water

$A_1 = 1.27$ $\quad A_2 = 4.7$ (see (2).
$Z_2 = 1.0$ centipoise
$M_1 = 60$ $\quad M_2 = 18$

$$D = 1.06 \times 10^{-5} \text{ cm}^2/\text{sec. at } 20°C$$

This is in fair agreement with the experimental value of 0.95×10^{-5} $\text{cm}^2/\text{sec.}$ (22).

Acetic Acid in Isopropyl Ether

Assume $A_1 = 1.27$ and $A_2 = 1.00$
$Z_2 = 0.379$ centipoises
$M_1 = 60$ $\quad M_2 = 102$

$$D = 2.5 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

Acetic Acid in Methyl Isobutyl Ketone

Assume $A_1 = 1.27$ and $A_2 = 1.00$
$Z_2 = 0.546$ centipoises
$M_1 = 60$ $\quad M_2 = 100$

$$D = 2.20 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

Acetic Acid in Ethyl Acetate

Assume $A_1 = 1.27$ and $A_2 = 1.00$
$Z_2 = 0.455$ centipoises
$M_1 = 60$ $\quad M_2 = 88$

$$D = 2.71 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

The diffusivities of acetic acid in the above solvents have not been determined experimentally hence their values must be calculated as above. Another empirical method

for estimating liquid diffusivities has been proposed by Wilke (26) but the results of this method are about 30% higher than the results calculated above.

The diffusion coefficients of acetic acid in the three solvents studied are seen to be approximately equal but all are higher than that for acetic acid in water.

The Newman Equation

Several authors especially Sherwood, Evans and Longcor (23) have employed the Newman Equation in an attempt to explain certain results of spray tower work concerned with liquid-liquid extraction.

Newman (19) has developed theoretical equations to express mathematically the drying of solids having different shapes. These equations apply to that portion of the drying time in which the surfaces are substantially dry and evaporation takes place as rapidly as liquid can diffuse from the interior to the surfaces. Fick's Law is applied to the transfer of water vapor and surface resistance is assumed negligible. For spheres the expression is as follows:

$$E = \frac{6}{\pi^2}\left[e^{\frac{-\pi^2 D\,\theta}{a^2}} + 1/4\; e^{\frac{-4\pi^2 D\,\theta}{a^2}} + \ldots\ldots 1/n^2\; e^{\frac{-n^2\pi^2 D\,\theta}{a^2}}\right]$$

where E is the fraction of solute remaining in the sphere after time θ

D is the diffusion coefficient

θ is the time

a is the radius of the sphere

n is the term number in the series

Applying this to extraction, E becomes the fraction of extractable solute left unextracted. It is not entirely correct to apply this equation to the extraction which occurs during drop formation since the radius of the drop is increasing. This calculation, however, is interesting since experimental values have been determined as previously discussed.

Sample Calculation:

For purposes of illustration the runs made using column #1, tip #1 and isopropyl ether will be employed. In this case the drop radius in its final form is 0.220 cm.; drop formation time is 1.3 seconds; the diffusion coefficient for acetic acid in water is 0.95×10^{-5} $cm^2/sec.$ (22).

Using ten terms of the above expression E is found to be 0.94. The agreement between this value and the value of 0.95 as experimentally determined is astonishing.

The equation, however, is of little use inasmuch as no account at all is taken of the solvent. In other words the above calculation would have yielded a value of E equal to 0.94 regardless of the solvent employed. That this would not be the case has already been found experimentally. The agreement obtained above must, therefore, be considered coincidental.

The Ilkovic Equation

In polarography, the Ilkovic Equation expresses the current flowing into a drop of mercury forming on the end of a capillary tip as a function of several variables. This equation has the form

$$i = \text{constant } (nF)\ C\ (V')^{2/3}\ D^{1/2}\ t^{1/6}$$

where i = current, amperes

n = valence of ion under consideration

F = Faraday's constant - 96,500 coulombs

C = concentration outside drop

V' = volume rate of increase of drop

D = diffusivity of ion under consideration in liquid media used

t = time, seconds

The value of the constant used in the above equation depends on the units of concentration, volume rate of increase of drop and diffusivity.

This equation for the dropping mercury cathode shows that the current increases with the sixth root of the time during the life of the drop. It is thus possible to calculate the instantaneous current at any time t, which is flowing into the forming drop.

This mechanism is similar to that of solute transfer during drop formation in spray tower operation. It should

be possible to formulate a similar equation for this process thus,

$$M = \text{constant } C\ (V')^{2/3}\ D^{1/2}\ t^{1/6}$$

where M = instantaneous rate, moles of solute transferred per unit time

C = concentration of solute outside drop

V' = volume rate of increase of drop

D = diffusivity of solute in liquid media outside drop

t = time of drop formation

This equation should make it possible to calculate the moles of solute being transferred at any time t. By integration of this equation over the drop formation time the total amount of solute transferred during drop formation is obtained;

$$W = \text{constant } C\ (V')^{2/3}\ D^{1/2}\ t^{7/6}$$

where W = total moles of solute transferred during drop formation.

The above equation, however, would be expected to apply, if at all, only to diffusion occurring from the continuous phase into the dispersed phase.

Furthermore, it seems necessary to modify this equation in some way to include the diffusivities of the solute in both phases. In any case this seems a logical starting point for further study.

A Study of Drop Behavior

Literature references concerned with the formation of liquid drops in a second liquid immiscible with the first are scarce. Further study in this regard seems desirable. The present research concerned as it was with drop formation may easily serve as the foundation for such a study.

Some insight into this subject, in the absence of detailed laboratory research, may be had from a study of the formation of liquid drops in air. Hauser, Edgerton, Holt and Cox (15) have made such a study and employed an ingenious photographic technique to record the mechanism of drop formation. Their description of drop formation is as follows:

> "The drop grows longer and larger on the end of the tip. Instability sets in and a neck forms between the part of the drop remaining on the tip and the part that eventually falls off. This neck grows longer and narrower until the drop finally separates. At this point the drop is slightly ellipsoidal with the long axis vertical. The neck of liquid connecting the two parts of the drop narrows down to a point at the point of separation. The main drop then separates and owing to the slight tension caused by attachment to the stem, it flattens out somewhat immediately after separation takes place. The main oscillation is marred slightly by secondary oscillations set up at the same time, so that the drop assumes somewhat irregular shapes though the main effect is a single oscillation about its form of equilibrium, a sphere. The neck of remaining liquid segments at first into a series of nearly equal-sized nodes. In all cases observed, the stem of water coalesces rapidly into one drop. Other substances give more secondary drops."

The above mechanism is very much the same as that observed when liquid drops are formed in liquids (the two liquids must, of course, be immiscible). The photographs presented earlier indicate this fact very clearly. The phenomenon of secondary drop formation was also observed as described in the section dealing with the calibration of the feed device. The appearance, disappearance and reappearance of secondary drops as described in that section are, however, unexplained.

The subject of drop formation is quite complex. The more important factors which seem to affect the size of a drop formed at a tip are: tip diameter, head of liquid, surface tensions of the two liquids, and the densities and viscosities of the two liquids. The effect of surface tension or interfacial tension on drop size was illustrated in the Preliminary Experiment #6 where it was shown that a high interfacial tension leads to large drops while a low interfacial tension leads to small drops.

Elgin and Browning (12) report that dispersion of isopropyl ether of relatively high acetic acid concentration in water gives large drops whereas dispersion of acid free ether into water of appreciable acid concentration produces small drops. This shows the effect of the surface tensions of the two phases on drop size. The presence of

acetic acid in isopropyl ether affects its surface tension very little hence approximately the same drop size will be obtained whether the acetic acid concentration of the dispersed isopropyl ether is low or high. As a matter of fact, pure isopropyl ether dispersed in water will give approximately the same drop size as isopropyl ether containing appreciable acetic acid merely because the acetic acid has little effect on the surface tension of this solvent. It seems, therefore, that the difference in surface tension between the two liquid phases has a pronounced effect on drop size. This point is further illustrated by considering the drop sizes produced when water of different acetic acid content is dispersed in isopropyl ether. Figure 27 shows the drop sizes obtained when water containing different amounts of acetic acid is dispersed in different solvents. Note that as the acidity increases the drop size decreases. Note, further, that as the acetic acid content increases the surface tension of the water phase decreases thus approaching that of the solvent. This figure further substantiates the above postulate that the difference between the surface tensions of the two liquid phases has a pronounced effect on drop size. A direct proportionality seems to exist between these two variables. (The data presented in Figure 27 were obtained using tip #1).

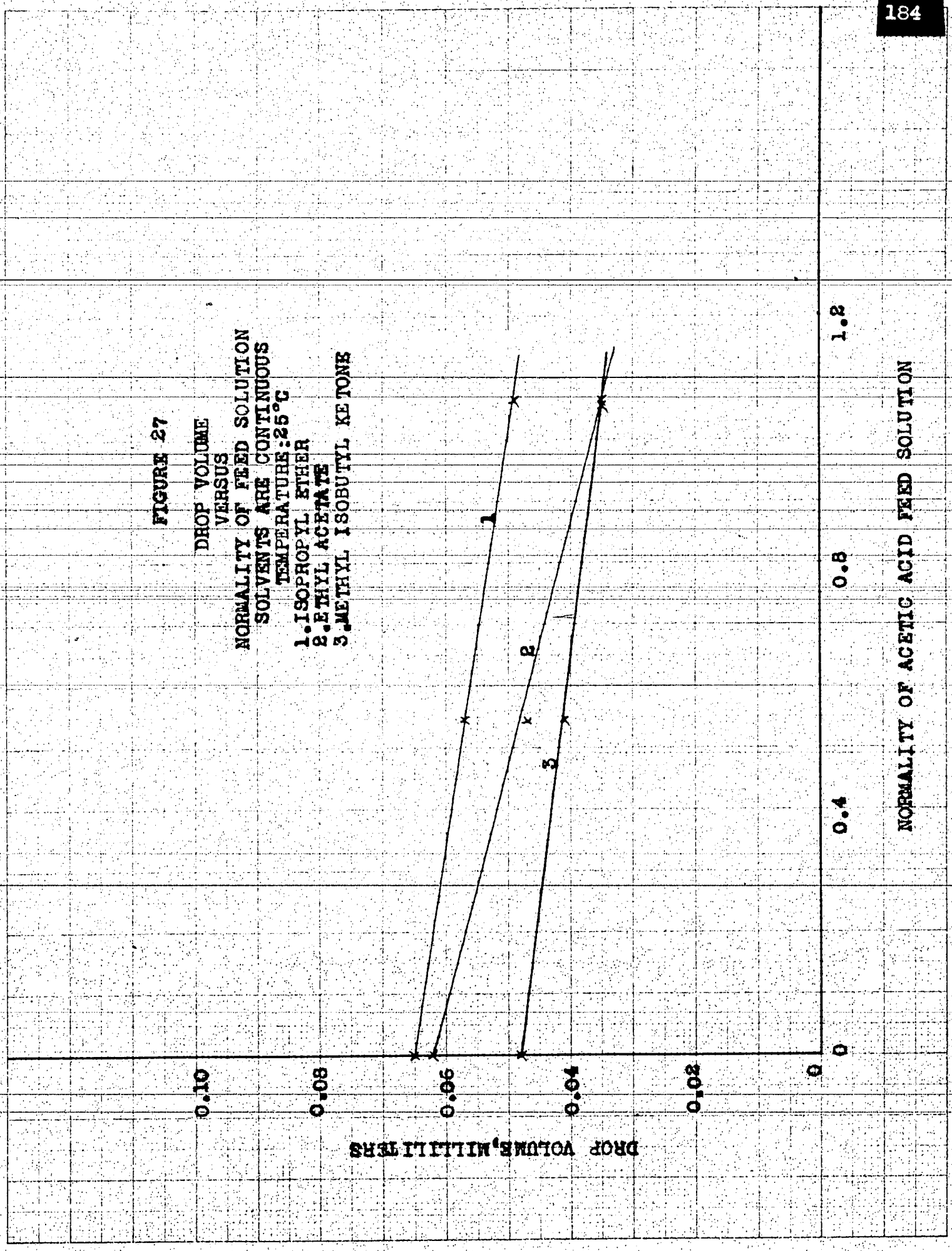


FIGURE 27

DROP VOLUME
VERSUS
NORMALITY OF FEED SOLUTION
SOLVENTS ARE CONTINUOUS
TEMPERATURE:25°C
1.ISOPROPYL ETHER
2.ETHYL ACETATE
3.METHYL ISOBUTYL KETONE

While working with ethyl acetate the effect of another variable on drop formation was indicated. In the discussion concerned with the materials to be used in the present research it was pointed out that a C.P. 99.5% grade of ethyl acetate had to be employed rather than the 85% grade. Operation with the latter was found to be impossible. When the feed solution (1.063 N acetic acid solution) was dispersed in the pure ethyl acetate the drops formed individually and periodically. The drop formation time was about 1.1 seconds and the drops could be counted very easily. This of course was at a certain liquid level in the burette. However, using the same liquid level in the burette and dispersing the same feed solution in the 85% grade of ethyl acetate an entirely different situation was obtained. The feed solution was emitted from the delivery end of the tip very rapidly and it was found impossible to either measure the drop formation time or count the drops. Furthermore, it was found impossible to reduce the liquid level in the burette enough to remedy this situation. This precluded the use of 85% ethyl acetate in the present experiment and hence the 99.5% grade was employed. As previously indicated the impurity in the 85% grade ethyl acetate is 15% of ethyl alcohol. The effect then of the physical properties of the continuous phase is clearly illustrated.

The unusual behavior here is probably due to the effect of viscosity. The ethyl alcohol impurity affects the surface tension and density of the ethyl acetate only slightly but alters its viscosity appreciably. Although this explanation is open to dispute the fact remains that impurities which affect the physical properties of the continuous phase also affect drop formation in this phase. The need for a comprehensive study of all the factors affecting drop formation in liquid-liquid systems still exists.

The factors affecting the falling of drops have also been studied but little. The development of an equation to express the rising or falling velocity of liquid drops in liquid media would be of considerable interest. Here again, however, the problem is a complex one with many factors influencing the phenomenon to be studied. The observations made in the preliminary experiments of this paper pointed out that the rise and fall of liquid drops do not take place smoothly. Drops in falling or rising are deflected periodically from their vertical paths which, of course, reduces their apparent velocities. Furthermore, these drops are vibrating constantly which also undoubtedly affects their velocity. Not only does this constant vibrating affect the longitudinal dimension of the drop but it also necessarily affects it latitudinally. In agreement

with the observations made by Hauser, Edgerton, Holt and Cox (15) for liquid drops falling through air, it was found here that liquid drops falling through liquids also seem to oscillate about their form of equilibrium, a sphere. The intensity of oscillation (both frequency and amplitude) was observed to be dependent upon several variables. For instance, the larger the drops the more intense the oscillation; also the physical properties of the continuous phase seem to affect this oscillation. Drops falling through ethyl acetate were seen to oscillate very little as compared to the drops falling through isopropyl ether.

Expressions for calculating the velocity of fall or rise of liquid drops in liquid media are few. Accurate expressions do not exist. Bond (4) and Bond and Newton (5) have made a rather limited study of this subject and have presented the following expression, which is merely a modification of Stoke's Law.

$$v = \frac{1}{k}\left[\frac{2}{9}\,\frac{(\rho' - \rho)\, g\, a^2}{\mu}\right]$$

where v is the terminal velocity of the drop, i.e., the velocity which it ultimately attains. This is the highest velocity the drop can obtain under a given set of conditions.

ρ' is the density of the liquid in the drop

ρ is the density of the continuous phase

a is the radius of the drop

g is the acceleration due to gravity

μ' is the viscosity of the liquid in the drop

μ is the viscosity of the continuous phase

$$k = \frac{2/3 + \mu'/\mu}{1 + \mu'/\mu}$$

(consistent units must be used throughout)

Applying this equation to the case of drops of 1.063 N acetic acid falling through isopropyl ether:

μ' = 1 centipoise = .000672 lbs./ft sec.

μ = .379 centipoise = .000255 lbs./ft. sec.

ρ' = 62.4 lbs./ft^3

ρ = .725 x 62.4 lbs./ft3

g = 32.2 ft/sec^2

$a = \frac{.0148}{2}$ ft.

k = 0.908

The calculated v is about 24 ft./sec. In contrast to this the observed velocity was 0.492 ft/sec. This work by Bond and Newton postulates that for any drop radius appreciably less than a certain critical value the drop behaves almost like a rigid sphere. This is probably true since as the drop diameter decreases the intensity of oscillation also decreases thus allowing the drops to fall smoothly.

It is felt that the equation proposed by the above authors is not applicable here inasmuch as viscous flow conditions were not realized in the present experiments. Furthermore, the equation proposed by Bond did not take into account mass transfer which also would prevent this equation from being directly applicable to the present work. It is probable that the drops studied in this research were much above the critical drop size mentioned above. Indeed, it was observed that the smaller drops studied fell faster than the larger drops. This behavior has been discussed previously.

It is interesting to apply to the present problem the theory developed for the settling of solid spheres in liquids. This theory is fully discussed by Walker, Lewis, McAdams and Gilliland (24). This application will be illustrated using the data of Table 1, Run #1.

volume per drop = 0.048 cm^3

diameter per drop = 0.45 cm = 0.0148 ft.

sp. gr. of ether = 0.725

viscosity of ether = 0.379 centipoises = .000255 lbs./ft/sec.

velocity (Figure 28) = 5.9 in/sec. = 0.492 ft./sec.

Reynolds Number of Falling Drop

$$\text{Re. No.} = \frac{D\,u\,\rho}{\mu} = \frac{.0148 \times 0.492 \times .725 \times 62.4}{.000255}$$

Re. No. = 1290 (This indicates turbulent motion)

In calculating the above Reynold's Number the observed velocity of fall was used. It is also possible to calculate the velocity of fall which would be possessed by spheres of a given size. (See Walker, Lewis, McAdams and Gilliland (24).

$$f\ (\text{Re. No.})^2 = \frac{4\ g\ D^3\ \rho\ (\rho_s - \rho)}{3\mu^2}$$

$$f\ (\text{Re. No.})^2 = 1.66 \times 10^6$$

from Figure 99 (24),

$$\text{Re. No.} = 2500$$

and the falling velocity is found to be 0.95 ft./sec.

The calculated falling velocity is thus greater than the observed velocity. This is probably due to the fact that attractive forces undoubtedly act on the liquid drops due to mass transfer and also to the fact that the drops are not spheres. It might also be due to the fact that the falling drops are being deflected during their descent which slows them down considerably.

If the equation for falling velocities in turbulent flow is employed (24)

$$u = K_e \sqrt{\frac{g\ D\ (\rho_s - \rho)}{\rho}}$$

where $K_e = 1.74$ for spheres, the velocity is found to be 1.03 ft/sec.

K_e for falling disks is given by (24)

$$K_e = 1.35\ \frac{t}{D}$$

where t = thickness
D = diameter

The value of K_e for disks is much lower than K_e for spheres hence this would lead to velocities much closer to the observed. Since the drops in falling have a disk-like shape, the use of the latter value of K_e seems more advisable.

Forces Acting on a Falling Drop

If the falling drops are assumed to be spherical, it is possible to develop a theory similar to that developed for solid particles falling in a fluid medium.

When a sphere of liquid falls through another liquid medium these are at least four forces acting on the drop;

1) the force of gravity

$$F_g = \frac{\pi D^3 \rho_s g}{6}$$

where D is the drop diameter

ρ_s is the density of the liquid in the drop

g is the acceleration due to gravity

2) the buoyant force

$$F_b = \frac{\pi D^3 \rho g}{6}$$

where ρ is the density of the continuous phase

3) the resistance drag which, assuming Newton's Law to apply, is

$$R_1 = \frac{k A \rho V^2}{2}$$

where k is a constant - "drag coefficient"

A is the frontal area of the drop

ρ is the density of the continuous phase

V is the velocity of fall

4) the retarding influence (due to solute transfer) caused by the attraction of the continuous phase for the material of the drop. This has not been evaluated but may be represented by R_2.

The net resultant force acting downward is $F_g - F_b$.

In falling, the drops assume a velocity that causes the forces acting on them to balance. This velocity is called the "free-settling velocity" or the "terminal velocity". Thus,

$$R_1 + R_2 = F_g - F_b$$

$$\frac{k A \rho V^2}{2} + R_2 = \frac{\pi D^3 g (\rho_s - \rho)}{6}$$

whence

$$V^2 = \frac{2}{k A \rho} \left[\frac{\pi D^3 g (\rho_s - \rho)}{6} - R_2 \right]$$

This equation indicates that in falling, the drops assume a velocity which is less than that calculated by Newton's Law for freely falling spheres.

It is possible to solve the previous equation for the term R_2;

$$R_2 = \frac{\pi D^3 g (\rho_s - \rho)}{6} - \frac{k A \rho V^2}{2}$$

Letting k = 0.43 as originally proposed by Newton, this equation can be used to calculate the attraction of the continuous phase for the dispersed.

Using the data on Table 1, Run #1,

$$R_2 = \frac{\pi(.0148)^3 \, 32.2 \, (.275) \, 62.4}{6} - \frac{0.43 \times \pi(.0148)^2 \, (.492)^2 \, .725 \times 62.4}{8}$$

$$= 937 \times 10^{-6} - 4.01 \times 10^{-4}$$

$$= .000937 - .000401 = .000536 \ \frac{\text{ft. pounds}}{\text{sec}^2}$$

R_2 = 7.41 dynes

Similar calculations can be made for the other systems studied and using the different drop sizes employed. These calculations lead to the following values of R_2:

System	Drop Diameter (cm)	R_2 (dynes)
Isopropyl Ether	0.451	7.41
	0.383	3.53
Methyl Isobutyl Ketone	0.406	3.94
	0.342	1.7
Ethyl Acetate	0.406	1.62

These values are quite reasonable and their dimensions are the same as surface tension (or interfacial tension) times distance in centimeters. Further study along these lines seems desirable.

The complexity of the forces acting on falling drops of liquid is further illustrated by reference to Figure 20. Note the velocity of fall for different size drops in isopropyl ether. The smaller size drops actually fall faster than the larger drops. This is somewhat unexpected inasmuch as large spheres of solids fall faster than smaller spheres. The reason for this unusual occurrence in the case of liquid drops is probably attributable to the oscillations taking place in the falling drops. As mentioned previously these oscillations decrease with decreasing drop diameter and hence the retarding effect which these oscillations undoubtedly exert also decreases. It is expected that a drop diameter exists below which normal behavior exists, i.e., decreasing the drop diameter results in decreased falling rates. This is in accord with the observations made by Bond and Newton (5) as already mentioned.

Figure 28, prepared from the data obtained in the present research indicates the velocity of fall of liquid drops at different column heights. Note that the drops attain their terminal velocity within three inches after their detachment from the tip. This fact is also indicated by the straight lines in Figure 20.

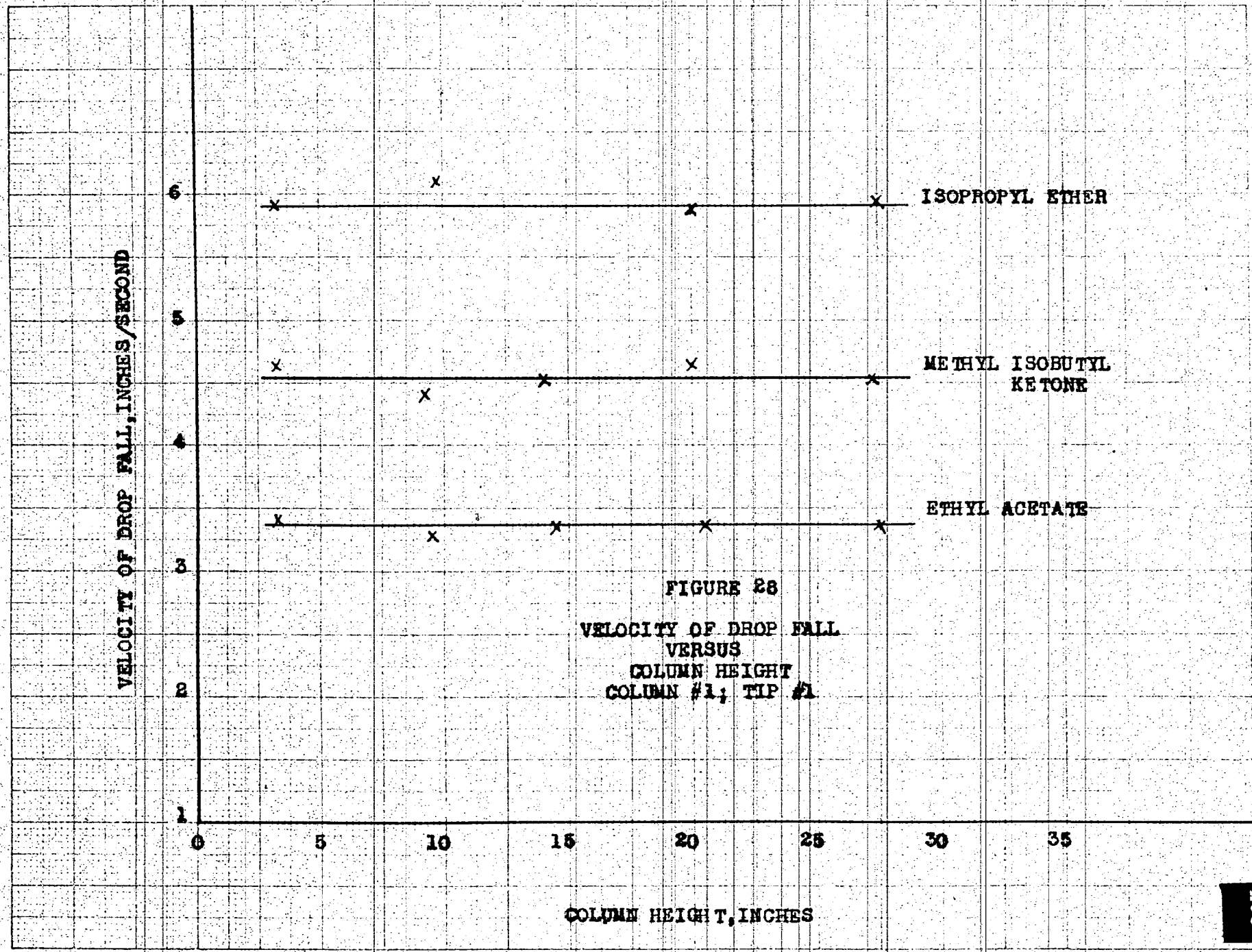


FIGURE 28

VELOCITY OF DROP FALL
VERSUS
COLUMN HEIGHT
COLUMN #1; TIP #1

SUMMARY AND CONCLUSIONS

The mechanism of solute transfer in spray towers was studied. A theory was proposed which postulated the existence of three separate stages of extraction. Stage 1 is during drop formation; stage 2 begins at the moment the drop is detached from the delivery tip and ends when the drop strikes the bottom interface; stage 3 involves the process in which the drops break across the bottom interface. The operating variables which seemed to effect each of the stages of extraction were discussed.

Experimental work was undertaken to prove the existence of the three separate stages of extraction. A feed device was designed by which the feed solution could be delivered dropwise into the continuous phase. This feed device also made it possible to measure quite accurately the volume of the drops delivered into the continuous phase.

The extraction of acetic acid from water with isopropyl ether, methyl isobutyl ketone and ethyl acetate was studied. The acetic acid-water solution was 1.063 N and was the dispersed phase. This dispersed phase fell through the solvents during the experimental runs.

Two special columns were designed and employed in obtaining the necessary experimental data. The data obtained made it possible to prove the existence of the three separate stages of extraction and also to evaluate the relative importance of each of these stages.

The amounts of acetic acid lost during drop formation, i.e., during stage 1, using isopropyl ether, methyl isobutyl ketone and ethyl acetate were found to be 5%, 8%, and 17% respectively. The value for the methyl isobutyl ketone system is much less than that reported earlier by Sherwood, Evans and Longcor (23). The difference here is thought to be due to the differences in the direction of extraction. These authors studied the extraction of acetic acid from the ketone.

The amounts of acetic acid lost during stage 3 using isopropyl ether, methyl isobutyl ketone and ethyl acetate were found to be 6%, 13%, and 11% respectively. The explanation of this phenomenon is probably that the solute is adsorbed at the bottom interface.

The experiments with isopropyl ether and methyl isobutyl ketone were repeated for two different drop sizes. The experimental results indicate that the same percentage of the solute is extracted during stage 1 irrespective of drop size. The same applies to stage 3. The percentages of the solute extracted were calculated on the basis of the solute present in the drop originally.

The solute extracted during stage 2 could be calculated by referring to the graphs plotted from the experimental data. The effect of drop size on the extraction occurring during stage 2 was indicated. It was found that

for a given volume of feed solution more solute was extracted when the smaller drops were employed. This was to be expected and is due, of course, to the increase in the transfer area.

Values for overall transfer coefficients based on the water phase were calculated for stage 2, i.e., the falling period. The falling drops were assumed to be spheres and the transfer area was calculated. These coefficients were calculated for an individual drop so that the transfer area was equal to the surface area of a sphere. These coefficients were calculated at various column heights and a plot of these calculations was prepared. The values were seen to vary slightly with column height. In the isopropyl ether system this was thought to be due to the fact that the concentration driving force decreased with column height while the amount of solute transferred per unit time remained constant with column height. The values of K_W for methyl isobutyl ketone and ethyl acetate were higher than those for isopropyl ether, indicating the superiority of these two solvents. Drop size was seen to have little effect on the overall transfer coefficient of stage 2.*

A study was made of the effect of drop formation time on the total amount of solute extracted. In these runs the column height was kept constant. Drop formation time was seen to have no affect on the amount of solute extracted

* See Addendum, Page 205, for calculation of overall transfer coefficients for stage 1.

at a given column height. This result suggests keeping drop formation time at a minimum.

The three solvents were compared as far as their ability to extract acetic acid from water was concerned. This comparison indicated that the solvents should be arranged in the following order of decreasing effectiveness: ethyl acetate, methyl isobutyl ketone, isopropyl ether. This order remains the same if these systems are arranged in a decreasing order of interfacial tension values. This corroborates the statement made by Johnson and Bliss (18) regarding the effect of interfacial tension on spray tower operation.

The time of drop fall was measured in all the systems studied. These data indicate that the drops attain their terminal velocities within the first three inches of their fall. Furthermore, it was found that the smaller drops of the feed solution fell more rapidly through the continuous phase than the larger drops. This is thought to be due to the oscillations occurring during drop fall. It is thought further that a critical drop size exists below which smaller drops fall with lower velocities.

Photographs were presented showing the different stages of drop formation. At detachment of the drop, the drop was seen to be slightly ellipsoidal with its long axis vertical. The stem of liquid springs back to the tip just after the drop is detached.

An analysis was made of previous research articles which pointed out the precautions to be observed when employing values of $K_w a$. The effect of increasing dispersed phase rates and inlet solute concentrations on the specific area coefficient "a" was discussed.

Certain special topics related to extraction were considered. A study of drop behavior was included in this section. Drop size was seen to be affected by such variables as tip diameter, head of liquid, density of the dispersed phase and the continuous phase, the surface tensions of both liquid phases, viscosities etc. It was shown experimentally that the difference between the surface tensions of the two phases has a pronounced effect on drop size. As the surface tension difference decreases the drop size also decreases. The factors influencing the rate of drop fall were also considered in this section.

The present thesis has pointed out some very important concepts. The existence of three separate stages of extraction in spray tower operation has been firmly established. It is felt that the recognition of these three stages of extraction and an understanding of the factors which affect them will lead to a proper interpretation of spray tower operation.

It is interesting to compare the values of K_w obtained previously for stage 2 with overall coefficients

calculated over the entire 3 stages. Values of the overall transfer coefficients over the entire 3 stages were calculated for the isopropyl ether and methyl isobutyl ketone systems using Tables 22, 23, 24 and 25 and Figures 21 and 23. These calculations were made for a drop formation time of 1 sec. and for a drop fall time of 3.4 seconds in all cases. K_W for the isopropyl ether system was found to be 0.70 lb. moles/hr. ft^2 lb. moles/ft^3 for both drop sizes; for the methyl isobutyl ketone system K_W was 1.31 for a drop diameter of 0.406 cm and 1.24 for a drop diameter of 0.342 cm. Compare these values with those listed in Table 7.

In the present thesis it was impossible to study all the factors which affect the three stages of extraction. Several of these factors have been evaluated and their effects have been discussed. The extraction occurring during stage 1 is independent of drop size. At least, this is true of the percentage of the total solute content of the drops. The extraction during this stage is also unaffected by drop formation time. Short drop formation times result in the same amount of extraction as do longer drop formation times. The only factor studied in stage 2 was drop area which of course was as expected. Increasing transfer area resulted in increased amounts of extraction. A direct proportion seems to exist here. The factors affecting stage 3 are difficult to evaluate. The amount of solute lost in this stage was, nevertheless, significant.

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ADDENDUM

Page 110, line 1

The layer was drained immediately at the end of each run. However, it was found that the amount of solute extracted was not affected if this layer was left in contact for appreciable lengths of time. A run was made in which the layers were left in contact for two and a half hours before the water layer was drained and analyzed. The results were found to be unaffected.

The Calculation of Overall Transfer Coefficients for Stage 1

Overall transfer coefficients for stage 1 were calculated in much the same way as the coefficients for stage 2 (see page 158), using equation (21) modified as described below.

The term M/θ was evaluated as follows: the initial acetic acid per drop was obtained by multiplying the drop volume by the normality of the feed; the amount of solute lost during drop formation was obtained by multiplying the value of the initial acetic acid per drop by the appropriate ordinate intercept of Figures 12, 13 or 14. The drop formation time was then employed to calculate the lb. moles of solute transferred per hour during this stage.

The concentration of the drop at the beginning and end of stage 1 was calculated in a manner similar to that employed for the calculations concerned with stage 2.

The area term was used in the form of an integrated mean area. The area increases from zero to a maximum during this stage and since the volumetric feed rate is constant it was possible to develop an expression for the area as a function of drop formation time, thus, assuming the drop to be spherical at all times:

$$A = \frac{3^{2/3}\left(\frac{dV}{dT}\right)^{2/3}}{\left(\frac{1}{4\pi}\right)^{1/3}} T^{2/3}$$

where A is the area of the drop in cm^2

$\frac{dV}{dT}$ is the volumetric feed rate in $\frac{cm^3}{sec.}$

T is the time of drop formation in seconds.

Since the above equation expresses the surface area of the drop as a function of time, it is possible to calculate an integrated mean area of the drop for its period of drop formation. The method of calculation is as follows:

$$A_m\ (T - 0) = \int_0^T A\, dT$$

whence

$$A = \frac{1}{T - 0} \int_0^T \frac{3^{2/3} \left(\frac{dV}{dT}\right)^{2/3}}{\left(\frac{1}{4\pi}\right)^{1/3}} T^{2/3}\, dT$$

This value was converted to ft^2 and used in the following equation:

$$K_w = \frac{M/\theta}{A_m \times (\Delta C)_{lm}}$$

It was possible to use the arithmetic mean concentration driving force as the change was not appreciable.

These calculations led to the following results for K_w for stage 1 (see Table 7a). The units of K_w are lb moles hr^{-1} $ft^{-2} \div$ lb moles ft^{-3}, or simply ft/hr.

The overall transfer coefficients for stage 1 are larger than those for stage 2 (except for the larger drop size in the methyl isobutyl ketone system). This is thought to be due to the convection currents set up within the forming drop causing rapid mass transfer. During stage 2 these convection currents are less intense and hence the transfer coefficients are less. A situation might exist, however, when the coefficient for stage 1 would be less than that for stage 2. This would be true if the drop formation time was increased to such an extent that the convection currents during drop formation would be less than those during stage 2.

The results presented in Table 7a clearly indicate the effect of drop size on the overall transfer coefficients for stage 1. A marked increase is noted with decrease in drop size whereas the coefficients for stage 2 were found to be substantially independent of drop size. It is felt that as the drop size decreases there is more convection currents set up within the drop during its formation and hence mass transfer is much more rapid (assuming of course equal volumetric feed rates). Thus the overall transfer coefficients increase with decrease in drop size.

TABLE 7a - Overall Transfer Coefficients for Stage 1

Solvent	Drop Size (cm.)	$\frac{M}{\theta}$ ($\times 10^5$) lb moles/hr.	Mean Area $ft^2 \times 10^3$	(C) mean lb moles/ft^3	K_w, ft/hr.
Isopropyl Ether	0.451	1.55	0.41	0.0645	0.585
Isopropyl Ether	0.383	1.55	0.297	0.0645	0.81
Methyl Isobutyl Ketone	0.406	1.83	0.336	0.0637	0.855
Methyl Isobutyl Ketone	0.342	1.79	0.243	0.0639	1.15
Ethyl Acetate	0.406	3.88	0.337	0.0607	1.90

APPENDIX

All the data contained in this section were obtained with either column #1 or column #2. The procedures followed in obtaining these data were as previously described. Two different capillary tips were used in connection with the feed device. Tip #1 was used in obtaining the larger drop sizes and tip #2 for obtaining the smaller drop sizes.

In the tables of data which follow, each table represents a series of experimental runs using a definite column, solvent and capillary tip on the feed device. It is to be noted that the duplicate and triplicate runs at a given column height have been included.

In all the runs made the normality of the feed solution was 1.063 N. (1.060 N being used in Tables 8, 14 and 15).

The data is presented in such a manner that all the information pertinent to a given series of runs is given at the head of each table. This information includes: column used (#1 or #2); solvent used; capillary tip employed in feed device; normality of feed solution and finally the number of drops of feed solution allowed to fall through the solvent in each run. The initial burette height employed is easily determined from the second column in each table.

The temperatures of the feed solution and solvent were taken before each set of runs. All runs were made at a temperature of 25°C ± 1°C.

Tables 8 through 17 indicate that the column heights were varied within each series. Thus a relation between the amount of solute extracted and column height was obtained. Tables 18 through 21, on the other hand, represent series of runs in which the column heights were constant and the drop formation time was varied. This was an attempt to show the effect of drop formation time on the amount of extraction occurring during drop formation. The procedure used in obtaining the data of Tables 18 through 21 was exactly the same as that previously described, the only difference being that at the start of a run the stopcock on the feed device was not opened all the way. The time of drop formation for these series of runs was varied by varying the amount by which this stopcock was opened during each run. Drop fall times were not measured. It was assumed that these would be approximately equal since the column heights employed were approximately the same.

The runs made in obtaining the data of Table 18 were made using the 50 ml. burette instead of the 10 ml. burette. As a matter of fact, these runs were made before the 10 ml. burette was obtained. It was not felt necessary to repeat these runs using the 10 ml. burette since they seem to serve the purpose. It is admitted that the accuracy is low when using the 50 ml. burette but the accuracy is not

low enough to prevent this series of runs from serving their purpose. Furthermore, the results obtained with this burette compare favorably with comparable runs made with the 10 ml. burette.

The following is an explanation of the items appearing in the following tables. The initial burette reading is the liquid level height which was read in the burette on the feed device before the start of the run. The final burette reading is the reading obtained after the number of drops, indicated at the head of each table, had been delivered from the tip. The volume is the difference in the two burette readings. The drop volume may be calculated by dividing this figure by the number of drops indicated at the head of each table.

Drop formation time was measured as the time between successive drop detachments from the tip. Drop fall time has already been explained. Column height has also been explained.

The value for the initial acetic acid is obtained by multiplying volume by normality of the feed solution.

Sodium hydroxide used is the amount required in the analysis of the samples obtained in each run (See Sampling Procedure). In some runs, a 25 ml. aliquot was withdrawn and titrated. These runs are indicated by prefixing a (25) before the value for the sodium hydroxide used.

The normality of the sodium hydroxide used in titrating the samples is given in the column following the volume of base used.

Values for the final acetic acid content are calculated by multiplying the volume of the base used by its normality, the answer being in milliequivalents. In the runs in which the volume of base used has a (25) prefixed to it a special calculation is needed. The product of the volume of the base used by the normality must further be multiplied by the factor

$$\frac{50 + \text{volume of feed solution}}{25}$$

(The volume of feed solution is obtained from the fourth column in the table).

In runs 67 through 80 the values for the volumes of sodium hydroxide used in each case have already been corrected for the hydrolysis of the ethyl acetate. This has been discussed previously. The titration values originally obtained were decreased by 1.25 ml. and are listed in their proper places. The value of 1.25 was obtained by running samples of known acetic acid content and finding that in the titrations 1.25 milliliters of 0.1104 normal sodium hydroxide were added in excess.

Sample Calculation

To find values for final acetic acid:

Run #1

Volume of NaOH = 22.40 ml

Normality of base = 0.0974

Final acetic acid = 22.40 x 0.0974

= 2.18 milliequivalents

Run #29

Volume = (25) 7.39

Normality = 0.0925

Volume of feed = 1.81

$$\text{Final acetic acid} = 7.39 \times 0.0925 \times \frac{50 + 1.81}{25}$$

= 1.415 milliequivalents

Values for the acetic acid lost are obtained by subtracting the final acetic acid from the initial, the answer being in milliequivalents of acetic acid.

TABLE 8 - Data on Total Extraction of Acetic Acid
Column #1; Tip #1; Isopropyl Ether
Normality of Feed = 1.060; 50 drops used
Drop Volume = 0.048 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
1	3.82	6.22	2.40	1.3	-	3 1/4	2.54	22.40	0.0974	2.18	0.36
2	3.81	6.21	2.40	1.3	-	3 3/8	2.54	22.30	0.0974	2.17	0.37
3	3.79	6.20	2.41	1.3	-	3 1/4	2.55	22.73	0.0974	2.21	0.34
4	3.84	6.19	2.35	1.3	0.55	3 1/4	2.49	22.05	0.0974	2.15	0.34
5	3.80	6.20	2.40	1.3	-	9 1/2	2.54	20.80	0.0974	2.03	0.51
6	3.83	6.29	2.46	1.3	1.6	9 3/4	2.61	21.70	0.0974	2.11	0.50
7	3.80	6.25	2.45	1.3	-	20 1/4	2.60	18.80	0.0974	1.83	0.77
8	3.84	6.26	2.42	1.3	-	20	2.56	18.74	0.0974	1.82	0.74
9	3.83	6.28	2.45	1.3	-	20	2.60	19.08	0.0974	1.86	0.74
10	3.78	6.22	2.44	1.3	3.4	20	2.59	18.80	0.0974	1.83	0.76
11	3.85	6.30	2.45	1.3	-	27 1/4	2.60	16.90	0.0974	1.65	0.95
12	3.81	6.29	2.48	1.3	4.65	27 1/2	2.63	17.35	0.0974	1.69	0.94

TABLE 9 - Data on Extraction of Acetic Acid in Stage 1 plus Stage 2
Column #2; Tip #1; Isopropyl Ether
Normality of Feed = 1.063 N; 50 drops used
Drop Volume = 0.048 ml

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
13	3.81	6.24	2.43	1.2	-	8	2.58	23.48	0.0981	2.30	0.28
14	3.80	6.21	2.41	1.2	-	8	2.56	20.52	0.1104	2.26	0.30
15	3.82	6.23	2.41	1.2	-	8	2.56	20.30	0.1104	2.24	0.32
16	3.81	6.21	2.40	1.2	-	8	2.55	20.30	0.1104	2.24	0.31
17	3.74	6.15	2.41	1.3	-	13 1/2	2.56	21.50	0.0981	2.11	0.45
18	3.775	6.19	2.415	1.3	-	14	2.57	21.53	0.0981	2.11	0.46
19	3.775	6.19	2.425	1.3	-	14	2.58	21.60	0.0981	2.12	0.46
20	3.85	6.40	2.55	1.3	-	20	2.715	21.08	0.0981	2.07	0.645
21	3.81	6.22	2.41	1.3	-	20	2.56	19.95	0.0981	1.955	0.605
22	3.85	6.285	2.435	1.3	-	20	2.59	20.14	0.0981	1.97	0.62
23	3.55	5.99	2.44	1.2	-	26	2.59	19.20	0.0981	1.88	0.71
24	3.70	6.17	2.47	1.2	-	26	2.63	19.60	0.0981	1.92	0.71
25	3.98	6.46	2.48	1.2	-	26	2.64	19.40	0.0981	1.90	0.74
26	3.85	6.27	2.42	1.3	-	25 1/2	2.57	16.70	0.1104	1.845	0.725
27	3.82	6.26	2.44	1.2	-	25	2.59	16.98	0.1104	1.875	0.715
28	4.06	6.505	2.445	1.3	-	25 1/2	2.60	16.97	0.1104	1.875	0.725

TABLE 10 - Data on Total Extraction of Acetic Acid
Column #1; Tip #1; Methyl Isobutyl Ketone
Normality of Feed = 1.063 N; 50 drops used;
Drop Volume = 0.035 ml

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
29	7.65	9.46	1.81	1.3	0.8	3 1/4	1.92	(25) 7.39	0.0925	1.415	0.505
30	7.05	8.75	1.70	1.3	0.7	3 1/8	1.81	(25) 6.86	0.0925	1.315	0.495
31	7.03	8.74	1.71	1.2	0.7	3 1/4	1.82	(25) 6.71	0.0925	1.285	0.535
32	7.06	8.86	1.80	1.3	2.1	9 1/4	1.91	(25) 5.75	0.0925	1.10	0.81
33	7.10	8.83	1.73	1.2	2.0	9 1/4	1.84	(25) 5.67	0.0925	1.085	0.755
34	7.09	8.80	1.71	1.2	2.1	9 3/8	1.82	(25) 5.45	0.0925	1.045	0.775
35	7.07	8.875	1.805	1.3	3.1	14	1.92	(25) 4.92	0.0925	0.945	0.975
36	7.08	8.83	1.75	1.2	3.1	14 1/4	1.86	(25) 4.85	0.0925	0.93	0.93
37	7.09	8.82	1.73	1.2	4.3	20	1.84	(25) 3.99	0.0925	0.765	1.075
38	7.09	8.82	1.73	1.2	4.3	20	1.84	(25) 3.97	0.0925	0.76	1.08
39	7.05	8.86	1.81	1.3	6.0	27 1/4	1.92	(25) 3.30	0.0925	0.63	1.29
40	7.05	8.79	1.74	1.3	6.0	27 3/8	1.85	(25) 3.10	0.0925	0.595	1.255
41	7.09	8.82	1.73	1.3	6.0	27 1/2	1.84	(25) 3.05	0.0925	0.585	1.255

TABLE 11 - Data on Extraction of Acetic Acid in Stage 1 plus Stage 2
Column #2; Tip #1; Methyl Isobutyl Ketone
Normality of Feed = 1.063 N; 50 drops used;
Drop Volume = 0.035 ml

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
42	7.03	8.78	1.75	1.3	-	8	1.86	12.67	0.1104	1.40	0.46
43	7.03	8.75	1.72	1.2	-	8	1.83	12.43	0.1104	1.37	0.46
44	7.09	8.82	1.73	1.3	-	8	1.84	12.70	0.1104	1.40	0.44
45	7.03	8.77	1.74	1.3	-	13 1/2	1.85	10.70	0.1104	1.18	0.67
46	7.045	8.76	1.715	1.3	-	13 3/4	1.825	10.66	0.1104	1.178	0.647
47	7.015	8.745	1.73	1.3	-	13 3/4	1.84	10.80	0.1104	1.19	0.65
48	7.05	8.77	1.72	1.2	-	20 1/4	1.83	8.80	0.1104	0.972	0.858
49	7.045	8.755	1.71	1.2	-	20	1.82	8.845	0.1104	0.977	0.843
50	7.03	8.745	1.715	1.3	-	20 1/4	1.825	8.74	0.1104	0.965	0.860
51	7.045	8.745	1.70	1.3	-	25 3/4	1.81	7.575	0.1104	0.837	0.973
52	7.04	8.77	1.73	1.3	-	25 3/4	1.84	7.81	0.1104	0.863	0.977
53	7.05	8.795	1.745	1.2	-	25 3/4	1.855	7.77	0.1104	0.858	0.997

TABLE 12 - Data on Total Extraction of Acetic Acid
Column #1; Tip #1; Ethyl Acetate
Normality of Feed = 1.063 N; 50 drops used
Drop Volume = 0.0352 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
54	7.23	9.06	1.83	1.3	1.0	3 1/4	1.95	(25) 5.69	0.1053	1.24	0.71
55	7.325	9.22	1.895	1.3	1.0	3 1/4	2.02	(25) 5.745	0.1053	1.255	0.765
56	7.22	8.98	1.76	1.2	1.0	3 1/4	1.87	(25) 5.275	0.1053	1.15	0.72
57	7.18	8.905	1.725	1.2	1.0	3 1/2	1.835	(25) 5.23	0.1053	1.14	0.695
58	7.215	9.155	1.94	1.2	1.0	3 1/4	2.06	(25) 5.93	0.1053	1.30	0.76
59	7.205	8.935	1.73	1.2	3.0	9 1/2	1.84	(25) 3.88	0.1053	0.845	0.995
60	7.20	8.915	1.715	1.2	2.9	9 1/2	1.825	(25) 3.91	0.1053	0.855	0.97
61	7.17	8.865	1.695	1.2	2.9	9 1/2	1.80	(25) 4.24	0.1053	0.925	0.875
62	7.21	8.91	1.70	1.2	4.3	14 1/2	1.81	(25) 3.05	0.1053	0.665	1.145
63	7.53	9.27	1.74	1.2	4.3	14 1/2	1.85	(25) 3.09	0.1053	0.675	1.175
64	7.51	9.285	1.775	1.2	5.9	20 1/2	1.89	(25) 2.15	0.1053	0.47	1.42
65	7.495	9.255	1.76	1.3	6.0	20 1/4	1.87	(25) 2.41	0.1053	0.46	1.41
66	7.53	9.305	1.775	1.3	8.2	27 1/2	1.89	(25) 1.76	0.1053	0.34	1.55

TABLE 13 - Data on Extraction of Acetic Acid in Stage 1 plus Stage 2
Column #2; Tip #1; Ethyl Acetate
Normality of Feed = 1.063 N; 50 drops used;
Drop Volume = 0.0352 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
67	7.22	8.99	1.77	1.3	-	8 1/4	1.88	11.32	0.1104	1.25	0.63
68	7.235	8.98	1.745	1.2	-	8 1/4	1.855	10.28	0.1104	1.14	0.715
69	7.21	9.03	1.82	1.3	-	8	1.935	11.05	0.1104	1.22	0.715
70	7.20	9.01	1.81	1.3	-	8	1.925	10.97	0.1104	1.21	0.715
71	7.16	9.00	1.84	1.3	-	8 1/4	1.955	10.92	0.1104	1.21	0.745
72	7.20	8.98	1.78	1.2	-	13 3/4	1.89	7.98	0.1104	0.882	1.01
73	7.215	8.99	1.775	1.3	-	13 3/4	1.89	8.00	0.1104	0.884	1.01
74	7.22	9.00	1.78	1.2	-	13 3/4	1.89	8.08	0.1104	0.892	1.00
75	7.25	9.005	1.755	1.3	-	20 1/4	1.865	5.82	0.1104	0.643	1.222
76	7.20	9.00	1.80	1.3	-	20	1.915	6.15	0.1104	0.680	1.235
77	7.27	9.08	1.81	1.3	-	20	1.925	5.99	0.1104	0.663	1.262
78	7.25	9.03	1.78	1.3	-	25 3/4	1.89	4.63	0.1104	0.512	1.38
79	7.25	9.035	1.785	1.3	-	25 3/4	1.89	4.62	0.1104	0.511	1.38
80	7.25	9.095	1.845	1.3	-	25 3/4	1.96	4.97	0.1104	0.550	1.41

TABLE 14 - Data on Total Extraction of Acetic Acid
Column #1; Tip #2; Isopropyl Ether
Normality of Feed = 1.060 N; 80 drops used
Drop Volume = 0.0295 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
81	3.84	6.20	2.36	0.8	-	3	2.50	22.20	0.0974	2.16	0.34
82	3.82	6.19	2.37	0.8	-	3 1/8	2.51	21.80	0.0974	2.12	0.39
83	3.81	6.17	2.36	0.8	-	3 1/4	2.50	21.62	0.0974	2.11	0.39
*84	3.81	6.17	2.36	0.8	0.55	3 1/8	2.50	22.18	0.0974	2.16	0.34
85	3.81	6.19	2.40	0.8	-	9 1/4	2.54	20.21	0.0974	1.97	0.57
*86	3.83	6.47	2.64	0.8	1.5	9 1/4	2.80	22.30	0.0974	2.17	0.63
87	3.81	6.17	2.36	0.8	-	20	2.50	17.36	0.0974	1.69	0.81
*88	3.81	6.25	2.44	0.8	3.25	20	2.59	17.70	0.0974	1.725	0.865
89	3.81	6.17	2.36	0.8	-	26 3/4	2.50	15.58	0.0974	1.52	0.98
*90	3.82	6.16	2.34	0.8	4.3	26 3/4	2.48	15.51	0.0974	1.51	0.97

* Drops not counted in 84, 86, 88 and 90. Evidently more than 80 drops in 86 and 88.

TABLE 15 - Data on Extraction of Acetic Acid in Stage 1 plus Stage 2
Column #2; Tip #2; Isopropyl Ether
Normality of Feed = 1.060 N; 80 drops used
Drop Volume = 0.0295 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
91	3.80	6.13	2.33	0.8	-	8 1/4	2.47	21.81	0.0974	2.13	0.34
92	3.80	6.11	2.31	0.8	-	8 1/4	2.45	21.96	0.0974	2.14	0.31
93	3.79	6.10	2.31	0.8	-	8 1/2	2.45	21.30	0.0974	2.08	0.37
94	3.79	6.09	2.30	0.8	-	8 1/2	2.44	21.40	0.0974	2.08	0.36
95	3.78	6.20	2.42	0.8	-	14 1/2	2.56	20.89	0.0974	2.04	0.52
96	3.80	6.24	2.44	0.8	-	14	2.59	21.10	0.0974	2.06	0.53
97	3.80	6.13	2.33	0.8	-	26	2.47	17.02	0.0974	1.66	0.81
98	3.81	6.16	2.35	0.8	-	26 1/4	2.49	17.11	0.0974	1.67	0.82
99	3.82	6.19	2.37	0.8	-	26 1/4	2.51	17.31	0.0974	1.69	0.82

TABLE 16 - Data on Total Extraction of Acetic Acid
Column #1; Tip #2; Methyl Isobutyl Ketone
Normality of Feed = 1.063 N; 90 drops used
Drop Volume = 0.0210 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
100	7.06	8.96	1.90	0.8	-	3 1/8	2.02	15.74	0.0922	1.45	0.57
101	7.08	8.96	1.88	0.8	-	3 1/8	2.00	15.62	0.0922	1.44	0.56
*102	7.06	8.95	1.89	0.8	0.7	3 1/4	2.01	15.88	0.0922	1.46	0.55
103	7.05	8.92	1.87	0.8	-	9 3/8	1.99	12.30	0.0922	1.13	0.86
104	7.06	8.93	1.87	0.8	-	9 1/2	1.99	12.04	0.0922	1.11	0.88
*105	7.10	8.98	1.88	0.8	2.0	9 3/4	2.00	12.18	0.0922	1.12	0.88
106	7.12	8.97	1.85	0.8	-	14 1/2	1.97	9.94	0.0922	0.916	1.054
107	7.055	8.94	1.885	0.8	-	14 3/8	2.00	9.96	0.0922	0.918	1.082
*108	7.04	8.93	1.89	0.8	2.95	14 1/2	2.01	10.23	0.0922	0.942	1.068
109	7.12	9.04	1.92	0.8	-	19 7/8	2.04	8.12	0.0922	0.748	1.292
*110	7.05	8.94	1.89	0.8	4.1	19 7/8	2.01	8.35	0.0922	0.770	1.24

* Drops not counted in 102, 105, 108, and 110.

TABLE 17 - Data on Extraction of Acetic Acid in Stage 1 plus Stage 2
Column #2; Tip #2; Methyl Isobutyl Ketone
Normality of Feed = 1.063 N; 90 drops used
Drop Volume = 0.0210 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
111	7.08	8.90	1.82	0.7	-	8	1.94	15.84	0.0922	1.46	0.48
112	7.07	8.915	1.845	0.8	-	7 3/4	1.96	15.06	0.0922	1.39	0.57
113	7.04	8.92	1.88	0.8	-	8	2.00	16.49	0.0922	1.52	0.48
114	7.05	8.97	1.92	0.8	-	8 1/4	2.04	16.20	0.0922	1.49	0.55
115	7.06	9.00	1.94	0.8	-	8 1/2	2.065	16.35	0.0922	1.505	0.56
116	7.07	9.00	1.93	0.8	-	8 3/4	2.055	16.25	0.0922	1.495	0.56
117	7.07	9.10	2.03	0.8	-	14	2.16	14.60	0.0922	1.35	0.81
118	7.05	9.00	1.95	0.8	-	13 3/4	2.08	13.99	0.0922	1.29	0.79
119	7.06	8.99	1.93	0.8	-	14	2.055	13.93	0.0922	1.285	0.77
120	7.05	8.91	1.86	0.8	-	13 1/2	1.98	13.18	0.0922	1.22	0.76
121	7.06	8.92	1.86	0.8	-	13 1/2	1.98	12.93	0.0922	1.19	0.79
122	7.055	8.95	1.895	0.8	-	13 1/4	2.02	13.52	0.0922	1.25	0.77
123	7.06	8.92	1.86	0.8	-	25 1/4	1.98	8.95	0.0922	0.825	1.155
124	7.05	8.95	1.90	0.8	-	25 3/4	2.02	9.20	0.0922	0.849	1.171
125	7.07	8.96	1.89	0.8	-	25 3/4	2.01	9.20	0.0922	0.849	1.161

TABLE 18 - Data on Total Extraction of Acetic Acid
Column #1; Tip #1; Isopropyl Ether
Normality of Feed = 1.063 N; 50 drops used
Drop Volume = 0.050 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
126	37.09	39.58	2.49	1.3	-	3	2.65	(25) 11.72	0.0925	2.27	0.38
127	37.03	39.52	2.49	1.3	-	3	2.65	(25) 11.67	0.0925	2.26	0.39
128	37.07	39.53	2.46	1.3	-	3	2.61	(25) 11.68	0.0925	2.26	0.35
129	37.10	39.58	2.48	1.4	-	3	2.64	(25) 11.77	0.0925	2.28	0.36
130	40.70	43.20	2.50	2.0	-	3	2.66	(25) 12.07	0.0925	2.34	0.32
131	38.50	41.01	2.51	3.5	-	3	2.67	(25) 12.19	0.0925	2.36	0.31
132	37.06	39.64	2.58	3.0	-	3	2.74	(25) 12.00	0.0925	2.33	0.41
133	37.09	39.65	2.56	2.0	-	3	2.73	(25) 12.17	0.0925	2.37	0.36
134	37.03	39.55	2.52	4.4	-	3	2.68	(25) 11.82	0.0925	2.30	0.38
135	37.02	39.55	2.53	3.9	-	3	2.69	(25) 12.02	0.0925	2.34	0.35
136	37.02	39.50	2.48	1.3	-	3	2.64	(25) 11.59	0.0925	2.25	0.39
137	37.07	39.52	2.45	1.3	-	3	2.61	(25) 11.67	0.0925	2.27	0.34

TABLE 19 - Data on Extraction of Acetic Acid in Stage 1 plus Stage 2
Column #2; Tip #1; Isopropyl Ether
Normality of Feed = 1.063; 50 drops used
Drop Volume = 0.050 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
138	3.80	6.21	2.41	1.2	-	8	2.56	20.52	0.1104	2.26	0.30
139	3.82	6.23	2.41	1.2	-	8	2.56	20.30	0.1104	2.24	0.32
140	3.81	6.21	2.40	1.2	-	8	2.55	20.30	0.1104	2.24	0.31
141	3.865	6.36	2.495	1.6	-	8 1/4	2.66	21.29	0.1104	2.35	0.31
142	3.83	6.34	2.51	1.9	-	8	2.67	21.24	0.1104	2.35	0.32
143	3.80	6.34	2.54	2.9	-	8	2.70	21.26	0.1104	2.35	0.35
144	3.805	6.31	2.505	4.5	-	8 1/4	2.66	20.84	0.1104	2.30	0.36
145	3.78	6.29	2.51	4.3	-	8 1/4	2.67	21.07	0.1104	2.33	0.34
146	3.81	6.24	2.43	1.2	-	8	2.58	23.48	0.1104	2.30	0.28

TABLE 20 - Data on Total Extraction of Acetic Acid
Column #1; Tip #2; Methyl Isobutyl Ketone
Normality of Feed = 1.063; 85 drops used
Drop Volume = 0.0218 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
147	7.05	8.90	1.85	0.7	-	3 1/8	1.97	15.22	0.0922	1.40	0.57
148	7.055	8.93	1.875	0.8	-	3 1/8	1.99	15.49	0.0922	1.43	0.56
149	7.05	8.90	1.85	0.8	-	3 1/4	1.97	15.11	0.0922	1.39	0.58
150	7.07	8.90	1.83	0.8	-	3 1/4	1.95	15.56	0.0922	1.43	0.52
151	7.05	8.93	1.88	1.5	-	3 3/8	2.00	15.29	0.0922	1.41	0.59
152	7.06	8.90	1.84	3.0	-	3 3/8	1.96	13.96	0.0922	1.29	0.67
153	7.06	8.91	1.85	3.0	-	3 1/4	1.97	15.06	0.0922	1.39	0.58

TABLE 21 - Data on Extraction of Acetic Acid in Stage 1 plus Stage 2
Column #2; Tip #2; Methyl Isobutyl Ketone
Normality of Feed = 1.063; 90 drops used
Drop Volume = 0.0227 ml.

Run	Initial Burette Reading (ml.)	Final Burette Reading (ml.)	Volume of Feed (ml.)	Drop Formation Time (sec.)	Drop Fall Time (sec.)	Column Height (in.)	Initial Acetic Acid (m.e.)	NaOH Used (ml.)	Normality of NaOH	Final Acetic Acid (m.e.)	Acetic Acid Lost (m.e.)
154	7.05	8.97	1.92	0.8	-	8 1/4	2.04	16.20	0.0922	1.49	0.55
155	7.06	9.00	1.94	0.8	-	8 1/2	2.065	16.35	0.0922	1.505	0.56
156	7.07	9.00	1.93	0.8	-	8 3/4	2.055	16.25	0.0922	1.495	0.56
157	7.04	8.97	1.93	1.9	-	8 1/2	2.055	16.23	0.0922	1.495	0.56
158	7.05	9.00	1.95	1.6	-	8 1/2	2.08	16.50	0.0922	1.520	0.56
159	7.05	8.99	1.94	1.9	-	8 1/4	2.065	16.20	0.0922	1.495	0.57

TABLE 22 - Calculations of Overall Transfer Coefficients For Stage 2 Isopropyl Ether System; Representative Drop Volume = 0.048 ml. Drop Diameter = 0.451 cm; Drop Area = 0.686×10^{-3} ft^2.

	Column Height, Inches					
	5	10	15	20	25	30
Initial acetic acid/drop (m.e.)	0.0509	0.0509	0.0509	0.0509	0.0509	0.0509
Acetic acid lost during drop formation (m.e.)	0.00254	0.00254	0.00254	0.00254	0.00254	0.00254
Acetic acid lost during drop breaking (m.e.)	0.00305	0.00305	0.00305	0.00305	0.00305	0.00305
Total acetic acid lost (m.e.)	0.0080	0.0103	0.0127	0.0150	0.0173	0.0197
Acetic acid lost during fall (m.e.)	0.0024	0.0047	0.0071	0.0094	0.0117	0.0141
Acetic acid/drop at detachment (m.e.)	0.0484	0.0484	0.0484	0.0484	0.0484	0.0484
Acetic acid/drop at bottom (m.e.)	0.0460	0.0437	0.0413	0.0390	0.0367	0.0343
Drop concentration at top, lb moles/ft^3	0.0629	0.0629	0.0629	0.0629	0.0629	0.0629
Drop concentration at end, lb moles/ft^3	0.0597	0.0568	0.0537	0.0507	0.0477	0.0446
Fall time (seconds)	0.83	1.7	2.54	3.4	4.24	5.1
W/θ, lb. moles/hour ($\times 10^5$)	2.29	2.20	2.22	2.19	2.19	2.19
Δ C, lb. moles/ft^3	0.0613	0.0598	0.0583	0.0568	0.0553	0.0538
K_W for Stage 2	0.545	0.537	0.555	0.563	0.578	0.594

TABLE 23 - Calculations for Isopropyl Ether System
Representative drop volume = 0.0295 ml.
Drop diameter = 0.383 cm; drop area = 0.493×10^{-3} ft^2

	Column Height, Inches					
	5	10	15	20	25	30
Initial acetic acid/drop (m.e.)	0.0313	0.0313	0.0313	0.0313	0.0313	0.0313
Acetic acid lost during drop formation (m.e.)	0.00156	0.00156	0.00156	0.00156	0.00156	0.00156
Acetic acid lost during drop breaking (m.e.)	0.00188	0.00188	0.00188	0.00188	0.00188	0.00188
Total acetic acid lost (m.e.)	0.00516	0.00688	0.00855	0.0102	0.0119	0.0136
Acetic acid lost during fall (m.e.)	0.00176	0.00348	0.00515	0.0068	0.0085	0.0102
Acetic acid/drop at detachment (m.e.)	0.0297	0.0297	0.0297	0.0297	0.0297	0.0297
Acetic acid/drop at bottom (m.e.)	0.0279	0.0262	0.0245	0.0229	0.0212	0.0195
Drop concentration at top, lb moles/ft^3	0.0628	0.0628	0.0628	0.0628	0.0628	0.0628
Drop concentration at end, lb moles/ft^3	0.0590	0.0554	0.0518	0.0485	0.0449	0.0412
Fall time (seconds)	0.8	1.6	2.4	3.2	4.0	4.8
W/θ, lb. moles/hour ($\times 10^5$)	1.75	1.73	1.70	1.69	1.69	1.69
ΔC, lb. moles/ft^3	0.0609	0.0591	0.0573	0.0556	0.0538	0.0520
K_W for Stage 2	0.583	0.593	0.602	0.617	0.638	0.659

TABLE 24 - Calculations for Methyl Isobutyl Ketone System
Representative drop volume = 0.035 ml.
Drop diameter = 0.406 cm; drop area = 0.555×10^{-3} ft^2

	Column Height, Inches				
	5	10	15	20	25
Initial acetic acid/drop (m.e.)	0.0372	0.0372	0.0372	0.0372	0.0372
Acetic acid lost during drop formation (m.e.)	0.0030	0.0030	0.0030	0.0030	0.0030
Acetic acid lost during drop breaking (m.e.)	0.0048	0.0048	0.0048	0.0048	0.0048
Total acetic acid lost (m.e.)	0.0119	0.0158	0.0194	0.0223	0.0246
Acetic acid lost during fall (m.e.)	0.0041	0.0080	0.0116	0.0145	0.0168
Acetic acid/drop at detachment (m.e.)	0.0342	0.0342	0.0342	0.0342	0.0342
Acetic acid/drop at bottom (m.e.)	0.0301	0.0262	0.0226	0.0197	0.0174
Drop concentration at top, lb moles/ft^3	0.0610	0.0610	0.0610	0.0610	0.0610
Drop concentration at end, lb moles/ft^3	0.0537	0.0467	0.0403	0.0351	0.0310
Fall time (seconds)	1.1	2.2	3.3	4.4	5.5
W/θ, lb. moles/hour ($\times 10^5$)	2.95	2.88	2.79	2.62	2.42
ΔC, lb. moles/ft^3	0.0573	0.0538	0.0506	0.0480	0.0443
K_W for Stage 2	0.928	0.965	0.995	0.983	0.983

TABLE 25 - Calculations for Methyl Isobutyl Ketone
Representative drop volume = 0.0210 ml.
Drop diameter = 0.342 cm; drop area = 0.394×10^{-3} ft^2

	Column Height, Inches				
	5	10	15	20	25
Initial acetic acid/drop (m.e.)	0.0224	0.0224	0.0224	0.0224	0.0224
Acetic acid lost during drop formation (m.e.)	0.0018	0.0018	0.0018	0.0018	0.0018
Acetic acid lost during drop breaking (m.e.)	0.0029	0.0029	0.0029	0.0029	0.0029
Total acetic acid lost (m.e.)	0.00745	0.0100	0.0123	0.0143	0.0157
Acetic acid lost during fall (m.e.)	0.00275	0.0053	0.0076	0.0096	0.0110
Acetic acid/drop at detachment (m.e.)	0.0206	0.0206	0.0206	0.0206	0.0206
Acetic acid/drop at bottom (m.e.)	0.0178	0.0153	0.0130	0.0110	0.0096
Drop concentration at top, lb moles/ft^3	0.0612	0.0612	0.0612	0.0612	0.0612
Drop concentration at end, lb moles/ft^3	0.0529	0.0455	0.0386	0.0327	0.0285
Fall time (seconds)	1.01	2.04	3.07	4.1	5.12
W/θ, lb. moles/hour ($\times 10^5$)	2.16	2.06	1.99	1.86	1.70
ΔC, lb. moles/ft^3	0.0570	0.0533	0.0499	0.0452	0.0427
K_W for Stage 2	0.965	0.980	1.01	1.05	1.01

TABLE 26 - Calculations for Ethyl Acetate System
Representative drop volume = 0.0352 ml.
Drop diameter = 0.406 cm; drop area = 0.555×10^{-3} ft^2

	Column Height, Inches				
	5	10	15	20	25
Initial acetic acid/drop (m.e.)	0.0374	0.0374	0.0374	0.0374	0.0374
Acetic acid lost during drop formation (m.e.)	0.00636	0.00636	0.00636	0.00636	0.00636
Acetic acid lost during drop breaking (m.e.)	0.00411	0.00411	0.00411	0.00411	0.00411
Total acetic acid lost (m.e.)	0.0155	0.0203	0.0246	0.0281	0.0303
Acetic acid lost during fall (m.e.)	0.0050	0.0098	0.0141	0.0176	0.0198
Acetic acid/drop at detachment (m.e.)	0.0310	0.0310	0.0310	0.0310	0.0310
Acetic acid/drop at bottom (m.e.)	0.0260	0.0212	0.0169	0.0134	0.0112
Drop concentration at top, lb moles/ft^3	0.0550	0.0550	0.0550	0.0550	0.0550
Drop concentration at end, lb moles/ft^3	0.0461	0.0376	0.0300	0.0238	0.0199
Fall time (seconds)	1.5	3.0	4.45	5.92	7.41
W/θ, lb. moles/hour ($\times 10^5$)	2.64	2.59	2.51	2.36	2.12
ΔC, lb. moles/ft^3	0.0505	0.0463	$(0.0413)_{lm}$	$(0.0374)_{lm}$	$(0.0345)_{lm}$
K_W for Stage 2	0.941	1.01	1.09	1.14	1.11