THE EFFECT OF PULSATION ON LIQUID-LIQUID MASS-TRANSFER RESISTANCES

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PREFACE

The study of individual mass-transfer resistances in liquid-liquid extraction and the effects on these of such variables as flow rates have received considerable attention, not only for design purposes, but also because of the possible light that such studies may shed on the mechanism of liquid-liquid mass transfer.

In recent years, pulsed columns have been extensively used, particularly in radiochemical separations, to obtain higher mass-transfer rates than are obtainable with unpulsed columns, such as spray and packed columns.

In this study, a partially miscible system was used in the determination of individual film mass-transfer resistances in a pulsed column and to investigate the effect of pulsed column variables, such as pulse frequency, pulse amplitude, and flow rates, on the individual resistances. Such a study, it is hoped, might not only help to explain the increased efficiencies obtainable with pulsed columns, but eventually to contribute towards better understanding of mass-transfer phenomena.

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PART I. INTRODUCTION

Liquid-liquid Extraction

Liquid-liquid extraction is that unit operation whereby a substance is transferred from one liquid to another by direct contact of the two liquids. In general, this unit operation may be divided into four categories: (1) batch extraction; (2) stagewise extraction; (3) continuous extraction; and (4) extraction by centrifugal action.

In batch extraction, definite amounts of the two liquids are placed in a vessel, mixed together, and then allowed to settle out into two phases which are then separated. Most laboratory extractions are done batchwise.

In stagewise extraction, the two liquids flow into one vessel where they mix, the mixture flows to another vessel where the two liquid phases separate, and the two phases flow out through separate outlets. One such combination of vessels is called a mixer-settler.

In continuous liquid-liquid extraction, the two liquids are contacted along the length of one vessel, usually a vertical column, or tower. One liquid is dispersed into, and flows countercurrently to, the other liquid. The first liquid disperses into the second liquid at one end of the vertical column, and settles out at the other end of the column. The dispersed liquid is referred to as the dispersed, discontinuous, or drop phase, while the other liquid is referred to as the continuous, or field phase.

In centrifugal extractors, the heavier liquid is thrown outward from a central rotor to the periphery of a rotating perforated drum, thereby displacing the lighter liquid which moves in the opposite direction.

Whatever the manner of extraction, it is necessary that the two liquids should, at least to a certain extent, be immiscible. In addition, a difference in density should exist between the two liquids to cause movement of one relative to the other.

The phenomenon involved in the transfer of a substance from one liquid phase to another liquid phase belongs to that general group of phenomena known as mass transfer. In the study of mass transfer phenomena, the rate at which a substance moves through another substance is of paramount importance, particularly when the study of mass transfer is directed towards the design of equipment to carry out such mass transfer, either on a laboratory, or on an industrial plant, scale.

When two liquids and a solute are mixed together, the solute will distribute itself between the two liquids. At equilibrium, the ratio of solute concentration in one liquid to the solute concentration in the other liquid is equal to a certain value called the distribution, or partition, coefficient:

$$\frac{c_1}{c_2} = m, \tag{1}$$

where:

c_1 = solute concentration in one liquid
c_2 = solute concentration in the other liquid
m = distribution coefficient.

The distribution or partition coefficient, m, may be a function of the concentrations, c_1 and c_2. The relationship between the two concentrations may be given in the form of a plotted curve, called the "equilibrium diagram."

In most applications of liquid-liquid extraction, the two liquids cannot be maintained in contact with one another for a very long period of time. This is particularly true of commercial applications where economic considerations place a limit on contact time. Consequently, the two liquids are maintained in contact with one another for a finite length of time during which mass transfer occurs. The rate of mass transfer can be expressed as:

$$N = K(c_1 - c_1^*), \qquad (2)$$

where:

N = rate of mass transfer per unit contact area

K = mass transfer coefficient

c_1 = solute concentration in the first liquid

c_1^* = concentration which would be in equilibrium with the solute concentration in the second liquid after infinite contact time.

In other words, if c_2 is the solute concentration in the second liquid, then:

$$c_1^* = mc_2, \qquad (3)$$

where:

m = distribution coefficient

as in equation (1).

The mass transfer coefficient, K, in equation (2) relates the amount of solute transferred per unit time per unit contact area to the concentration "driving force" $(c_1 - c_1^*)$. Its reciprocal, 1/K, may be considered as the resistance to mass transfer, such that equation (2) may be re-written as:

$$N = \frac{c_1}{R},$$

where:

c_1 = concentration "driving force" $(c_1 - c_1^*)$

R = mass transfer resistance, $1/K$.

It is generally believed that the interface between two liquids offers no resistance to mass transfer, and that equilibrium exists at such an interface. Hence, the rate equation for mass transfer may also be written as:

$$N = k_1(c_1 - c_{i1}) \qquad (4)$$

where:

N = rate of mass transfer per unit contact area

k_1 = individual mass transfer coefficient for the first liquid

c_1 = bulk solute concentration in the first liquid

c_{i1} = solute concentration at the interface, referred to the first liquid, such that:

$$c_{i1} = mc_{i2} \qquad (5)$$

where:

c_{i2} = interfacial concentration, referred to the second liquid.

In the foregoing discussion, the assumption was implied that the bulk concentration in either liquid is different from the interfacial concentration referred to that liquid, i. e.,

$$c_1 \neq c_{i1}$$

and

$$c_2 \neq c_{i2}.$$

Theoretically, it would require an infinite number of mixer-settler stages, or an infinite height of column for c_1 and c_{i1} to become equal, or for c_2 and c_{i2} to become equal. However, in certain systems, such as the system used in this study, the mass transfer resistances are so small that c and c_i become substantially equal even for a finite height of column.

In most liquid-liquid extraction equipment, it is difficult to measure the interfacial area between the two liquids. Hence, the effect of interfacial area is combined with the coefficient K so that for vertical columns equation (2) may be re-written as:

$$N' = Ka(c_1 - c_1^*)dh \qquad (6)$$

where:

N' = rate of mass transfer per unit cross-sectional area of the column

K = coefficient, as defined in equation (2)

a = interfacial area per unit volume of the column

dh = differential height of column.

In order that equation (6) can be integrated, the interfacial area, a, is assumed to be uniform over the cross-sectional area of the column.

The volumetric coefficient, Ka, has been found to be a function of column geometry (such as the type and size of packing), as well as of the system properties. In general, the greater the turbulence, or agitation, in the column, the greater the value of Ka. While turbulence caused by the dispersion of one liquid in the other is sometimes sufficient to give the desired value of Ka, the degree of turbulence and the interfacial, or contact, area may be increased by any of several means. The column may be filled with packing material which provide greater contact area for the two liquids. Or, one liquid may be dispersed through a series of perforated plates, while the other liquid passes through chimneys, or downcomers, on each plate. The mass transfer rate may also be increased by providing external means of agitation, such as stirrers, or by applying a pulsating, or pulsing, motion to the liquids in the column. These different types of columns taken in order are known, respectively, as: spray columns; packed columns; sieve-plate columns; agitated columns; and the last, with which we are most concerned, pulsed columns.

Pulsed Columns

The use of pulsation to increase mass transfer rate in an extraction column was the subject of a patent issued to Van Dijck (21) in 1935. In his device, pulsation is accomplished by alternately raising and lowering a series of perforated plates in a column. However, Van Dijck also discussed the possibility of accomplishing the desired agitation by moving the column liquids up and down through stationary plates.

Recently the use of such devices, now called pulsed columns, has aroused considerable interest. This is particularly true in the field of radiochemical processing, where space limitations imposed by shielding requirements place a premium on extraction efficiency. Indeed, it has repeatedly been shown that column heights can be drastically cut down by means of pulsation.

Pulsed columns can be divided into two main types (3, 20). The first type of pulsed column consists of an ordinary packed column in which a pulsing motion is imparted to the liquids in the column by means of a reciprocating piston pump, diaphragm, or bellows. The second type consists of a sieve-plate column, without downcomers, in which pulsing motion is likewise imparted by means of a reciprocating pump. The plate perforations are ordinarily too small for the two liquids to flow through countercurrently without pulsing. To this second type of pulsed column has been given the name "pulse column" (4). Van Dijck's original idea of moving the plates has not gained wide acceptance.

Individual Mass-transfer Resistances

According to equation (6) a solute moves from one liquid into another at a certain rate. In order that there ~~by~~ be no accumulation of solute, this same solute must move from the main body, or bulk, of one liquid to the interface between the two liquids at the same rate as that given by equation (6), thus:

$$N' = k_1 a(c_1 - c_{i1})dh; \tag{7}$$

likewise, it must move from the interface to the bulk of the other liquid:

$$N' = k_2 a(c_{i2} - c_2)\ dh, \tag{8}$$

where:

k_1 = individual mass-transfer coefficient for the first liquid

k_2 = individual mass-transfer coefficient for the second liquid.

We can therefore picture the solute as moving from the bulk of one liquid to the interface between the two liquids across a resistance $1/k_1a$, and then moving from the interface to the bulk of the other liquid across a second resistance $1/k_2a$. Ordinarily, the interfacial concentrations cannot be determined; hence, the individual resistances $1/k_1a$ and $1/k_2a$ cannot be calculated. However, bulk concentrations in the two liquids can be easily determined, and the over-all resistance $1/Ka$ can be calculated by suitable manipulations of equation (6).

According to equation (6) the total concentration driving force across the two liquids is given by:

$$c_{tot} = (c_1 - c_1^*) = (c_1 - mc_2).$$

Assuming no resistance at the interface, the total concentration driving force is equal to the sum of the driving forces across the two liquids:

$$(c_1 - mc_2) = (c_1 - c_{i1}) + (mc_{i2} - mc_2).$$

Substituting from equations (6), (7), and (8):

$$\frac{N'}{Kadh} = \frac{N'}{k_1adh} + \frac{mN'}{k_2adh}$$

or:

$$\frac{1}{Ka} = \frac{1}{k_1a} + \frac{m}{k_2a}.$$

If either of the two resistances is large compared to the other, it becomes approximately equal to the total resistance.

Colburn and Welsh (5) developed an ingenious technique for measuring individual mass-transfer resistances by using two partially miscible liquids. When two such liquids are contacted with one another, one liquid transfers, or diffuses, into the second liquid until the equilibrium, or saturation, concentration of the first liquid in the second is reached. Likewise, the second liquid transfers into the first until its equilibrium concentration is reached. Thus, the first liquid serves as the solute in the second liquid, and vice-versa. It is assumed that equilibrium exists at all times at the interface of the two liquids. Therefore, if c_1 is the concentration of the first liquid in the second, its concentration at the interface is c_{s1}, where c_{s1} is the equilibrium, or saturation, concentration.

Equations analogous to equations (7) and (8) may be written, for the first liquid:

$$N' = k_1 a \, (c_{s1} - c_1) dh \tag{9}$$

and for the second liquid:

$$N'' = k_2 a \, (c_{s2} - c_2) dh. \tag{10}$$

Because the solute in the first liquid is different from the solute in the second liquid, N' is not necessarily equal to N".

From the foregoing, it is easily seen that if one liquid is made the dispersed phase and the second be made the continuous phase, the resistances of the two phases can be determined separately, since the concentrations c_1 and c_2 are easily obtainable, and the saturation values c_{s1} and c_{s2} can be obtained by contacting the two liquids for a sufficiently long period of time, and then measuring the concentrations. It should be noted that c_{s1} and c_{s2} are functions of temperature.

This technique of using two partially miscible liquids, which is analogous to that in gas-liquid absorption where a pure gas and a pure liquid are contacted, was therefore adopted for the purpose of investigating the effect of pulsation on the dispersed and continuous phase resistances, i. e., on the mass-transfer coefficients k_1a and k_2a in equations (9) and (10). The methods used in the problems associated with, and the results obtained from, such a study make up the subject matter of this thesis.

PART II. RECENT LITERATURE

Individual Mass-transfer Resistances

Colburn and Welsh (5) used the partially miscible system isobutanol-water to study individual transfer resistances in a 3-11/16 in. x 21 in. column packed with 1/2-inch clay Raschig rings. Individual "film" HTU's were determined by calculating the number of transfer units for each phase:

$$\mathrm{NTU} = \int_{y_1}^{y_2} \frac{dy}{y_s - y}, \qquad (11)$$

which is an approximation of the more general form:

$$\mathrm{NTU} = \int_{y_1}^{y_2} \frac{(1 - y)_f \, dy}{(1 - y)(y_s - y)}, \qquad (11\text{-a})$$

where:

y = concentration in mole-fraction or weight fraction

y_s = concentration at saturation

$(1 - y)_f$ = logarithmic mean concentration of the non-diffusing component;

and by converting NTU's to HTU's (height of a transfer unit):

$$\mathrm{HTU} = \frac{h}{\mathrm{NTU}}, \qquad (12)$$

where:

h = height of the column.

For dilute solutions, $(1 - y)_f$ and $(1 - y)$ are approximately equal. Therefore, equation (11) simplifies to:

$$NTU = 2.3 \log \frac{y_s}{y_s - y_2} . \qquad (13)$$

For the dispersed phase, HTU_D was found to be substantially constant and independent of the flow rates:

$$HTU_D = \text{constant}. \qquad (14)$$

On the other hand, for the continuous phase HTU_C was found to be a power function of the flow ratio, W_C/W_D, such that

$$HTU = \alpha\left(\frac{W_C}{W_D}\right)^{0.75} , \qquad (15)$$

where:

α = constant

W_C, W_D = flow rates by weight of the continuous and dispersed phases, respectively.

The following correlations were recommended for over-all HTU's:

$$HTU_{OD} = c_1 + c_2\left(\frac{W_C}{W_D}\right)^{0.75}\left(\frac{mW_D}{W_C}\right); \qquad (16)$$

$$HTU_{OC} = c_2\left(\frac{W_C}{W_D}\right)^{0.75} + c_1\left(\frac{W_C}{mW_D}\right), \qquad (17)$$

where:

HTU_{OD} = over-all HTU based on the dispersed phase

HTU_{OC} = over-all HTU based on the continuous phase

c's = constants

W_D = flow rate by weight of the dispersed phase

W_C = flow rate by weight of the continuous phase

m = distribution coefficient, equal to the slope of the equilibrium line.

Comings and Briggs (6) attempted to determine the relative magnitudes of the individual transfer resistances by using caustic and acid solutions to reduce the over-all resistance. Benzoic acid, aniline, and acetic acid were transferred between water and benzene in wetted-wall and packed columns. The results were correlated by equations of the form:

$$Ka = \alpha V_D^r V_C^s , \tag{18}$$

where:

Ka = over-all coefficient

V's = superficial velocities

r, s = exponents

α = constant.

A qualitative determination of the resistance offered by each "film" was made, and it was believed that the individual coefficients could also be represented by equations of the form

$$ka = \alpha' V_W^m V_B^n ; \tag{19}$$

where:

V_W, V_B = water and benzene flow rates, respectively.

Approximate values of the exponents m and n for wetted-wall columns are also given in this study.

Brinsmade and Bliss (2) used a wetted-wall tower to resolve over-all coefficients into individual coefficients. From the general equation:

$$\frac{1}{K_c a} = \frac{1}{k_c a} + \frac{H}{k_w a} ; \tag{20}$$

and the assumed relationships:

$$k_c = \alpha_c L_c^n L_w^p \tag{21}$$

and

$$k_w = \alpha_w L_w^{\,r} L_c^{\,s} , \qquad (22)$$

where:

H = distribution coefficient

L's = flow rates by weight

c,w = subscripts which refer to core and wall liquids, respectively;

the exponents n, p, r, and s, were evaluated by plotting reciprocal coefficients against reciprocal flow rates.

Over-all coefficients were evaluated as

$$\frac{1}{K_c a} = \frac{\alpha}{L_c^{0.63}} + \frac{\beta}{L_w} ; \qquad (23)$$

from equations (20), (21), (22), and (23), the individual coefficients were resolved into

$$k_c a = \alpha_c L_c^{0.63} \qquad (24)$$

and

$$k_w a = \alpha_w L_w . \qquad (25)$$

These coefficients were compared with those derived from Colburn and Welsh's study:

$$k_D a = \alpha_D \, L_D \qquad (26)$$

and

$$k_C a = \alpha_C L_C^{0.25} L_D^{0.75} . \qquad (27)$$

The partially miscible systems isobutyraldehyde-water and 3-pentanol-water were used by Laddha and Smith (12) to study individual transfer resistances in 2-inch spray and packed towers. The results parallel those of Colburn and Welsh.

For the dispersed phase:

$$HTU_D = \text{constant} \tag{28}$$

and for the continuous phase:

$$HTU_C = \beta \left(\frac{L_C}{L_D}\right)^n. \tag{29}$$

End Effects

End effects were studied by Geankoplis and Hixson (9) who used a bent-tube device to sample the continuous phase in a spray column at different points. Ferric chloride was transferred from water as the continuous to isopropyl ether as the dispersed phase. A significant end effect was found at the continuous phase inlet but none at the other end. This inlet effect was found to increase with the mass transfer efficiency of the column, and also to increase with the dispersed phase (ether) flow rate. This inlet effect, however, decreased with increasing feed concentration in either phase. On the other hand, column geometry and interface level (with respect to the feed inlet level) did not have any appreciable influence on the end effect.

In a later study, Geankoplis, et. al. (10) studied acetic acid extraction from dispersed toluene to continuous water phase in a 3-3/4-inch diameter glass column, 6 feet tall, fitted with the same kind of sampling device used in the previous study by Geankoplis and Hixson (9). It was found that the inlet effect occurred at the continuous phase inlet, as before, and it was therefore concluded that the inlet effect was independent of the direction of solute transfer. As in the previous study, logarithms of the concentrations were plotted against linear distance along the column and found to be approximately straight. The slopes of these lines were related to HTU values. However, at the dispersed phase inlet, the mass transfer rate was less than expected, and this was believed due to the flaring section at that point. Concentration gradients in the dispersed phase were related to those in the continuous phase by material balances.

Correlation of inlet effect with HTU values inside the column shows a linear decrease of inlet effect with increasing HTU. Furthermore, the inlet effect decreases as the dispersed phase flow rate is decreased and becomes zero at zero dispersed phase flowrate. The effect of concentration is opposite to that found previously when transfer was from continuous to dispersed phase (9). In this latter study, when mass transfer was from dispersed to continuous phase, inlet effect increased with dispersed phase feed concentration.

End effects in the dispersed phase were investigated by Licht and Conway (16). According to their findings, mass transfer in the dispersed phase occurs in three stages: (1) at the dispersed phase inlet; (2) as the dispersed phase moves up or down the column through the continuous phase; and (3) at the interface where the dispersed phase recoalesces. Columns of different heights were used to eliminate the second stage; and a special column was used to eliminate the second and third stages. By difference, the respective effects of the three stages were obtained.

Representative figures for the extraction of acetic acid from water (dispersed) are:

Solvent (continuous)	% extracted stage 1	% extracted stage 3
Isopropyl ether	5	6
Methyl isopropyl ketone	8	13
Ethyl acetate	17	11

Pulsed Columns

A diagram of Van Dijck's original pulsed column is given by Morello and Poffenberger (17) in a survey of commercial extraction equipment.

Rubin and Lehman (18) studied the systems water-uranyl nitrate-cyclohexanone and water-uranyl nitrate-pentaether in a 1/2-inch diameter, 3-foot tall pulse column, with teflon perforated plates. While they agree with other investigators (5, 12) that the dispersed phase HTU is essentially constant with respect to flow rates, they believe that the continuous phase HTU can better be expressed as a linear function of the continuous and dispersed phase flow rates, independently, rather than as a function of the flow ratio. This assumption leads to the HTU-surface concept, according to which, over-all HTU's can be plotted in three dimensions with over-all HTU on one coordinate axis, flow rate of one phase on the second coordinate axis, and the reciprocal of the other flow rate on the third coordinate axis.

Their data were correlated in terms of over-all HTU's:

$$\mathrm{HTU}_{OG} = \alpha G + \beta \frac{G}{L} \qquad (30)$$

and

$$\mathrm{HTU}_{OL} = \gamma \qquad (31)$$

where:

G, L = flow rates of organic and aqueous phases, respectively

α, β, γ = constants.

By means of certain assumptions and mathematical manipulations, equations (30) and (31), were converted to individual HTU's:

$$HTU_G = \alpha G \qquad (32)$$

and

$$HTU_L = \gamma' . \qquad (33)$$

Lehman (14) used trace concentrations of plutonium between aqueous nitric acid and TTA (thenoyltrifluoroacetone) organic solvent, at different acid and TTA concentrations to vary the distribution coefficient and thereby obtain individual HTU's from the relationship:

$$H_{OG} = H_G + \frac{mG}{L} H_L \qquad (34)$$

or

$$H_{OL} = H_L + \frac{L}{mG} H_G . \qquad (35)$$

A few such calculations were made to illustrate the method, but no general correlations of individual HTU's were made. However, over-all HTU's were correlated by the HTU-surface concept developed by Rubin and Lehman.

Cohen and Beyer (4) studied the system isoamyl alcohol-boric acid-water in a 1-inch diameter, 20-inch tall pulse column with 10 ducoflex perforated plates. At a given pulse frequency and amplitude, the effect of flow rates on the over-all HTU was correlated by:

$$HTU_{OG} = \alpha \left(\frac{G}{L}\right)^{0.39} . \qquad (36)$$

However, at low frequencies, over-all HTU's appeared to vary with individual flow rates, rather than flow ratio, possibly because at low frequencies neither phase was truly continuous. At high frequencies, the pulse column behavior was "similar to that of a spray column."

The effect of pulse amplitude and frequency were correlated in terms of HETS (height equivalent to a theoretical stage) as a function of the product amplitude x frequency (Af). The change with Af was greater at low Af, possibly because of back-mixing due to small droplets at high Af.

Belaga and Bigelow (1) correlated HTU's as a function of the product Af, using the system hexone-acetic acid-water, with hexone as the continuous phase, in a pulsed perforated-plate column. HTU increased, then decreased, and finally increased with increasing Af, although the variation was not appreciable (the range in HTU values was between HTU = 2.63 inches and HTU = 6.25 inches). Column behvaior at different pulse frequencies and amplitudes was used to explain this HTU variation.

Sege and Woodfield (19) used a 3-inch diameter perforated-plate pulse column, and the system nitric acid (aq. solution) -uranyl nitrate-tributyl phosphate in CCl_4 or hydrocarbon, to study pulse column variables. Three types of phase-dispersion behavior were observed as a function of throughput rates and pulsing conditions: (a) the mixer-settler type of operation; (b) emulsion type of operation; and (c) unstable operation.

Chantry, Von Berg, and Wiegandt (3) give a comprehensive survey of the literature on pulsed columns, as well as the results of a series of investigations on a 4-foot tall, 40-mm diameter pulsed packed column, and pulsed sieve-plate column of the same general dimensions. Frequencies of 0 to 300 cycles per minute were available at column amplitudes of 0 to 10 mm. Two systems were used in this study: methyl isobutyl ketone-acetic acid-water and ethyl acetate-acetic acid-water. Water was the continuous phase in almost all the runs.

It was found that the HETS varied as the 0.37 power of the dispersed phase flow rate when the column was pulsed and was almost independent of the continuous phase flow rate. In general, HETS decreased as the amplitude was increased at a given frequency, and likewise decreased as the frequency was increased at a given amplitude. The curves given, however, show minima, beyond which, the HETS tend to increase with either pulse amplitude or frequency. Such points were usually close to flooding conditions.

An approximate correlation was proposed which gives the amplitude as a function of frequency at a given HETS; thus, at HETS = 7:

$$A = 10{,}000\ f^{-2} \tag{37}$$

where:

A = pulse amplitude in mm

f = pulse frequency in cycles per minute.

Lane (13) investigated the four-component system pentaether-uranyl nitrate-nitric acid-water, and "pseudo-equilibrium" concentrations in terms of activities and activity coefficients were calculated. Runs were made in 1-inch diameter bottom-pulsed and top-pulsed columns, and HTU's based on the pseudo-equilibrium lines were calculated. However, no correlations relating HTU's to flow rates or pulse variables were given.

Reynolds number was used by Li and Newton (15) to correlate mass transfer coefficients of the system toluene-benzoic acid-water in a perforated-plate pulsed column consisting of eleven segments of 2-in. x 2 in. Pyrex pipe spacers. The perforated plates were of 5/32-inch thick brass, perforated with 85 holes of 1/16-inch diameter, with a fractional open area of 8.51%.

Their results were expressed in the form:

$$\frac{K_W a H}{(Re)^d} = \phi_T (V_T)^n (V_W)^m \qquad (38)$$

where:

H = reciprocal of the distribution coefficient

ϕ_T = constant.

The Reynolds number through the perforations was calculated by using the density and viscosity of a two-phase liquid mixture composed of the average hold-up analysis of all the runs at an average room temperature of 80°F. "The term v, the arithmetic average velocity of liquid mixture through the perforations, was calculated from the volume of displacement of the plunger in the pump and the area of perforations on the plate."

Two kinds of behavior were observed: a "streamline," and a "turbulent" region, as indicated by a break in the Reynolds number plots. The Reynolds number exponent in the "streamline" region was 0.175 and the exponent in the "turbulent" region was 1.07. The "streamline" region was characterized by a "cell-like formation with large drops of water phase (the continuous phase) surrounded by toluene films." This phase-inversion behavior obviously retards mass transfer to the extent that the effect of pulsation is diminished.

The hold-up was an increasing function of Reynolds number in both regions, but a sudden drop in hold-up was noticed at the transition from the "streamline" to the "turbulent" region. It is believed that a transition from cell to drop structure occurred at this point, and because the drops moved faster, they contributed less hold-up. It was also observed that, "the hold-up was affected mainly by the flow rate of the discontinuous phase and was practically independent of the flow rate of the continuous phase."

PART III. EXPERIMENTAL APPARATUS

Column and Accessories

The extraction column was built from two sections of Pyrex pipe, 2 inches in internal diameter, each section having a length of 1 foot. The entire apparatus is schematically shown in Figure 1-2. Orginally, the column consisted of a 2-foot length of Pyrex pipe and was to be packed with 6 x 6-mm. Pyrex Raschig rings. However, the results of a few trial runs showed that in such a pulsed column the isobutanol-water system would saturate easily. Hence, instead of packing, a perforated plate was inserted between the two sections of the glass column. The perforated plate was 1/16-inch thick stainless steel drilled with 19 holes of 5/32-inch diameter spaced at a center-to-center distance of 3/8 inch on an equilateral triangular pattern. These holes comprise a free area of 11.6% of the column cross-sectional area. "Fel-pro" compressed asbestos sheets were cut and used as gaskets.

The feed inlet lines were 1/4-inch O. D. stainless steel tubing, which extended up to the feed rotameters. The aqueous effluent line was also 1/4-inch stainless steel tubing up to the aqueous effluent valve. The rest of the feed and effluent lines were 1/4-inch O. D. copper tubing. The feed and effluent tanks were 55-gallon stainless steel drums. The feed valves and the aqueous effluent valve were 1/8-inch needle valves. All other valves were 1/4-inch globe valves, except for one solenoid valve which controlled the cooling water line

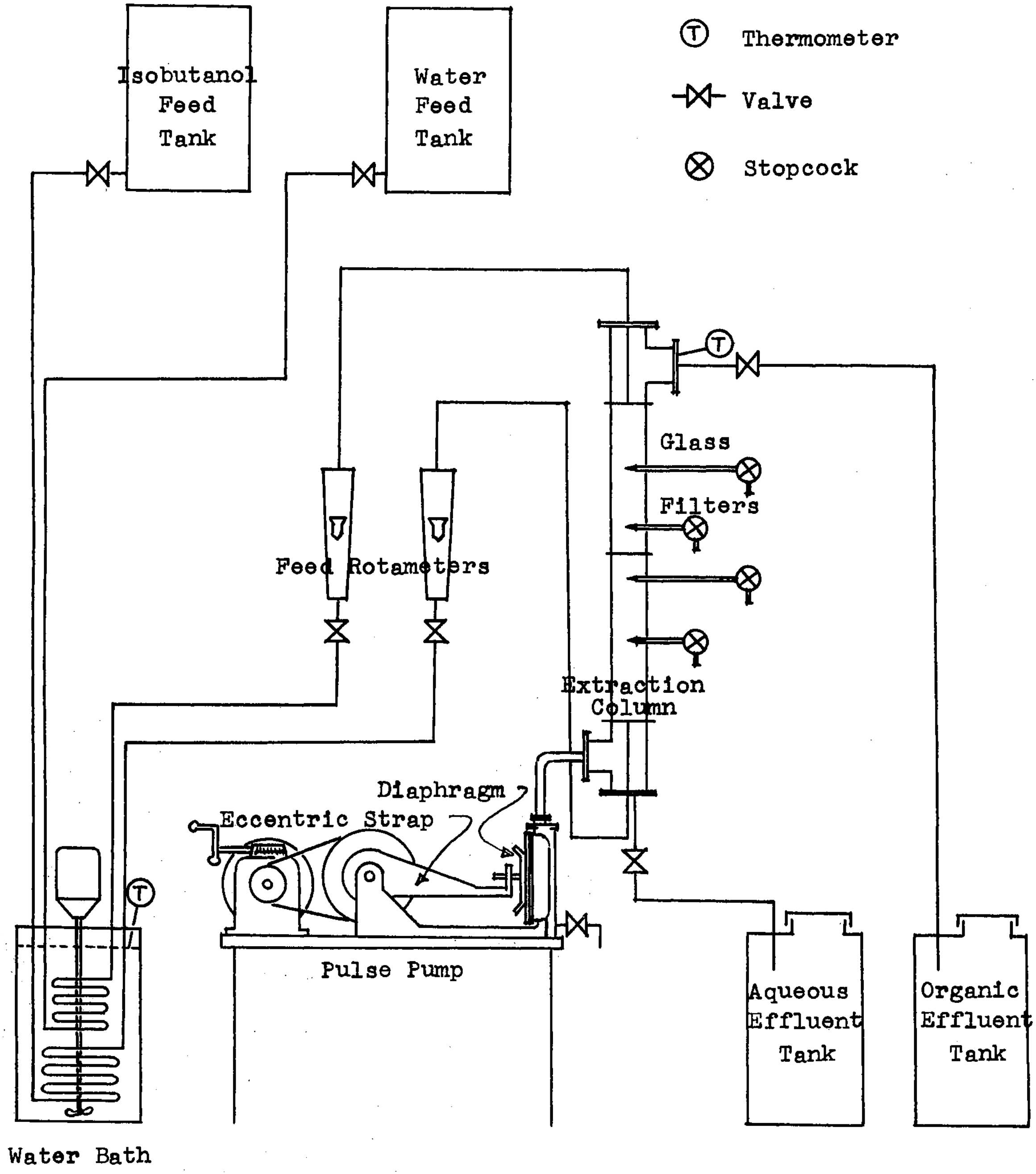
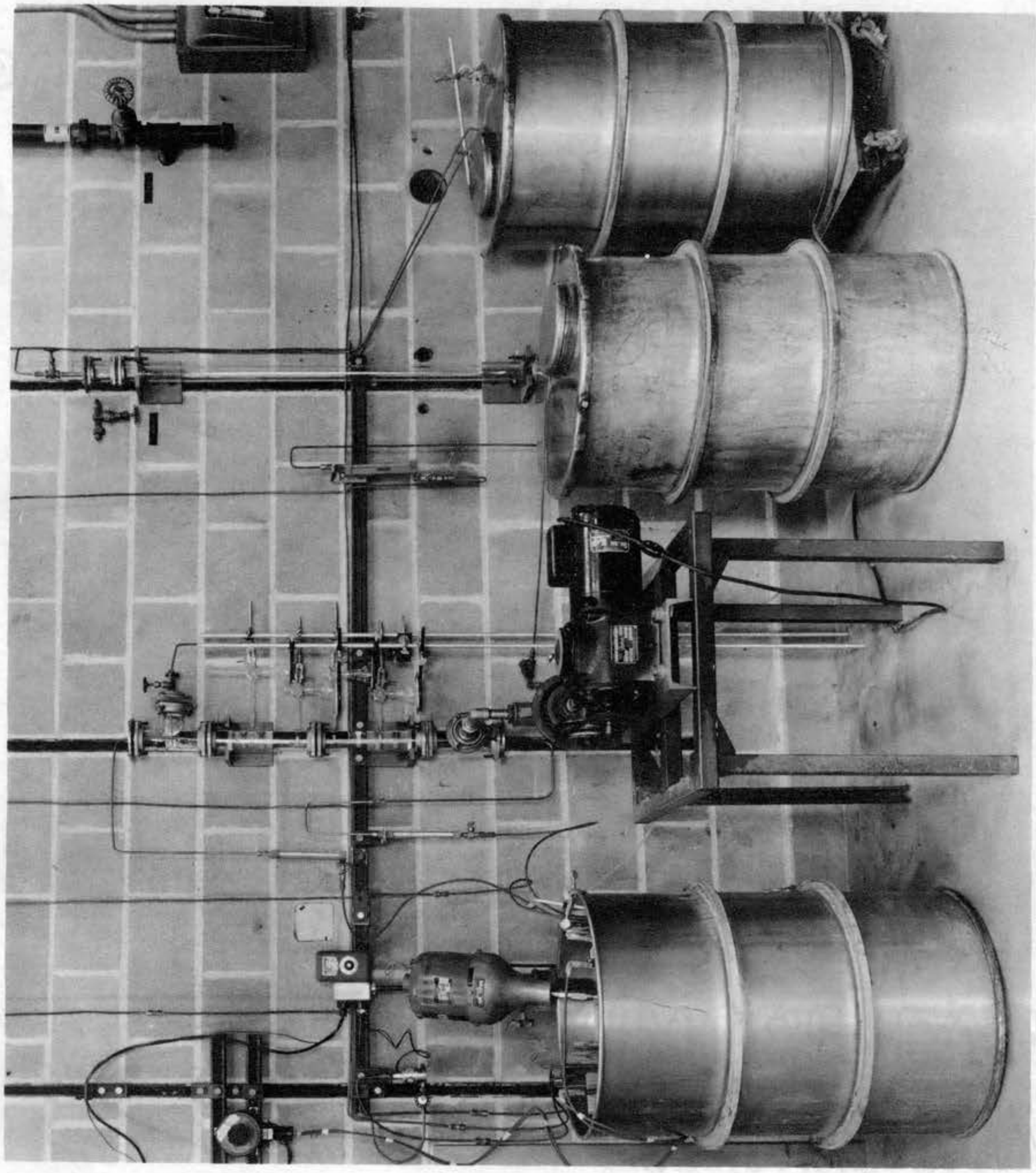


Fig. 1-a. Diagram of Experimental Apparatus

Fig. 1-b. Photograph of the Experimental Apparatus.



to the feed water bath.

The temperature in the column was maintained at approximately 25°C by immersing coils of the feed lines in a 55-gallon water bath which was maintained at the desired temperature by a cold-water line and a Cal-rod immersion heater connected to a Chromalox model AR 2529 thermostatic relay. A dial thermometer was attached to the column at the organic, or upper, effluent line, and the temperature was controlled by adjusting the water bath temperature such that the dial thermometer reading was 25°C. On hot days, when the room temperature was approximately 30°C, the water bath temperature was set at about 23.5-24°C to maintain the column at 25°C.

The feed tanks were located on a balcony approximately 12-1/2 feet above floor level. The organic feed inlet was 4 feet above floor level. Both feeds flowed by gravity head independently of the pulse pump. The feed flow rates were measured by Fischer and Porter precision-bore Flowrators: a 150-cc per min rotameter for the organic feed, and a 500-cc per min rotameter for the aqueous feed. After installation, the rotameters were calibrated with isobutanol and water, respectively.

Pulse Pump

The pulsator, or pulser, was a Denver Equipment Co. cast-iron body, neoprene diaphragm pump. The 5-1/2-inch diameter neoprene diaphragm was connected to an adjustable stroke eccentric. One ball check-valve was removed prior to use. The pump was driven by a 1/2-h. p. electric motor through a Graham variable speed transmission with an output range of 0 to 550 cycles per minute. In this study, the frequencies used were limited to a range of 0 to approximately 100 cycles per minute. Pulse amplitudes of 1/4 inch and 1/2 inch were studied. The pulser was connected to the column through 1-inch stainless steel piping.

Glass Filters

In the latter course of this work, four Ace glass filters of C porosity were fused into the column to sample the continuous phase and to provide a better picture of the concentration gradient within the column. The use of these filters was, however, limited to the case when the aqueous phase was continuous. It is believed that preferential sampling of the aqueous phase by the glass filters is due to preferential wetting of the sintered glass surface of the filter by the aqueous phase. When the organic phase was made continuous, films of the aqueous phase formed on the sintered glass surface, making it impossible to draw off either phase alone.

Dehydrator Column

A 1-1/2-inch column, 4 feet tall, was also assembled in an attempt to recover the spent isobutanol with anhydrous $CaSO_4$ (Drierite). However, its use was discontinued after a trial run gave unfavorable results. Approximately 4 lb of Drierite charged into the column was able to bring down the water concentration from 11.5% to 7.2% on the first throughput, at a feed rate of 50 ml per min. After 10 minutes, the concentration was 9.5%; after 15 minutes, 10.2%; and after 20 minutes, 10.5%.

The chemicals used in this study were technical-grade isobutanol from the Celanese Corporation of America, and once-distilled water from the 10-gallon per hour Barnstead still supplying distilled water to Building D-310.

PART IV. EXPERIMENTAL PROCEDURES

Start-up Procedure

On the day previous to a run, isobutanol and water were poured into their respective feed tanks if the remaining amounts in the tanks were deemed insufficient for the contemplated runs. This was done on the preceding day because it was noticed that filling the tanks on the same day caused minor fluctuations in the rotameter readings, particularly on the aqueous feed line. This must have been due to motion of the liquid inside the feed tank immediately after pouring in the feed.

Before a run was made, the water bath was adjusted to the required temperature (from 23.5°C to 26°C, depending on the ambient temperature) by means of the thermostatic relay. When the water batch had reached the desired temperature, the column was filled with water until it reached the upper interface level, which was approximately 1 inch above the aqueous feed inlet, if the water phase was to be the continuous phase. If water was to be dispersed, the water was allowed to fill the column only up to the lower interface level, which was approximately 1 inch below the organic feed inlet.

While the column was being filled with water, the pulse pump was switched on. The pulsing motion pushed out trapped air through the plate perforations on the up-stroke, and sucked in water on the down-stroke. The pump was directly connected to the bottom of the column; hence, the pump casing filled with water when feed water was charged into the column.

If the water phase was to be continuous, the column was filled with water up to the upper interface level, then the two effluent valves were opened, and the aqueous feed valve was set at the desired flow rate. There were two effluent valves leading from the bottom of the column: one was attached to the pump casing just below the diaphragm, and the other was attached to the effluent line leading from the column bottom. The pulse pump effluent valve was installed so that the liquid in the pump casing would not be stagnant; the valve allowed a continuous stream of aqueous effluent to discharge from the pump, thereby keeping the concentration of the liquid in the pump the same as that of the liquid at the bottom of the column. The other aqueous effluent valve was used to draw off samples from the bottom of the column and also to regulate the interface level when the column was in operation.

With the water at the upper interface level (water continuous), and the pump running at the desired pulse frequency and amplitude, the organic feed valve was opened to the desired flow rate as indicated by the organic feed rotameter. As the organic phase entered the column, the water level moved up due to the organic phase hold-up. The aqueous effluent valves were adjusted to maintain the desired level.

If the organic phase was to be continuous, the start-up procedure was slightly different. The column was filled with water up to the lower interface level, organic feed was let into the column until it had filled the upper part of the column up to the organic effluent outlet, and the organic feed valve was set at the desired flow rate as indicated by the rotameter reading. With the pulse pump running at the desired frequency, the water feed valve was opened and set at the desired flow rate.

Sampling Procedure

Samples were taken at least one-half hour after start-up, when the column was not pulsed, or at least one hour after start-up, when pulsed. The former corresponded to approximately 5 throughputs for the continuous aqueous phase, and this was deemed sufficient to achieve steady-state conditions. In this study, all the runs were made with water continuous, except for a few where wet isobutanol was continuous, and in these runs only the dispersed phase was analyzed.

When sampling through the glass filters, the stop-cocks connected to the glass filters were set so that samples could be collected in 50-ml Erlenmeyer flasks at such a rate that the flasks could be filled in 15 minutes. Samples obtained during the early portions of a run were discarded, and only the samples collected during the last 15 minutes were kept for analysis.

Sample Analysis

For both phases, sample analyses were accomplished by density weighings in 25-ml pycnometers. Density-concentration cruves were prepared by mixing known amounts of isobutanol and water at 25°C. Because the room temperature was variable from day to day, density-concentration curves (see Figure 2) for 26°C and 27°C were calculated from that at 25°C by the formula given by Heertjes, et. al. (11):

$$\frac{1}{\rho_{m,t}} = \frac{1}{\rho_{m,25}} + (1 - q)\left(\frac{1}{\rho_{w,t}} - \frac{1}{\rho_{w,25}}\right) + q\left(\frac{1}{\rho_{i,t}} - \frac{1}{\rho_{i,25}}\right), \tag{39}$$

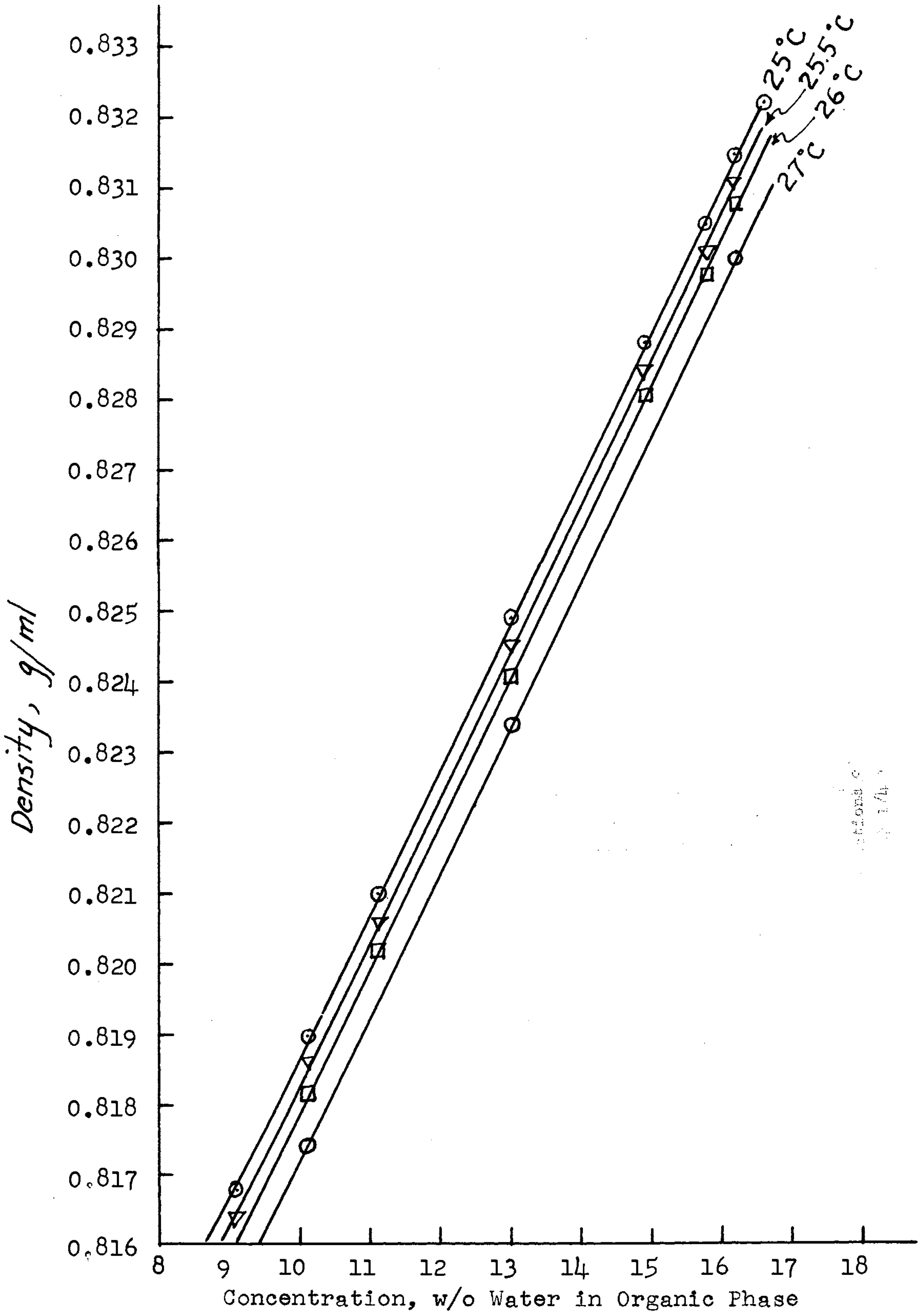


Fig. 2-a. Concentration-Density Diagram for the Organic Phase.

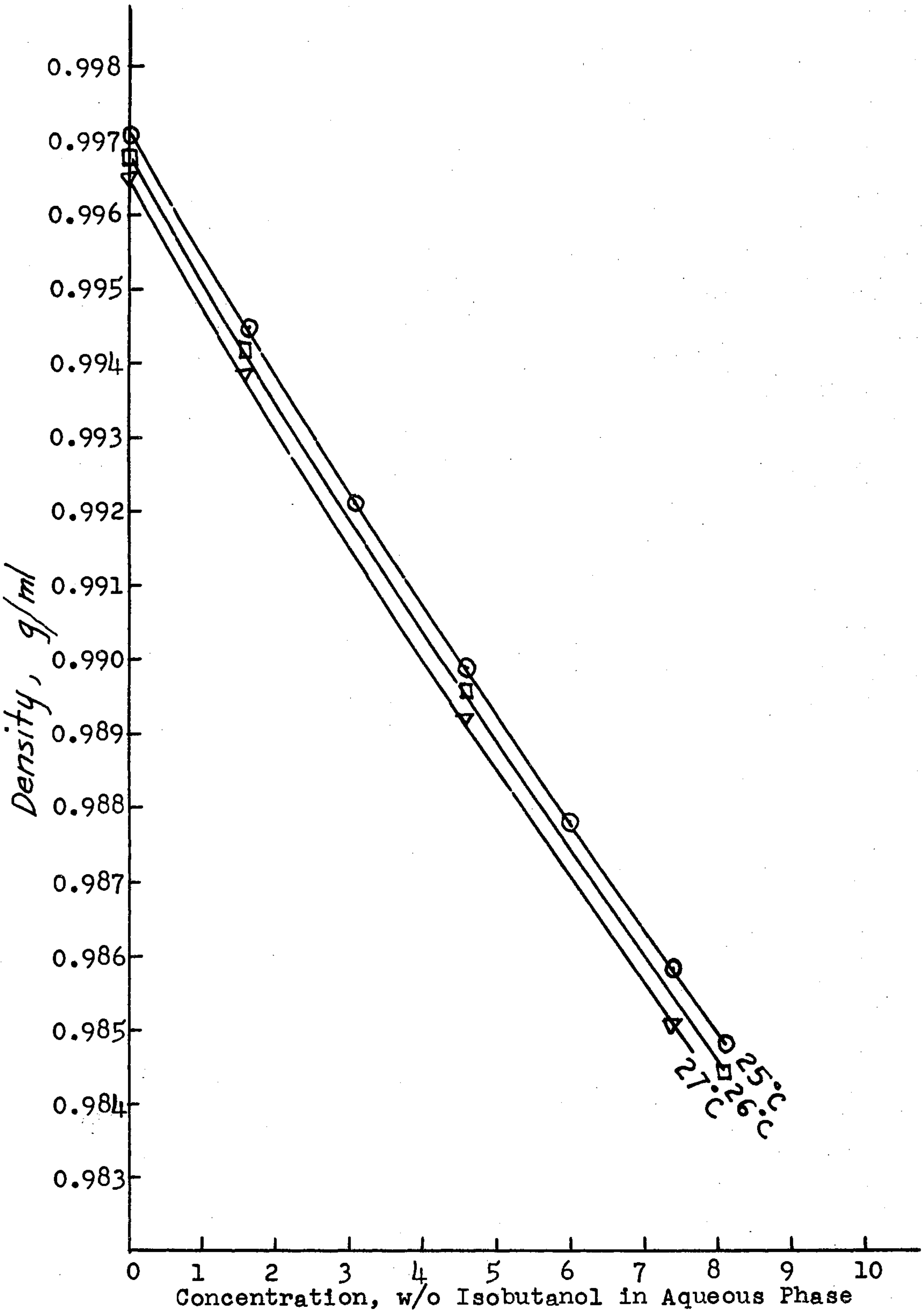


Fig. 2-b. Concentration-Density Diagram for the Aqueous Phase.

where:

ρ = density

q = weight fraction isobutanol

m, w, i, t, 25 = subscripts denoting: mixture, water, isobutanol, temperature, and 25°C, respectively.

The room temperature did not drop below 25°C because of steam heating during the cold season.

The room temperature was recorded and the sample temperature in the pycnometer was taken to be approximately half-way between 25°C and the room temperature. The error involved in this approximation is believed to be less than 0.1% concentration by weight. Sample temperatures were occasionally checked by a special pycnometer with a thermometer cap. The temperature obtained agreed quite well with the estimated temperature.

Hold-up Measurement

Two methods of measuring the dispersed phase hold-up were used. In the first method, when the column was deemed to be at steady-state, the interface level was noted and the feed and effluent valves were shut off as quickly as possible. After the dispersed phase hold-up had settled-out, the interface level was again noted, and the difference in interface level was converted to volumetric hold-up.

In the second method, after the valves were shut off and the dispersed phase hold-up had settled out, the continuous phase feed valve was opened, and enough of the continuous phase was let into the column to restore the interface level to its original position. The dispersed phase liquid pushed out of the column was collected, and the volume collected gave the dispersed phase hold-up directly.

The first method was used at low values of the dispersed phase hold-up and is believed to be the more accurate of the two methods. The second method, however, had to be resorted to at high values of the hold-up for this reason: the interface level, upon settling out of the dispersed phase, would go down to about or below the column joint, and could not be measured because the clamps holding the column sections together obstructed visual observation.

PART V. EXPERIMENTAL RESULTS

Method of Computation

The method of computation followed was essentially the same as that of Colburn and Welsh (5).

Consider an extraction column in which the flow rate of one liquid phase is L, weight per unit time. As this phase moves through the column over a small distance dh, the amount of solute transferred into it is

$$N' = \frac{L\,dc}{A}, \qquad (40)$$

where:

N' = rate of solute transfer per unit cross-sectional area of the column

L = flow rate of the phase under consideration, weight per unit time

A = cross-sectional area of the column

dc = change in solute concentration, weight fraction, over the short distance dh.

This rate of mass transfer can also be expressed by

$$N' = ka(c_s - c)dh, \qquad (41)$$

where:

N' = rate of solute transfer per unit cross-sectional area of column

k = mass transfer coefficient for this phase at this particular section of the column

a = effective interfacial, or contact, area per unit volume of the column

$c_s - c$ = concentration driving force

dh = differential height of column.

The "drift-term," $(1 - c)_f$, analogous to $(1 - y)_f$ in equation (11-a), is omitted from equation (41) because the diffusion is assumed to be approximately equi-molal in both directions.

Combining equations (40) and (41):

$$L\,dc = ka(c_s - c)A\,dh. \tag{42}$$

For the partially miscible system isobutanol-water, the amount of material leaving each phase just about balances the amount of material entering into that phase. We may therefore assume L to be approximately constant throughout the column, rather than L(1 - c) as indicated by equation (11-a) (See Appendix F).

Although ka may not be truly constant over the entire column, we assume an average value in order that equation (42) can be integrated:

$$\frac{L}{A}\int_{c_1}^{c_2}\frac{dc}{c_s - c} = ka\int_{0}^{h} dh\ , \tag{43}$$

where:

c_1 and c_2 = terminal concentrations of the liquid phase

h = column height.

Following Colburn (5), the integral on the left-hand side of equation (43) can be considered as equal to the number of transfer units:

$$NTU = \int_{c_1}^{c_2}\frac{dc}{c_s - c} \tag{44}$$

At a given temperature, c_s is constant, and equation (44) can be integrated to give

$$NTU = \ln \frac{c_s - c_1}{c_s - c_2}. \tag{45}$$

If the feed is essentially pure liquid, $c_1 = 0$, and equation (45) simplifies to

$$NTU = \ln \frac{c_s}{c_s - c_2}, \tag{46}$$

where:

c_s = saturation concentration

c_2 = effluent concentration of theparticular phase.

This is the form used in this study.

Substituting equation (44) into equation (43):

$$\frac{L}{A} (NTU) = ka\ h. \tag{47}$$

upon rearrangement,

$$\frac{L}{A} = ka(HTU). \tag{48}$$

HTU is the height of a transfer unit defined by

$$HTU = \frac{h}{NTU}, \tag{49}$$

where:

h = effective height of the column.

These equations may be used for either the continuous or the dispersed phase. The subscripts C and D will be used to differentiate one from the other.

For the pulsed runs, the number of transfer units, NTU were used to correlate the data, rather than HTU's. The reasons for this choice were two-fold: firstly, the NTU's are increasing functions of the pulse operating variables, frequency and amplitude, at least within the range of operation in this study; and secondly, according to equation (47), the volumetric mass transfer coefficient, ka, is directly proportional to NTU; therefore, NTU values can be easily converted to mass transfer coefficients by multiplication with a suitable constant. In this work, however, NTU values were retained because they are easier to handle and there seems to be no advantage gained in converting to ka values.

The results of this study also showed that, for this system, and for this column, the effect of pulsation on mass transfer efficiency can best be correlated by expressing the increase in mass transfer, due to pulsation, as Δ NTU, which is given by

$$\Delta \text{ NTU} = \text{NTU} - \text{NTU}_o, \tag{50}$$

where:

NTU = number of transfer units at the given pulse frequency and amplitude

NTU_o = NTU at zero pulse frequency.

Δ NTU can then be plotted against the pulsed column variables.

For a given set of continuous and dispersed-phase flow rates, multiplication of equation (50) by a suitable constant leads to

$$\Delta \text{ ka} = \text{ka} - \text{ka}_o. \tag{51}$$

Equations (50) and (51) are used with the proper subscript C, or D, to denote either the continuous phase, or the dispersed phase.

Preliminary Runs

Preliminary runs No. 5 to 35 were made without pulsing, without column packing, andwithout a perforated plate, in the same 2-inch diameter column used subsequently as a pulsed column. Effluent analyses were made by the density-concentration method explained in Part IV. However, for these preliminary runs, instead of 25-ml pycnometers, weighings were made in 25-ml volumetric flasks, four flasks per phase sample, and the average of the four flasks taken.

HTU_C values from these preliminary runs were calculated by using equations (46) and (49), and are plotted in Fig. 3 as linear functions of the continuous phase flow rate L_C, with dispersed phase flow rate L_D as parameter, according to Rubin and Lehman's HTU-surface concept (18). In Fig. 4, HTU_C is plotted on log-log coordinates as a function of the flow ratio L_C/L_D. It can be seen that the data can be represented by a relationship of the form

$$HTU_C = \propto\left(\frac{L_C}{L_D}\right)^n , \tag{52}$$

where the exponent n is approximately 1.0 with a probable deviation of ±0.1. On the other hand, Fig. 5 shows that HTU_D is approximately constant, as expected.

While HTU_C may perhaps be more accurately represented as a linear function of L_C and $1/L_D$, the results of these preliminary runs show that, for this system and column, HTU_C may be expressed as a power function of the flow-ratio L_C/L_D, with a reasonable degree of accuracy.

To explain why HTU_D should be independent of flow rates, it has been suggested (5, 18) that the interfacial, or contact, area per unit volume, a, in equation (6) or (41), is most probably directly proportional to the dispersed phase flow rate L_D. This seems to be a reasonable assumption because the dispersed-phase hold-up can be observed to increase with increasing L_D. Furthermore, the smaller

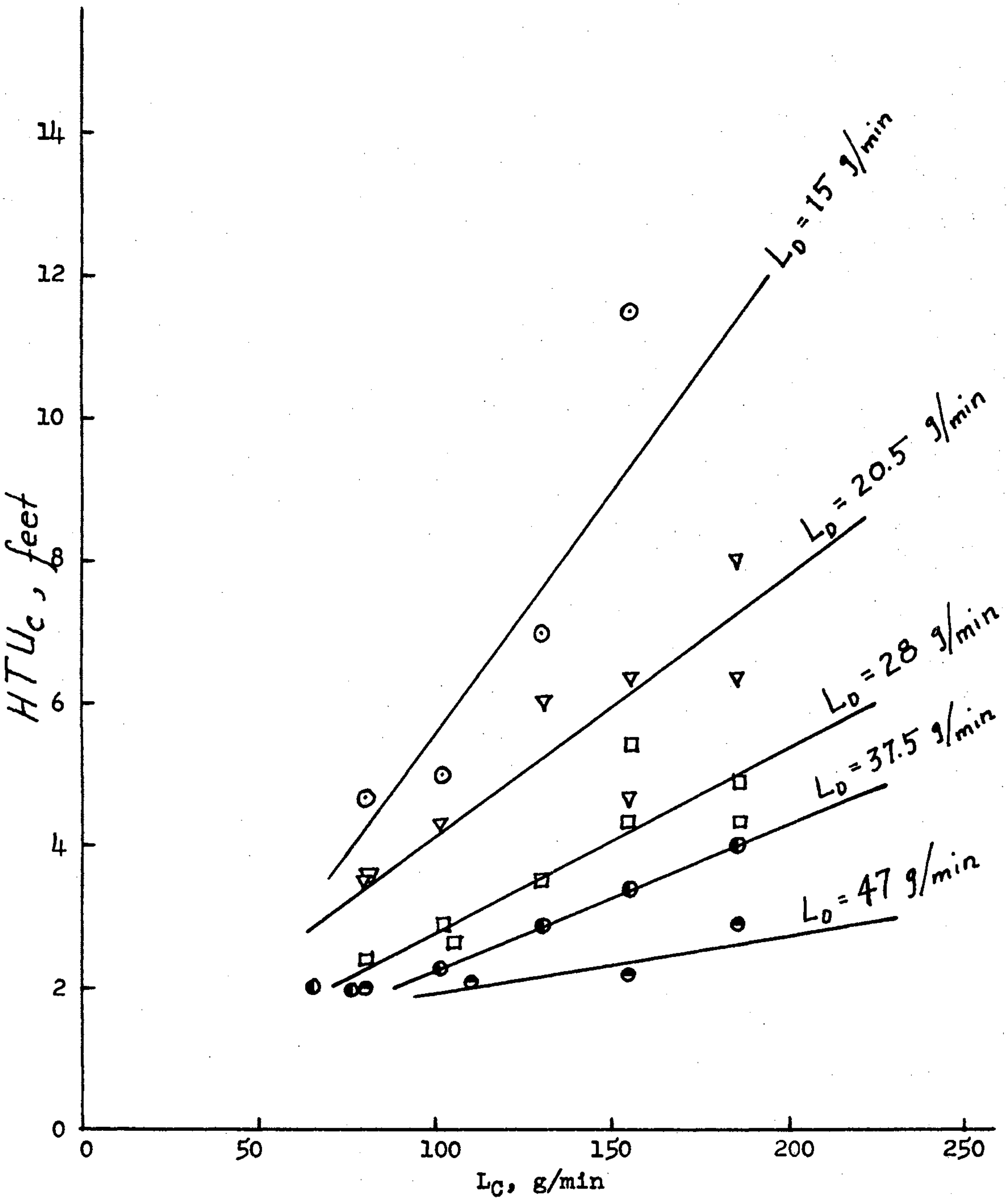


Fig. 3. HTU of the Continuous Phase as Linear Functions of the Flow Rates.

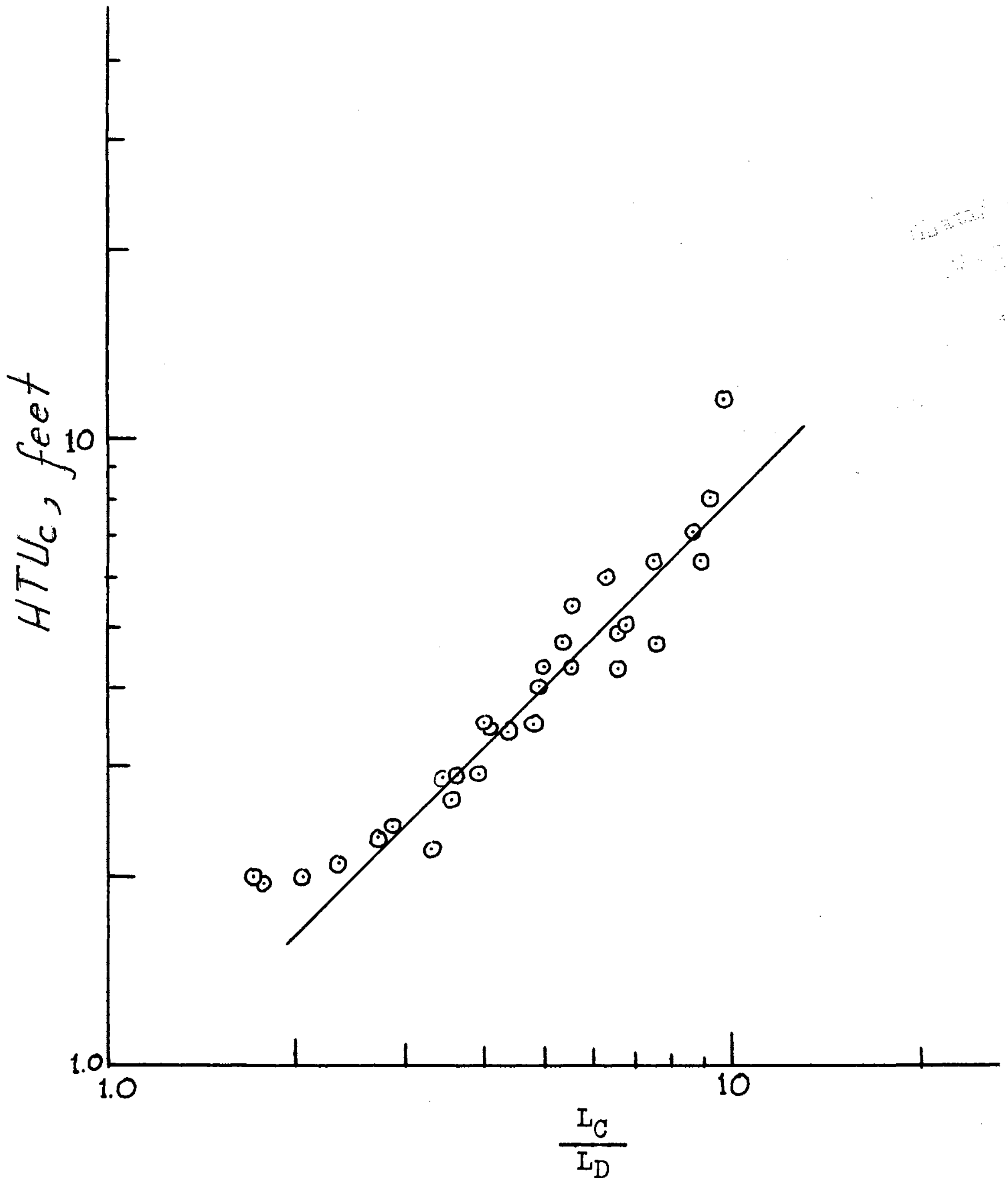


Fig. 4. HTU of the Continuous Phase as a Power Function of the Flow Ratio.

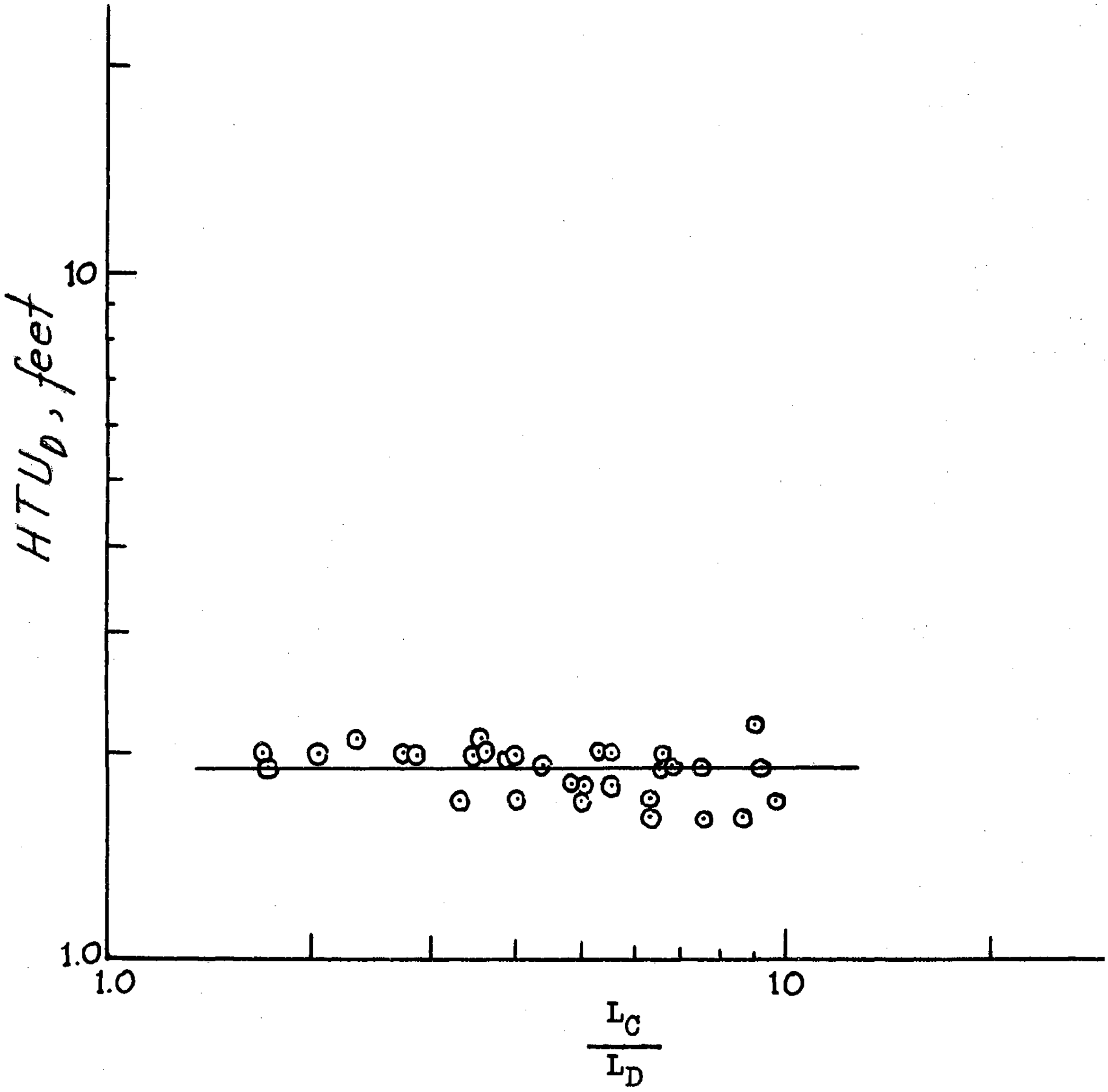


Fig. 5. HTU of the Dispersed Phase as a Function of the Flow Ratio.

size of the droplets formed at higher L_D should provide greater interfacial area, a, at higher L_D.

According to equation (48), for the dispersed phase

$$HTU_D = \frac{1}{k_D a} \left(\frac{L_D}{A}\right). \qquad (53)$$

If a is directly proportional to L_D, then

$$\frac{L_D}{a} = \text{constant}. \qquad (54)$$

Taking an average value of the coefficient k_D over the entire column, equation (53) reduces to:

$$HTU_D = \text{constant}. \qquad (55)$$

On the other hand, for the continuous phase, if HTU_C is taken to be a power function of the flow-ratio L_C/L_D, as in equation (52), then we may write:

$$k_C a = \alpha \frac{L_C}{A} \left(\frac{L_D}{L_C}\right)^n. \qquad (56)$$

The experimental results of previous investigators (2, 5, 6, 12) and of this work seem to indicate that the exponent n lies between 0 and 1. If the interfacial area, a, for the continuous phase is assumed to be identically equal, or at least proportional, to the interfacial area for the dispersed phase, equation (56) may be re-written:

$$k_C = \frac{\alpha'}{A} \left(\frac{L_C}{L_D}\right)^{1-n}. \qquad (57)$$

When $n<1$, k_C increases as L_C increases, and increases as L_D decreases.

If, as Rubin and Lehman (18) suggest, HTU_C is a linear function of L_C and $1/L_D$, i. e.,

$$HTU_C = b + cL_C + \frac{d}{L_D} + e\frac{L_C}{L_D} \qquad (58)$$

and as before, interfacial area, a, is proportional to L_D; then, from equations (48) and (54):

$$k_C = \frac{L_C}{AL_D} \cdot \frac{1}{b' + c' L_C + \frac{d'}{L_D} + e' \frac{L_C}{L_D}}, \quad (59)$$

which can be simplified to

$$k_C = \frac{1}{A} \cdot \frac{1}{b' \frac{L_D}{L_C} + c' L_D + \frac{d'}{L_C} + e'}, \quad (60)$$

which indicates, as does equation (57), that k_C increases as L_C increases, and increases as L_D decreases.

Thus, it seems that increasing the continuous phase flow rate favors mass transfer in the continuous phase, possibly because of increasing turbulence; and that mass transfer in the continuous phase in also favored by decreasing L_D, possibly because of the larger droplets formed which may also contribute to greater turbulence in the continuous phase.

In this study, the exponent n in equations (56) and (57) was found to have a value approximately equal to 1.0, which means that the flow rates do not affect the continuous phase mass transfer, if interfacial area a is indeed proportional to L_D. Colburn andWelsh (5), however, found n equal to 0.75 for the same isobutanol-water system, isobutanol dispersed, in a column packed with 1/2-inch clay Raschig rings. Packing probably tends to make the effect of turbulence more pronounced. A more detailed comparison between the results from these two studies is given in Appendix G.

Pulsed Runs

The data for the pulsed runs from run No. 35 to run No. 64, Series

A, and from No. 11 to No. 80, Series B, are plotted in Fig. 6. All of these runs were made with the perforated plate, described in Part III inserted at the middle of the column. All runs were made at flow rates of 130 ml per min and 59 ml per min for the aqueous and organic phases, respectively, except for runs No. 68-80, Series B, which were made at 200 ml per min and 71 ml per min for the aqueous and organic phases, respectively. On the plots, and in the Appendices, these flow rates are designated by the numbers 6.0-11.0 and 8.5-12.0, which refer to the rotameter readings. The pulse amplitude was fixed at approximately 1/4 inch, measured on the column itself.

In Figs. 6-a and 6-b, Δ NTU$_C$ and Δ NTU$_D$ are plotted as functions of the pulse frequency f, and in Fig. 6-c, the increase in dispersed phase hold-up, due to pulsation, Δ H, in ml, is plotted as a function of the pulse frequency.

There are two lines in Fig. 6-a. The lower line represents Δ NTU$_C$ from runs No. 35-64, Series A, when samples were taken after only 15 minutes to one-half hour. It is believed now that this length of time was not sufficient for the column to achieve steady-state conditions, hence, the lower Δ NTU$_C$ values for these runs. Δ NTU$_D$ values for these runs, however, agreed with subsequent values, probably because of the higher linear throughput of the dispersed organic phase, approximately 2 ft in 10 sec (it takes approximately 10 sec for a dispersed organic phase droplet to rise from top to bottom of the column), as compared to that of the aqueous phase, 0.21 ft per min which corresponds to about 3 throughputs in one-half hour. The upper line in Fig. 6-a represents runs when samples were taken at least one hour after start-up.

According to Fig. 6, the following relationships may be written:

$$\Delta\ NTU_C = \alpha\ f^n \tag{61}$$

$$\Delta\ NTU_D = \beta f^n \tag{61-a}$$

$$\Delta H = \gamma f^n\ , \tag{61-b}$$

where the value of the exponent n lies between 2.5 and 3.5, which the probably average value being $n = 3.0$.

At higher pulse frequencies ($f > 45$, approximately), the ΔNTU_C and ΔNTU_D values do not show as much increase with pulse frequency as do the ΔH values. It is possible that at these high frequencies, some of the very small droplets reach an equilibrium, or saturation, condition before they coalesce at the interface; hence, they do not contribute very much to the total mass transfer.

At very high frequencies ($f > 70$, approximately), the ΔH values fall below the line, probably because at these very high frequencies the column operation starts to become unstable and some of the smaller-sized dispersed phase droplets are swept out with the continuous phase effluent.

The main conclusion to be drawn from these plots is, however, the similarity of the dependence of ΔNTU_C and ΔNTU_D on pulse frequency, and their similarity to the variation of ΔH with frequency. If the volumetric interfacial area, a, is proportional to the dispersed phase hold-up, it would seem that the increase in mass transfer due to pulsation is, for the most part, due to the increase in the interfacial area available for mass transfer. This is the conclusion reached by Feick and Anderson (8). They compared the mass transfer rates of two solutes, whose main diffusional. resistances lay in the continuous, and dispersed phases, respectively. Because the increase in mass transfer, due to

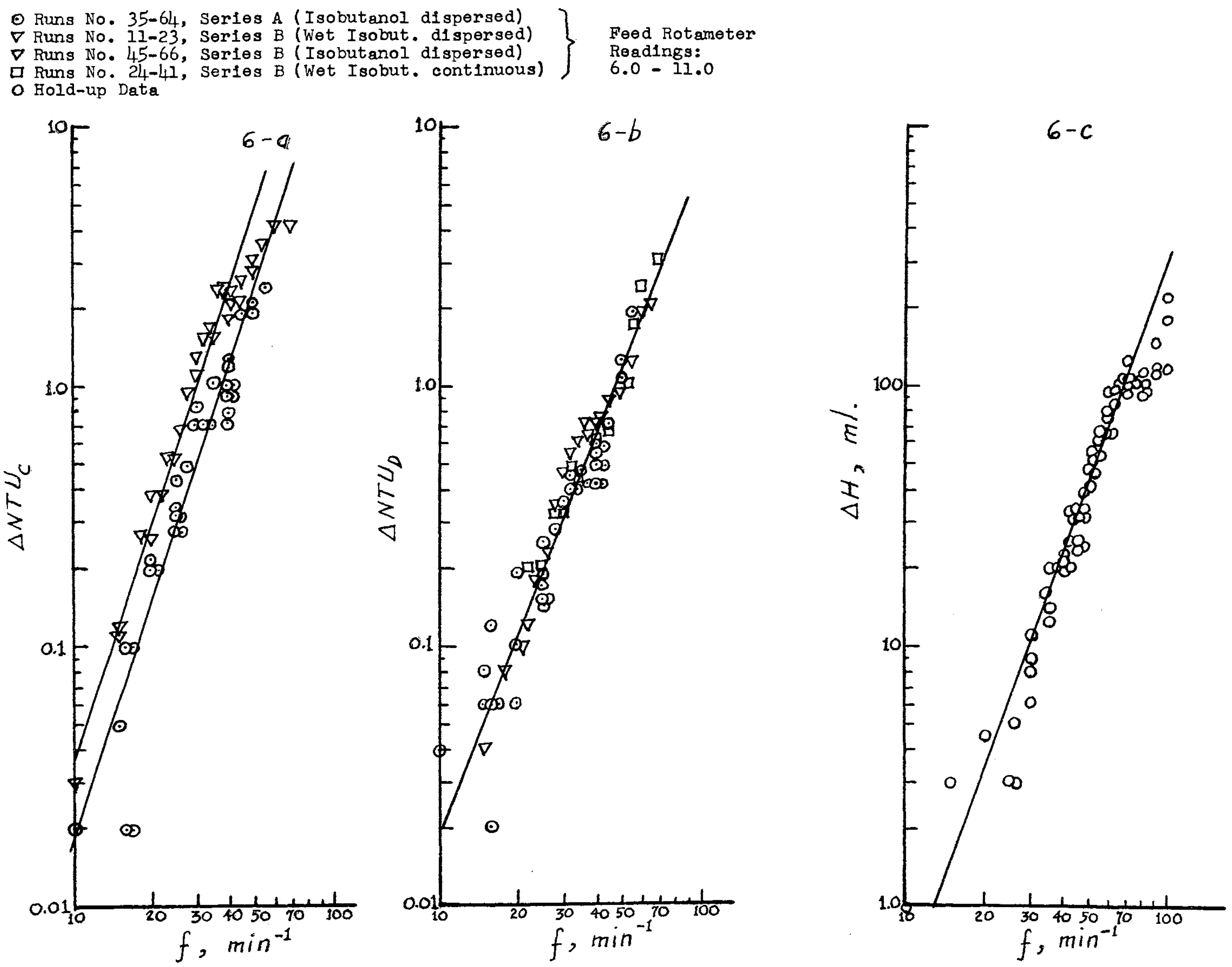


Fig. 6. ΔNTU_C, ΔNTU_D, and ΔH as Functions of the Pulse Frequency f at a Pulse Amplitude of 1/4 inch.

pulsation, was the same in order of magnitude for both solutes, they concluded that "the chief effect of the agitation is on the area of contact between the phases."

The next series of runs, No. 81-106, was made to determine the effect of flow rates on mass transfer efficiency when the column was pulsed. As in the previous set of runs, the plate was located at the middle of the column. Runs No. 107-128 were also made to determine the effect of flow rates under pulsed conditions, with the sole difference that the plate was now located at the bottom of the column.

At a given frequency, values of ΔNTU_C were plotted against flow ratio (as in Fig. 7) and the data seemed to be best correlated by the equation

$$\Delta NTU_C = \alpha \left(\frac{L_D}{L_C}\right)^{0.8} \qquad (62)$$

at a given pulse amplitude and frequency.

In Fig. 8, $\Delta NTU_C \, (L_C/L_D)^{0.8}$ are plotted against pulse frequency f for both sets of runs (No. 81-106 and 107-128). The data can be correlated by the equation

$$\Delta NTU_C = \alpha' \left(\frac{L_D}{L_C}\right)^{0.8} f^{3.0}, \qquad (63)$$

where:

f = pulse frequency in pulses, or cycles, per minute

α' = 0.10×10^{-3} for the runs with the plate at the middle of the column

α' = 0.03×10^{-3} for the runs with the plate at the bottom of the column.

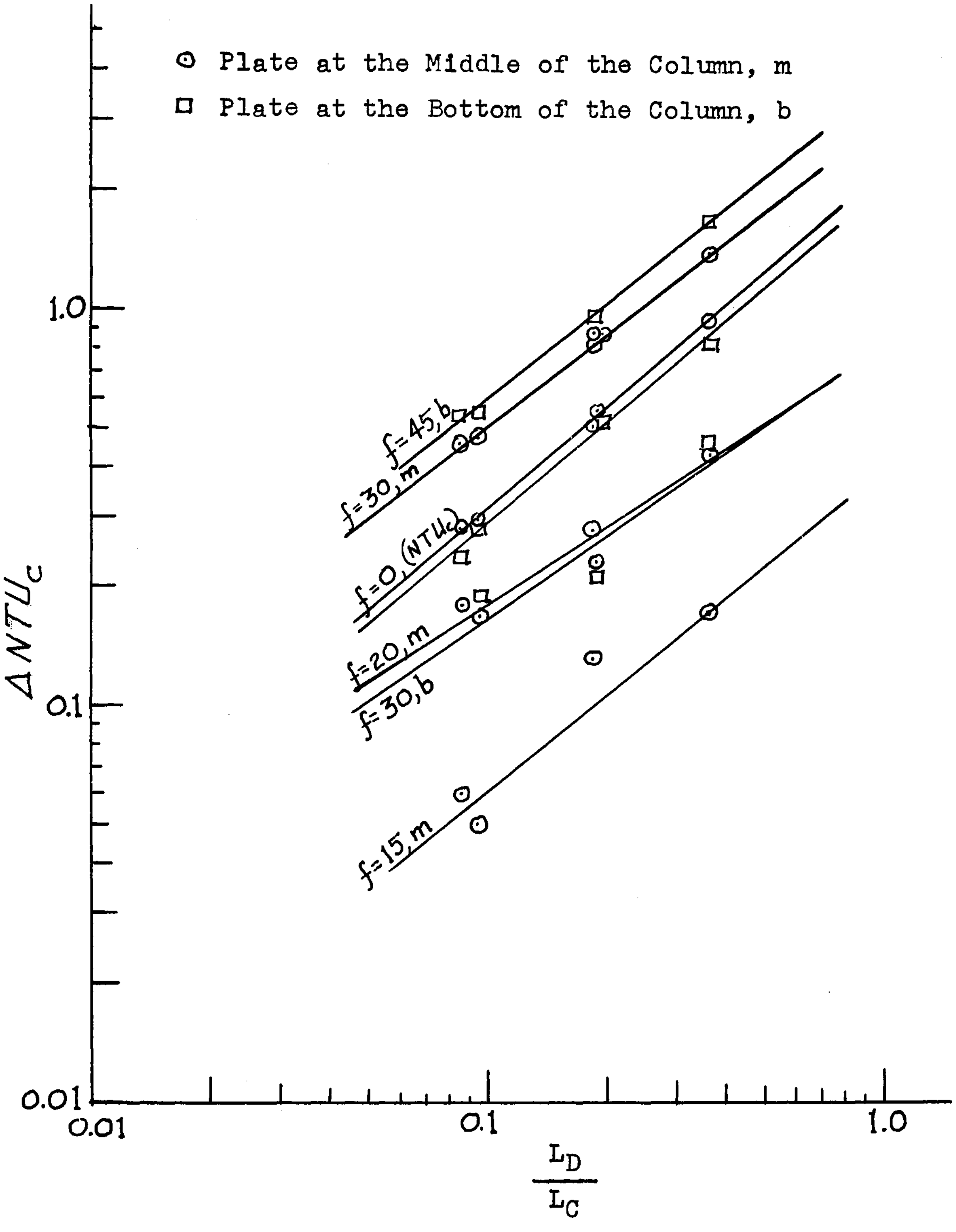


Fig. 7. Δ NTU$_C$ as a Function of the Flow Ratio at Constant Pulse Frequency.

The values of ΔNTU_D apparently do not depend on the flow rates, but they show more scatter than the values of ΔNTU_C. The following correlation may be written for the dispersed phase ΔNTU:

$$\Delta NTU_D = \beta f^{3.0}, \qquad (64)$$

where:

f = pulse frequency in pulses per minute

$\beta = 0.02 \times 10^{-3}$ for the runs with the plate at the middle

$\beta = 0.002 \times 10^{-3}$ for the runs with the plate at the bottom.

It should be noted that the plate perforations were large enough so that a truly continuous phase was maintained at all times in all of the runs.

All of these data, taken from the pulsed and unpulsed runs, column with perforated plate, can be summarized in the following equations: for the continuous phase, at a column pulse amplitude of approximately 1/4 inch:

$$NTU_C = \alpha_1 \left(\frac{L_D}{L_C} \right)^{0.9} + \alpha_2 \left(\frac{L_D}{L_C} \right)^{0.8} f^{3.0}, \qquad (65)$$

and for the dispersed phase, also at a pulse amplitude of 1/4 inch:

$$NTU_D = \beta_1 + \beta_2 f^{3.0}, \qquad (66)$$

where:

$\alpha_1 = 2.5$ for both plate positions

$\beta_{\cancel{2}1} = 1.0$ for both plate positions

$\alpha_2 = \alpha'$ in equation (63)

$\beta_2 = \beta$ in equation (64).

A few runs were made at a pulse amplitude of 1/2 inch (Runs No. 129-140). However, because of the difficulty in adjusting the pulse amplitude accurately, the data have not been correlated. Furthermore, because of inconsistencies in the data for the dispersed phase ΔNTU at A = 1/2 inch, only those for the continuous phase are shown in Fig. 8.

Glass-filter Data

In order to obtain a better picture of the concentration gradient within the column, Ace glass filters of C porosity were fused into the column at four points to sample the continuous phase. Unfortunately, these glass filters could sample only the aqueous continuous phase, as mentioned in Part III. All runs starting from run No. 81, Series B, were made with glass filters on the column. Comparison of these runs with previous runs without the glass filters showed an increase in the continuous aqueous effluent due to the presence of the glass filters of at most 0.1% by weight concentration. For the dispersed phase, any difference due to the glass filters could not be detected and probably was within the experimental error in column operation and sample analysis.

Plate at the Middle of the Column

Perhpas the most outstanding feature of the glass-filter curves (Figs. 9 to 13) was the considerable end effect found at the continuous phase inlet. The end effect found in this study paralleled that found by Geankoplis and co-workers (9, 10). This end effect also increases with increasing mass-transfer efficiency, and increases with dispersed phase flow rate and with decreasing continuous phase flow rate.

It can also be seen that, for the unpulsed runs, there is an apparent discontinuity at the perforated plate which shows considerable mass transfer into the continuous phase taking place at this section of

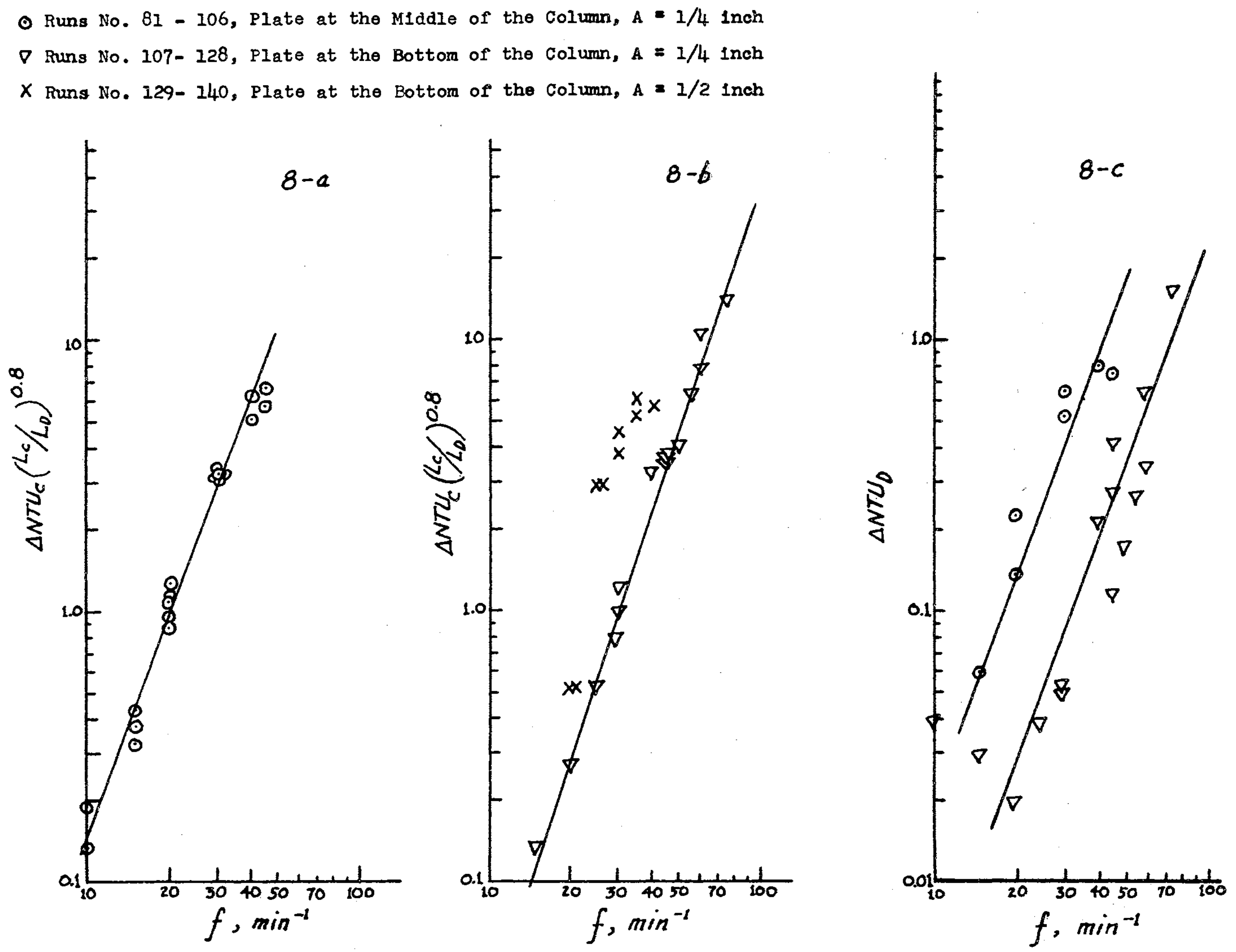


Fig. 8. ΔNTU_C and ΔNTU_D as Functions of Flow Ratio and Pulse Frequency f.

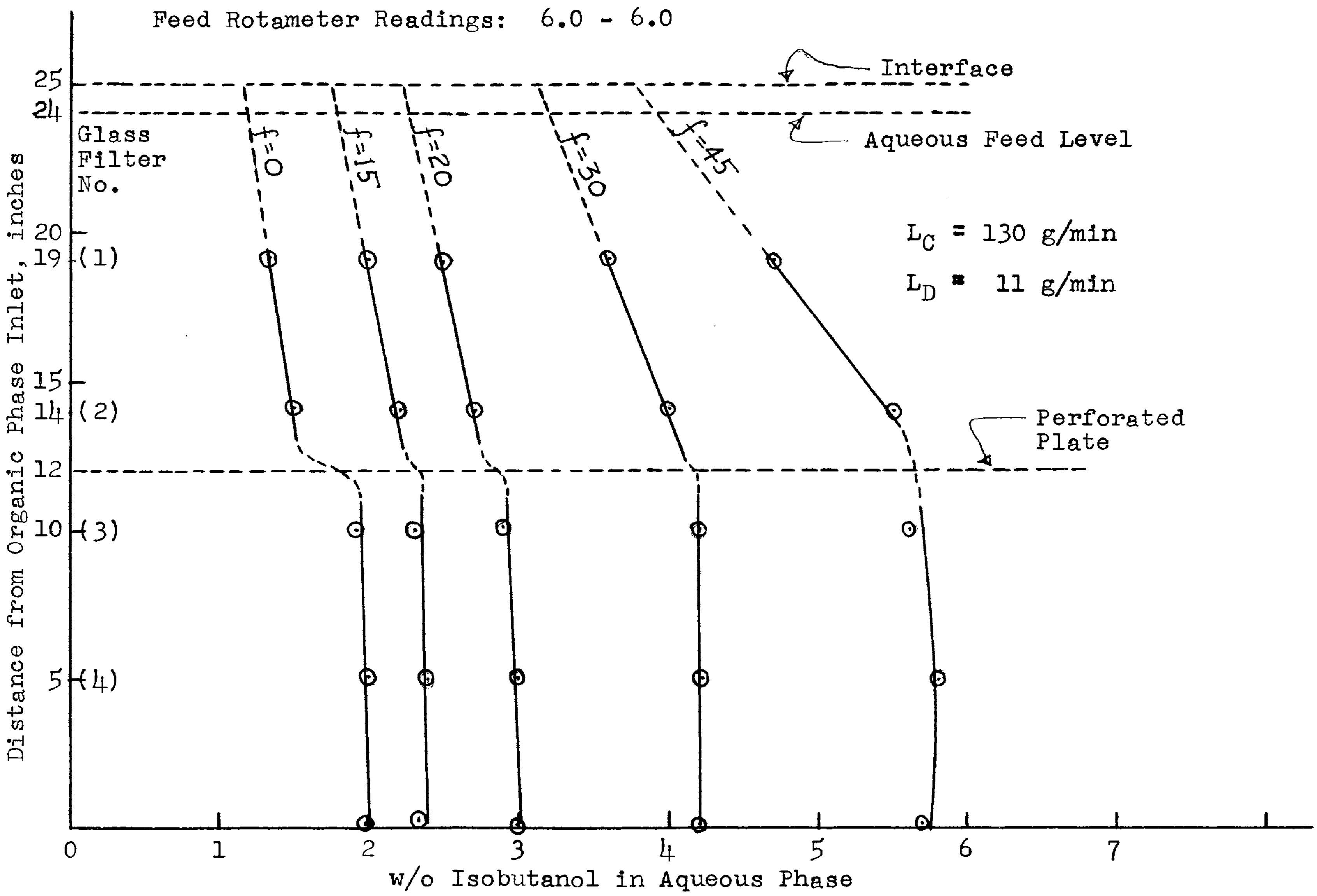


Fig. 9. Continuous Phase Profile, Plate at the Middle.

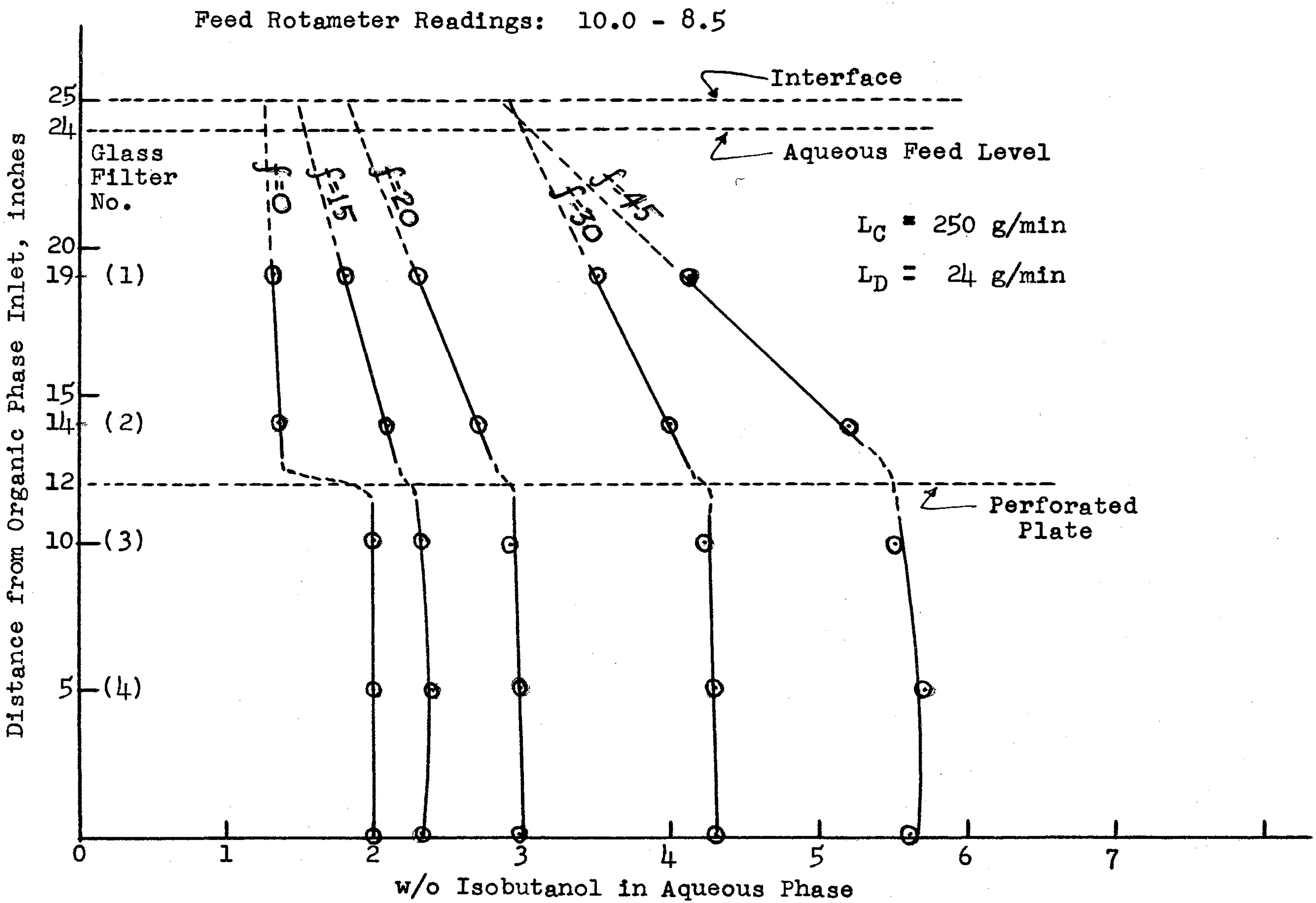


Fig. 10. Continuous Phase Profile, Plate at the Middle.

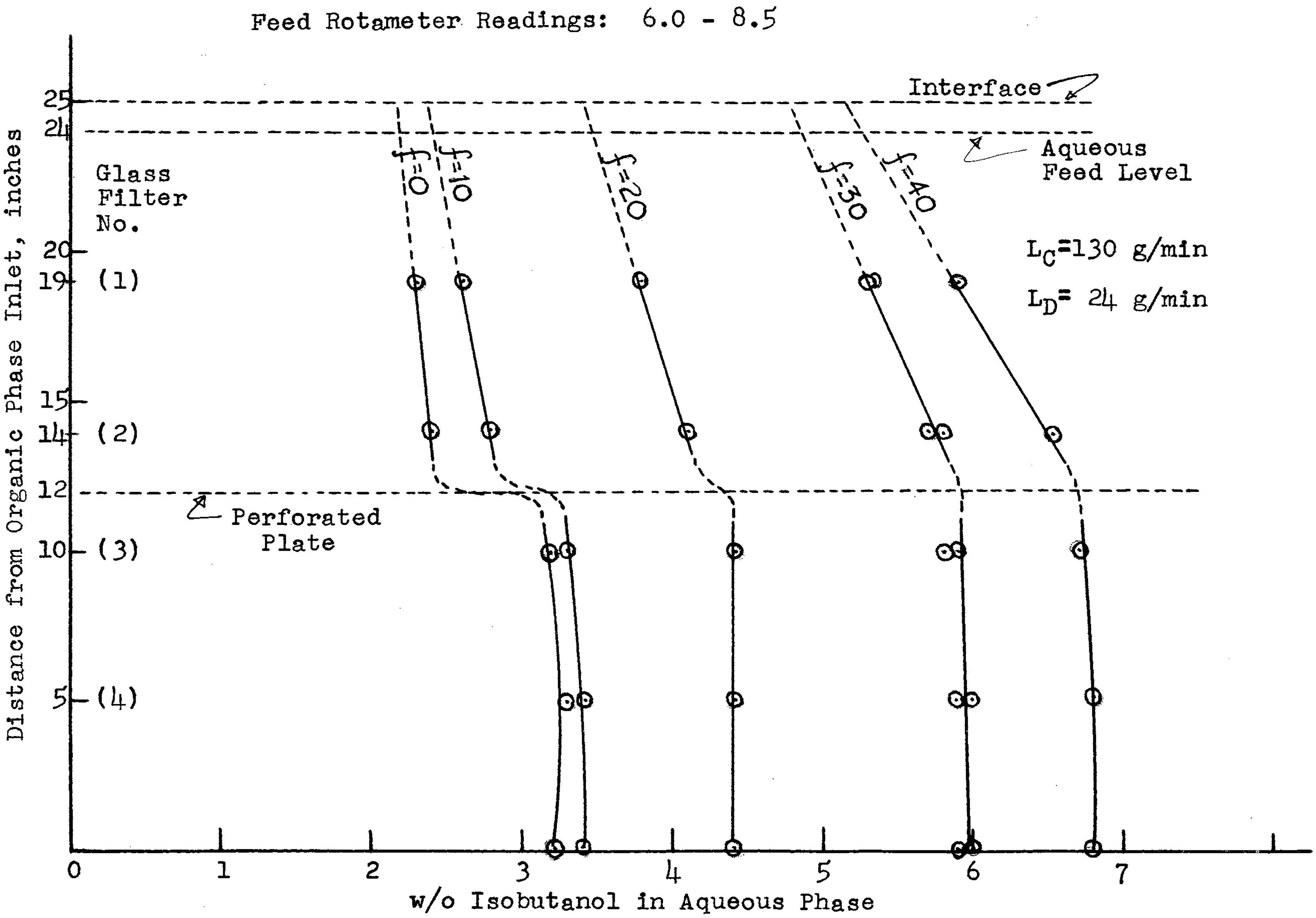


Fig. 11. Continuous Phase Profile, Plate at the Middle.

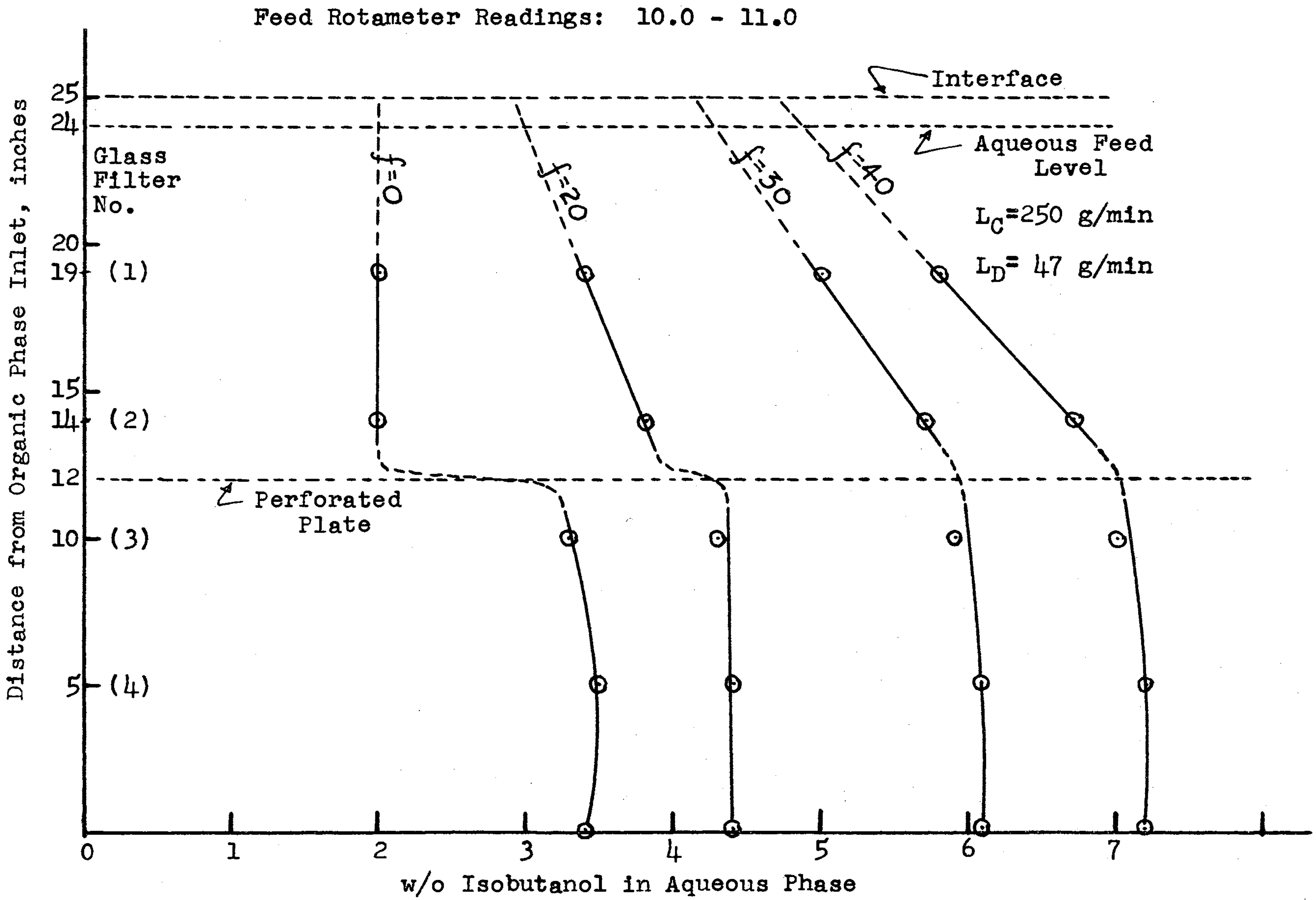


Fig. 12. Continuous Phase Profile, Plate at the Middle.

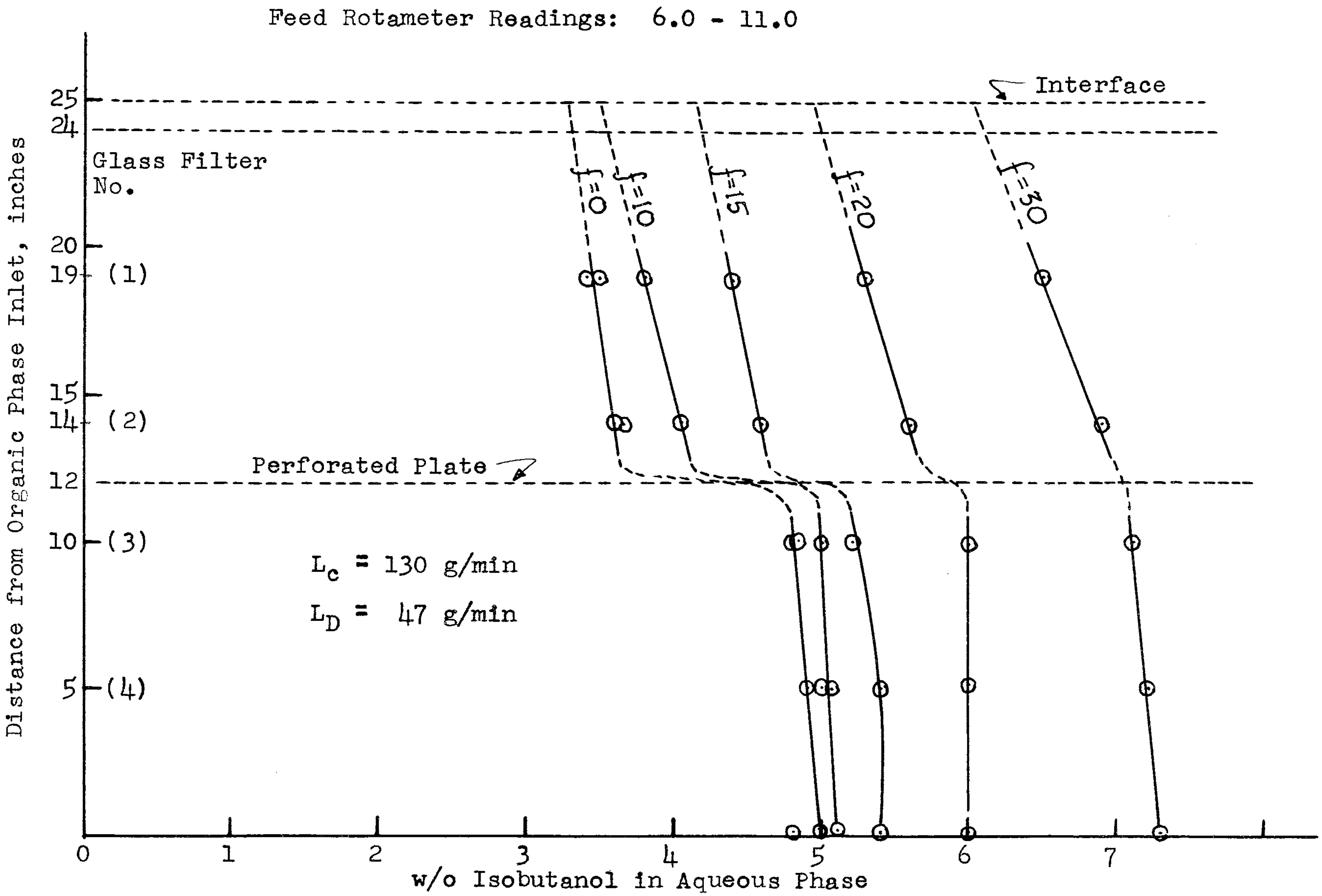


Fig. 13. Continuous Phase Profile, Plate at the Middle.

the column. This mass transfer at the plate increases with dispersed phase flow rate and decreases with increasing continuous phase flow rate, although the dispersed phase flow rate seems to have a greater effect on the extent of this discontinuity.

At increasing pulse frequencies, the plate discontinuity becomes less pronounced, probably because of the mixing caused by the pulsation.

On the other hand, there is apparently no end effect for the continuous phase at the dispersed phase inlet, and the value of the effluent concentration sometimes goes below that of the lowest glass filter on the column, by about 0.1% by weight concentration. This means that in a few cases there is probably additional mass transfer at the sintered-glass surface. The effect on sample concentration of flow rate through the glass filters has also been investigated, and the results are tabulated in Appendix H. The results indicate that, in general, the glass-filter data can be taken as being truly representative of the concentrations within the column. Samples should, however, be drawn off very carefully to minimize additional mass transfer due to passage through the glass filters.

These glass-filter data seem to support the contention that the continuous phase end effect is due to the coalescence of the dispersed phase droplets at the interface, and that the increased efficiency obtainable from a pulsed column is due to the dispersion and recoalescence that apparently takes place at the perforated plate; or, in the case of pulsed packed columns, as a result of drop impact on packing material.

Back-mixing could probably account for this inlet effect to some extent, as, indeed, mixing due to pulsation probably accounts for smoothing out the plate discontinuity at high pulse frequencies. However, at very high frequencies, the inlet effect tends to approach a constant value, and the change in concentration along the column, dc/dh, becomes greater, which is contrary to the effect expected if back-mixing were mainly responsible. Back-mixing, it seems, would tend to equalize the concentrations along the column, rather than increase the concentration change; and back-mixing would be expected to increase with increasing pulse frequency. Although back-mixing is undoubtedly present in the column, it is believed that the inlet effect is more a result of droplet coalescence at the interface.

Plate at the Bottom of the Column

The data taken from runs No. 107 to 140 (Figs. 14 to 17) still show the continuous phase inlet effect found previously, and, again, the same effects caused by changing the flow rates can be observed. As before, the end effect increases with increasing pulse frequency and also with increasing pulse amplitude.

At very high pulse frequencies ($f > 60$ cycles per minute), the concentration gradient becomes linear, and the inlet end effect seems to approach a constant value, as mentioned above. Apparently, there is a greater proportion of mass transfer taking place at the lower section of the column, which is to be expected because the perforated plate is now located at the bottom of the column.

The effect of pulsation on the dispersed phase can be seen in the timed sequence of photographs (Fig. 18-28) taken at a pulse frequency of 40 cycles per min.

Interpretation of Results

From the different sets of data obtained in this study, the following picture of the mass-transfer process likely to exist in

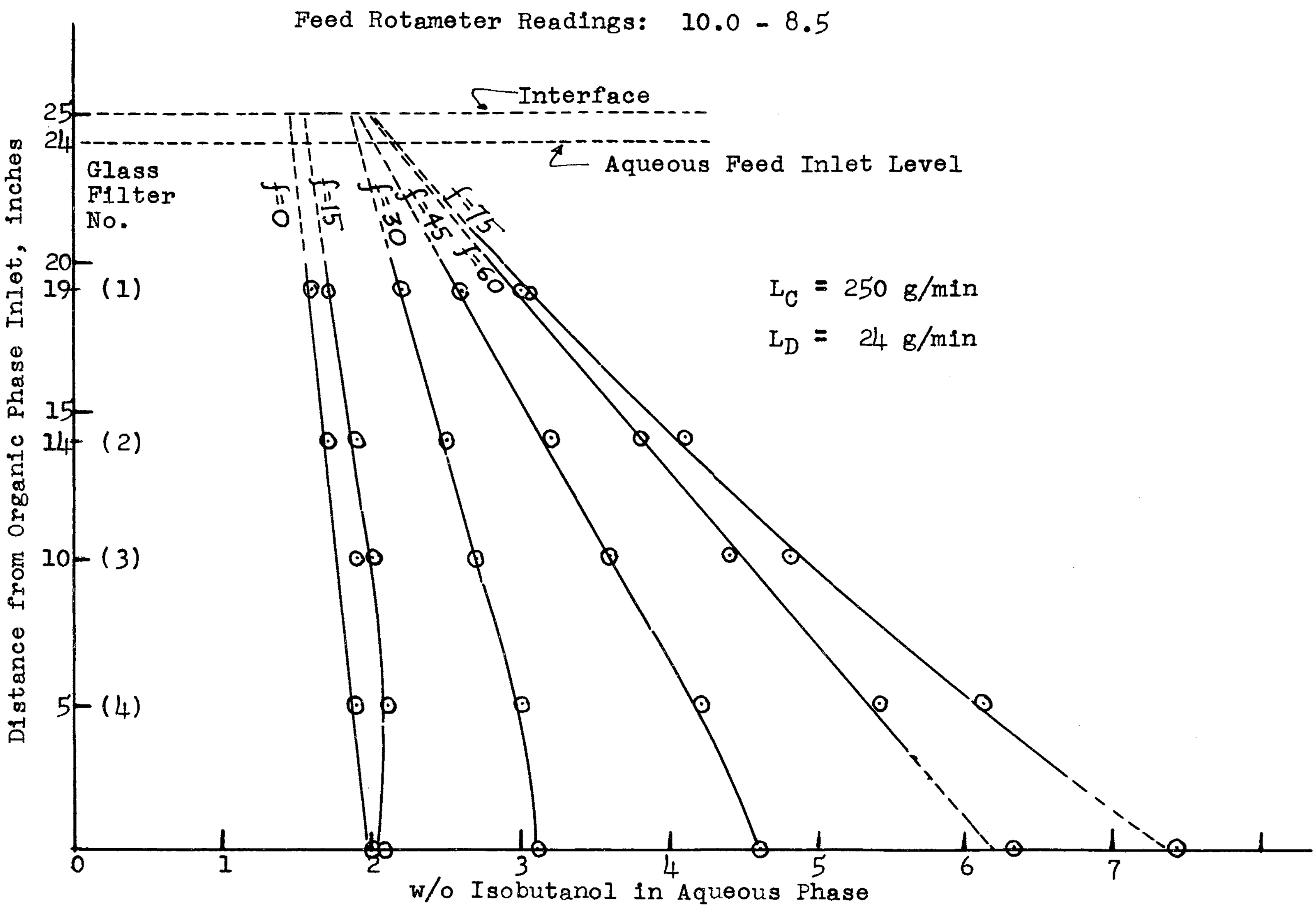


Fig. 14. Continuous Phase Profile, Plate at the Bottom.

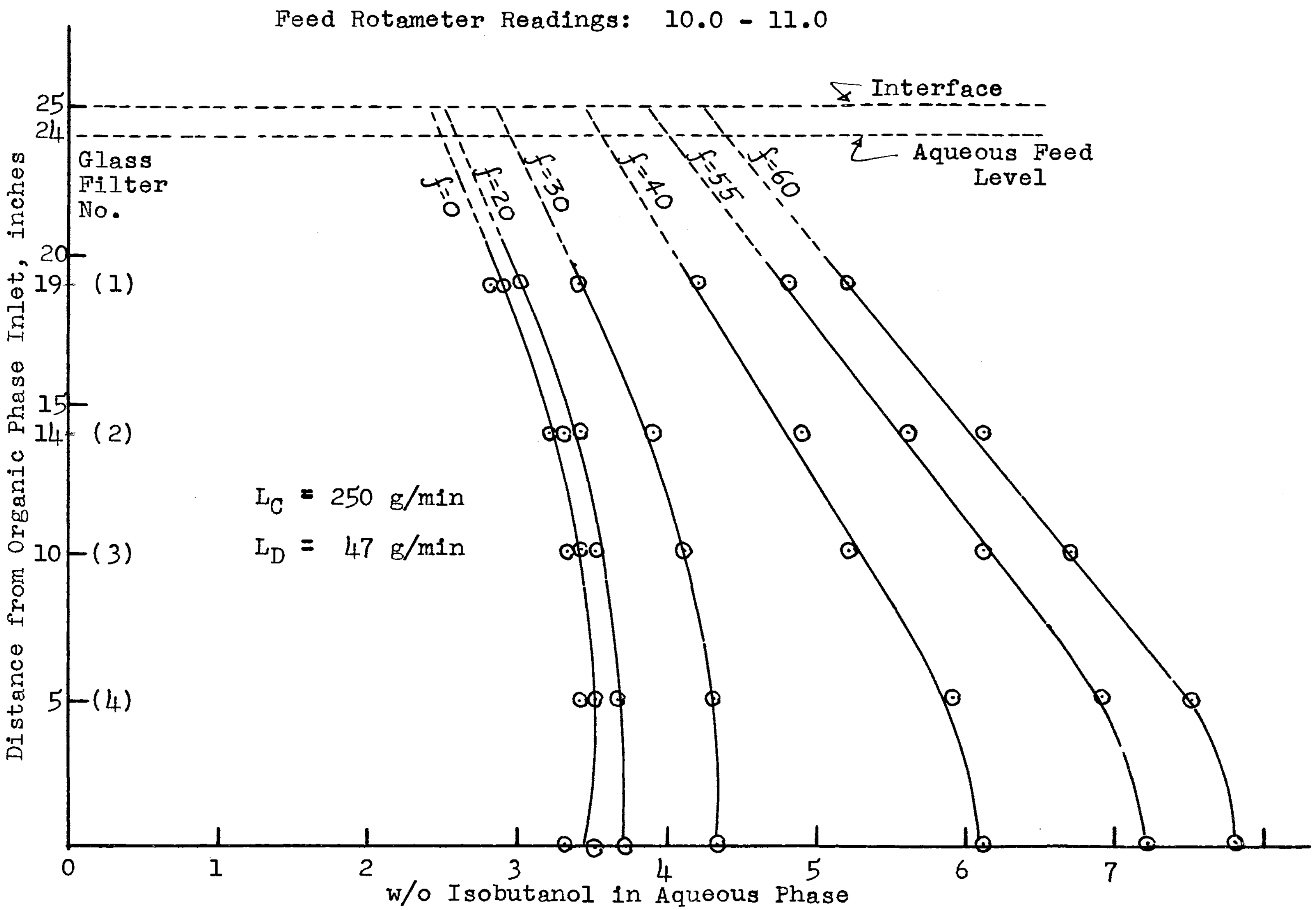


Fig. 15. Continuous Phase Profile, Plate at the Bottom.

Feed Rotameter Readings: 6.0 - 11.0

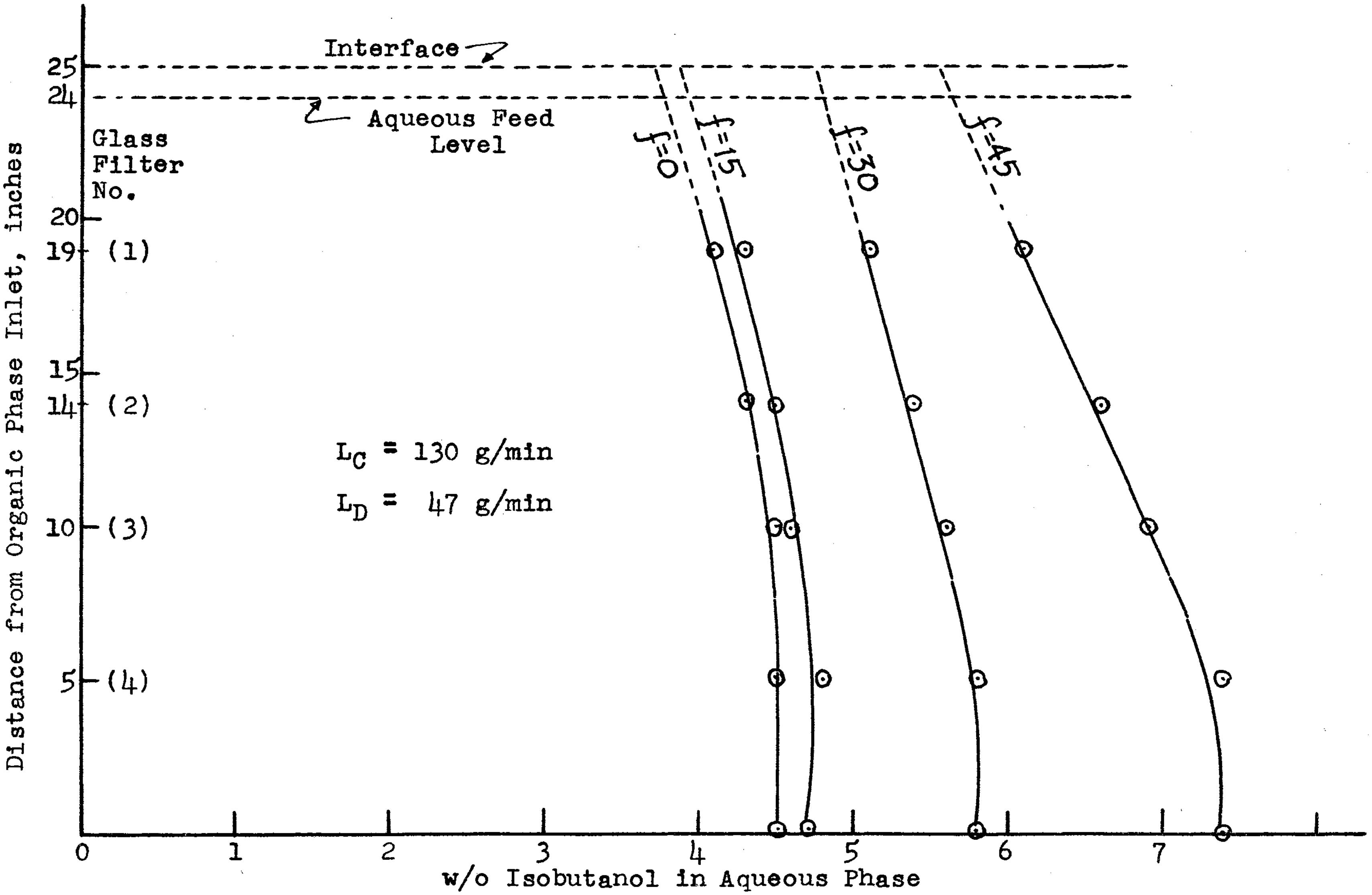


Fig. 16. Continuous Phase Profile, Plate at the Bottom.

Feed Rotameter Readings: 10.0 - 8.5

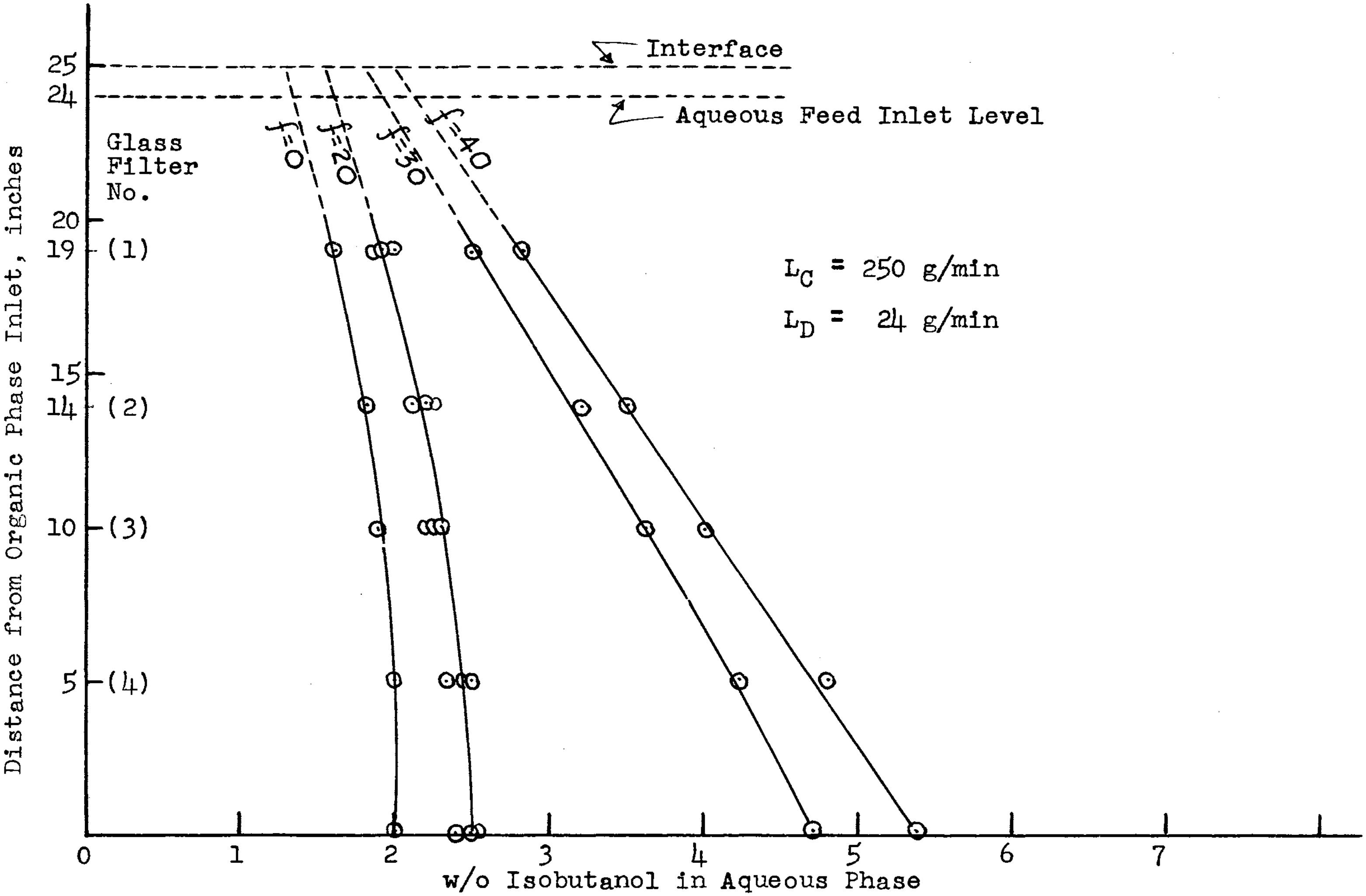


Fig. 17. Continuous Phase Profile, Plate at the Bottom, Pulse Amplitude = 1/2 inch.

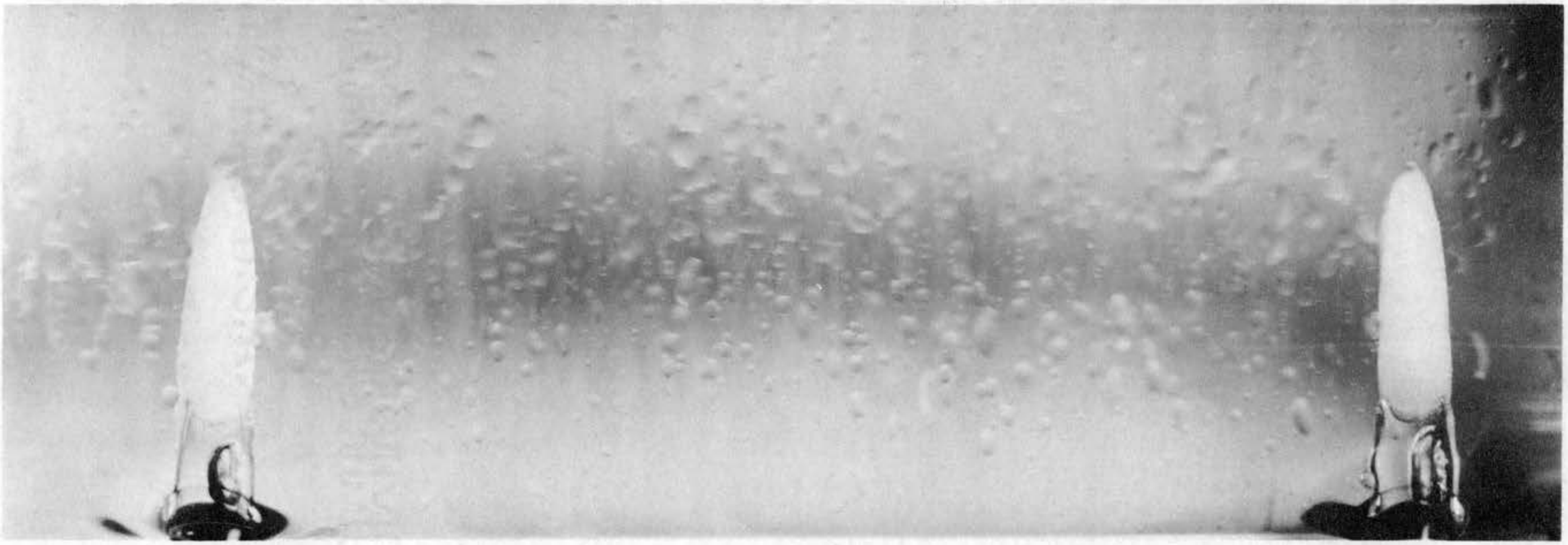


Fig. 18. Photograph of Column Showing Droplets at Start of Pulser.

Fig. 19. Photograph of Column Showing Droplets at Time t = 5 seconds after Start of Pulser.

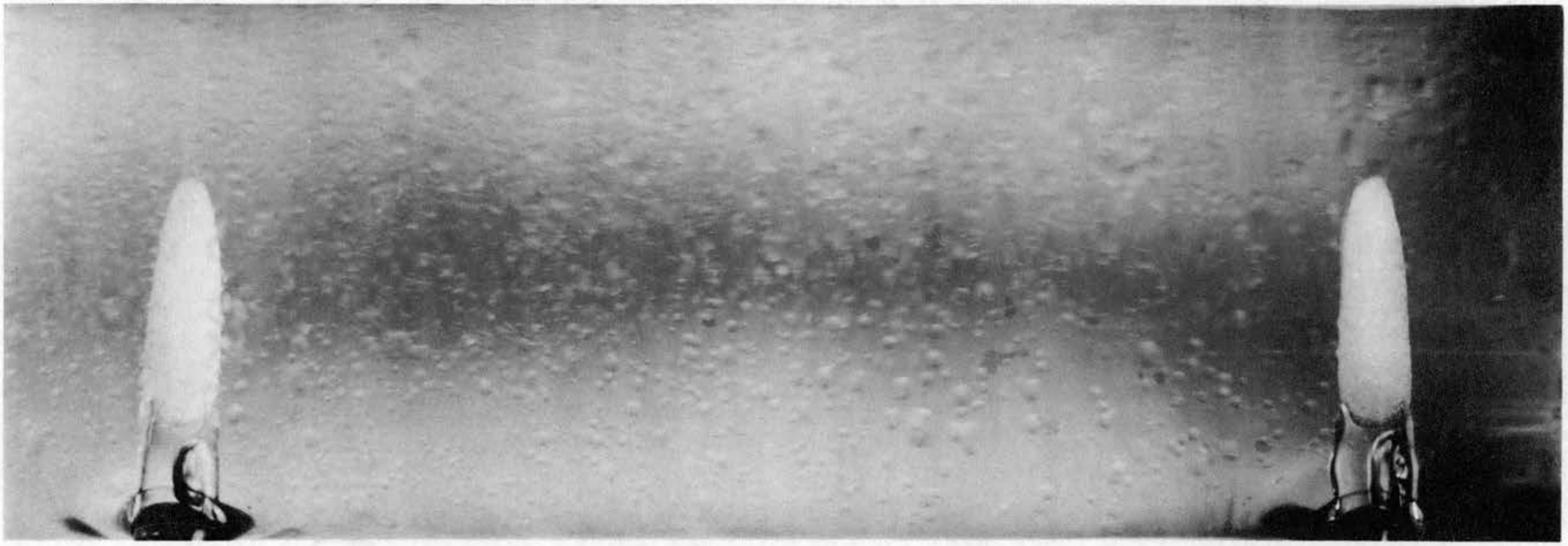


Fig. 20. Photograph of Column Showing Droplets at Time t = 10 seconds after Start of Pulser.

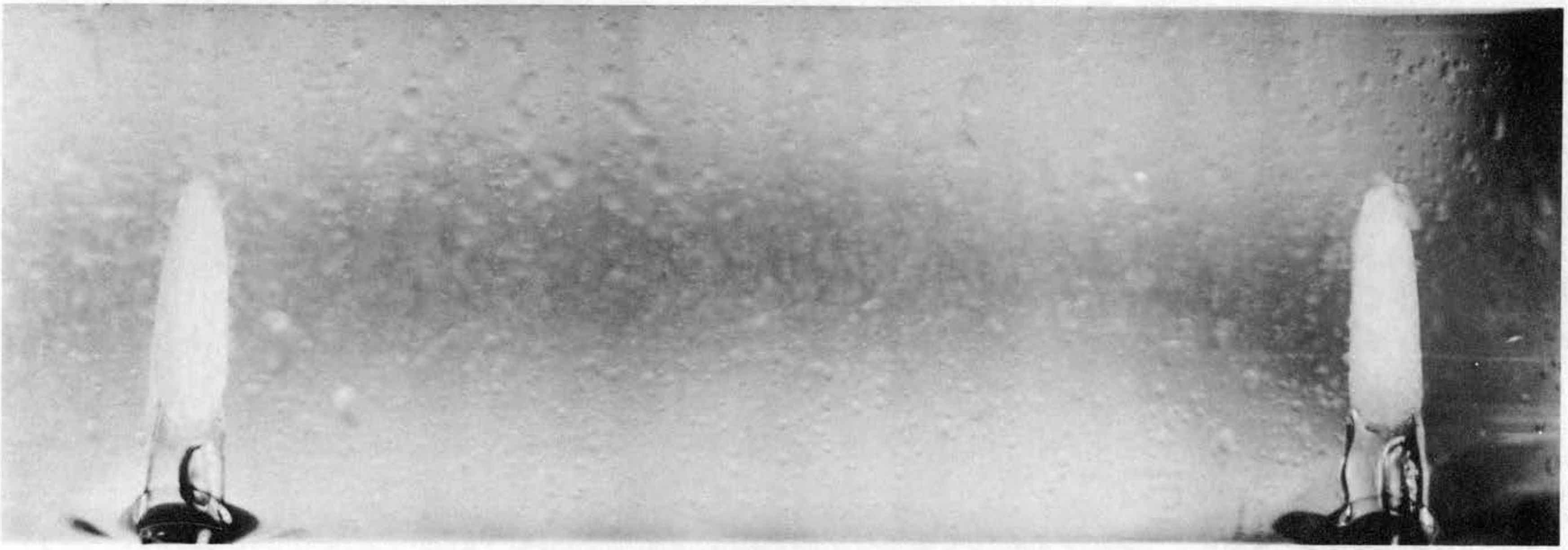


Fig. 21. Photograph of Column Showing Droplets at Time t = 15 seconds after Start of Pulser.

Fig. 22. Photograph of Column Showing Droplets at Time t = 30 seconds after Start of Pulser.

Fig. 23. Photograph of Column Showing Droplets at Time t = 45 seconds after Start of Pulser.

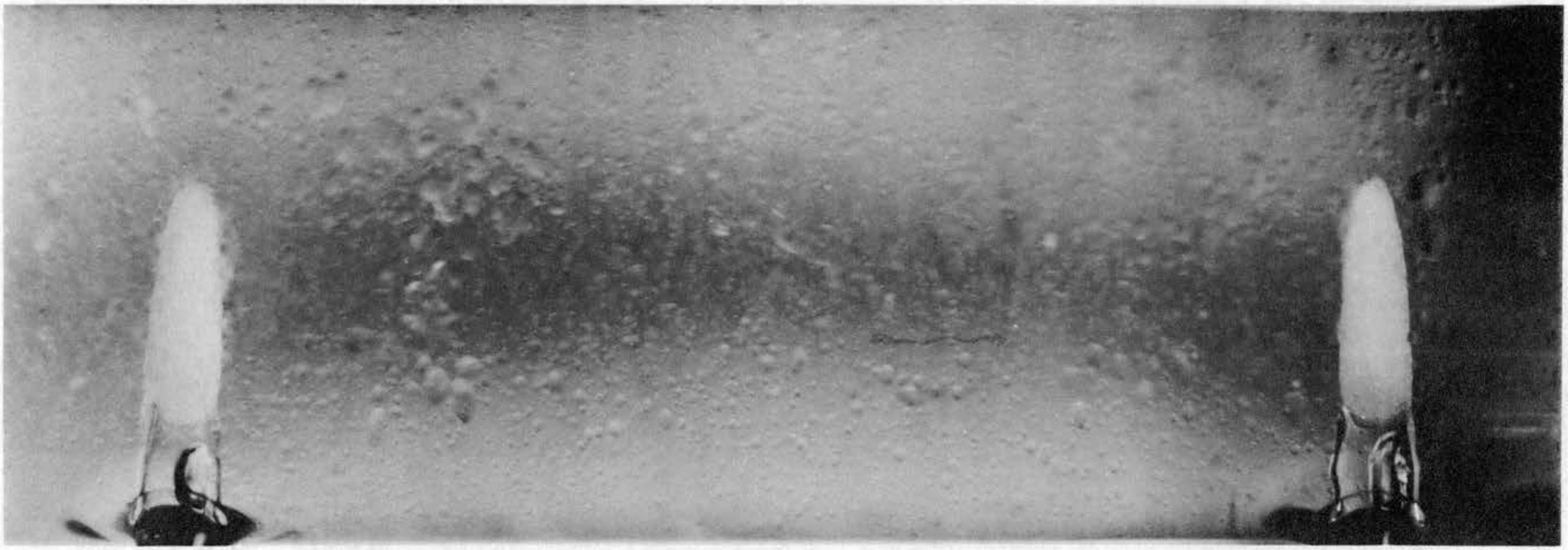


Fig. 24. Photograph of Column Showing Droplets at Time t = 1 minute after Start of Pulser.

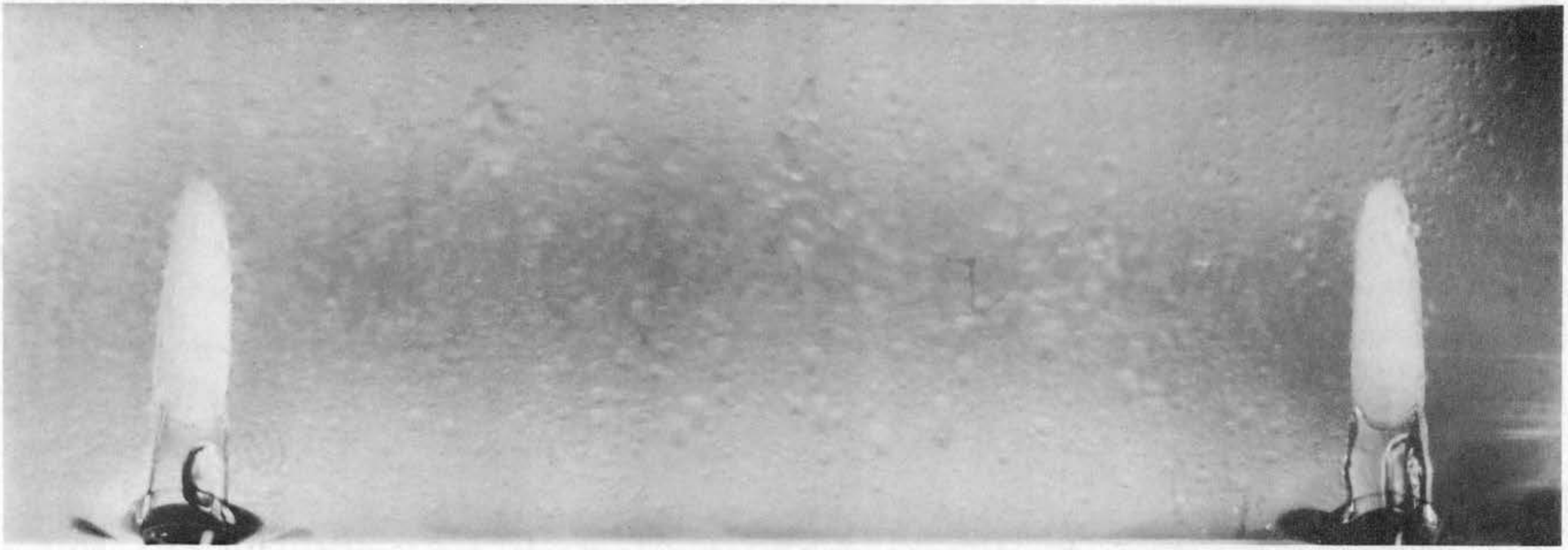


Fig. 25. Photograph of Column Showing Droplets at Time $t = 1\frac{1}{2}$ minutes after Start of Pulser.

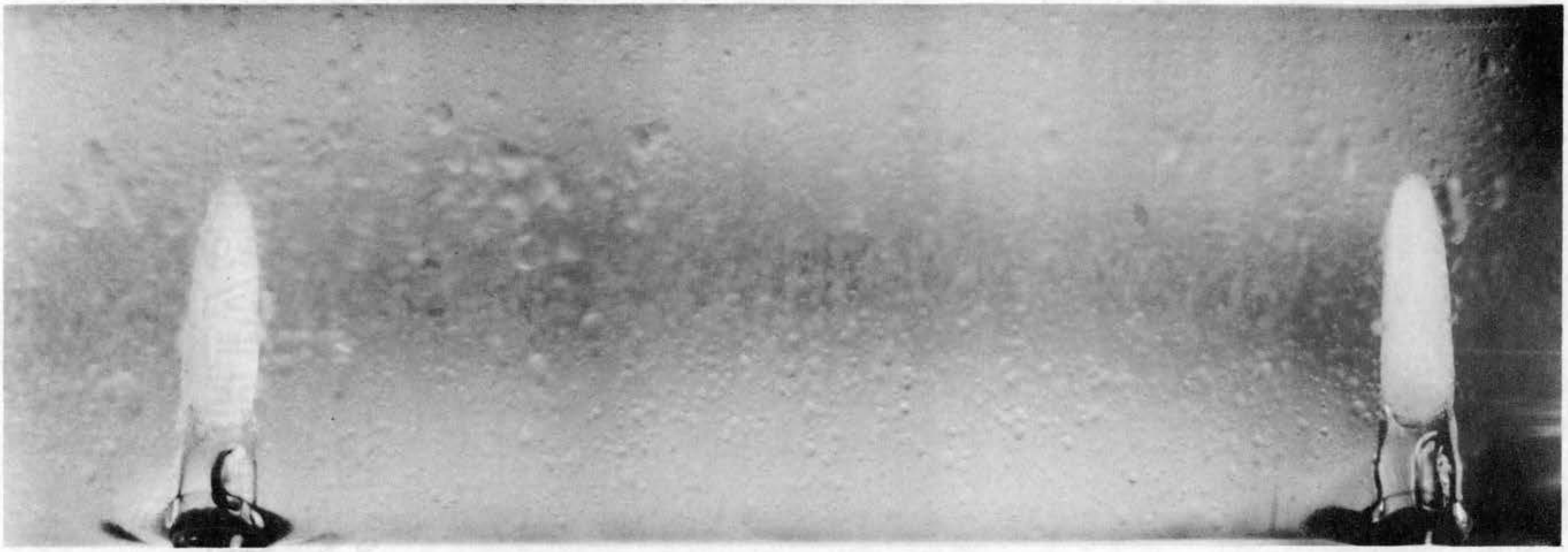


Fig. 26. Photograph of Column Showing Droplets at Time t = 2 minutes after Start of Pulser.

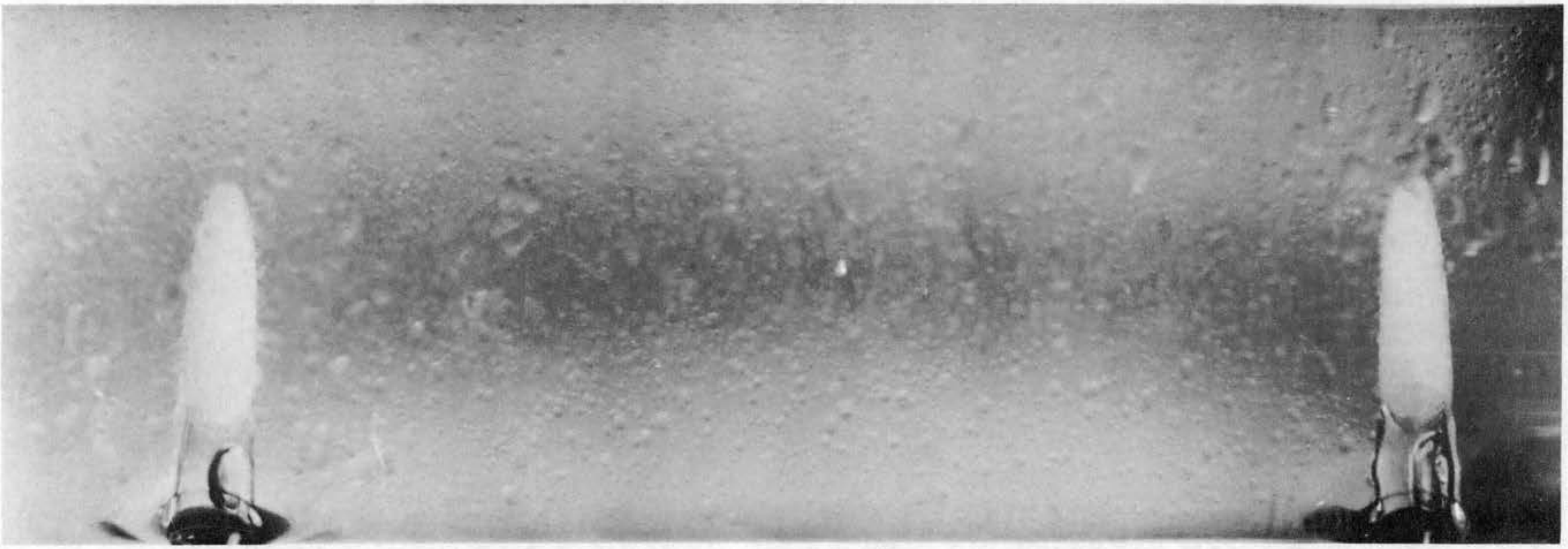


Fig. 27. Photograph of Column Showing Droplets at Time t = 3 minutes after Start of Pulser.

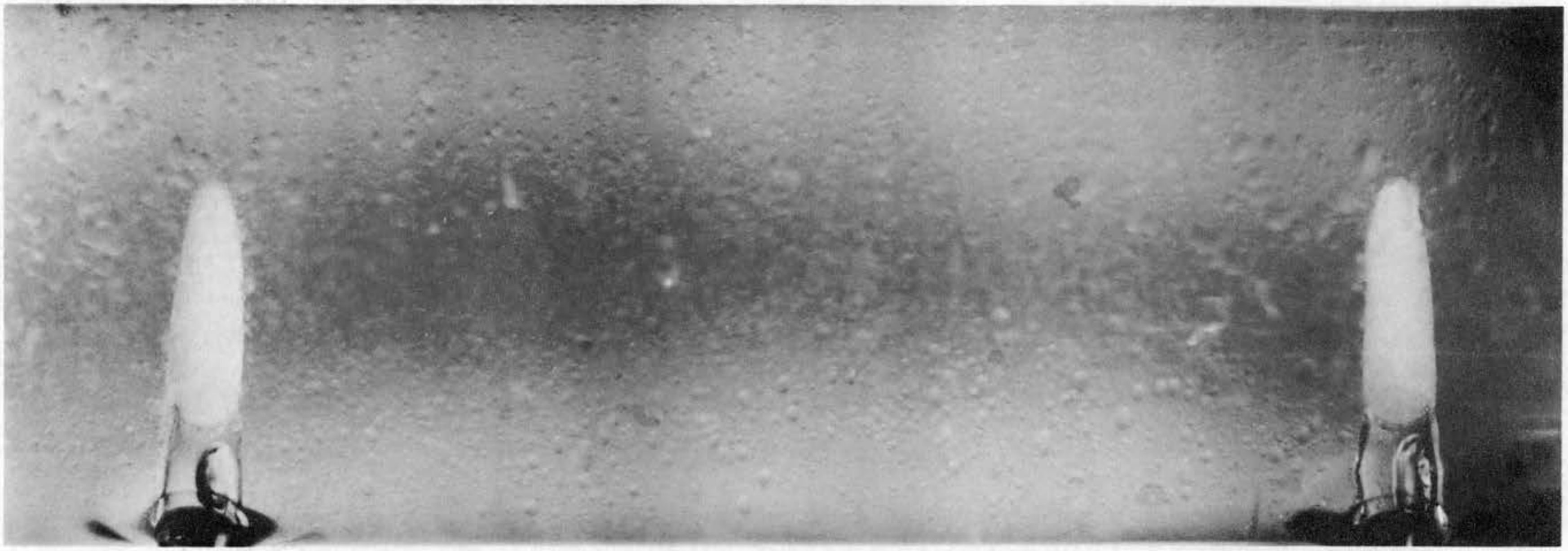


Fig. 28. Photograph of Column Showing Droplets at Time t = 5 minutes after Start of Pulser.

liquid-liquid extraction equipment may be drawn:

At the dispersed phase inlet the main stream of liquid flowing through the inlet tube or pipe breaks up into globules or droplets. As the dispersed phase liquid leaves the inlet tube, a thin film of the continuous phase liquid probably forms around the stream of dispersed phase liquid. This gives rise to a certain amount of mass transfer, into or out of, the dispersed phase liquid which is at its initial concentration. At the instant that the main stream breaks up into droplets, this film is broken and then reformed as the droplets move away from the main stream.

As a droplet moves through the continuous phase, turbulence effects, particularly at the wake of the droplet, cause the film surrounding the droplet to thin out, thereby increasing the mass-transfer rate into the continuous phase. The presence of packing in the column probably hastens mass transfer by the impact of droplets on the packing, which causes film rupture, film re-formation, an increase in the total number of droplets, and an increased turbulence in the continuous phase.

The presence of a perforated plate would also have a similar effect, that of promoting drop dispersion and re-coalescence, which would result in more frequent rupturing and re-formation of the droplet films. This probably accounts for the increased mass-transfer efficiencies obtainable with perforated-plate columns, particularly when pulsed. Pulsing would also increase the extent of droplet break-up and re-coalescence in packed columns.

As the droplets reach the interface, the thin films probably break up, or "slough off", resulting in considerable mass transfer at this section of the column. This accounts for the inlet effect discussed in the preceding sections. In some instances, these films can be seen extending into the coalesced dispersed phase layer beyond the interface: in the isobutanol-water system this effect is very pronounced when water is dispersed.

It seems, therefore, that the presence of a film around the dispersed phase droplet cannot be easily dismissed. This film seems to retard, rather than promote, mass transfer, and the increased efficiency obtainable with industrial extraction equipment must be due to the continuous break up and re-formation of such films. Danckwerts (7) has presented a theory of mass transfer in liquids based on a "surface renewal" concept. Equations are derived giving the mass-transfer coefficient in terms of the diffusivity of the solute, and a constant, s, the "rate of surface renewal", which is the fractional rate of change of the surface area. Danckwerts' supposition that mass transfer takes place to a great extent across fresh liquid surface is perfectly compatible with the theory that mass transfer takes place to a large extent during film break up and re-formation.

Although film rupture and re-formation probably play a major part in the mass-transfer process, the total extent of mass transfer still depends on the total number and the average size of the droplets; hence, we can conclude that the rate of mass transfer is proportional to the total interfacial area, which is related to the total number and size distribution of the droplets.

PART IV. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

From this study on the effect of pulsation on liquid-liquid mass-transfer rates, the following general conclusions were reached:

a) Without pulsation, mass-transfer rates can be expressed as power functions of the flow ratio, or, alternatively, as linear functions of the flow rates.

b) If it is assumed that the volumetric interfacial area, a, is proportional to the dispersed phase flow rate L_D, then the dispersed phase mass-transfer coefficient k_D is fairly independent of flow rates, and the continuous phase coefficient k_C is an increasing function of the continuous phase flow rate L_C and a decreasing function of the dispersed phase flow rate L_D.

c) In all extraction columns, whether pulsed, or unpulsed, there are end effects which contribute to the total mass transfer, and within certain ranges of operation, these end effects are porportional to the total mass transfer.

d) With the pulsed column used in this study, the effect of flow rates and pulse frequency, at constant pulse amplitude, on the mass-transfer rates were correlated as follows: for the continuous phase, at a column pulse amplitude of 1/4 inch:

$$NTU_C = \alpha_1 \left(\frac{L_D}{L_C}\right)^{0.9} + \alpha_2 \left(\frac{L_D}{L_C}\right)^{0.8} f^{3.0}$$

and for the dispersed phase, also at a pulse amplitude of 1/4 inch:

$$NTU_D = \beta_1 + \beta_2 f^{3.0}.$$

It should be noted that the mass-transfer rates were averaged over the entire column, and include the contributions due to end effects and plate discontinuity, as well as that due to mass transfer over the column.

e) The dependence of both correlations in section (d) on the same power of the pulse frequency suggest that the major effect of pulsation is to increase the average volumetric interfacial area, a.

f) A "film" theory of liquid-liquid mass transfer is presented to explain the findings on column operation given in the preceding sections.

Recommendations

After evaluating the results of this study, the following recommendations are made, in the hope that they might contribute towards better understanding of mass-transfer phenomena in liquid-liquid extraction:

a) A pulsed column consisting of perforated plates clamped between the column sections should be built, with flexible feed and effluent connections to the column, such that the number of plates and sections can be changed to study end effects in pulsed columns, as well as the relationship between end effects and operating variables.

b) Chemical reactions should be utilized further to substantially eliminate the resistance of either phase in liquid-liquid extraction. The results of such studies, combined with ordinary mass-transfer studies, might prove of value in understanding transfer mechanisms.

c) The use of a fourth component to alter the distribution coefficient of a solute should be utilized further to determine individual transfer resistances, and the results of such a study compared with those obtained from theuse of partially-miscible systems. In this connection, one system which might profitably be investigated is the system uranyl nitrate transferring between water and hexone (methyl isobutyl ketone), with either aluminum nitrate or nitric acid as the salting-out agent.

d) The effects of feed concentrations and direction of mass transfer on column efficiencies should be investigated further.

A SELECTED BIBLIOGRAPHY

1. Belaga, M. W., and Bigelow, J. E., "Effect of Pulse-column Operating Variables on HTU," KT-133 (Jan 1952).

2. Brinsmade, D. S., and Bliss, H., "Extraction of Acetic Acid in Methyl Isobutyl Ketone with Water in a Wetted-wall Tower," Trans. Am. Inst. Chem. Engrs., 39, 679 (1943).

3. Chantry, W. A., Von Berg, R. L., and Wiegandt, H. F., "Applications of Pulsation to Liquid-liquid Extraction," Ind. Eng. Chem., 47, 1153 (1955).

4. Cohen, R. M., and Beyer, G. H., "Performance of a Pulse Extraction Column," ISC-294 (Dec 1952).

5. Colburn, A. P., and Welsh, D. G., "Experimental Study of Individual Transfer Resistances in Countercurrent Liquid-liquid Extraction," Trans. Am. Inst. Chem. Engrs., 38, 179 (1942).

6. Comings, E. W., and Briggs, S. W., "Liquid-liquid Extraction in Wetted-wall andPacked Columns," Trans. Am. Inst. Chem. Engrs., 38, 143 (1942).

7. Danckwerts, P. V., "Significance of Liquid-film Coefficients in Gas Absorption," Ind. Eng. Chem., 43, 1460 (1951).

8. Feick, G., and Anderson, H. M., "Performance of a Packed Liquid-liquid Extraction Column under Controlled Agitation," Ind. Eng. Chem., 44, 404 (1952).

9. Geankoplis, C. J., and Hixson, A. N., "Mass-transfer Coefficients in an Extraction Spray Tower," Ind. Eng. Chem., 42, 1141 (1950).

10. Geankoplis, C. J., Wells, P. L., and Hawk, E. L., "Extraction in a Pilot-unit Spray Tower," Ind. Eng. Chem., 43, 1848 (1951).

11. Heertjes, P. M., Holve, W. A., and Talsma, H., "Mass-transfer between Isobutanol and Water in a Spray-column," Chem. Eng. Sci., 3, 122 (1954).

12. Laddha, G. S., and Smith, J. M., "Mass-transfer Resistances in Liquid-liquid Extraction," Chem. Eng. Progress, 46, 195 (1950).

13. Lane, A. F., Jr., "Prediction of Concentration Gradients in Multicomponent Mass Transfer," UCRL-2983 (May 1955).

14. Lehman, H. R., "Mechanical Characteristics and Performance of Liquid-liquid Extraction Columns," UCRL-1558 (Nov 1951).

15. Li, W. H., and Newton, W. M., "Liquid-liquid Extraction in a Pulsed Perforated-plate Column," A. I. Ch. E. Journal, 3, 56 (1957).

16. Licht, W., Jr., and Conway, J. B., "Mechanism of Solute Transfer in Spray Towers," Ind. Eng. Chem., 42, 1151 (1950).

17. Morello, V. S., and Poffenberger, N., "Commercial Extraction Equipment," Ind. Eng. Chem., 42, 1021 (1950).

18. Rubin, B., and Lehman, H. R., "Performance of Liquid-liquid Extraction Equipment," UCRL-718 (May 1950).

19. Sege, G., and Woodfield, F. W., "Pulse Column Variables," Chem. Eng. Prog., 50, 396 (1954).

20. Treybal, R. W., "Mechanically Aided Liquid Extraction," Advances in Chemical Engineering, ed. Drew, T. B., and Hooper, J. W., Jr., New York, Academic Press Inc. (1956).

21. Van Dijck, W. J. D., U. S. Patent 2,011,186 (Aug. 1935).

APPENDIX A

CONCENTRATION-DENSITY DATA

TABLE I

CONCENTRATION-DENSITY FOR THE ISOBUTANOL-WATER SYSTEM AT 25°C.

Organic Phase

Conc., w/o water	Density, g per ml
0	0.7980
2.4	0.8031
4.8	0.8078
7.0	0.8126
9.1	0.8168
10.1	0.8190
11.1	0.8210
13.0	0.8249
14.9	0.8288
15.8	0.8305
16.2	0.8315
16.6	0.8322

Aqueous Phase

Conc., w/o isobutanol	Density, g per ml
0	0.9971
1.6	0.9945
3.1	0.9921
4.6	0.9899
6.0	0.9878
7.4	0.9858
8.1	0.9848

TABLE II

CONCENTRATION-DENSITY DATA AT 25.5, 26, and 27°C CALCULATED BY THE FORMULA OF HEERTJES, ET AL. (11).

Organic Phase

Conc., w/o water	Density, g per ml 25.5°C	26°C	27°C
0	0.7976	0.7972	0.7964
7.0	0.8122	0.8118	-
9.1	0.8164	0.8160	-
10.1	0.8186	0.8182	0.8174
11.1	0.8206	0.8202	-
13.0	0.8245	0.8241	0.8234
14.9	0.8284	0.8281	-
15.8	0.8301	0.8298	-
16.2	0.8311	0.8308	0.8300

Aqueous Phase

Conc., w/o isobutanol	Density, g per ml 25.5°C	26°C	27°C
0	0.99695	0.9968	0.9965
1.6	0.9943	0.9942	0.9939
3.1	0.9919	-	-
4.6	-	0.9896	0.9892
6.0	0.9876	-	-
7.4	-	-	0.9851
8.1	0.9846	0.9844	-

APPENDIX B

RESULTS OF PRELIMINARY RUNS WITHOUT PULSING

TABLE III

PRELIMINARY SPRAY-COLUMN RUNS WITHOUT PULSING ORGANIC PHASE DISPERSED

Run No.	Phase	Conc.,% by Wt.	Rot. Read.	L_C or L_D (g/min)	$\frac{L_C}{L_D}$	HTU, ft.
5	aq.	4.3	5.05	105	3.56	2.65
	org.	10.1	9.3	29.5		2.1
6	aq.	5.0	5.2	110	2.34	2.1
	org.	10.2	11.0	47		2.1
7	aq.	2.5	7.1	155	5.54	5.4
	org.	11.2	9.1	28		1.8
8	aq.	4.8	7.0	155	3.30	2.2
	org.	11.5	11.0	47		1.7
9	aq.	1.3	7.0	155	9.70	11.5
	org.	11.5	7.2	16		1.7
10	aq.	2.6	5.0	102	6.80	5.0
	org.	10.9	7.0	15		1.9
11	aq.	2.0	6.0	130	8.67	7.0
	org.	12.0	6.95	15		1.6
12	aq.	0.5	6.0	130	6.35	32.0
	org.	12.0	8.05	20.5		1.6
13	aq.	3.5	5.95	130	4.82	3.5
	org.	11.2	8.9	27		1.8
14	aq.	2.3	6.0	130	6.34	6.0
	org.	11.5	8.0	20.5		1.7
15	aq.	4.0	5.0	102	3.64	2.9
	org.	10.6	9.1	28		2.0
16	aq.	2.8	7.0	155	7.55	4.7
	org.	11.8	8.0	20.5		1.6
17	aq.	3.0	5.0	102	5.0	4.3
	org.	11.5	8.0	20.5		1.7
18	aq.	3.5	4.0	80	4.0	3.5
	org.	10.6	8.0	20.5		2.0

TABLE III (Continued)

Run No.	Phase	Conc.,% by wt.	Rot. Read.	L_C or L_D (g/min)	$\frac{L_C}{L_D}$	HTU, ft.
19	aq.	3.5	4.0	80	4.0	3.5
	org.	11.5	8.0	20.5		1.7
20	aq.	2.2	7.0	155	7.55	6.35
	org.	11.0	8.0	20.5		1.9
21	aq.	2.8	4.0	80	5.33	4.7
	org.	10.5	7.0	15		2.0
22	aq.	4.6	4.0	80	2.86	2.4
	org.	10.6	9.0	28		2.0
23	aq.	5.1	4.05	80	1.70	2.0
	org	10.5	11.0	47		2.0
24	aq.	5.2	4.0	77	2.05	2.0
	org.	10.5	10.0	37.5		2.0
25	aq.	4.7	5.0	102	2.72	2.3
	org.	10.5	10.0	37.5		2.0
26	aq.	4.0	6.0	130	3.47	2.9
	org.	10.6	10.0	37.5		2.0
27	aq.	3.6	7.0	155	4.4	3.4
	org.	11.0	10.0	37.5		1.9
28	aq.	5.2	3.5	65	1.73	2.0
	org.	10.7	10.0	37.5		1.9
29	aq.	2.2	8.0	185	9.0	6.35
	org.	10.0	8.0	20.5		2.2
30	aq.	3.0	8.0	185	6.6	4.3
	org.	10.8	9.0	28		1.9
31	aq.	3.2	8.0	185	4.94	4.0
	org.	11.0	10.0	37.5		1.8
32	aq.	4.0	8.0	185	3.94	2.9
	org.	10.7	11.0	47		2.0
33	aq.	2.7	8.0	185	6.6	4.9
	org.	10.4	9.0	28		2.0
34	aq.	3.0	7.0	155	5.53	4.3
	org.	10.4	9.0	28		2.0
35	aq.	1.8	8.0	185	9.25	8.0
	org.	10.7	7.9	20		1.9

APPENDIX C

PULSED COLUMN DATA AT CONSTANT FLOW-RATIO

TABLE IV

Runs No. 35-64, Series A

Feed Rotameter Readings: 6.0-11.0

Dispersed Phase: Isobutanol
Continuous Phase: Water

Run No.	$f(\text{min}^{-1})$	%AE	NTU_C	ΔNTU_C	%OE	NTU_D	ΔNTU_D
35-1	40	6.7	1.80	0.92	13.4	1.65	0.49
35-2	40	6.4	1.60	0.72	13.4	1.65	0.49
36-1	40	6.5	1.68	0.80	13.6	1.71	0.55
36-2	40	6.8	1.89	1.01	13.2	1.58	0.42
37	40	6.7	1.80	0.92	13.7	1.74	0.58
38	40	6.8	1.89	1.01	13.2	1.58	0.42
39.1	0	4.7	1.88	0	11.4	1.16	0
40	40	7.0	2.08	1.20	13.2	1.58	0.42
41-1	16	5.0	0.98	0.10	12.0	1.28	0.12
41-2	16	5.0	0.98	0.10	11.7	1.22	0.06
42	16	4.7	0.88	0	11.5	1.18	0.02
43-1	16	4.8	0.90	0.02	11.7	1.22	0.06
43-2	16	4.8	0.90	0.02	11.7	1.22	0.06
44-1	25	5.6	1.20	0.32	12.1	1.31	0.15
44-2	25	5.5	1.16	0.28	12.1	1.31	0.15
45	25	5.5	1.16	0.28	12.2	1.33	0.17
46	25	5.6	1.20	0.32	12.3	1.35	0.19
47-1	32	6.4	1.61	0.73	13.1	1.56	0.40
47-2	32	6.4	1.61	0.73	13.1	1.56	0.40
48	32	6.4	1.61	0.73	13.3	1.61	0.45
49	20	5.3	1.08	0.20	11.7	1.22	0.06
50	20	5.3	1.08	0.20	11.9	1.26	0.10
51	28	6.0	1.38	0.50	12.3	1.35	0.28
52	50	7.6	3.00	2.12	14.8	2.22	1.06
53	0	4.5	0.83	0	11.2	1.12	0
54	10	4.6	0.85	0.02	11.4	1.16	0.04
55	20	5.2	1.05	0.22	12.1	1.31	0.19
56	30	6.5	1.68	0.85	12.8	1.48	0.36
57	40	7.0	2.08	1.25	13.6	1.71	0.59
58	50	7.5	2.77	1.94	15.1	2.40	1.28
60	55	7.7	3.28	2.45	15.8	3.03	1.91
61	45	7.5	2.77	1.94	13.9	1.82	0.70
62	35	6.8	1.89	1.06	13.2	1.59	0.47
63-1	25	5.5	1.16	0.33	11.9	1.26	0.14
63-2	25	5.8	1.28	0.45	12.4	1.37	0.25
64	15	4.7	0.88	0.05	11.6	1.20	0.08

TABLE V

Runs No. 11-23, Series B

Feed Rotameter Readings: 6.0-11.0

Dispersed Phase: Wet Isobutanol
Continuous Phase: Water

Run No.	f(min^{-1})	%AE	NTU$_C$	ΔNTU$_C$
11	0	4.6	0.86	0
12	10	4.9	0.95	0.09
13	15	5.0	0.98	0.12
14	20	5.4	1.12	0.26
15	25	6.0	1.39	0.53
16	30	6.9	1.98	1.12
17	35	7.3	2.43	1.57
18	40	7.5	2.68	1.82
19	45	7.6	3.00	2.14
20	50	7.8	3.69	2.83
21	55	7.9	4.38	3.52
22	60	7.95	5.08	4.22
23	70	7.95	5.08	4.22

TABLE VI

Runs No. 24-41, Series B

Feed Rotameter Readings: 6.0-11.0

Dispersed Phase: Water
Continuous Phase: Wet Isobutanol

Run No.	f(min^{-1})	%AE	NTU_D	ΔNTU_D
24	0	6.9	1.98	0
25	10	6.9	1.98	0
38	12	7.1	2.18	0.20
26	15	6.9	1.98	0
27	20	6.9	1.98	0
39	22	7.1	2.18	0.20
28	25	7.1	2.18	0.20
40	28	7.2	2.30	0.32
29	30	7.2	2.30	0.32
41	32	7.3	2.43	0.45
30	35	7.3	2.43	0.45
31	40	7.4	2.59	0.61
32	45	7.45	2.65	0.67
33	50	7.6	3.00	1.02
34	55	7.8	3.69	1.71
35	60	7.9	4.38	2.40
36	70	7.95	5.07	3.09
37	0	6.9	1.98	0

TABLE VII

HOLD-UP DATA CORRESPONDING TO RUNS NO. 35-64 SERIES A AND RUNS NO. 11-41 SERIES B.

Direct Volume Measurement

Pulse frequency f(min^{-1})	Hold-up (ml)	ΔH (ml)
40	41	21
45	45	25
0	20	0
15	20	0
25	23	3
30	29	9
45	43.5	23.5
55	74	54
70	114	94
62	104	84
52	66	46
45	44	24
35	34	14
80	110	90
0	19	0
20	19	0
26	25	5
34	36	16
38	40	20
42	40	20
44	45	25
46	51	31
48	53	33
58	100	80
62	117	97
68	128	108
76	122	102

TABLE VII (Continued)

Pulse frequency f(min^{-1})	Hold-up (ml)	ΔH (ml)
30	31	11
50	62	42
36	40	20
40	42	22
54	86	66
52	72	52
55	88	68
46	53	33
52	74	54
54	82	62
58	97	77
64	118	98
68	126	106
74	124	104
78	126	106
84	121	101
48	59	39
70	128	108
82	112	92
90	130	110
100	136	116

TABLE VIII

Runs No. 45-66, Series B

Feed Rotameter Readings: 6.0-11.0

Dispersed Phase: Isobutanol
Continuous Phase: Water

Run No.	f(min^{-1})	%AE	NTU$_C$	ΔNTU$_C$	%OE	NTU$_D$	ΔNTU$_D$
45	0	4.7	0.87	0	11.1	1.10	0
46	10	4.8	0.90	0.03	11.1	1.10	0
47	15	5.05	0.98	0.11	11.3	1.14	0.04
48	18	5.5	1.14	0.27	11.5	1.18	0.08
49	20	5.8	1.26	0.39	11.6	1.20	0.10
50	22	5.8	1.26	0.39	11.7	1.22	0.12
51	24	6.1	1.40	0.53	12.0	1.28	0.18
52	26	6.4	1.56	0.69	12.2	1.33	0.23
53	28	6.8	1.83	0.96	12.6	1.42	0.32
54	30	7.2	2.20	1.33	13.1	1.56	0.46
55	32	7.4	2.45	1.58	13.4	1.65	0.55
56	34	7.5	2.60	1.73	13.6	1.71	0.61
57	36	7.8	3.29	2.42	13.9	1.82	0.72
58	38	7.8	3.29	2.42	13.7	1.74	0.64
59	40	7.8	3.29	2.42	13.9	1.82	0.72
60	42	7.7	3.00	2.13	14.0	1.85	0.75
61	45	7.85	3.45	2.61	14.3	1.98	0.88
62	50	7.95	3.99	3.12	14.4	2.02	0.92
63	60	8.1	-	-	15.8	3.03	1.93
65	55	8.1	-	-	15.0	2.34	1.24
66	65	8.1	-	-	15.9	3.16	2.06

TABLE IX

HOLD-UP DATA CORRESPONDING TO RUNS NO. 45-66, SERIES B MEASUREMENT BY LINEAR SCALE AND CONVERSION TO VOLUME

$f(min^{-1})$	Hold-up (inches)	Hold-up (ml)	ΔH (ml)
0	3/16	10	0
10	7/32	11	1
15	1/4	13	3
20	9/32	14.5	4.5
25	1/4	13	3
30	11/32	18	8
30	5/16	16	6
35	7/16	22.5	12.5
40	19/32	30.5	20.5
45	13/16	42	32
50	18/16	58	48
45	0.3	41	31
60	1.45	75	65

Direct Volume Measurement

45		44	34
60		105	95
70		138	128
70		120	110
80		122	112
90		158	148
100		230	220
120		225	215
140		200	190
100		140	180

APPENDIX D

PULSED COLUMN DATA AT DIFFERENT FLOW-RATIOS

TABLE X

Runs No. 81-106

Perforated Plate at the Middle of the Column

Dispersed Phase: Isobutanol
Continuous Phase: Water

(No dispersed phase analysis up to Run No. 97)

Feed Rotameter Readings: 6.0-6.0; $\frac{L_C}{L_D} = 11.6$ g./g. $\left(\frac{L_C}{L_D}\right)^{0.8} = 7.1$

f(min^{-1})	%AE	NTU$_C$	ΔNTU$_C$	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$
0	2.0	0.28	0	0
15	2.35	0.34	0.06	0.43
20	3.0	0.46	0.18	1.28
30	4.2	0.73	0.45	3.2
45	5.7	1.22	0.94	6.7

Feed Rotameter Readings: 6.0-8.5; $\frac{L_C}{L_D} = 5.41$ g./g. $\left(\frac{L_C}{L_D}\right)^{0.8} = 3.86$

f(min^{-1})	%AE	NTU$_C$	ΔNTU$_C$	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$
0	3.2	0.50	0	0
10	3.4	0.55	0.05	0.193
20	4.4	0.78	0.28	1.08
30	5.9	1.30	0.80	3.09
30	6.0	1.35	0.85	3.28
40	6.8	1.83	1.33	5.14

Feed Rotameter Readings: 6.0-11.0; $\frac{L_C}{L_D} = 2.75$ g./g. $\left(\frac{L_C}{L_D}\right)^{0.8} = 2.25$

f(min^{-1})	%AE	NTU$_C$	ΔNTU$_C$	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$
0	4.9	0.93	0	0
10	5.1	0.99	0.06	0.135
15	5.4	1.10	0.17	0.38
20	6.0	1.35	0.42	0.95
30	7.3	2.31	1.38	3.1

TABLE X (Continued)

Feed Rotameter Readings: 10.0-8.5; $\frac{L_C}{L_D}$ = 10.4 g./g. $(\frac{L_C}{L_D})^{0.8}$ = 6.5

$f(\min^{-1})$	%AE	NTU_C	ΔNTU_C	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$	%OE	NTU_D	ΔNTU_D
0	2.0	0.29	0	0	11.2	1.12	0
15	2.3	0.34	0.05	0.33	11.5	1.18	0.06
20	3.0	0.46	0.17	1.11	11.9	1.26	0.14
30	4.3	0.76	0.47	3.05	13.8	1.78	0.66
45	5.6	1.18	0.89	5.79	14.1	1.89	0.77

Feed Rotameter Readings: 10.0-11.0; L_C/L_D = 5.30 g./g. $(L_C/L_D)^{0.8}$= 3.8

$f(\min^{-1})$	%AE	NTU_C	ΔNTU_C	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$	%OE	NTU_D	ΔNTU_D
0	3.4	0.55	0	0	11.2	1.12	0
20	4.4	0.78	0.23	0.87	12.3	1.35	0.23
30	6.1	1.40	0.85	3.23	13.4	1.65	0.53
40	7.2	2.20	1.65	6.3	14.2	1.94	0.82

TABLE XI

Runs No. 107-128

Perforated Plate at the Bottom of the Column

Dispersed Phase: Isobutanol
Continuous Phase: Water

Feed Rotameter Readings: 6.0-6.0; $\frac{L_C}{L_D}$ = 11.6 g./g. $(\frac{L_C}{L_D})^{0.8}$ = 7.1

f(min^{-1})	%AE	NTU$_C$	ΔNTU$_C$	$\frac{\Delta NTU_C}{(L_C/L_D)^{0.8}}$	%OE	NTU$_D$	ΔNTU$_D$
0	1.7	0.24	0	0	11.3	1.14	0
45	4.4	0.78	0.54	3.84	13.1	1.56	0.42

Feed Rotameter Readings: 10.0-8.5; $\frac{L_C}{L_D}$ = 10.4 g./g. $(\frac{L_C}{L_D})^{0.8}$ = 6.5

f(min^{-1})	%AE	NTU$_C$	ΔNTU$_C$	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$	%OE	NTU$_D$	ΔNTU$_D$
0	2.0	0.29	0	0	10.5	1.00	0
15	2.0	0.29	0	0	10.7	1.03	0.03
30	3.1	0.48	0.19	1.23	10.8	1.05	0.05
45	4.6	0.84	0.55	3.58	11.2	1.12	0.12
60	6.3	1.50	1.21	7.9	12.3	1.35	0.35
75	7.4	2.45	2.16	14.0	15.3	2.55	1.55

Feed Rotameter Readings: 10.0-11.0; $\frac{L_C}{L_D}$ = 5.30 g./g. $(\frac{L_C}{L_D})^{0.8}$= 3.8

f(min^{-1})	%AE	NTU$_C$	ΔNTU$_C$	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$	%OE	NTU$_D$	ΔNTU$_D$
0	3.4	0.54	0	0	11.0	1.08	0
10	3.4	0.54	0	0	11.2	1.12	0.04
20	3.7	0.61	0.07	0.27	11.1	1.11	0.03
25	4.0	0.68	0.14	0.53	11.2	1.12	0.04
30	4.3	0.76	0.21	0.80	11.0	1.08	0
40	6.1	1.40	0.86	3.27	12.1	1.31	0.22
50	6.5	1.62	1.08	4.10	11.9	1.26	0.18
55	7.2	2.20	1.66	6.3	12.3	1.35	0.27
60	7.8	3.30	2.76	10.5	13.7	1.74	0.66

Feed Rotameter Readings: 6.0-11.0; $\frac{L_C}{L_D}$ = 2.75 g./g. $(\frac{L_C}{L_D})^{0.8}$ = 2.25

f(min^{-1})	%AE	NTU$_C$	ΔNTU$_C$	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$	%OE	NTU$_D$	ΔNTU$_D$
0	4.5	0.81	0	0	10.8	1.05	0
15	4.7	0.87	0.06	0.14	10.8	1.05	0
30	5.8	1.26	0.45	1.01	11.1	1.11	0.06
45	7.4	2.45	1.64	3.7	12.2	1.33	0.28

TABLE XII

Runs No. 129-140

Perforated Plate at the Bottom of the Column
Pulse Amplitude = 1/2 inch (approx.)

Dispersed Phase: Isobutanol
Continuous Phase: Water

Feed Rotameter Readings: 10.0-8.5; $(\frac{L_C}{L_D})^{0.8} = 6.5$

$f(\text{min}^{-1})$	%AE	NTU_C	ΔNTU_C	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$
0	2.0	0.29	0	0
20	2.5	0.37	0.08	0.52
20	2.5	0.37	0.08	0.52
30	5.1	0.99	0.70	4.55
35	5.6	1.18	0.89	5.26
40	5.4	1.10	0.81	5.7
30	4.7	0.87	0.58	3.77

Feed Rotameter Readings: 10.0-11.0; $(\frac{L_C}{L_D})^{0.8} = 3.8$

$f(\text{min}^{-1})$	%AE	NTU_C	ΔNTU_C	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$
25	5.1	0.99	0.45	2.92
25	5.1	0.99	0.45	2.92

Feed Rotameter Readings: 6.0-6.0; $(\frac{L_C}{L_D})^{0.8} = 7.1$

$f(\text{min}^{-1})$	%AE	NTU_C	ΔNTU_C	$\frac{\Delta NTU_C}{(L_D/L_C)^{0.8}}$
35	5.4	1.10	0.86	6.1

APPENDIX E

GLASS-FILTER DATA

TABLE XIII

Runs No. 81-106

Perforated Plate at the Middle of the Column

Dispersed Phase: Isobutanol
Continuous Phase: Water

Feed Rotameter Readings: 6.0-6.0

		Conc., w/o Isobutanol in Water				
		Glass Filter No.				Aqueous Effluent
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)	
87	0	1.35	1.5	1.9	2.0	2.0
88	15	2.0	2.2	2.3	2.4	2.35
91	20	2.5	2.7	2.9	3.0	3.0
89	30	3.6	4.0	4.2	4.2	4.2
90	45	4.7	5.5	5.6	5.8	5.7

Feed Rotameter Readings: 10.0-8.5

		Glass Filter No.				Aqueous Effluent	Organic Effluent
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)		
98	0	1.3	1.35	2.0	2.0	2.0	11.2
99	15	1.8	2.1	2.3	2.4	2.3	11.5
100	20	2.3	2.7	2.9	3.0	3.0	11.9
101	30	3.5	4.0	4.2	4.3	4.3	13.8
102	45	4.1	5.2	5.5	5.7	5.6	14.1

Feed Rotameter Readings: 6.0-8.5

		Glass Filter No.				Aqueous Effluent
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)	
92	0	2.3	2.4	3.2	3.3	3.2
95	10	2.6	2.8	3.3	3.4	3.4
93	20	3.8	4.1	4.4	4.4	4.4
96	30	5.3	5.7	5.8	5.9	5.9
97	30	5.3	5.8	5.9	6.0	6.0
94	40	5.9	6.5	6.7	6.8	6.8

Feed Rotameter Readings: 10.0-11.0

		Glass Filter No.				Aqueous Effluent	Organic Effluent
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)		
103	0	2.0	2.0	3.3	3.5	3.4	11.2
104	20	3.4	3.8	4.3	4.4	4.4	12.3
105	30	5.0	5.7	5.9	6.1	6.1	14.2
106	40	5.8	6.7	7.0	7.2	7.2	14.2

TABLE XIII (Continued)

Feed Rotameter Readings: 6.0-11.0

Run No.	f(min^{-1})	Glass Filter No. (1)	(2)	(3)	(4)	Aqueous Effluent
82	0	3.5	3.6	4.8	5.0	4.8
83	0	3.4	3.6	4.8	4.9	5.0
85	10	3.8	4.05	5.0	5.05	5.1
86	15	4.4	4.6	5.2	5.4	5.4
84	20	5.3	5.6	6.0	6.0	6.0
81	30	6.5	6.9	7.1	7.2	7.3

TABLE XIV

Runs No. 107-128

Perforated Plate at the Bottom of the Column

Dispersed Phase: Isobutanol
Continuous Phase: Water

Feed Rotameter Readings: 6.0-6.0

		Conc., w/o Isobutanol in Water					
		Glass Filter No.				Aqueous Effluent	Organic Effluent
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)		
112	0	1.4	1.5	1.6	1.7	1.7	11.3
113	45	2.8	3.3	3.6	4.1	4.4	13.1

Feed Rotameter Readings: 10.0-8.5

		Glass Filter No.				Aqueous Effluent	Organic Effluent
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)		
108	0	1.6	1.7	1.9	1.9	2.0	10.5
110	15	1.7	1.9	2.0	2.1	2.0	10.7
107	30	2.2	2.5	2.7	3.0	3.1	10.8
109	45	2.6	3.2	3.6	4.2	4.6	11.2
111	60	3.0	3.8	4.4	5.4	6.3	12.3
115	75	3.0	4.1	4.8	6.1	7.4	15.3

Feed Rotameter Readings: 10.0-11.0

		Glass Filter No.				Aqueous Effluent	Organic Effluent
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)		
117	0	2.9	3.3	3.4	3.5	3.5	11.0
118	0	2.8	3.2	3.3	3.4	3.3	10.9
120	10	2.8	3.1	3.2	3.4	3.4	11.2
119	20	3.0	3.4	3.5	3.65	3.7	11.1
121	30	3.4	3.9	4.1	4.3	4.3	11.0
116	40	4.2	4.9	5.2	5.9	6.1	12.1
124	55	4.8	5.6	6.1	6.9	7.2	12.3
114	60	5.2	6.1	6.7	7.5	7.8	13.7

Feed Rotameter Readings: 6.0-11.0

		Glass Filter No.				Aqueous Effluent	Organic Effluent
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)		
125	0	4.1	4.3	4.5	4.5	4.5	10.8
126	15	4.3	4.5	4.6	4.8	4.7	10.8
127	30	5.1	5.4	5.6	5.8	5.8	11.1
128	45	6.1	6.6	6.0	7.4	7.4	12.2

TABLE XV

Runs No. 129-140

Perforated Plate at the Bottom of the Column

Pulse Amplitude = 1/2 inch (approx.)

Dispersed Phase: Isobutanol
Continuous Phase: Water

Feed Rotameter Readings: 6.0-6.0

		Conc., w/o Isobutanol in Water				
		Glass Filter No.				Aqueous
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)	Effluent
132	35	3.2	3.8	4.2	4.9	5.4

Feed Rotameter Readings: 10.0-8.5

		Glass Filter No.				Aqueous
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)	Effluent
138	0	1.6	1.8	1.9	2.0	2.0
139	15	1.7	1.9	2.0	2.1	2.0
134	20	2.0	2.2	2.3	2.5	2.5
136	20	1.9	2.2	2.3	2.5	2.5
137	20	1.9	2.1	2.2	2.35	2.4
129	30	2.7	3.4	3.9	4.4	5.1
140	30	2.5	3.2	3.6	4.2	4.7
133	35	2.7	3.5	4.1	4.9	5.6
135	40	2.8	3.5	4.0	4.8	5.4

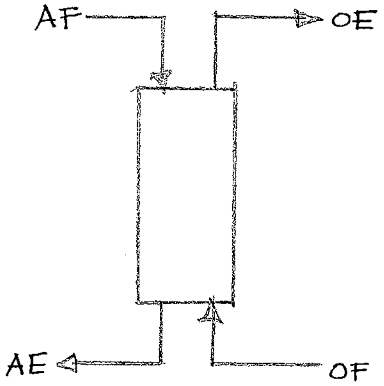
Feed Rotameter Readings: 10.0-11.0

		Glass Filter No.				Aqueous
Run No.	f(min^{-1})	(1)	(2)	(3)	(4)	Effluent
130	25	3.9	4.5	4.7	5.1	5.1
131	25	3.7	4.3	4.6	4.9	5.1

APPENDIX F

SAMPLE OF MATERIAL BALANCES TO PROVE APPROXIMATE CONSTANCY OF L_C AND L_D

Sample Material Balances to Prove Constancy of L_C and L_D



Pulse frequency: 0

Aqueous Feed: 130 ml/min = 129.6 g/min
= 0.9971

Organic Feed: 59 ml/min = 47.1 g/min
= 0.7980

Aqueous Effluent Conc. (AE) = 4.7%

Organic Effluent Conc. (OE) = 11.1%
= 0.8210

Water balance:

$$129.6 = AE(1 - 0.047) + OE(0.111)$$

Isobutanol balance:

$$47.1 = AE(0.047) + OE(1 - 0.111)$$

$$\begin{aligned} 129.6 &= 0.953\ AE + 0.111\ OE \\ 47.1 &= 0.047\ AE + 0.889\ OE \\ \hline 1039.1 &= 7.650\ AE + 0.889\ OE \\ 47.1 &= 0.047\ AE + 0.889\ OE \\ \hline 992.0 &= 7.603\ AE; \\ AE &= 130.5\ g/min \\ 47.1 &= 6.229 + 0.889\ OE; \\ OE &= 46.0\ g/min \end{aligned}$$

APPENDIX G

COMPARISON OF COLBURN AND WELSH'S RESULTS WITH RESULTS FROM THIS WORK

Comparison of Colburn and Welsh's Data with Data from this Work

	Colburn and Welsh	This Work
Type of Column:	Packed with 1/2-inch clay Raschig rings	Unpacked (spray column)
Column Dimensions:	3-11/16 in. x 21 in.	2 in. x 24 in.
Water Dispersed:	$HTU_D = 0.6$	None
	$HTU_C = 2.0\left(\frac{W_C}{W_D}\right)^{0.75}$	
Isobutanol Dispersed:	$HTU_D = 0.9$	$HTU_D = 1.9$
	$HTU_C = 1.0\left(\frac{W_D}{W_C}\right)^{0.75}$	$HTU_C = 0.8\left(\frac{L_C}{L_D}\right)$
	$NTU_D = 2.0$	$NTU_D = 1.0$
	$NTU_C = 1.75\left(\frac{W_D}{W_C}\right)^{0.75}$	$NTU_C = 2.5\left(\frac{L_D}{L_C}\right)$
	$k_Ca = \frac{W_D}{Ah}(1.75)\left(\frac{W_C}{W_D}\right)^{0.25}$	$k_Da = \frac{L_D}{Ah}(2.5)$
	$k_Da = \frac{W_D}{Ah}(2.0)$	$k_Da = \frac{L_D}{Ah}(1.0)$

APPENDIX H

GLASS FILTER FLOW-RATE DATA

Effect of Flow Rate Through the Glass Filter on Sample Concentration

All samples taken from the lowest glass filter on the column.

Unpulsed runs

Feed rotameter readings: 10.0 - 11.0

Run No. 146

Flow-rate, ml/min	6.25	7.0	11.1	20.6
Conc., weight per cent	3.45	3.45	3.5	3.45

Run No. 147

Flow-rate, ml/min	3.1	4.4	26.0	43.5
Conc., weight per cent	3.4	3.4	3.4	3.5

Pulsed run

Pulse frequency: 30 cycles per min
Pulse amplitude: 1/2 inch (approximately)
Feed rotameter readings: 10.0 - 8.5

Run No. 149

Flow-rate, ml/min	3.3	7.4	13.2	20.0
Conc., weight per cent	3.7	3.7	3.7	3.8

Note: a) Samples were not taken in order of increasing flow rate.

b) For run No. 149, temperature in the column was 22°C.

VITA

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