

EFFECT OF 400-KILOCYCLE INSONATION ON THE
EXTRACTION OF ACETONE FROM CARBON
TETRACHLORIDE WITH WATER

by

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I. INTRODUCTION

A solute introduced into a mixture of two immiscible liquids, if soluble in both liquids, distributes itself between the two liquids in a definite equilibrium concentration, the distribution normally favoring one of the liquids in preference to the other. The distribution principle finds important applications in the process of solvent extraction, which, in recent years, has assumed marked importance as a chemical engineering unit operation.

In general practice, a solute which is dissolved in one solvent is removed by bringing the solution into contact with a second solvent in which the solute is more soluble than the first; the solute distributes itself between the two solvents, passing from one solvent phase to the other. In the transference of a solute from one liquid phase to another immiscible liquid phase across an interface, there is a resistance to this mass transfer that has a definite influence on the rate and quantity of mass transferred. A concept, known as the fluid film concept of diffusion, recognizes that at the interface between two relatively immiscible liquids, there is a thin film on either side

of the interface through which the solute must pass in diffusing from one solvent to the other. The rate of mass transfer depends on the interfacial area, the film thickness, and the differential concentration of the solute in the solvent at the interface and in the two phases. Any factor that would reduce the resistance, i.e., increase the interfacial area, decrease the film thickness, and increase the differential concentration of the solute, would increase the rate and the quantity of mass transferred.

Ultrasonic waves are reported to produce microagitation and thermal effects in dispersions and emulsions, particularly at an interface where the waves encounter a phase boundary.

The purpose of this investigation was to study the effect of an ultrasonic field on the rate of transfer of acetone from a carbon tetrachloride phase to a water phase.

II. LITERATURE REVIEW

According to Treybal⁽⁹⁷⁾ three major factors must be considered in the design and construction of a liquid-liquid extraction process. These factors are: (1) the phase equilibrium relations, (2) the rate at which extraction proceeds, and (3) the equipment used. This review covers these factors after fundamental concepts and definitions are presented.

Concepts and Definitions

Selected concepts and definitions are given: first, to recall for the reader broad principles and general theory underlying liquid-liquid extraction and ultrasonics; and second, to present the meaning within which controversial terms are used in this review.

Liquid-Liquid Extraction. Several techniques have been developed for separating components of a liquid solution⁽⁹⁷⁾; however, one particular method or another is usually advantageous in a given system either because of the properties of the system or because of the economics involved. In general, it is desired to effect separation

by physical methods rather than by chemical methods. Examples of methods of separation of components of a liquid system are: distillation, evaporation, sorption, and liquid-liquid extraction.

All of these separation techniques depend upon the tendency of a liquid, when distributed between two phases at equilibrium⁽⁹⁷⁾, to occur in different concentrations in each of the phases. Liquid-liquid extraction⁽³²⁾ is the separation process wherein one or more liquid components are transferred from one liquid phase to another.

Liquid-liquid extraction may be carried out in several different ways, the most important of which is to add another solvent that is immiscible, or nearly immiscible, with one or more of the components of the feed⁽⁹⁷⁾. Alternately, the original solution may be heated or cooled to form two phases. A third component, that takes no direct part in the extraction method, may be added to cause the feed to form two phases. Finally, the feed solution may be treated with two immiscible liquids each of which dissolves a separate component of the original solution⁽³²⁾.

Uses of Liquid-liquid Extraction. According to Elgin⁽³²⁾ extraction may be preferable to other separation operations when: (1) the boiling points of the components of the liquid mixture are within a very few degrees of each other, (2) one or more of the liquids are sensitive to heat, (3) a comparatively small amount of solute is present in the original mixture and the solute is less volatile than the other components, and (4) the solvent used has a lower heat of vaporization than the original solution. Brown⁽¹⁹⁾ suggests that in addition to the foregoing reasons extraction may be employed when the two liquids are non-volatile or nearly so.

Treybal⁽⁹⁷⁾ emphasizes that the following points must be considered before one decides to use any extraction operation. First, the addition of more than one component has several disadvantages (a large amount of capital is tied up in inventories, corrosion problems are increased, handling and storage problems are increased, and dangers of contamination of final product are increased). Second, the extraction process must be followed by a solvent recovery process, usually distillation. This solvent recovery step quite often represents a major portion of the final cost of the extraction process.

Benedict⁽⁶⁾ focuses attention on the fact that all physical separation processes require power to perform separation. In extraction the principal power requirement is the heat needed to recover the solvent. Thus, if the power expended to effect a given separation is the least for extraction this is the most economical process. However, this should not be used as the sole criterion of selection⁽⁶⁰⁾ as other factors, such as solvent loss or product contamination, may become important.

A few of the many industrial uses of liquid-liquid extraction that should be mentioned are refining of lubricating oils⁽²⁾, extraction of acetic acid from pyroligneous acid liquors⁽⁴²⁾, recovery of phenol⁽⁶¹⁾, purification and concentration of vitamins and antibiotics⁽⁹⁸⁾, refining of vegetable oils^(41,51), and recovery of alcohols from Fischer-Tropsch synthesis gas⁽⁵²⁾.

Feed. The original liquid solution that is to be separated is referred to as the feed⁽³²⁾.

Solute. Solute⁽³²⁾ is the dissolved component of the feed to be extracted. The solute is not necessarily the desired final product. In the refining of lubricating

oils, for example, impurities are extracted from the oil stocks and hence, are the solute, but are not the desired final product.

Solvent. Solvent⁽²²⁾ is the immiscible liquid that is added to dissolve selectively the solute from the feed, and occurs in the greatest concentration, exclusive of the solute, in the extract phase.

Carrier Solvent. Carrier solvent⁽²²⁾ consists of all the components in the original feed except the solute.

Extract Phase. The extract phase⁽⁸²⁾ consists of the solvent after it has contacted and has been separated from the feed. This layer contains, in addition to the solvent, the solute and whatever other components it has gained. This phase is often referred to as the solvent-rich phase.

Extract. After the solvent has been removed from the extract phase it is referred to as the extract⁽⁸²⁾.

Raffinate Phase. The raffinate phase⁽⁸²⁾ consists of the original feed after it has been contacted and separated from the solvent.

Raffinate. After the solvent has been removed from the raffinate phase it is called the raffinate⁽⁸²⁾.

Selectivity. The solvent is said to be selective⁽⁸²⁾ for that component of the feed which occurs in the greater ratio in the extract than in the feed. That is, the solvent is selective for the solute by definition. For extraction to take place in a desired direction, the selectivity coefficient, β , must be greater than unity⁽¹⁹⁾. The selectivity coefficient, β , and the distribution coefficient, m , are often confused. The distribution coefficient is an expression of the equilibrium between the two phases in liquid-liquid extraction (See equation 1, page 9), while the selectivity coefficient (See equation 5, page 28) is an expression of the relative enrichment of the solute in the extract phase.

Distribution. Glasstone⁽⁴⁰⁾ states the distribution law in the following manner: "If to a system of two liquid layers, made up of two immiscible or slightly miscible components, is added a quantity of a third substance soluble in both layers, then the substance is found to distribute, or divide, itself between the two layers in a definite manner." The definite manner being

that the ratio of solute concentration in the two phases is constant, as shown in the following equation⁽³⁰⁾:

$$y = m x \quad (1)$$

where:

m = distribution coefficient, dimensionless

y = concentration of solute in the extract phase, mol fraction

x = concentration of solute in the raffinate phase, mol fraction.

It was once thought that this ratio was independent of the absolute concentration; but it is now known that this fact is true for very few systems, and in these systems, only at low concentration⁽⁹⁹⁾.

Ideal Stage. If after the extraction stage the two phases leave in equilibrium, that is, if the solute is distributed according to the distribution law, the stage is called an ideal stage⁽³³⁾. An ideal stage represents the limiting amount of extraction for any stage.

Stagewise Contact. In any extraction process, if the two liquid phases are alternately mixed and separated the process is said to be one of stagewise contact⁽⁸⁰⁾. A more

rigorous definition of a stagewise extractor would be any extractor⁽⁴⁶⁾ in which the interfacial area between the two phases varies with position in the equipment or with time. The classical example of stagewise contact is the bubble-cap column.

Continuous Contact. Instead of bringing the solution to be extracted and the extracting solvent into contact in separate stages with intermediate settling, it is possible to cause the liquid phases to flow continuously past each other. This type of contact is called continuous contact⁽⁸⁰⁾. Continuous contact may be further defined as any extraction process in which the interfacial area does not vary substantially with position in the column or with time during the operation of the column.

Transfer Unit. Colburn^(28,29) points out that the concept of "ideal stages" is not applicable to continuous contact. The difference in the physical mechanism of contact invalidates the ideal stage calculation. He^(28,29) proposed the use of the transfer unit as a basis with which to compare the efficiency of the continuous extraction process. The Colburn transfer unit (See equation 6, page 31) is the concentration change experienced per unit

of concentration difference causing this change. The transfer unit is a measure of standard difficulty of extraction. Just as one equilibrium contact is a measure of extraction independent of the system, so is one transfer unit. The former applies to continuous and the latter to stagewise contact extraction.

Classification of Extraction Operations by Solvent Systems. A convenient method of classifying⁽¹⁰¹⁾ extraction operations is as follows:

- I. Single solvent systems, including all those which consist of or which may be reduced to the equivalent of, three components, the two to be separated and the solvent.
 - A. Stagewise contact
 - B. Continuous contact
- II. Mixed solvents
 - A. Stagewise contact
 - B. Continuous contact
- III. Double solvents (fractional extraction)
 - A. Stagewise contact
 - B. Continuous contact

Classification of Extraction Operations by Flow Sheets. Elgin⁽³¹⁾ has proposed a useful classification of extraction operations depending upon the arrangement of the equipment. His classification is as follows:

- I. Single contact
- II. Multiple contact
 - A. Cocurrent
 - 1. Multistage
 - 2. Differential
 - B. Countercurrent
 - 1. Continuous
 - a. With reflux
 - b. Without reflux

Differential cocurrent contact is the limiting case of multistage cocurrent contact in which the solvent is added in differential portions and the extract removed as fast as it is formed. Its inclusion as a separate class is due to the work of Treybal⁽¹⁰¹⁾ and Varteressian and Fenske⁽¹⁰⁵⁾. The familiar Soxhlet extractor is an example of a differential cocurrent extractor⁽¹⁰⁸⁾.

Equilibrium Relations

In studies of chemical engineering equipment the equilibrium relations of the systems involved are important as a basis for comparisons and further calculations. By equilibrium relations is meant the studies on distribution and phase relations.

Distribution. The equilibrium⁽⁹⁹⁾ that is of importance in liquid-liquid extraction is the distribution equilibrium, or the phase relation studies of solute distribution. The ideal form of the distribution law, however, is inadequate in liquid-liquid extraction. Several reasons for this fact are presented in the following paragraph.

Nernst⁽²⁵⁾ suggested that all deviations from the distribution law are caused by either association or disassociation of the solute in either or both phases. Nernst's explanation may well be correct, but his equations become impossibly cumbersome when applied to most systems. These deviations, if caused by the mechanism postulated by Nernst, are also complicated by a change in the relative amount of disassociation or association when the absolute concentration of the solute changes.

Brancker, Hunter, and Nash⁽¹⁸⁾ found that the mol fraction of A in the A-rich phase when plotted against the equilibrium concentration of B in the B-rich phase gave a curved line. However, if the coordinates of the concentration of A in the A-rich phase are adjusted to obtain a straight line these same coordinates will give a straight line for most other systems. This method is similar to the method of Cox⁽³⁰⁾ for vapor pressure data. Brancker et al⁽¹⁸⁾ state that solutropic systems cannot be correlated by this method. A solutropic system⁽⁸³⁾ is one in which the distribution ratio changes from greater than one to less than one, or vice versa, as the concentration of the solute changes.

Bachman⁽³⁾ found that the equations of the straight lines on the Brancker, Hunter, and Nash coordinates are as follows:

$$X_{AA}X_{BB} = aX_{AA} + bX_{BB} \quad (2)$$

where:

X_{AA} = concentration of solvent in the extract phase, weight fraction

X_{BB} = concentration of carrier solvent in raffinate phase, weight fraction

a = constant, weight fraction

b = constant, weight fraction.

Thus, if X_{BB} is plotted against X_{BB}/X_{AA} on rectangular coordinate paper straight lines should be obtained.

Othmer and Tobias⁽⁶⁴⁾ found that a plot of equilibrium values of $(1 - X_{AA})/X_{AA}$ against $(1 - X_{BB})/X_{BB}$ on double logarithmic coordinate paper produced straight lines.

The three previous modifications of the distribution law all suffer from the disadvantage that the concentration of the solute, C , is not in the expression. Hand⁽⁴⁴⁾ showed that a double logarithmic plot of X_{CB}/X_{AA} against X_{CB}/X_{BB} is usually rectilinear. This method is generally

considered to be the most satisfactory of the many forms of the distribution law. Hand's method amounts to writing the distribution law in the following form:

$$\frac{X_{CB}}{X_{BB}} = k \left(\frac{X_{CA}}{X_{AA}} \right)^n \quad (3)$$

where:

X_{CB} = concentration of solute in raffinate
phase, weight fraction

X_{BB} = concentration of carrier solvent in
raffinate phase, weight fraction

X_{CA} = concentration of solute in extract
phase, weight fraction

X_{AA} = concentration of solvent in extract
phase, weight fraction

k = constant, dimensionless

n = constant, dimensionless.

Distribution Data for the System Carbon Tetrachloride-Acetone-Water. The distribution data⁽²¹⁾ for the system carbon tetrachloride-acetone-water at several temperatures are given in Table I, page 18. In Figure 1, page 19, the distribution curve is drawn on rectangular coordinates.

As this system is solutropic, it cannot be represented by the Hand equation. Distribution and refractive index data for the system are presented in Table II, page 20. Specific gravity of equilibrium solutions for the system are presented in Figure 2, page 21. Refractive index of equilibrium solutions for the system are plotted in Figure 3, page 22. Distribution of acetone between carbon tetrachloride and water is illustrated in Figure 4, page 23.

Binodal Curves. In addition to the distribution data the composition of the saturated solutions of A and C in B and of B and C in A are needed⁽³³⁾. This type of information is usually plotted on a triangular composition diagram. The use of this type of diagram for presenting solubility and phase composition data for ternary systems has been adequately covered by Bull and Coli⁽²²⁾, Brown⁽¹⁹⁾, Elgin⁽³³⁾, and Treybal⁽¹⁰¹⁾. An example of this type of diagram for the system carbon tetrachloride-acetone-water is presented in Figure 5, page 24, from data presented in Table III, page 25.

TABLE I

Distribution Data for the System Carbon
Tetrachloride-Acetone-Water

Temperature, °C	Acetone Concentration	
	Carbon Tetrachloride Phase, wt %	Water Phase, wt %
30.0	0.80	3.35
30.0	3.95	10.30
30.0	4.60	11.50
30.0	13.90	22.30
30.0	16.50	24.40
30.0	24.20	30.40
30.0	33.30	35.80
30.0	39.60	40.20
30.0	47.20	46.00
30.0	51.90	49.80
30.0	59.04 ^a	59.04 ^a
20.8	2.10	6.90
20.8	6.20	14.30
20.8	13.80	22.50
4.0	2.21	9.50
4.0	4.90	14.90
4.0	9.00	20.60
4.0	13.80	25.30

^a Plait point.

Buchanan, R. H.: Liquid-liquid Equilibrium Data for
the System Carbon Tetrachloride-Acetone-Water,
Ind. Eng. Chem., 44, 2449 (1952).

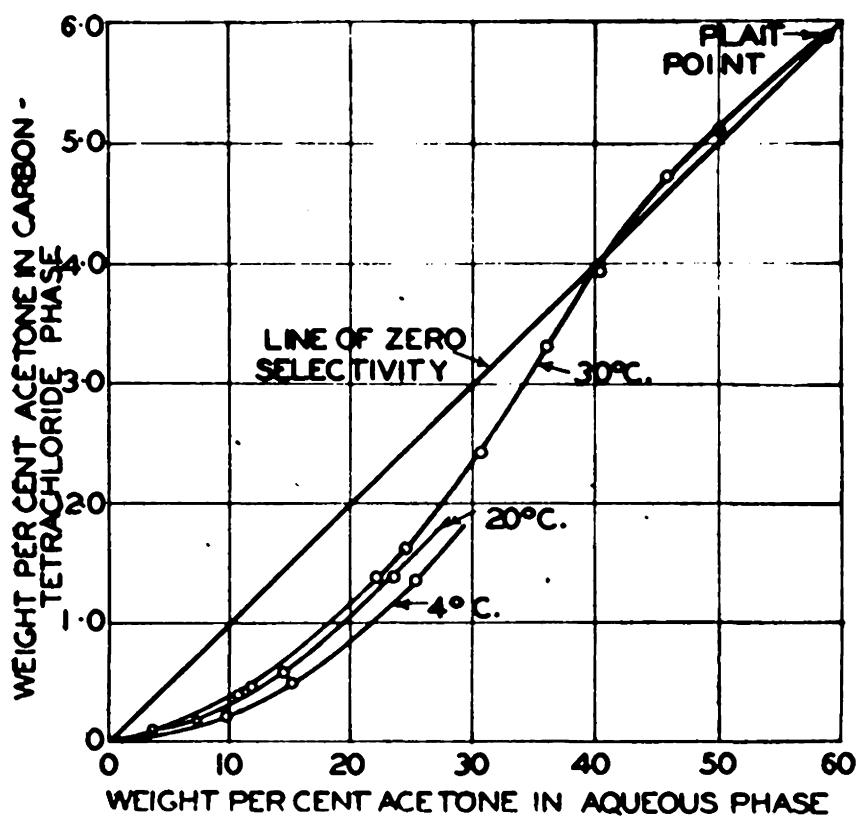


Figure 1. Distribution Data for the System
Carbon Tetrachloride-Acetone-Water

Buchanan, R. H.: Liquid-liquid Equilibrium Data for the System Carbon Tetrachloride-Acetone-Water, Ind. Eng. Chem., 44, 2449 (1952).

TABLE II

Distribution and Refractive Index Data for the System

Carbon Tetrachloride-Acetone-Water

Carbon Tetrachloride Phase			Water Phase		
Acetone Concentration	Specific Gravity	Refractive Index	Acetone Concentration	Specific Gravity	Refractive Index
wt %	30°/4°C	n_D^{20}	wt %	30°/4°C	n_D^{20}
0.00 ^a	1.5768	1.4628	0.00 ^a	0.9946	1.3320
0.00 ^b	1.5764	1.4594	0.00 ^b	0.9952	1.3330
0.49	1.5698	1.4588	2.87	0.9913	1.3341
1.73	1.5531	1.4568	5.98	0.9872	1.3365
2.38	1.5418	1.4558	8.14	0.9844	1.3376
5.53	1.4947	1.4503	14.83	0.9758	1.3419
8.68	1.4480	1.4446	17.79	0.9709	1.3449
12.81	1.3966	1.4377	21.93	0.9643	1.3479
17.39	1.3419	1.4302	26.88	0.9566	1.3508

^a Analysis of original component.

^b Analysis of original component saturated with other phase.

Hayford, D. A.: The Design, Construction and Operation of a Liquid-liquid Pulse Extractor.: Unpublished M. Sc. Thesis, Library, Virginia Polytechnic Institute, Blacksburg, Va., p. 93 (1953).

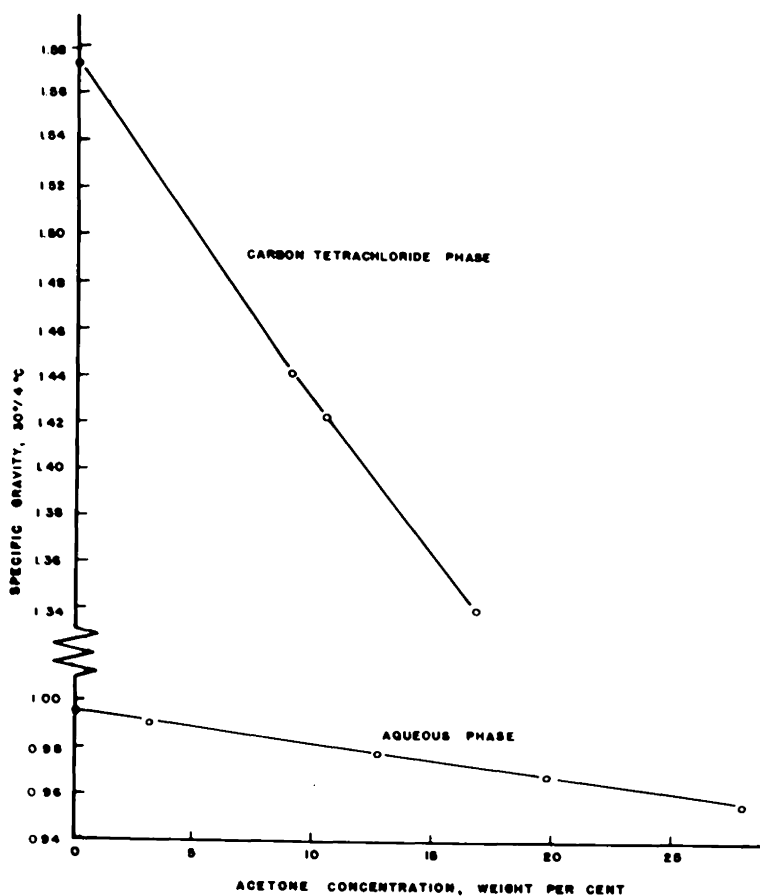


Figure 2. Specific Gravity of Equilibrium Solutions for
The System Carbon Tetrachloride-Acetone-Water

Hayford, D. A.: The Design, Construction and Operation of
a Liquid-Liquid Pulse Extractor. Unpublished M. Sc.
Thesis, Library, Virginia Polytechnic Institute,
Blacksburg, Va., p. 94 (1953).

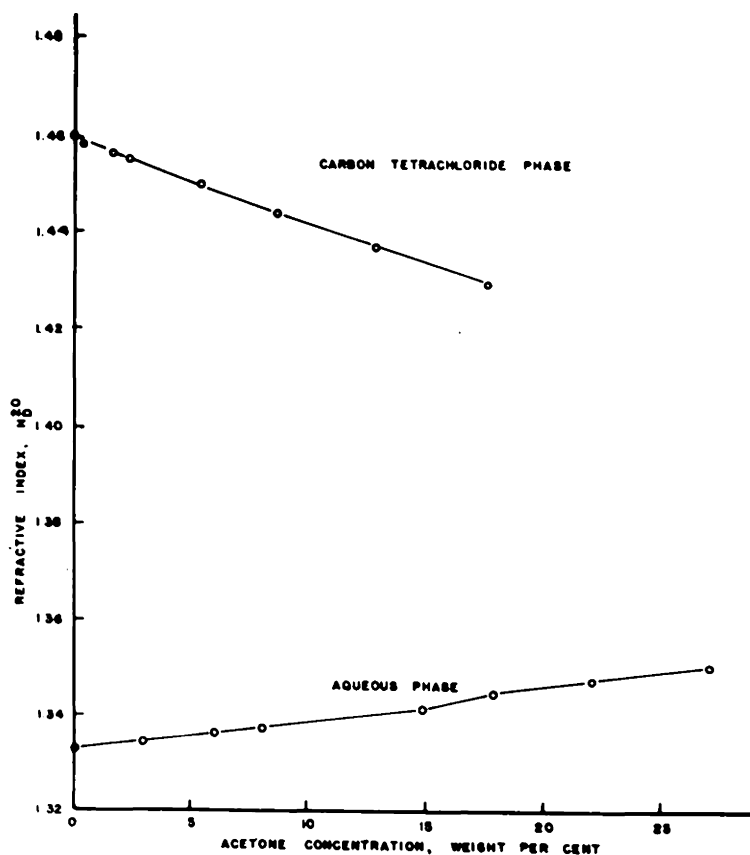


Figure 3. Refractive Index of Equilibrium Solutions for
The System Carbon Tetrachloride-Acetone-Water

Hayford, D. A.: The Design, Construction and Operation of a
Liquid-liquid Pulse Extractor. Unpublished M. Sc.
Thesis, Library, Virginia Polytechnic Institute,
Blacksburg, Va., p. 95 (1953).

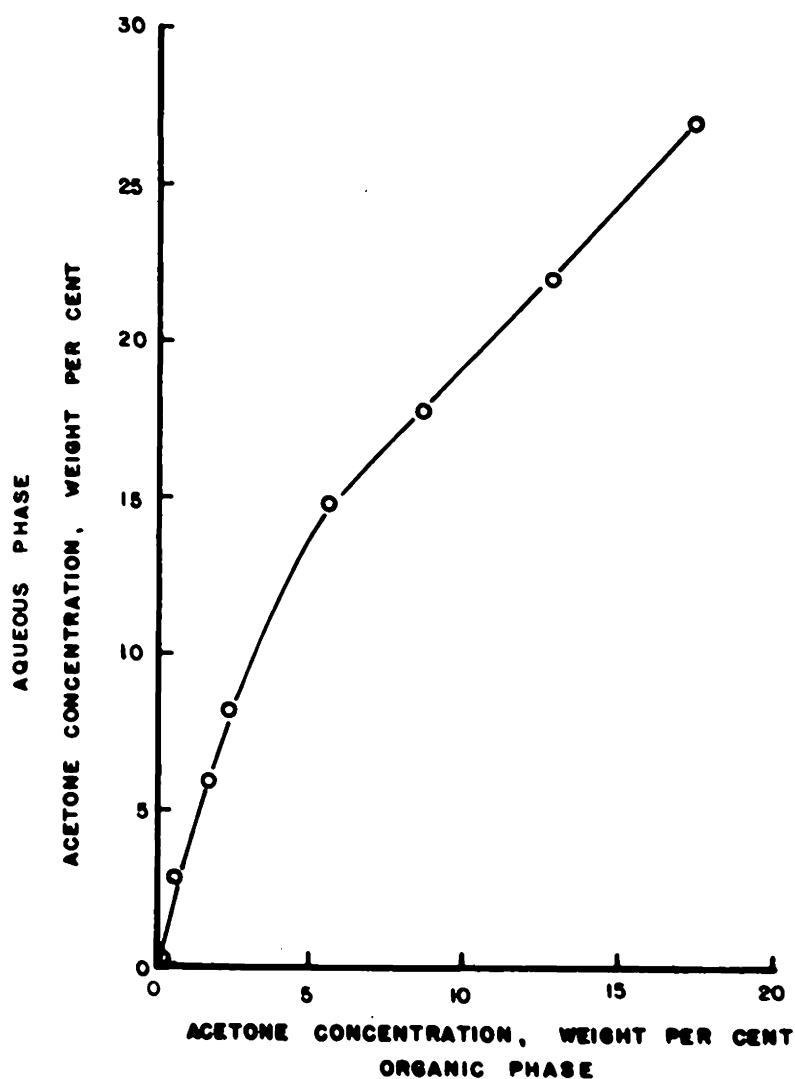


Figure 4. Distribution of Acetone between Carbon
Tetrachloride and Water at 20 °C

Hayford, D. A.: The Design, Construction and Operation of a
Liquid-liquid Pulse Extractor. Unpublished M. Sc.
Thesis, Library, Virginia Polytechnic Institute,
Blacksburg, Va., p. 96 (1953).

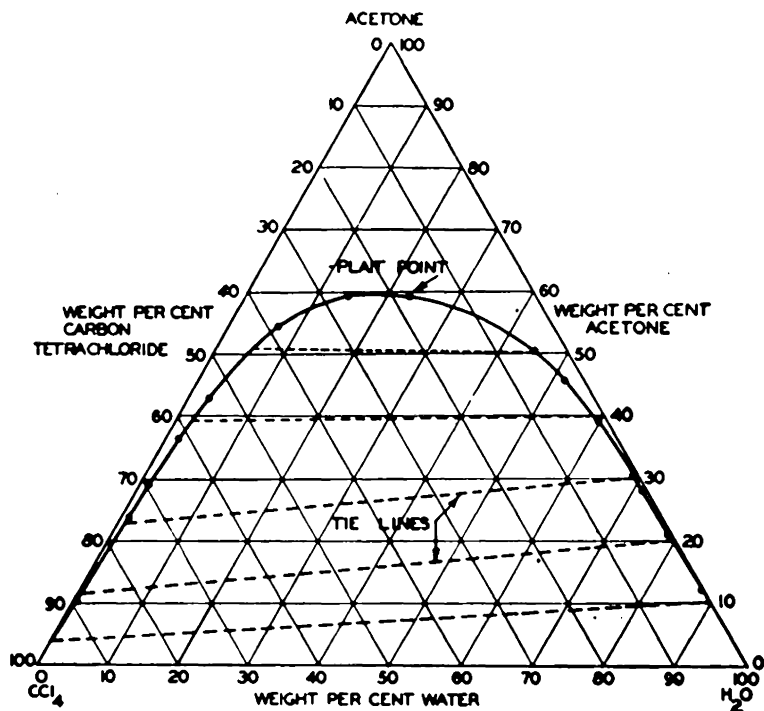


Figure 5. Solubility Data for the System
Carbon Tetrachloride-Acetone-Water

Buchanan, R. H.: Liquid-liquid Equilibrium Data for the System Carbon Tetrachloride-Acetone-Water, Ind. Eng. Chem., 44, 2449 (1952).

TABLE III

Solubility Data for the System Carbon

Tetrachloride-Acetone-Water

Acetone	CCl ₄	Water	Specific Gravity
wt %	wt %	wt %	30°/4°C
0.00	100.00	0.00	1.5750
9.14	90.78	0.08	1.4410
10.58	89.19	0.23	1.4230
22.17	76.98	0.85	1.2852
29.32	69.61	1.07	1.2120
36.40	61.90	1.62	1.1470
24.63	54.67	2.70	1.0936
54.34	38.73	6.93	1.0000
59.46	26.15	14.39	0.9524
59.04	18.01	22.95	0.9330 ^a
54.83	7.57	37.60	0.9197
50.27	4.69	45.05	0.9325
45.77	2.73	51.50	0.9292
47.32	1.36	61.32	0.9411
31.58	0.69	67.73	0.9494
21.08	0.40	78.52	0.9657
19.82	0.39	79.78	0.9680
12.83	0.28	96.90	0.9780
3.22	0.22	96.56	0.9910
0.00	0.00	100.00	0.9956

^a Plait point.

Buchanan, R. H.: Liquid-liquid Equilibrium Data for the System Carbon Tetrachloride-Acetone-Water, Ind. Eng. Chem., 44, 2449 (1952).

Equilibrium in Extraction Processes. Extraction may be carried out either in discrete steps or as a continuous countercurrent process. The former process is called countercurrent stagewise extraction, and the latter process is called continuous countercurrent extraction. The equilibrium relations, representing optimum operation, are different for these two processes.

Equilibrium in Stagewise Extraction. If, in any stagewise contactor, the two exit streams are in equilibrium the stage is called an ideal stage⁽⁸²⁾. In actual practice the stages are always less than perfect, and the two liquids leave each stage before equilibrium has been reached. This suggests that the various types of stages or contactors can be compared by means of their relative approach to equilibrium. The stage efficiency, defined as the percentage ratio of the approach to equilibrium for any given stage, was formulated⁽³³⁾ for this purpose.

The following equation is an expression of stage efficiency for stagewise extraction:

$$S = \frac{Y_A - Y_O}{Y_E - Y_O} \times 100 \quad (4)$$

where:

S = stage efficiency, per cent

Y_A = actual concentration of acetone in
extract phase, weight per cent

Y_E = ideal concentration of acetone in
extract phase, weight per cent

Y_O = concentration of acetone in the
solvent, weight per cent.

In practice, where several stages are mounted together to form a tower, the total number of equilibrium stages to perform the actual separation is found. The number of real stages making up the tower divided into the number of ideal stages gives the average stage efficiency⁽³³⁾ for the column.

Equilibrium in Countercurrent Extraction. For continuous countercurrent extraction the ideal relation between the two countercurrent streams at any point is given by the following equation⁽³³⁾:

$$Y = \frac{\beta X}{1 - X(\beta - 1)} \quad (5)$$

where:

Y = solute concentration in the extract
phase, weight fraction

X = solute concentration in the raffinate
phase, weight fraction

β = selectivity coefficient, dimensionless.

Thus, a measure of efficiency, similar to stage efficiency, may be calculated by comparing the ideal $\underline{Y}$ from the above equation to the real $\underline{Y}$ at any given point. This method, although valid and general, is seldom used.

Rate Relations

Once the equilibrium rates on performance are fixed, the rate relations make it possible to calculate the time required to approach equilibrium under actual conditions. In the more general case, if the time is fixed, the actual approach to equilibrium can, itself, be calculated.

Mass Transfer Concept. The closest available approximation to completely describe extraction behavior, although undoubtedly inadequate, is the two-film theory⁽³⁰⁾. In this theory the interface between the two phases is believed to be formed of two compressed, laminar films analogous to the type encountered in heat transfer. It is assumed that all the resistance to transfer of the solute, from one phase to the other, takes place between the films. Experimental results show that there is a measurable resistance⁽⁸²⁾ to the transfer of solute from phase to phase. In effect, this means that a finite time is required for a system to approach equilibrium. The reciprocal of the equilibrium time function is called the overall, mass-transfer coefficient. The overall, mass-transfer coefficient is a measure of the rate at which extraction takes place.

There have been many^(72,82) attempts to correlate the physical properties of the extraction system and the rate constant. However, as yet, no really satisfactory method of predicting the overall, mass-transfer coefficient for commercial equipment is available.

The Transfer Unit. The performance of stagewise equipment can be adequately described in terms of the stage efficiency. In order to obtain a measure of equal utility for use with continuous countercurrent extraction Colburn introduced the transfer unit. Colburn^(28,29) defined the number of transfer units as equal to the integral of the differential change in concentration divided by the difference in concentration tending to

cause transfer. Stated in symbols the number of transfer units may be defined as follows:

$$N = \int_{y_2}^{y_1} \frac{dy}{y^* - y} \quad (6)$$

where:

- N = the number of Colburn mass transfer units,
dimensionless
- y = concentration of solute in one phase, mol
fraction
- y* = concentration of solute in the extract
phase that is in equilibrium with the
concentration of solute in the raffinate
phase at the same point, mol fraction
- y₁ = concentration of solute in the extract phase
at the feed end of the column, mol fraction
- y₂ = concentration of solute in the extract phase
at the solvent end of the column, mol
fraction.

Methods of Calculation. Algebraic methods for calculating the number of theoretical stages have been reported by Varteressian and Fenske^(105,106) and Hunter and Nash^(48,49). These methods are extremely difficult to apply except in rather special cases. Graphical simplifications of the above methods have been proposed by Maloney and Schubert⁽⁵⁸⁾, Hunter and Nash^(48,49), and Varteressian and Fenske^(105,106).

Maloney and Schubert⁽⁵⁸⁾ have modified the method of Ponchon and Savaritt to apply to extraction. This method makes use of the solvent content-concentration diagram for a ternary system. It is covered in detail by Brown⁽²⁰⁾, Perry⁽³³⁾, and Bull and Coli⁽²²⁾.

The triangular phase diagram, an example of which is shown on page 24, supplies the necessary relation between the composition and quantity of the extract layer leaving any stage and those of the raffinate layer leaving the same stage. Simultaneous graphical solutions of the material balances on this chart furnish a graphical solution to a countercurrent stagewise extraction operation. This method was proposed by Hunter and Nash^(48,49) and is covered in detail by Perry⁽³³⁾ and Bull and Coli⁽²²⁾.

The McCabe-Thiele method may be modified to present a graphical solution to extraction problems. This method was first proposed by Varteressian and Fenske^(105,106) and covered by them and Perry⁽³³⁾.

Equipment

Classification of liquid-liquid extractors with mention of the commercial and experimental variations available is discussed in this section.

Liquid-liquid Extractors. A liquid-liquid extractor may be defined⁽³⁴⁾ as any type of equipment that may be used to effect liquid-liquid extraction. Liquid-liquid extractors, like most unit operations equipment, are exemplified by a great variety of commercially used types. This diversification was caused by a number of factors⁽⁶⁰⁾ which include: (1) lack of reliable performance data on available equipment, (2) development of extractors by different industries before the emphasis on unit operations began, (3) modification of existing distillation and absorption apparatus to extraction, (4) specialization of extractors for several purposes,

(5) development of existing equipment rather than design of new equipment.

Classification of Liquid Extractors. Three methods of classification of extractors are those presented by Elgin⁽³⁴⁾, Treybal⁽¹⁰²⁾, and Morello and Poffenberger⁽⁶⁰⁾. Elgin⁽³⁴⁾ classifies extraction equipment according to either mixer-settler (batch) or continuous extractors. He subclassifies further as follows:

I. Mixer-settler extractor

- A. Air agitators
- B. Mechanical mixers
- C. Flow mixers
- D. Column mixers
- E. Pumps

II. Countercurrent columns operating continuously

- A. Wetted wall
- B. Spray
- C. Packed
- D. Sieve or perforated plate
- E. Modified bubble plate
- F. Baffle column
- G. Columns with internal agitators.

Treybal⁽¹⁰²⁾ borrowed Elgin's classification and modified it to further subdivide the continuous columns.

Morello and Poffenberger⁽⁶⁰⁾ used an entirely different scheme of classification. They divided equipment into classes depending upon the method used to separate the phases. Their further subdivisions are:

I. Two phases separated by gravity

A. Contact made through the interfacial area as a film

1. Extended surfaces
2. Packed towers

B. Contact made through the interfacial area with one phase dispersed as droplets

1. No additional power required for dispersion
 - a. Spray towers
 - b. Baffle towers
 - c. Perforated plate towers
 - d. Bubble-cap towers
 - e. Packed towers
2. Additional power required to redisperse the phases
 - a. Mixer and settler combinations
 - b. Baffle tower with movable membranes

II. Two phases separated by centrifugal force.

Use of External Power in Extraction Equipment. One of the most important questions to be solved in liquid-liquid extractor design is the utility of extractors using external power⁽¹⁰²⁾. External power⁽⁶⁰⁾ may be defined as any power supplied to the extractor in addition to that power necessary to cause flow of the liquid phases.

The additional power supplied--if efficiently utilized--will cause the formation of a very high interfacial area and, consequently, achieve better extraction⁽⁷⁵⁾. However, this gain in extraction rate is set against the additional mechanical complexity of the extractor and the additional cost of operation. Some of the mechanical features of power extractors that often cause trouble are leaks in stuffing boxes, undesirable flexing and straining in long shafts, and increased erosion and corrosion of moving parts⁽⁶⁰⁾.

Available Types of Extractors. A partial list of the more commonly used types of extractors will be presented in this section. Operating performance and design characteristics are not included, but may be found in each separate reference.

Centrifugal Extractor. The only successful extractors of the centrifugal type are modifications of the extremely versatile Podbielinak⁽⁶⁵⁾ extractor. Extractors of the centrifugal type are widely used in the pharmaceutical industry (penicillin, streptomycin, etc.) where the product can easily absorb the higher first and operating costs⁽⁹⁶⁾.

Film Type Extractors. There are three different types of film extractors. The first two, the wetted-wall and the horizontal-tube extractor, are examples of laboratory experimental columns. The last, the film-type extractor of Gordon and Zeigler⁽⁴³⁾, is an example of a commercial extractor.

Spray Tower Extractor. The spray tower extractor is the simplest and cheapest continuous countercurrent extractor⁽¹⁰³⁾. Although widely used in laboratory studies because of its simplicity, the spray tower is little used industrially⁽⁶⁰⁾, partly because the dispersed phase has a tendency to coalesce, and the continuous phase to recirculate. Blanding and Elgin⁽¹²⁾ present a thorough discussion on spray tower design.

Packed Extraction Column. The successful use of packed towers in gas absorption and, to a lesser extent, in distillation suggested their use in liquid-liquid extraction. The overall efficiency of this type column may be poor⁽¹⁴⁾, because of channeling and recirculation of the continuous phase. Packed columns are being used at present to refine vegetable oils^(41,51,100), lubricating oils⁽⁶⁰⁾, and recover phenol^(60,100).

Baffle Extractor. Although most extractor designs are modifications of equipment for other unit operations, the baffle extractor⁽¹⁰³⁾ was developed solely for extraction. Elgin⁽³⁴⁾ defines the baffle extractor as "a vertical tower containing horizontal baffles to direct the flow of liquids. There are three types: disk and doughnut, side to side, and center to side." Baffle extractors are used in acetic acid recovery⁽⁴²⁾, and hydrocarbon oil extraction⁽⁶⁰⁾.

Perforated-Plate Extractor. The perforated-plate extractor⁽¹⁰³⁾ operates by having the dispersed phase repeatedly coalesced and dispersed. The liquids are forced through a series of trays in which a large number of holes have been punched or drilled. The

perforated-plate extractor is used extensively in the phenol-lubricating oil refining process⁽²⁾.

Bubble-Cap Extractors. The bubble-cap tray contactor in distillation and gas absorption is generally considered to be the most efficient type of contactor. However, when this contactor is used in extraction very poor results are obtained. Both Treybal⁽¹⁰³⁾ and Morello and Poffenberger⁽⁶⁰⁾ believe that a bubble-cap column, designed exclusively for liquid-liquid extraction, should be quite an efficient contactor.

Mixer and Settler Extractors. Mixer and settler type extractors⁽¹⁰²⁾ consist of a mixing chamber of suitable design followed by a settling chamber for each stage. Mixer-settler extractors were undoubtedly the earliest type of extraction equipment used, and although bulky, it is quite dependable. Many modifications^(62,63,74,75) of this type of contactor have been proposed.

Nature of Ultrasonics

Existing literature on ultrasonics focuses attention on the theoretical aspects as well as experimental observations but practical industrial applications of ultrasonic phenomena are limited. In many of the cases where ultrasonic energy has been demonstrated to accentuate certain physical and chemical phenomena, experimental work has been on a batch scale, employing conventional, research-type generators. Although fundamental concepts are included in most textbooks on physics and acoustics, the following definitions are presented as a matter of convenience.

Definition of Ultrasonic Waves. Ultrasonic waves are defined as high frequency, inaudible sound waves above approximately 18,000 cycles per second^(7,53). The term ultrasonics has been used synonymously with "supersonics" in many reports; however, the latter term has now become associated with the velocity of projectiles and aircraft in air, relative to the velocity of sound, while the former is more commonly associated with the frequency of sound waves.

Wave Motion. A wave is a temporary change in the shape or condition of a medium, which moves through the medium and transmits energy outward from the source⁽⁷¹⁾. If the source of the waves is continuous, they follow one another at equal intervals of time in a procession which is known as a train of waves. If the source is discontinuous, the deformation of the transmitting medium may consist of a single pulse known as a wave pulse.

Types of Waves. Waves are classified on the basis of how the particles of the medium move with reference to the direction of propagation of the wave form⁽⁷¹⁾.

Transverse Waves. A transverse wave is a wave in which the particles of the medium vibrate or the condition of the medium changes, at right angles to the direction of propagation of the wave. Light, radio waves, and x-rays are examples of transverse waves.

Longitudinal Waves. Longitudinal, or compressional, waves are those in which the particles of the medium vibrate, or the condition of the medium changes, in the direction of propagation of the wave. Sound waves fall in this category.

Characteristics of Wave Motion. Waves, whether they are longitudinal or transverse, have three distinct characteristics⁽⁷¹⁾. They are: (1) frequency, (2) wave length, and (3) amplitude. At a given frequency, the wave length is determined by the velocity which in turn is dependent upon the medium of transmission.

Frequency. The frequency of a wave is the number of complete vibrations which a particle of the transmitting medium makes in one second.

Wave Length. Wave length is the distance that the wave form advances while a particle makes one complete vibration. In a transverse wave, a wave length includes one crest and one trough; in a longitudinal wave, one compression and one rarefaction. The wave length of sound waves varies directly with the velocity and inversely with the frequency. At 20,000 cycles per second, the wave length of sound in water at 20 degrees centigrade is 0.72 centimeter--decreasing to 0.0072 centimeter at a frequency of 2,000,000 cycles per second.

Amplitude. The amplitude of a wave is the maximum distance that a particle of the medium of

transmission vibrates to either side of its equilibrium position⁽⁷¹⁾ and is a measure of the intensity of the acoustical energy being propagated.

Velocity. Ultrasonic wave velocity, although varying with the properties of the medium, is approximately 1 million times slower than electromagnetic waves; velocity of sound in air being 1,100 feet per second as compared to 186,000 miles per second for the electromagnetic waves.

Generator Classification. Several types of acoustical generators are available commercially. These vary from low frequency, high amplitude sirens and whistles, used for insonating gases, to high frequency, low amplitude, piezoelectric and magnetostriction generators used for detecting flaws in solids. Figure 6, page 44, illustrates the ranges of intensity and frequency for the different types of generators. The piezoelectric generator is the most convenient type for studying effects of ultrasonics on liquid systems.

Piezoelectric Generators. Commercial piezoelectric generators are usually quartz or barium titanate, although EDT (ethylene diamine tartrate), ADP (ammonium dihydrogen

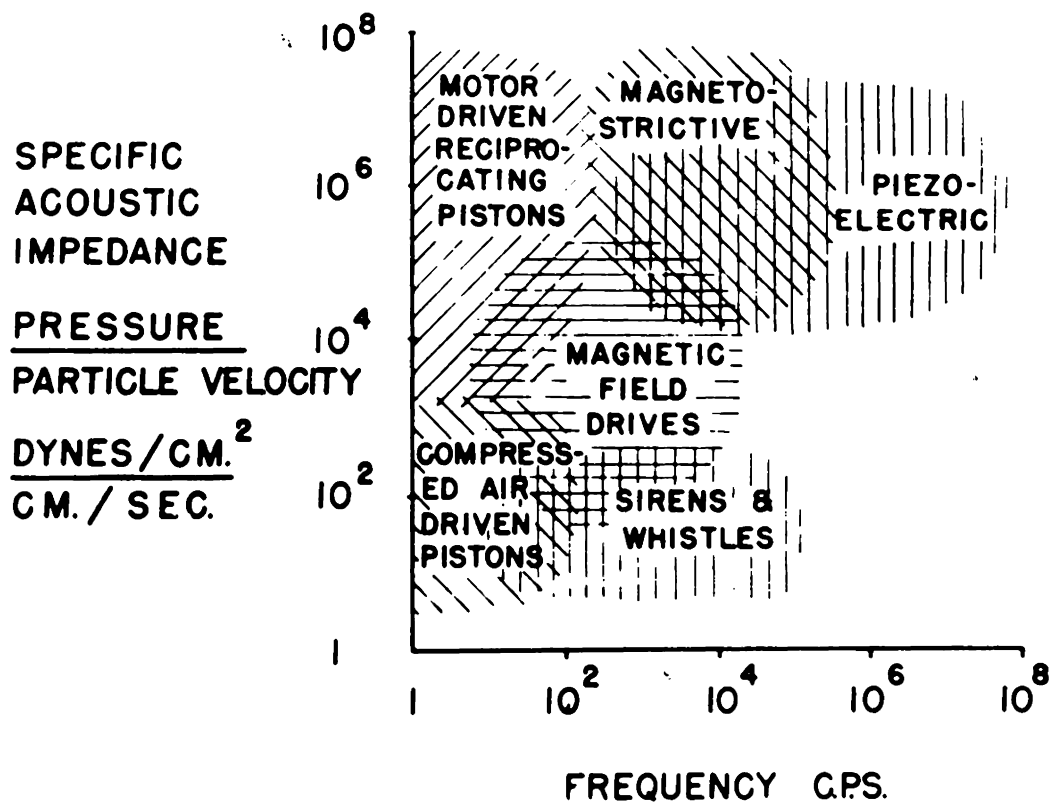


Figure 6. Available Transducer Types Usable at High
Power Levels for Various Regions of Specific
Acoustic Impedance vs. Frequency

Samsel, R. W.: Physical and Economic Limitations in the
Application of Sonic and Ultrasonic Energy to
Industrial Processes, "Ultrasonics--two symposia."
Chem. Engr. Prog. Sym. Series, No 1, 47, 80 (1951).

phosphate), lithium sulfate and other piezoelectric crystals are employed for specialized purposes⁽²³⁾.

The comparison chart, Table IV, page 46, indicates some of the desirable properties of barium titanate. Its electrical characteristics make barium titanate eminently suitable for high power ultrasonic applications with liquids and solids⁽²³⁾. The chart shows, for instance, that with a given applied voltage, the obtainable physical motion of the barium titanate is approximately 80 times greater than that of quartz. It shows also that the dielectric constant is unusually high, and that the material has a very low electrical impedance. This matter of electrical impedance is very important because it means that high potentials, in the order of thousands of volts, customary with quartz, are not required for the generation of ultrasonic power with this material. Its excellent motion-voltage characteristic (190×10^{-12} meter/volt) makes barium titanate particularly suitable for use in ultrasonic power generators. Barium titanate may be extruded, cast or pressed into various sizes and shapes to meet many anticipated physical or technical specifications.

TABLE IV

Comparative Chart of Physical Properties
of Piezoelectric Crystals

Expander Modes	$\frac{\text{Motion Out}}{\text{Voltage in } d}$ 10^{-12} m/V	Dielectric Constant K	$\frac{\text{Voltage Out}}{\text{Force in } g}$ $\frac{\text{V}\cdot\text{m}}{\text{Newton}}$	Elastic Modulus Y $10^9 \frac{\text{Newton}}{\text{m}^2}$	$\frac{\text{Voltage Out}}{\text{Motion in } Y\cdot g}$ 10^9 V/m	Coupling Coefficient $k = \sqrt{dg Y}$	Frequency Constant short- circuited kc.mm
Rochelle Salt (34°C)							
X cut lateral	165	200	.093	19.3	2.9	.54	2100
Y cut lateral	27	9.2	.33	10.7	3.6	.31	1180
ADP							
Lateral	24	15.3	.177	19.3	3.4	.29	1630
Quartz Lateral and) Parallel)							
	2.3	4.5	.058	80	4.6	.103	2700
Lithium Sulfate (LH)							
Parallel	16.0	10.3	.175	46	8.0	.36	2360
DKT							
Lateral	11.0	6.5	.192	25	4.8	.23	1770
EDT							
YX cut Lateral	11.3	8.2	.156	26	4.0	.22	2050
Tourmaline							
Parallel	1.93	6.6	.033	160	5.3	.10	3600
Barium Titanate, Prepolarized							
Parallel	190	1700	.0125	87	1.10	.46	2000 - 2500
Lateral	78	1700	.0052	87	.45	.19	2000

Prepared by Dr. H. Jaffe, Brush Development Co.

Butterworth, J. W.: Kilowatts of Ultrasonic Power for
Industry, "Ultrasonics--two symposia." Chem. Engr.
Prog. Sym. Series, No 1, 47, 71 (1951).

Figure 7, page 48, illustrates the increased intensity obtained by focusing ultrasonic waves. This is accomplished by means of a bowl-shaped barium titanate ceramic element.

Ultrasonic Absorption. Dissipation of acoustic energy in the medium itself is the determining factor in the transmission of sound through an unbounded medium. Since the absorption of sound increases with the frequency, it is considerably greater for ultrasound than

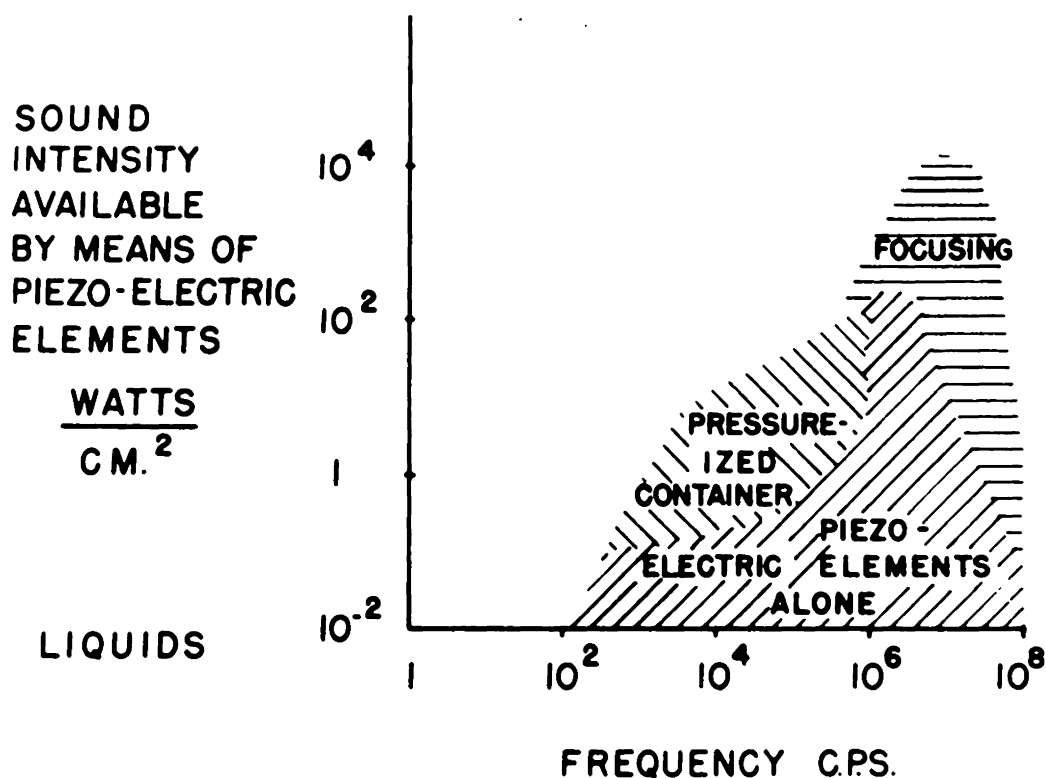


Figure 7. Spectrum of the Sounds that can be Produced
by Means of Piezoelectric Generators

Samsel, R. W.: Physical and Economic Limitations in the Application of Sonic and Ultrasonic Energy to Industrial Processes, "Ultrasonics--two symposia." Chem. Engr. Prog. Sym. Series, No 1, 47, 79 (1951).

for ordinary sound. For an estimate of the absorption, the following formula may be used:

$$\alpha = \frac{16 \pi^2 \nu \eta}{3 \nu^2 \rho} \quad (7)$$

where:

- ν = speed of propagation, centimeters per second
- ν = frequency of the sound, cycles per second
- η = viscosity coefficient, dimensionless
- ρ = density of the medium, grams per cubic centimeter
- π = constant, 3.1416
- α = absorption coefficient, which is defined by the equation:

$$I = I_0 e^{-\alpha(x/\lambda)} \quad (8)$$

where:

- λ = wave length of the sound, centimeters
- x = distance traveled, centimeters
- I_0 = initial intensity of sound, watts per square centimeter
- I = intensity after passing through distance x , watts per square centimeter
- e = constant, 2.7183.

Several investigators^(9,26,70) note that the experimental values are considerably higher than those computed by classical theory. Some of the explanations offered⁽¹⁰⁷⁾ for this discrepancy involve forces exerted between bonds or dipoles; relaxation specific heats; molecular rearrangements; phase differences; thermal density variations; and adjustment of thermal equilibrium states.

Figure 8, page 51, shows the velocity and absorption of sound waves in acetone-water mixtures, while Figure 9, page 52, presents the same data for acetone-benzene mixtures.

Effect of pressure on the velocity and absorption of sound waves is presented in Figure 10, page 53, and the effect of temperature on the coefficient of absorption is illustrated in Figure 11, page 54.

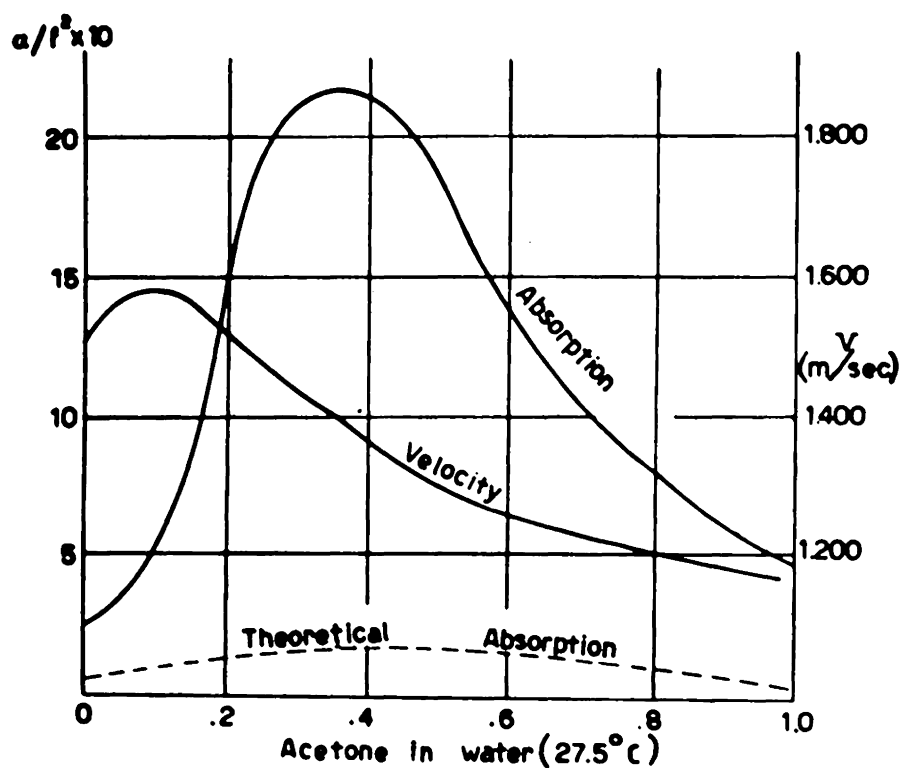


Figure 8. Velocity and Absorption of Sound Waves
in Acetone-Water Mixtures

Richardson, E. G.: "Ultrasonic Physics," p. 180. Elsevier
Publishing Company, New York, N. Y., 1952.

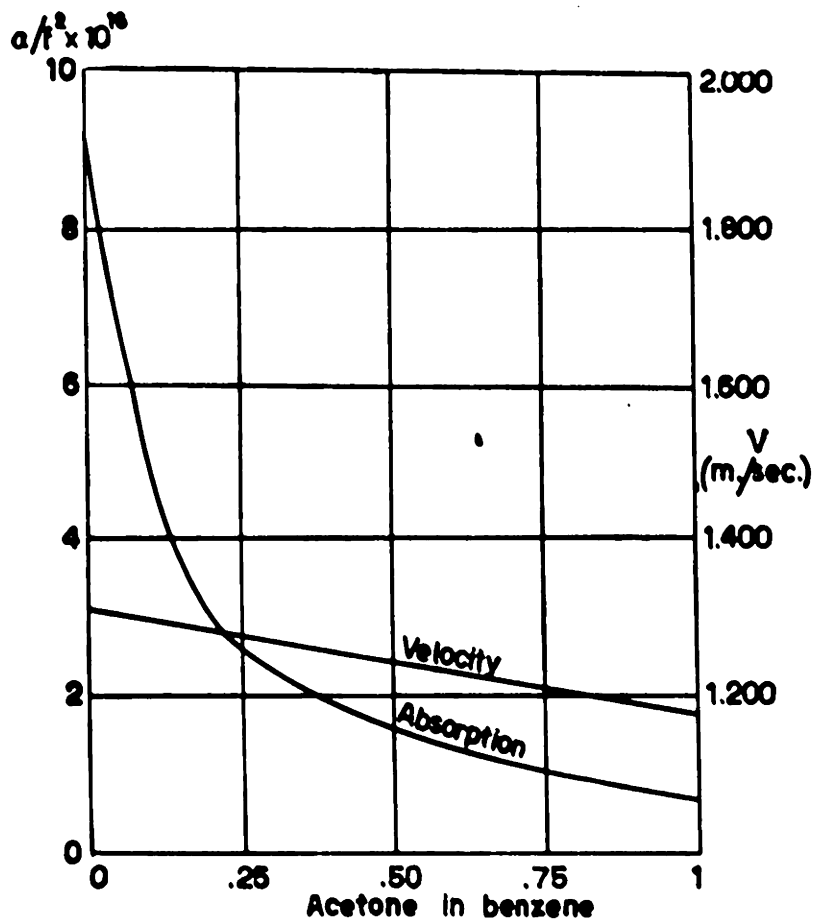


Figure 9. Velocity and Absorption of Sound Waves
in Acetone-Benzene Mixtures

Richardson, E. G.: "Ultrasonic Physics," p. 179. Elsevier
Publishing Company, New York, N. Y., 1952.

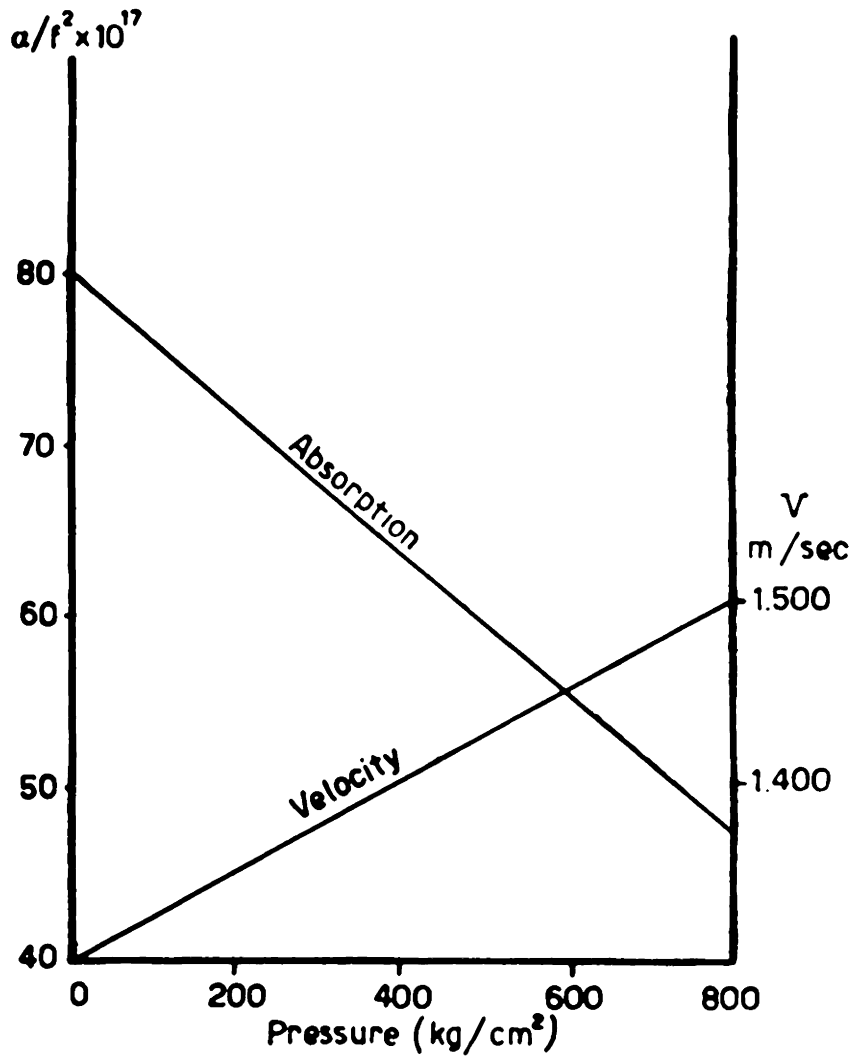


Figure 10. Velocity and Absorption of Sound Waves
in Liquids as a Function of Pressure

Richardson, E. G.: "Ultrasonic Physics," p. 182. Elsevier
Publishing Company, New York, N. Y., 1952.

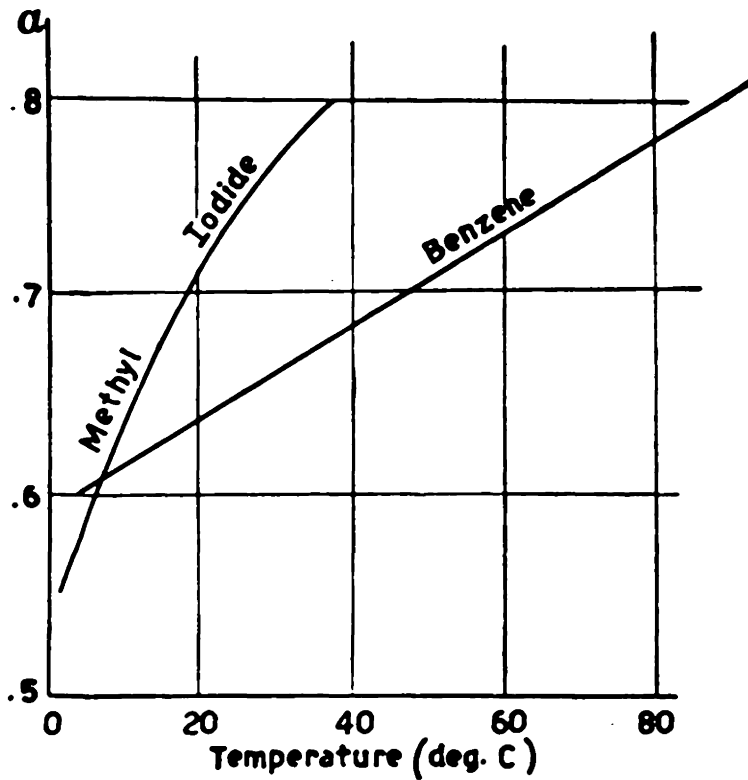


Figure 11. Absorption Coefficient in Benzene and
in Methyl Iodide as a Function of Temperature

Richardson, E. G.: "Ultrasonic Physics," p. 183. Elsevier
Publishing Company, New York, N. Y., 1952.

Effects of Ultrasonics

For the purpose of this investigation the effects of ultrasonics may be conveniently categorized into:

- (1) effects of cavitation, (2) thermal effects, and
- (3) chemical effects.

Cavitation. An important consequence of the passage of intense sound waves through liquids is cavitation^(15,16,47). Cady⁽²⁴⁾ defines cavitation as "a term applied both to the liberation of bubbles of air or other absorbed gases from a liquid and to the tearing apart of the liquid itself with the production of hollow spaces filled with vapor." These cavities tend to form layers a half wave length apart at the nodes since the dispersed substance is less dense than the medium (and at anti-nodes if it is denser), and then collapse with great violence due to external pressure. According to Weissler⁽¹⁰⁹⁾, a one megacycle sound wave of about 10 watts per square centimeter intensity, traveling through water, will cause an amplitude of motion of the molecules of about 10^{-5} centimeters. But, the acceleration of these molecules attains very high values, about 250,000 times greater than the acceleration due to gravity. The maximum instantaneous velocity is about 40 centimeters per

second. The pressure at a given point in the water changes from plus five atmospheres to minus five atmospheres, one million times each second. The negative portion of this sound wave tends to fracture the liquid and release any dissolved gas as minute bubbles. The cavities that are formed will collapse with a violent hammering action which generates local pressures on an order of magnitude of 10^3 atmospheres. Calculation⁽¹¹¹⁾ shows that the pressure of the blow, when a vortex cavity collapses upon a central nucleus one-twentieth the diameter of the original cavity, may reach 68 tons per square inch, or 765 tons per square inch if the diameter of the nucleus is only one per cent of that of the cavity initially. Cady⁽²⁴⁾ states that the optimum pressure for pronounced cavitation effects is about two atmospheres pressure, but at atmospheric pressure this effect sets in at intensities of about 0.3 watt per square centimeter in the ultrasonic range^(17,24). Its importance lies in the fact that almost all of the phenomena to be described subsequently, disappear if easily visible cavitation is suppressed, either by degassing the liquid, or by applying to it a large hydrostatic pressure^(45,50,56,77,91).

Formation of Cavities. Measured values of the fracture pressure of water range from the positive vapor pressure to a negative pressure of about 350 atmospheres⁽³⁵⁾. However, the theoretical fracture pressure of water has been calculated to be 1320 negative atmospheres⁽³⁵⁾, assuming that the vapor bubble responsible for fracture took place in the interior of the liquid. Fisher⁽³⁵⁾ states that the low experimental values may result from the fact that the initial bubble forms instead at the interface between the liquid and the container, or between the liquid and a suspended particle, where, in the case of a paraffin-water interface, the fracture pressure is only 62 per cent of that for the fracture in the interior of the liquid.

Collapse of Cavities. Rayleigh⁽⁶⁹⁾ has calculated the pressure developed during the collapse of a spherical cavity, and found that thousands of atmospheres may be developed at the moment when the cavity collapses to a small fraction of its original diameter. Sollner⁽⁸⁴⁾ has stated that, if cavitation arises, it acts as a disruptive mechanical force, the collapsing

cavities hammering at the material in the sound field, preferentially at the weaker spots which are the phase boundaries. Sollner⁽⁸⁴⁾ states further, that the action of sound waves in producing emulsions and dispersions is fundamentally the same as mechanical agitation. However, besides the mechanical aspect of cavitation it is believed that there are three more probable phenomena which occur during cavitation: chemical, electrical, and thermal effects. Weyl and Marbae⁽¹¹⁰⁾ have considered the chemical aspect as the fracture of molecules to form ions when a liquid is subjected to high negative pressure such as is produced by an ultrasonic field. The electrical aspect has been considered from the standpoint of luminescence of liquids transversed by ultrasonic waves^(27,37,112), in that the luminescence is produced by electrical discharges associated with the interfacial area of bubbles formed by cavitation. Finally, the thermal aspect is evidenced by considerable heat development at phase boundaries where cavitation is most likely to occur⁽⁵⁷⁾.

It is generally agreed that cavitation occurs preferentially at weak spots represented by phase

boundaries such as an oil-water interface^(13,85). And at these boundaries, cavitation induces microagitation-- defined as the selective, point-wise mixing encountered when insonated particles, either solid or liquid, move or vibrate in relation to each other, as compared to the bulk mixing produced by commercial agitators such as impellor mixers or moving baffles. For maximum microagitation at an interface, the sound wave must be absorbed or reflected rather than transmitted. Optimum conditions for the transmission of sound energy through an interface exist when the value of ρc (ρ is the density of the medium and c refers to the speed of sound in the medium) is equal for both phases. Conversely, the greatest microagitation occurs when there is a mismatch of the ρc values.

Cavitation, hence microagitation, is favored where emulsification may occur⁽⁵⁷⁾. Similarly, dissolved gases may act as weak spots as they are driven out by insonation, thus forming nuclei for bubbles⁽¹³⁾.

Sollner and Bondy⁽⁸⁸⁾ have studied the coagulation or demulsification of oil emulsions and concluded that, if cavitation does not occur, many stabilized

emulsions may be broken by prolonged application of sound intensities below 0.3 watt per square centimeter at atmospheric pressure.

Thermal Effects. Marinesco⁽⁵⁹⁾ reports that small regions of very high temperature exist in the insonated liquid because of the presence of cavitated bubbles. Several investigators^(8,10,38,87) have reported that maximum thermal changes occur at the interface between two substances traversed by ultrasonic waves. Freundlich, Sollner, and Ragowski^(38,39) found that when a given oil mixture contained equal weights of macroscopic objects such as glass beads or lead shot, the heat developed by ultrasonic waves increased with decreasing ball radius, that is, with increasing object-oil interface. They also reported that sound absorption by liquids is strongly increased by gas bubble formation during cavitation, and that heat produced by the sonic waves in the liquid is thus increased. Attention has been called^(8,10,87) to the fact that propagation of sound in a liquid is poorer if gas bubbles are present, because of the greater tendency toward conversion of sonic to thermal energy. Further

evidence of the proportional relationship of heat formation and area of interface is the fact that emulsions and suspensions heat many times faster than do corresponding homogeneous macro-phases.

Chemical Effects. Thompson⁽⁹⁴⁾ has reported the works of many investigators concerning the chemical effects produced by ultrasonic waves. Such effects include: acceleration of reaction rates, electrolytic effects, oxidation, luminescence, polymerization, decomposition, inversion of sucrose, increased crystallization and the determination of molecular properties. However, the effect of oxidation warrants consideration for this investigation because a basic assumption for liquid-liquid extraction requires that there be no chemical reaction.

Of the many chemical effects produced by ultrasonic insonation, the phenomenon of oxidation has attracted the most wide-spread interest.

Schmitt, Johnson, and Olson⁽⁷⁶⁾ believe that when carbon tetrachloride was added to potassium iodide and starch solution, an intense blue color developed immediately upon radiation. Other tests supported the fact that carbon tetrachloride does not act catalytically in the

oxidation of potassium iodide, but is itself decomposed, giving rise to some free chlorine. Schmitt, Johnson, and Olson⁽⁷⁶⁾ also think that by treatment of water containing dissolved air and a little potassium iodide, free iodine results. The reason for this process is believed to be due to the production of hydrogen peroxide by insonation of water containing dissolved air or oxygen, which in turn oxidizes the potassium iodide to iodine^(55,73,76,89).

Weissler⁽¹⁰⁹⁾ has found that the rate of iodine liberation from an insonated aqueous potassium iodide solution was over 15 times greater when the potassium iodide solution was kept fully saturated with carbon tetrachloride, and five times greater when the solution was half saturated with carbon tetrachloride at the start, than when none was present at all. The proposed theory for this "sonochemical" reaction⁽¹⁰⁹⁾ is that the carbon-to-chlorine bond is broken by the mechanical or possibly electrical forces generated at the collapse of cavitation bubbles which had been facilitated by the presence of air or some other dissolved gas. Once this chlorine is set free, it will react with the potassium iodide to produce free iodine.

It has been found by a number^(54,66,67,78,104) of investigators that ultrasonic insonation of water containing dissolved air not only activates the oxygen, but the nitrogen as well, forming nitrous and nitric acids.

Solov'eva⁽⁸⁹⁾ has demonstrated that ultrasonic waves will catalyze the oxidation of aqueous potassium iodide to potassium iodate and of aqueous ferrous sulfate to ferric sulfate by atmospheric oxygen. He⁽⁸⁹⁾ found that the rate of oxidation increases with sound intensity, although the relation was not linear.

In the insonation of water by ultrasonic waves, Beuthe⁽¹¹⁾ has shown that hydrogen peroxide is formed only in water saturated with oxygen or air, and the same might be concluded for all such chemical reactions observed. He⁽¹¹⁾ states that the vibratory motion produced by the ultrasonic waves causes oxygen molecules to be ionized at the comparatively large boundary between liquid and gas, perhaps by the action of electric charges. The oxygen atoms thus formed are then absorbed by the water with the formation of hydrogen peroxide.

Applications of Ultrasonics. Acoustical energy has been successfully utilized on a commercial scale for applications such as flaw detection, thickness gaging, agglomeration of aerosols, cleaning of small metal parts, and cutting and grinding. However, there is an urgent need⁽⁹³⁾ for fundamental, quantitative research to outline the limitations that bound the application of ultrasonic energy. Such research should point out potentialities that have some reasonable basis for scientific development.

In general, effects induced by acoustical energy will be of importance largely in multiphase systems⁽⁹⁰⁾, or more specifically (1) systems in which liquids or solids are suspended in liquids or gases, and (2) systems in which gases are entrapped in liquids. However, important effects may be expected in single phase fluid systems in which the sound energy employed brings about relative motion between molecules of different sizes or a significantly increased rate of collision between molecules. Unless the sound energy of the frequency employed in a given case can distinguish in some way between the "particles" of the system, ordinarily little useful effect can be expected.

"Chemical engineers⁽⁹⁰⁾ are continually encountering problems where rate processes are controlled by diffusion of material at an interface. One is familiar with the dependence of these diffusion rates, within limits, on the relative velocities at such interfaces. It is to be expected that because of the high local velocities associated with high-frequency, high-intensity sound energy a substantially increased rate of diffusion may be obtained at the mass transfer boundary."

III. EXPERIMENTAL

The experimental section of this thesis includes: purpose of the investigation, plan of experimentation, materials and apparatus used, method of procedure, data and results obtained, and sample calculations.

Purpose of Investigation

The purpose of this investigation was to study the effects of an ultrasonic field on the rate of transfer of acetone from a carbon tetrachloride phase to a water phase.

Plan of Experimentation

In general, the plan of experimentation was to subject a two-phase, three-component liquid-liquid extraction system to an ultrasonic field in a mixing chamber, separate the phases in a settling column, and subsequent to insonation observe the effects produced on the rate of mass transfer. Exploratory investigations indicated that carbon tetrachloride-acetone-water would serve as a suitable system.

Specifically, the plan of experimentation consisted of the following operations: reviewing the literature on liquid-liquid extraction and ultrasonics; planning and assembling extraction apparatus; developing techniques; planning methods of procedure; conducting exploratory investigations in regard to the system to be used; performing experimental tests to determine the effect of solvent-to-feed ratio, flow rate, and intensity of insonation on the rate of mass transfer for the system; conducting control and reproducibility tests; and evaluating, analyzing and discussing the results of the investigation.

Materials

Specifications of materials used in this investigation are presented in the following section.

Acetone. N. F., Baker and Adamson, lot No H 297J. Obtained from the General Chemical Division, Allied Chemical and Dye Corporation, New York, N. Y. Used as the solute in the liquid-liquid extraction system.

Carbon Tetrachloride. Technical grade, Baker and Adamson, lot No B 052. Obtained from the General Chemical Division, Allied Chemical and Dye Corporation, New York, N. Y. Used as the carrier solvent in the liquid-liquid extraction system.

Water. Tap water, analysis in Table V, page 69, at extractor site, obtained from lines located in the Ultrasonic Research Laboratory, Room A-102, McBryde Hall, Virginia Polytechnic Institute, Blacksburg, Va. Used as the solvent in the liquid-liquid extraction system.

TABLE V

Analysis of College Water Supply, Blacksburg, Virginia

Qualitative Analysis	Quantitative Analysis, ppm
pH - 7.4	-
Methyl orange alkalinity	200.0
HCO ₃	244.0
Cl (halide)	1.45
Nitrates and nitrites	None
Free CO ₂	28.2
Total dissolved solids	240.0
Volatile matter	84.0
Mineral residue	156.0
Dissolved silica as SiO ₂	2.4
Iron and aluminum oxides	3.0
Calcium	45.19
SO ₄ ion	7.08
Magnesium	24.42
Soap hardness	204.0
Calculated hardness	223.0

Fish, F. H.: Personal Communication, January 5, 1954.
Blacksburg, Virginia.

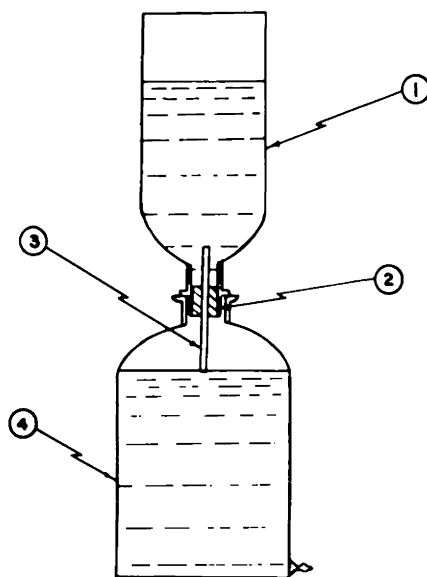
Apparatus

The apparatus used in this investigation is considered under the following subheadings: (1) extraction apparatus; (2) ultrasonic generator; and (3) auxiliary equipment.

Extraction Apparatus. The mixer-settler, single contact extractor employed in this investigation may be conveniently divided into the component parts of the system: (1) constant head tanks; (2) mixing chamber; and (3) settling column.

Constant Head Tanks. Flow rate control necessitated the use of constant-head tanks for storage of the feed and solvent. Figure 12, page 71, illustrates the type assembly used.

Mixing Chamber. The mixing chamber, or reactor, was constructed from a 2-1/4 inch section of pyrex tubing, 32-millimeter outside diameter and 28-millimeter inside diameter. A 0.001-inch nickel sheet was bonded to one end of the tube to form the bottom of the reactor and also act as an "acoustic window" to facilitate transmission of sound waves into the liquid system. Figure 13, page 72, shows a detail drawing of the mixing chamber, and Figure 14, page 73, presents a photographic representation of the reactor used in this investigation.



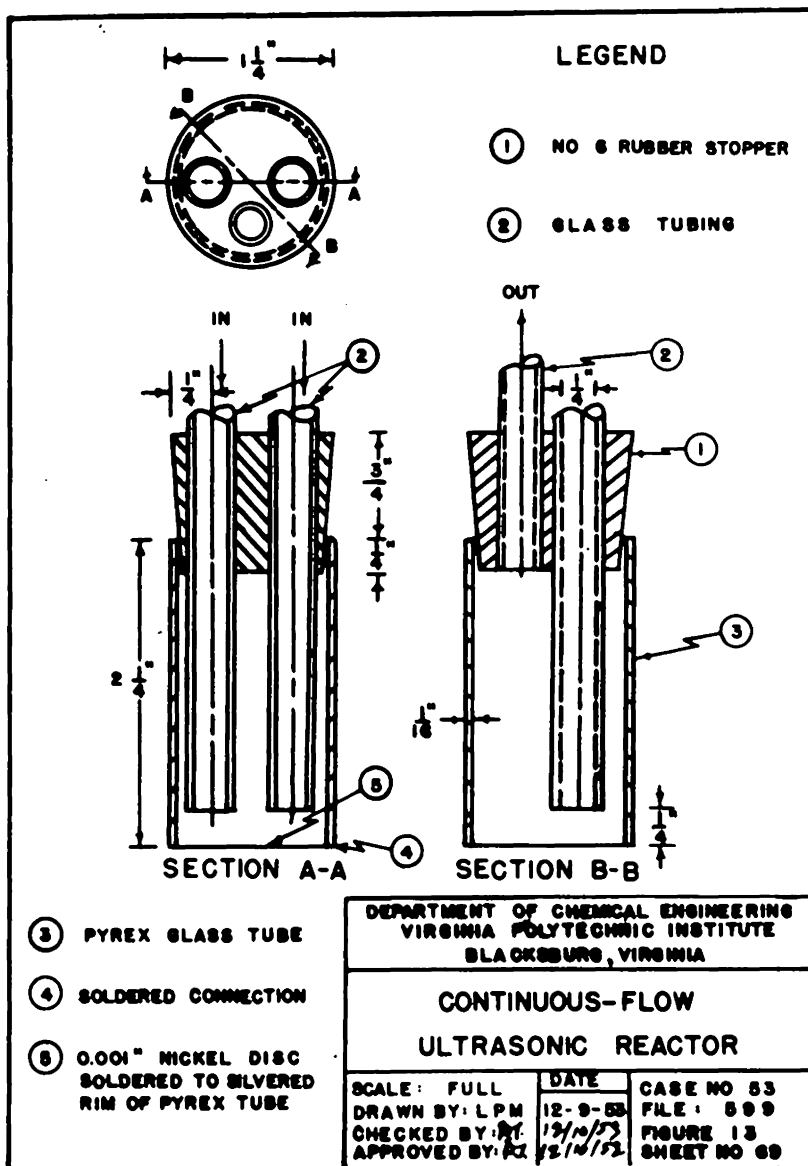
LEGEND

- ① GLASS BOTTLE, 1 GAL.
- ② NO 6 RUBBER STOPPER
- ③ GLASS TUBING, 3/8" I.D.
- ④ ASPIRATOR BOTTLE, 1 GAL.

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

CONSTANT HEAD TANK

SCALE: 1" = 6"	DATE	CASE NO
DRAWN BY: LPM	12-9-53	FILE 599
CHECKED BY: <i>DT</i>	12/10/53	FIGURE 12
APPROVED BY: <i>DT</i>	12/10/53	SHEET NO 68



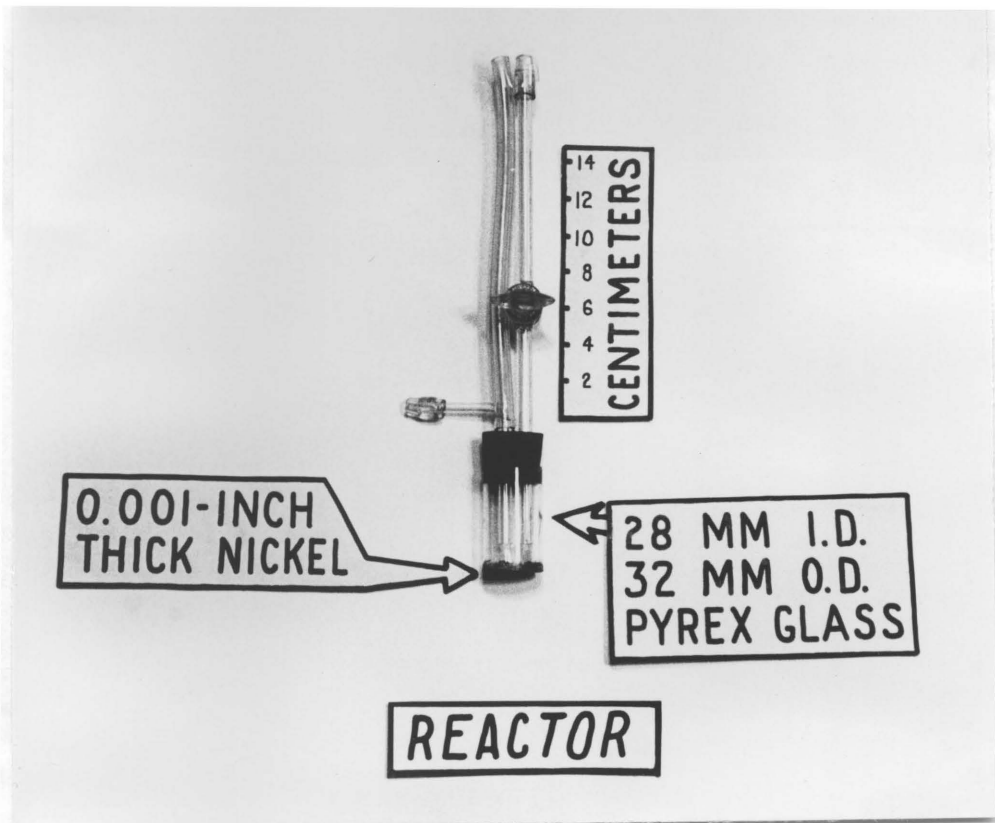


Figure 14. Reactor Employed in Ultrasonic
Extraction

Settling Column. A settling column was constructed from a six-inch section of pyrex tubing, 32-millimeter outside diameter and 28-millimeter inside diameter. Rubber stoppers, size No 6, were used for the top and bottom of the column. Inlet and outlet lines were 1/4-inch glass tubing. The settling column employed in this investigation is shown in Figure 15, page 75.

Ultrasonic Generator. An ultrasonic generator is an instrument which converts high-frequency electrical power into high-frequency mechanical vibrations. This is accomplished with a high-frequency electric oscillator which drives a piezoelectric crystal at its resonant frequency. The ultrasonic generator used for this investigation was the "Hypersonic Generator," model No BU-204, produced by Brush Development Company, Cleveland, Ohio. Major constituents of this equipment include: (1) generator, (2) transducer, and (3) tuning unit.

Generator. Hypersonic generator, model No BU-204, serial No 52 B 071. Input power 115 v, 6.5 amp, 660 w, 60 cy, single phase. Output power 250 w, 300-1000 kilocycles per second. Panel view shown in Figure 16, page 76. Manufactured by Brush

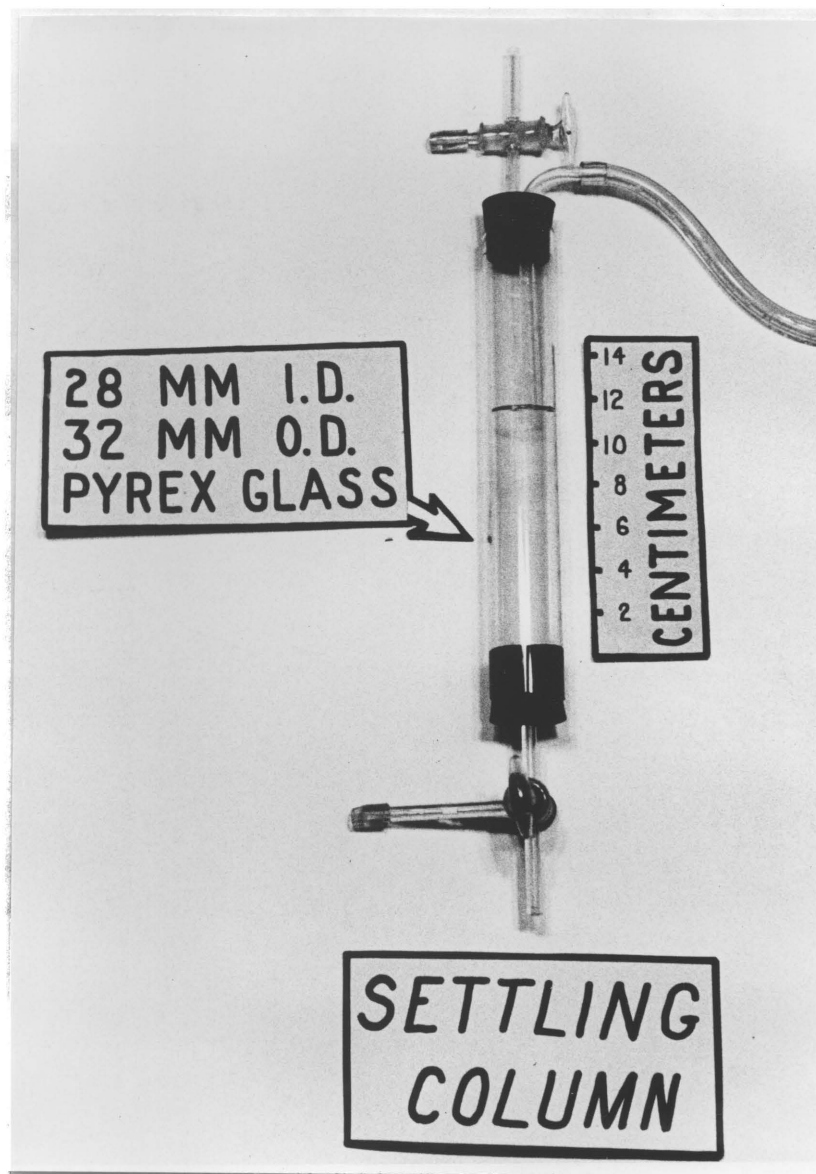


Figure 15. Settling Column Employed in
Ultrasonic Extraction

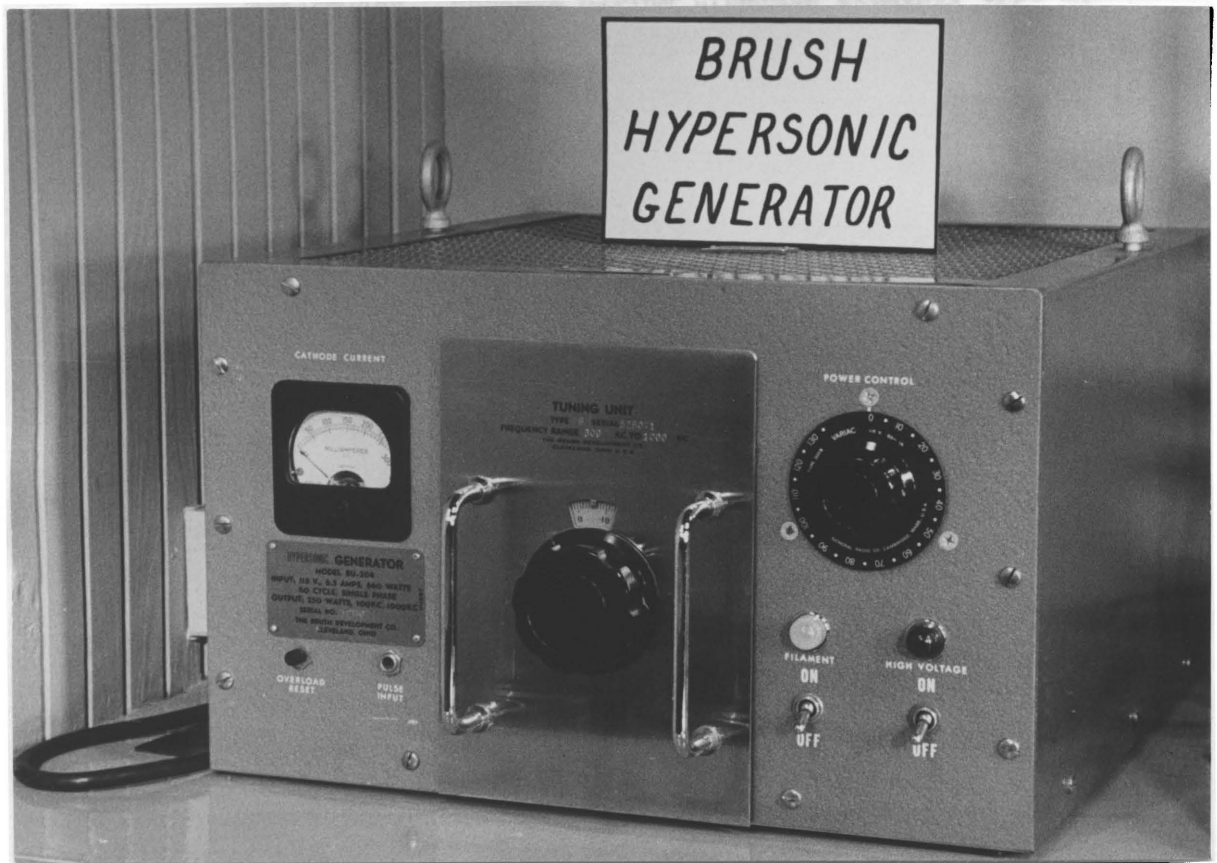


Figure 16. Panel View of Ultrasonic Generator

Development Co., Cleveland, Ohio. Used to supply high-frequency electrical current to transducer.

Transducer. Concave barium titanate element, type B, serial No 51 B 062, model No BU-305-A, frequency 400 kc. Front view of transducer in operation and sectional view are shown in Figure 17, page 78. Used to transform high-frequency electrical impulses into mechanical vibrations.

Tuning Unit. Removable, type B, serial No 52 B 071, range 300 to 1000 kc. Front view of removable tuning unit shown in Figure 18, page 79. Used to match electrical frequency of generator to the resonant frequency of the transducer crystal.

Distinguishing characteristics of the Brush Hypersonic Generator include: (1) concave barium titanate element in transducer which focuses ultrasonic energy, resulting in higher ultrasonic intensities; (2) transducer attached to the generator by a 6-foot cable to permit greater flexibility; and (3) frequency tuner unit that makes possible the use of any crystal with a frequency between 300 and 1000 kilocycles. A cooling coil is incorporated in the design of the transducer (see Figure 17, page 78) to maintain the temperature of the coupling medium constant. Ultrasonic

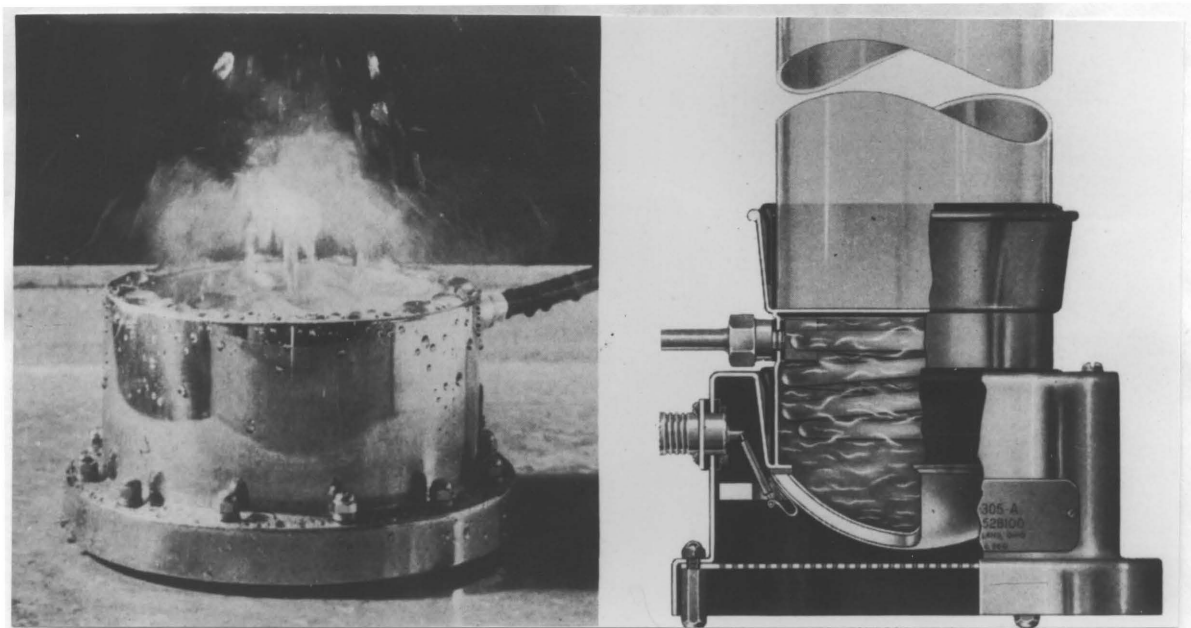


Figure 17. Brush Hypersonic Transducer Unit



Figure 18. Front View of Removable Frequency
Tuning Unit of Brush Hypersonic
Generator

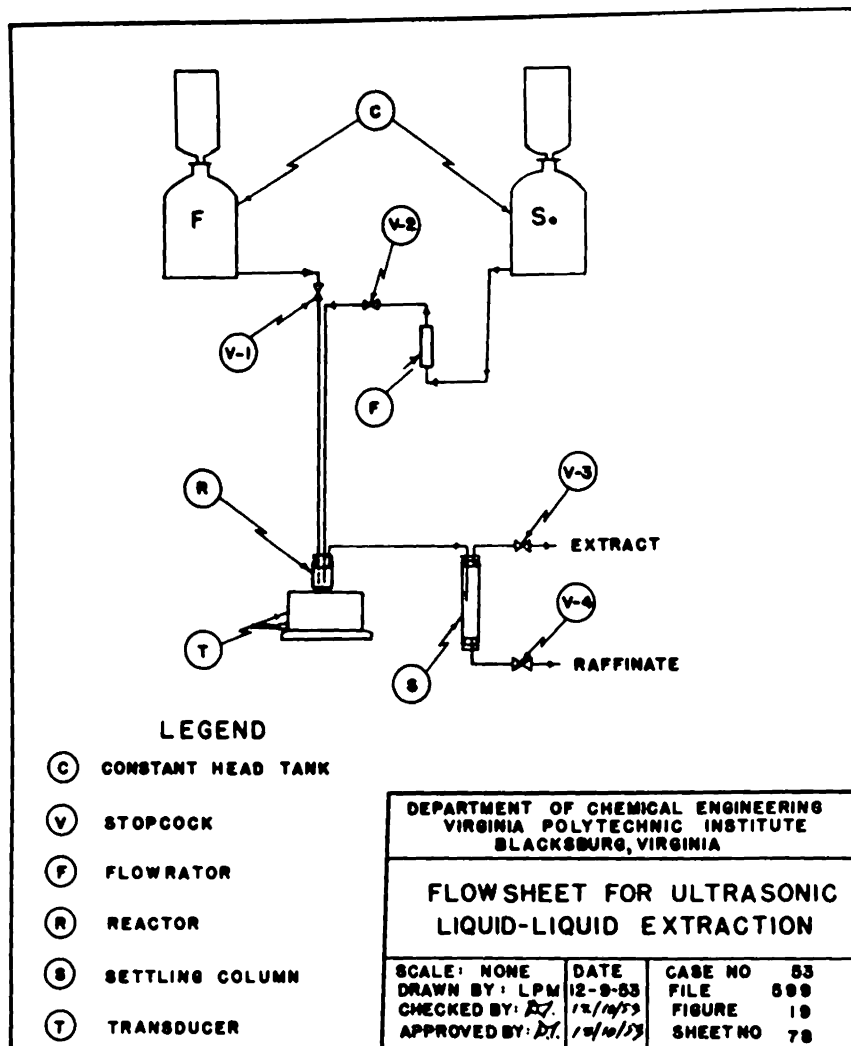
intensity output of the generator is controlled by a powerstat that regulates the plate current of the unit. Power potential requirements are automatically controlled by a voltage control within the generator. A general flow sheet for the entire system is presented in Figure 19, page 81, and the pictorial representation may be seen in Figure 20, page 82.

Auxiliary Equipment. Equipment not previously discussed is described below:

Balance. Triple beam. Capacity 0 to 610 grams, 0.1 gram increments. Manufactured by Ohaus Scale Co., Newark, N. J. Obtained from Phipps and Bird Co., Richmond, Va. Used to weigh the extract and raffinate samples from the extractor.

Constant-temperature Bath. Fisher Unitized Constant-temperature Bath, guaranteed to maintain set temperature at ± 0.025 °C. Obtained from the Fisher Scientific Co., Silver Spring, Md. Used for a constant-temperature bath during specific gravity determinations.

Constant-temperature Bath. Constant-temperature bath constructed by the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Controlled by an Aminco Thermal Switch, manufactured by the American



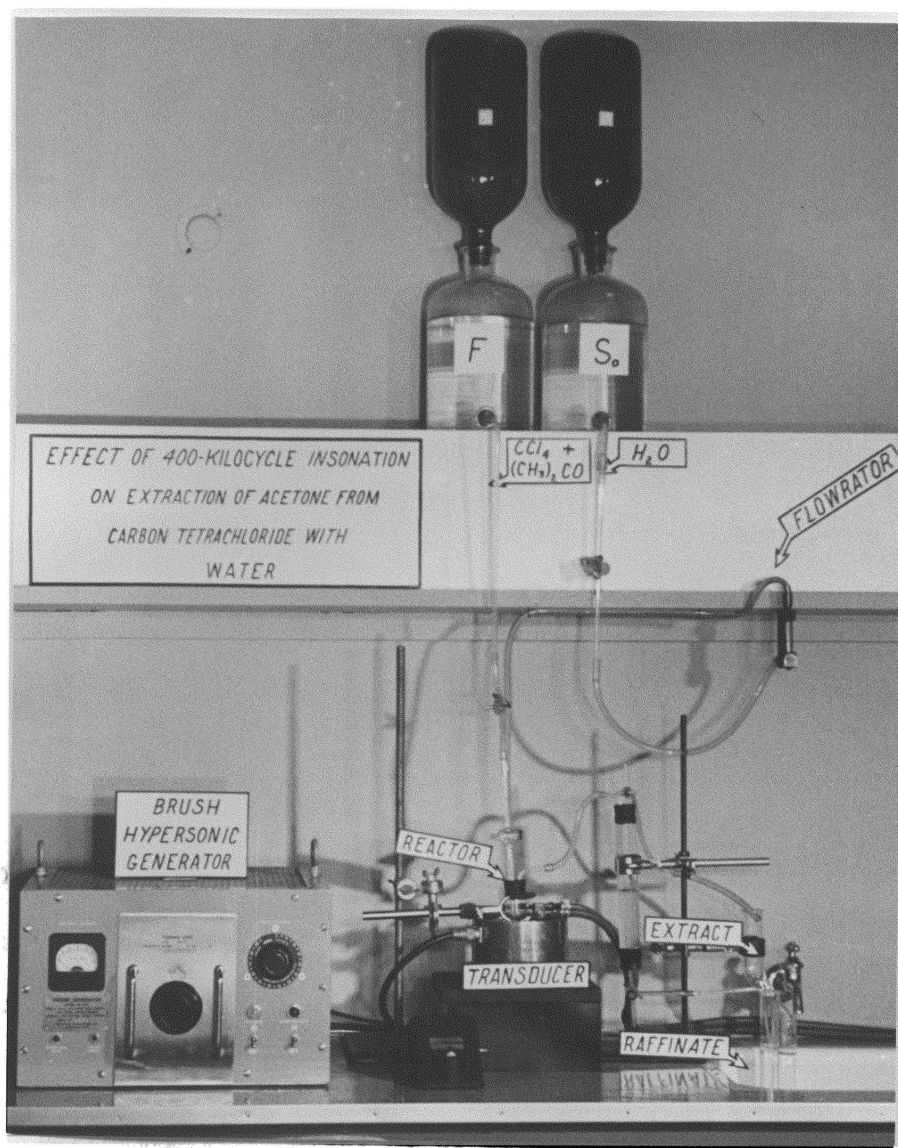


Figure 20. Apparatus for Liquid-liquid Extraction
in an Ultrasonic Field

Instrument Company, Silver Spring, Md. Used as a source of constant-temperature water for the refractometer.

Flowrator. Standard air flowrator, tube No 04-38-A, 0 to 2 standard cubic feet air. Modified for solvent stream measurement by replacement of glass indicating sphere with tungsten carbide ball-bearing. Manufactured by Fischer and Porter Co., Hatboro, Pa. Used to measure flow rate of solvent into extractor.

Miscellaneous Glassware. Laboratory glassware obtained from the Fisher Scientific Co., Silver Spring, Md. Used for standard analytical and laboratory purposes.

Mixer. "Lightnin" model L mixer, serial No 502260, 110 v, 50-60 cy, single phase. Manufactured by the Mixing Equipment Company. Obtained from the Fisher Scientific Co., Silver Spring, Md. Used to mix the feed for the extraction system.

Refractometer. Abbe, A. G. Spencer model 1777, range 1.3000 to 1.7100, sensitivity 0.0002, reads directly in n_D units, serial No 789326721. Obtained from the Fisher Scientific Co., Silver Spring, Md. Used to determine the refractive index of samples.

Thermometer. Mercury in glass, range -10 to 120 °C.
Obtained from the Fisher Scientific Co., Silver Spring, Md.
Used to measure temperature of samples.

Timer. Electric "Precision Time-It," graduated in
1/10 of a second, continuous with 4 digits, 115 v, 60 cy,
5 w. Obtained from Precision Scientific Co., Chicago, Ill.
Used for timing tests.

Tygon Tubing. Outside diameter, 3/8-inch by 1/4-inch
inside diameter; three feet required. Obtained from Julius
Blum and Co., Inc., New York, N. Y. Used to connect glass
tubing in the feed and solvent lines and also to join the
reactor outlet with the inlet line of the settling column.

Westphal Balance. Specific gravity, stainless steel,
Reinman-type plummet. Obtained from the Fisher Scientific
Company, Silver Spring, Md. Used to determine the specific
gravity of samples.

Methods of Procedure

The methods of procedure by which the experimental phase of this investigation was pursued are considered under the headings of literature review, records and reports, design and construction, methods of analysis, preparation of feed, exploratory investigations, and plan of evaluation.

Literature Review. A literature survey was conducted which considered basic concepts of both liquid-liquid extraction and ultrasonics. Consideration was given, also, to the means by which ultrasonic energy is transmitted into and absorbed by the medium, including theoretical values as well as actual experimental data for ultrasonic absorption in similar liquid systems. Solubility and equilibrium data are presented for the system carbon tetrachloride-acetone-water.

Records and Reports. All original data and notes for this investigation were kept in bound notebooks with consecutively-numbered pages. Separate sheets of drawings were attached to the notebook pages. Weekly and quarterly reports were submitted concerning progress of the investigation.

Design and Construction. Consideration of facilities necessary for the evaluation of a continuous-flow, ultrasonic liquid-liquid extraction unit, was prerequisite to a design drawing and construction of the equipment. Those facilities decided upon were: (1) constant head tanks for storage of the feed and solvent; (2) a mixing chamber, incorporating an ultrasonic field, through which the liquid system could flow continuously; and (3) a settling column, where the phases would separate while in continuous flow.

Constant Head Tanks. Flow rate control necessitated the use of constant head tanks for storage of the feed and solvent. Since the system insonated was in continuous flow, it was necessary to prepare an adequate amount of feed to last for at least one series of tests, with an additional amount available as a safety factor. Five gallons of feed were prepared at a time, and two-gallon containers were employed for the feed and solvent constant head tanks.

Mixing Chamber. In subjecting a liquid system in continuous flow to an ultrasonic field, it was desired to have a special container, the bottom of which would permit maximum transmission of the

ultrasonic waves from the transducer to the system flowing through the reactor. In a previous investigation, Thompson⁽⁹²⁾ has shown that a 0.001-inch nickel sheet gave the best transmission in comparison with a number of other materials such as copper, aluminum, and glass. Accordingly, a 0.001-inch nickel disc was bonded to one end of a pyrex tube, 2-1/4 inches high with a 32-millimeter outside diameter and a 28-millimeter inside diameter. Figure 13, page 72, is a drawing of the mixing chamber.

Settling Column. The settling column separated the two phases of the system, without disturbing the interface, while the liquid was in continuous flow. This was accomplished by using a pyrex tube, six inches high and having a 32-millimeter outside diameter and a 28-millimeter inside diameter. The inlet line from the mixing chamber entered the column through the rubber stopper at the top, and extended down into the column three inches. This discharge point served as a guide for controlling the interface of the system in the column. Outlet lines for both phases were provided with stopcocks to facilitate control of the interface.

Figure 15, page 76, illustrates the settling column employed in this investigation.

Method of Analysis. The analytical procedure consisted of the determination of the specific gravity (30 °C) and refractive index of the samples.

Determination of Specific Gravity. The specific gravity of samples was determined with a Wesphal balance. Standard techniques were used in these determinations⁽³⁾. For tests at a constant temperature of 30 ± 0.05 °C, the balance was located above a constant temperature bath that had been adjusted to this temperature.

Determination of Refractive Index. Samples, the refractive index of which was desired, were taken in culture tubes, sealed, and stored until such time as the refractometer was employed. The refractive index of these samples was determined using standard techniques⁽⁴⁾.

Preparation of Feed. During experimental tests, a feed consisting of 13.78 ± 2.72 weight per cent acetone in carbon tetrachloride was used. The mixture of carbon

tetrachloride in acetone, prepared in batches of five gallons, was placed in a five-gallon carboy and agitated with a Lightnin' mixer, in the presence of a slight excess of water, for at least 20 minutes. Analyses of the feed for acetone concentration were conducted before and after each test.

Apparatus Operation. Constant head tanks were filled with feed and solvent. The required solvent flow rate was obtained by adjusting stopcock V-2 until flowrator F-1 indicated the required solvent rate. All symbolic representations in this section refer to Figure 19, page 81. Table VI, page 90, presents the calibration of flowrator F, using tap water at 25 °C, and Figure 21, page 91, presents the calibration curve for this instrument.

Feed rate to the reactor R was regulated by means of stopcock V-1 until the proper quantity was indicated by a material balance. The phase boundary in the settling column S was maintained at a constant level by adjustment of stopcock V-4, while stopcock V-3 remained wide open. After steady flow rate conditions had existed for 15 minutes, indicated by a stationary interface without adjustment of stopcocks V-1 or V-4, both the extract and raffinate phases were collected for one minute and then

TABLE VI

Calibration of Solvent Stream Flowrator,

Using Tap Water^a at 25 °C

Flowrator Unit	Actual Flow Rate, gm/min
0.0	2.0
0.2	6.0
0.4	10.0
0.6	14.0
0.8	18.0
1.0	22.0
1.2	26.0
1.4	30.0
1.6	34.0
1.8	38.0
2.0	42.0

^a See Table V, page 69, for
analysis of water.

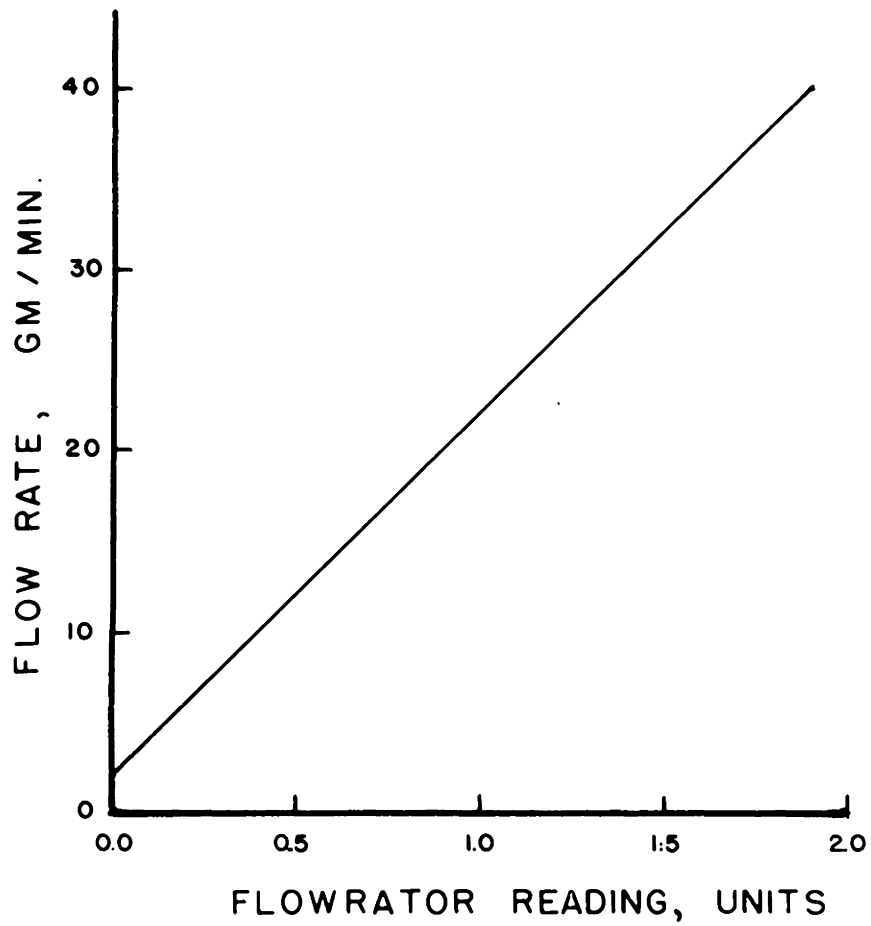


Figure 21. Calibration Curve for the Solvent
Stream Flowrator

weighed. This total weight minus the weight of solvent introduced per minute resulted in the flow rate of the feed to the reactor. This procedure was also employed to check the flow rates of the system periodically throughout each series of tests.

Ultrasonic intensity was controlled by the variac incorporated in the generator. Before each test the frequency tuning unit was adjusted until maximum ultrasonic intensity was obtained for the required power input of the test. The maximum intensity was determined by visual observation of the height of the water "spout" (see Figure 17, page 78) in the transducer with the reactor removed. The bottom of the reactor was then centered 5.5 centimeters above the transducing element.

The system was operated for 15 to 30 minutes before any samples were taken in order for the phases to attain a steady state condition⁽⁴⁶⁾. Ten minutes were allowed for the system to reach steady state conditions after each change of input power.

Exploratory Investigations. In order to fix certain variables and direct the choice of experimental tests to be made, the following exploratory investigations were

conducted: (1) selection of system; (2) flow rate; (3) solvent-to-feed; and (4) intensity (input power) of the ultrasonic field.

Selection of System. Availability of components, availability of equilibrium data, ease of analysis, and near immiscibility of the extracting solvent in the carrier solvent were characteristics that led to the selection of the system carbon tetrachloride-acetone-water.

Flow Rate. After construction of the apparatus, incremental increases in flow rate were attempted until the first signs of an emulsion appeared--this flow rate was approximately 200 grams per minute. The flow rates selected for investigation varied from 32 grams per minute to 120 grams per minute--well below this critical value in order to eliminate the complications introduced by emulsion formation. During this exploratory investigation, no ultrasonic energy was employed.

Solvent-to-Feed Ratio. Selection of solvent-to-feed ratios was based upon typical ratios that are practical for batch extraction operations⁽²¹⁾. The

solvent-to-feed ratios selected for this investigation were 1:1, 1:2, and 1:3 (on a weight basis).

Intensity of Insonation. The Brush Hypersonic Generator used in this investigation was equipped with an automatic overload switch that prevented the use of an input power greater than 250 milliamperes plate current. No discernible effects of the ultrasonic field occurred below 100 milliamperes plate current. Accordingly, power input readings selected for this investigation were 100, 150, and 200 milliamperes.

Plan of Evaluation. In the study of liquid-liquid extraction in an ultrasonic field, the variables of flow rate, intensity of insonation, and solvent-to-feed ratio were investigated to determine their effect on the rate of mass transfer. Flow rates of 32, 40, 72, 90, and 120 grams per minute were studied when insonated at power inputs of 100, 150, and 200 milliamperes. Solvent-to-feed ratios of 1:1, 1:2, and 1:3 on a weight basis were also investigated. Control and reproducibility tests were also conducted. Evaluation of the extraction was expressed as stage efficiency. Representative data were selected and plotted to illustrate the relation between the above variables and the stage efficiency.

Data and Results

The data and results of this investigation are presented in the following sections: (1) operating data, (2) material balance, (3) stage efficiencies, (4) effect of flow rate on ultrasonic liquid-liquid extraction, (5) effect of solvent-to-feed ratio on ultrasonic liquid-liquid extraction, and (6) reproducibility tests of ultrasonic liquid-liquid extraction.

Operating Data. In Table VII, page 96, the operational data for ultrasonic liquid-liquid extraction are presented.

Material Balance. As an aid in the evaluation of the accuracy of the experimental technique, a summary of the acetone material balances is shown in Table VIII, page 97. The average value of the deviation for these tests was 1.60 per cent.

Stage Efficiencies. The stage efficiencies for the various experimental tests are presented in Table IX, page 98. Included in this table, also, are the operational parameters that were studied: flow rate, solvent-to-feed ratio, and insonation intensity expressed as plate-current power input.

TABLE VII

Operational Data for Ultrasonic Liquid-liquid Extraction
of Acetone from Carbon Tetrachloride with Water

Test No	Plate Current, ^a ma	Phase	Flow Rate, gm/min	Refractive Index, 20 n _D	Acetone wt %
1	0	Extract Raffinate Feed Solvent	15.8 16.2 16.0 16.0	1.3380 1.4534 1.4409 1.3330	7.94 3.74 11.55 0.00
2	100	Extract Raffinate Feed Solvent	15.5 16.5 16.0 16.0	1.3382 1.4534 1.4409 1.3330	8.25 3.74 11.55 0.00
3	150	Extract Raffinate Feed Solvent	15.8 16.2 16.0 16.0	1.3380 1.4530 1.4409 1.3330	7.94 3.75 11.55 0.00
4	200	Extract Raffinate Feed Solvent	15.7 16.3 16.0 16.0	1.3380 1.4532 1.4409 1.3330	7.94 3.87 11.55 0.00
5	0	Extract Raffinate Feed Solvent	15.9 16.1 16.0 16.0	1.3381 1.4536 1.4404 1.3330	8.10 3.67 11.87 0.00
96	100	Extract Raffinate Feed Solvent	15.8 16.2 16.0 16.0	1.3381 1.4535 1.4404 1.3330	8.10 3.69 11.87 0.00
7	150	Extract Raffinate Feed Solvent	15.7 16.3 16.0 16.0	1.3380 1.4534 1.4404 1.3330	7.94 3.71 11.87 0.00
8	200	Extract Raffinate Feed Solvent	15.6 16.4 16.0 16.0	1.3380 1.4534 1.4404 1.3330	7.94 3.71 11.87 0.00
9	0	Extract Raffinate Feed Solvent	19.5 20.5 20.0 20.0	1.3378 1.4510 1.4390 1.3330	7.62 5.25 12.80 0.00
10	100	Extract Raffinate Feed Solvent	19.8 20.2 20.0 20.0	1.3380 1.4510 1.4390 1.3330	7.94 5.25 12.80 0.00
11	150	Extract Raffinate Feed Solvent	19.7 20.3 20.0 20.0	1.3387 1.4521 1.4390 1.3330	9.05 4.54 12.80 0.00
12	200	Extract Raffinate Feed Solvent	19.9 20.1 20.0 20.0	1.3390 1.4529 1.4390 1.3330	9.46 4.05 12.80 0.00
13	0	Extract Raffinate Feed Solvent	35.8 36.2 36.0 36.0	1.3389 1.4487 1.4336 1.3330	9.25 6.68 16.10 0.00
14	100	Extract Raffinate Feed Solvent	35.8 36.2 36.0 36.0	1.3391 1.4491 1.4336 1.3330	9.55 6.45 16.10 0.00
15	150	Extract Raffinate Feed Solvent	35.7 36.3 36.0 36.0	1.3396 1.4502 1.4336 1.3330	10.40 5.73 16.10 0.00
16	200	Extract Raffinate Feed Solvent	35.8 36.2 36.0 36.0	1.3399 1.4510 1.4336 1.3330	11.05 5.25 16.10 0.00
17	0	Extract Raffinate Feed Solvent	30.5 59.5 60.0 30.0	1.3419 1.4441 1.4330 1.3330	14.10 9.55 16.50 0.00
18	100	Extract Raffinate Feed Solvent	30.3 59.7 60.0 30.0	1.3420 1.4443 1.4330 1.3330	14.30 9.45 16.50 0.00
19	150	Extract Raffinate Feed Solvent	31.0 59.0 60.0 30.0	1.3427 1.4454 1.4330 1.3330	15.43 8.77 16.50 0.00
20	200	Extract Raffinate Feed Solvent	30.6 59.4 60.0 30.0	1.3432 1.4461 1.4330 1.3330	16.17 8.35 16.50 0.00
21	0	Extract Raffinate Feed Solvent	29.9 90.1 90.0 30.0	1.3399 1.4443 1.4387 1.3330	10.88 9.45 12.95 0.00
22	100	Extract Raffinate Feed Solvent	29.5 90.5 90.0 30.0	1.3399 1.4448 1.4387 1.3330	10.88 9.15 12.95 0.00
23	150	Extract Raffinate Feed Solvent	28.8 91.2 90.0 30.0	1.3417 1.4460 1.4387 1.3330	13.78 8.38 12.95 0.00
24	200	Extract Raffinate Feed Solvent	29.1 90.9 90.0 30.0	1.4389 1.4473 1.4387 1.3330	14.05 7.55 12.95 0.00

^a Brush Hypersonic Generator, model No BU-204, serial No 52-B-071, 400 kilocycle insonation.

TABLE VIII

Summary of Acetone Material Balances for Ultrasonic
Liquid-liquid Extraction of Acetone from
Carbon Tetrachloride with Water

Test No	Acetone Out, gm/min	Acetone In, gm/min	Deviation, gm/min	Deviation ^a , %
1	1.86	1.85	+ 0.01	0.54
2	1.89	1.85	+ 0.04	2.14
3	1.87	1.85	+ 0.02	1.08
4	1.88	1.85	+ 0.03	1.61
5	1.88	1.90	- 0.02	1.06
6	1.89	1.90	- 0.01	0.53
7	1.85	1.90	- 0.05	2.67
8	1.85	1.90	- 0.05	2.67
9	2.55	2.56	- 0.01	0.39
10	2.53	2.56	- 0.03	1.18
11	2.60	2.56	+ 0.04	1.55
12	2.69	2.56	+ 0.13	4.90
13	5.73	5.80	- 0.07	1.04
14	5.76	5.80	- 0.04	0.69
15	5.80	5.80	0.00	0.00
16	5.99	5.80	+ 0.19	3.23
17	9.98	9.90	+ 0.08	0.81
18	9.96	9.90	- 0.06	0.41
19	9.51	9.90	- 0.39	4.02
20	9.91	9.90	+ 0.01	0.01
21	11.76	11.65	+ 0.11	0.94
22	11.47	11.65	- 0.18	1.56
23	11.62	11.65	- 0.03	0.01
24	10.95	11.65	+ 0.70	6.18

^a Based upon average value of acetone in and acetone out.

TABLE IX

Stage Efficiency for Ultrasonic Liquid-liquid Extraction of
Acetone from Carbon Tetrachloride with Water

Test No	Plate Current, ma	Flow Rates			Acetone in Feed, wt %	Stage Efficiency, %
		Raffinate Phase, gm/min	Extract Phase, gm/min	Ratio ^a		
1	0	16.2	15.8	1.03	11.55	94.5
2	100	16.5	15.5	1.06	11.55	98.3
3	150	16.2	15.8	1.02	11.55	94.5
4	200	16.3	15.7	1.04	11.55	94.5
5	0	16.1	15.9	1.01	11.87	93.0
6	100	16.2	15.8	1.02	11.87	93.0
7	150	16.3	15.7	1.04	11.87	91.3
8	200	16.4	15.6	1.05	11.87	91.3
9	0	20.5	19.5	1.05	12.80	82.8
10	100	20.2	19.8	1.02	12.80	85.2
11	150	20.3	19.7	1.03	12.80	98.2
12	200	20.1	19.9	1.01	12.80	102.8
13	0	36.2	35.8	1.01	16.10	84.0
14	100	36.2	35.8	1.01	16.10	86.9
15	150	36.3	35.7	1.02	16.10	94.5
16	200	36.2	35.8	1.01	16.10	100.5
17	0	59.5	30.5	1.95	16.50	87.6
18	100	59.7	30.3	1.97	16.50	89.0
19	150	59.0	31.0	1.91	16.50	95.1
20	200	59.4	30.6	1.94	16.50	99.9
21	0	90.1	29.9	3.01	12.95	75.1
22	100	90.5	29.5	3.07	12.95	75.1
23	150	91.2	28.8	3.16	12.95	95.0
24	200	90.9	29.1	3.12	12.95	96.9

^a The flow rate ratio is equal to the raffinate-phase flow rate divided by the extract-phase flow rate.

Effect of Flow Rate on Ultrasonic Liquid-liquid

Extraction. In Figure 22, page 100, the effect of flow rate on ultrasonic liquid-liquid extraction is presented graphically.

Effect of Solvent-to-feed Ratio on Ultrasonic Liquid-

liquid Extraction. Figure 23, page 101, illustrates the effect of solvent-to-feed ratio on ultrasonic liquid-liquid extraction.

Reproducibility. Reproducibility tests indicated an

average deviation of 1.65 per cent from the mean stage efficiency. The results of these tests are shown in Figure 24, page 102.

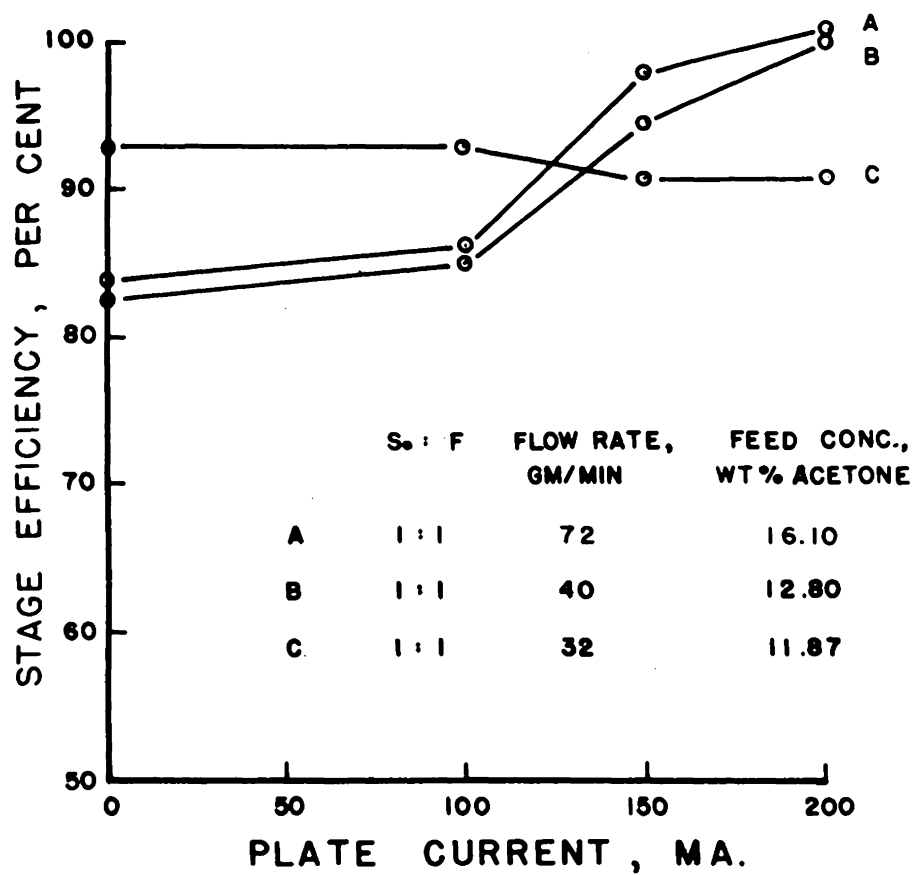


Figure 22. Effect of Flow Rate on Ultrasonic Liquid-
liquid Extraction of Acetone from Carbon
Tetrachloride with Water

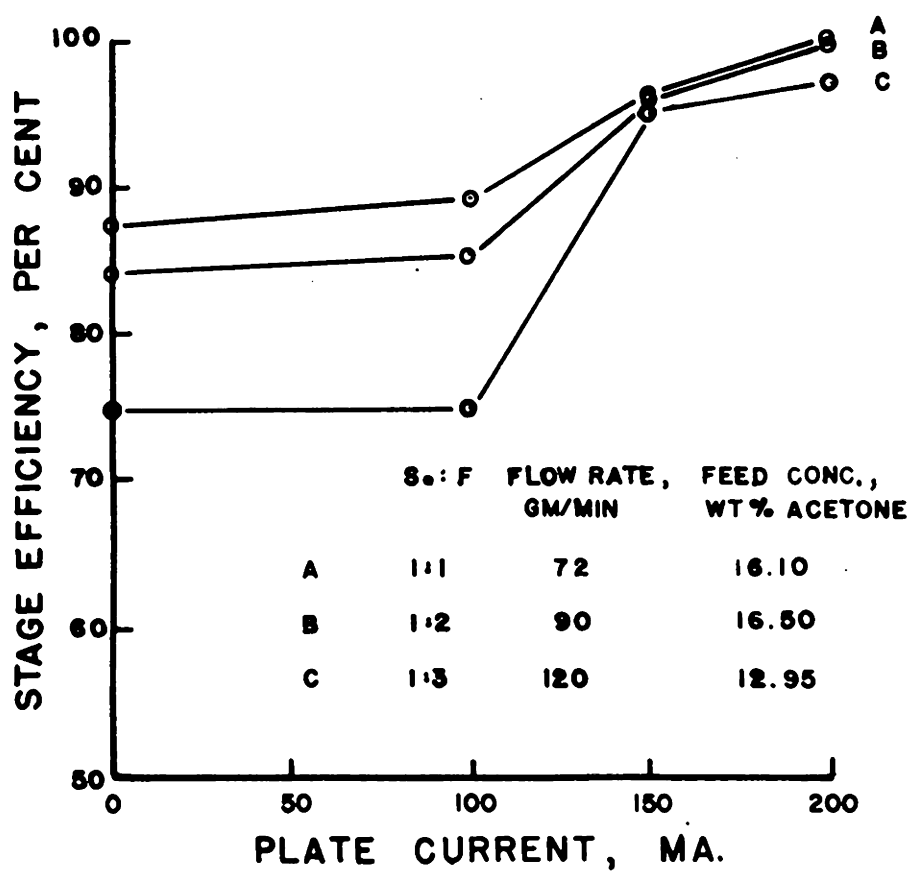


Figure 23. Effect of Solvent-to-feed Ratio on
Ultrasonic Liquid-liquid Extraction of Acetone
from Carbon Tetrachloride with Water

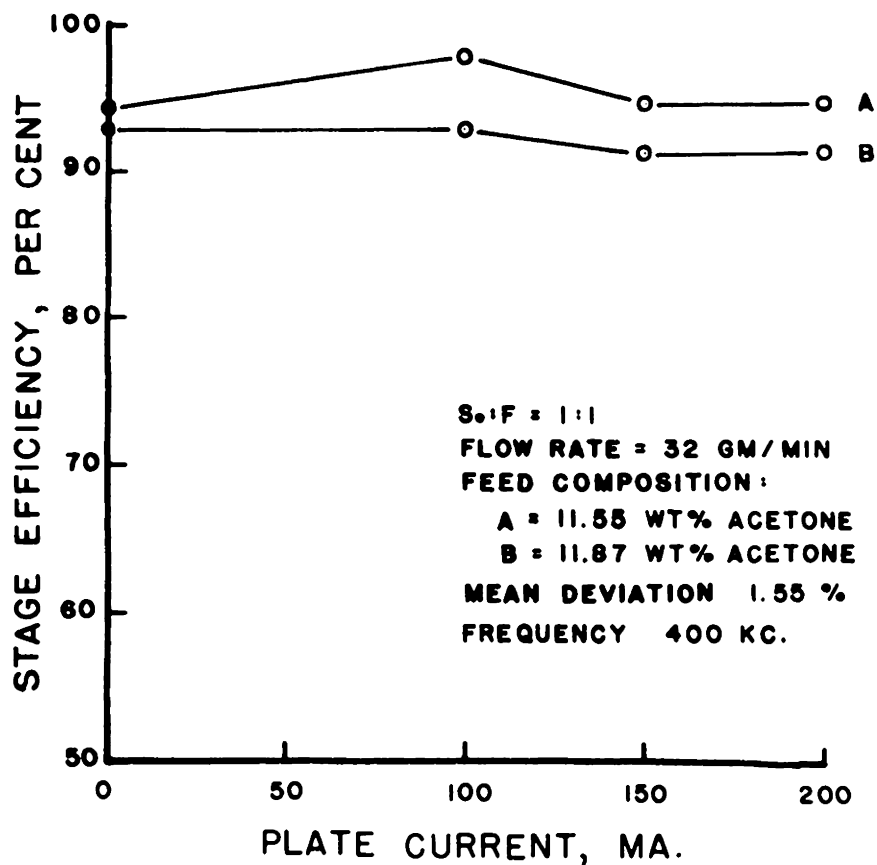


Figure 24. Reproducibility Tests of Ultrasonic Liquid-liquid
Extraction of Acetone from Carbon Tetrachloride
with Water

Sample Calculations

In this section examples of the calculations used in this investigation are presented.

Acetone Material Balance. As a check on the experimental accuracy, an acetone material balance was calculated for each test. The summary of these balances is contained in Table VIII, page 97. This calculation is illustrated using data from the second experimental test given, in Table VII, page 96.

The acetone leaving the extractor or the "acetone out" was calculated as shown below:

$$A_o = R x_1 + E y_2 \quad (9)$$

where:

A_o = acetone leaving extractor, grams per minute

R = raffinate phase flow rate, grams per minute

E = extract phase flow rate, grams per minute

x_1 = concentration of acetone in the raffinate phase, weight fraction

y_2 = concentration of acetone in the extract phase, weight fraction

$$A_o = (16.5 \times 0.0374) + (15.5 \times 0.0825)$$

$$A_o = 1.89 \text{ grams per minute.}$$

The acetone entering the extractor or the "acetone in" was calculated as shown below:

$$A_1 = Fx_0 + Sy_0 \quad (10)$$

where:

A_1 = acetone entering the extractor, grams per minute

F = feed flow rate, grams per minute

S = solvent flow rate, grams per minute

x_0 = concentration of acetone in the feed, weight fraction

y_0 = concentration of acetone in the solvent, weight fraction

$$A_1 = (16.0 \times 0.1155) + (16.0 \times 0.000)$$

$$A_1 = 1.85 \text{ grams per minute.}$$

The deviation is the absolute difference between the acetone in and the acetone out. The deviation is more often expressed as per cent of the average of the acetone in and the acetone out. This was computed, and may be seen in Table VIII, page 97.

Calculation of the Stage Efficiency. Before the stage efficiency was calculated, the maximum acetone concentration of the extract phase had to be determined. The maximum acetone concentration of the extract phase was calculated by the graphical method introduced by Hunter and Nash^(47,48). This method is more familiar in the form presented by Elgin⁽³³⁾ and Bull and Coli⁽²¹⁾.

The graphical solution for the ~~maximum~~ acetone concentration of the extract phase for the second experimental test presented in Table VII, page 96, is shown in Figure 25, page 106. The distribution data, that are also used, are presented in Figure 4, page 23.

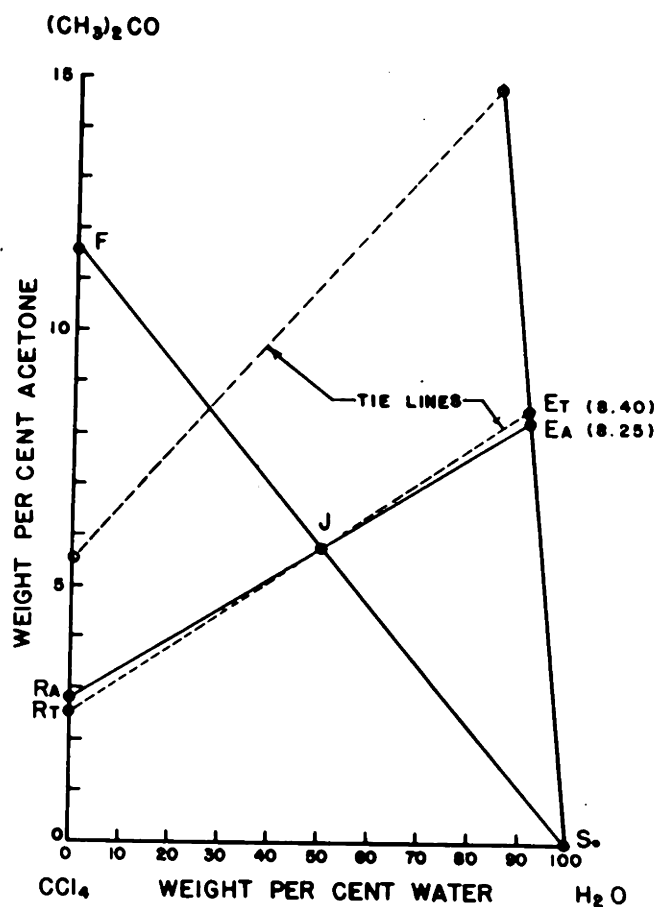


Figure 25. Graphical Solution for Second Experimental Test
Employing Acetone (Solute), Carbon Tetrachloride (Carrier
Solvent), and Water (Extracting Solvent)

The stage efficiency was calculated as shown below:

$$S = \frac{y_A - y_o}{y_E - y_o} \times 100 \quad (11)$$

where:

S = stage efficiency, per cent

y_A = actual concentration of acetone in the
extract phase, weight per cent

y_o = concentration of acetone in the solvent,
weight per cent

y_E = ideal concentration of acetone in the
extract phase, weight per cent

$$S = \frac{8.25 - 0.00}{8.40 - 0.00} \times 100$$

$$S = 98.3 \text{ per cent.}$$

IV. DISCUSSION

An analysis and discussion of the results obtained in this investigation are included in this section of the thesis together with recommendations for future work and a summary of the limitations imposed upon the investigation.

Discussion of Results

It has been hypothesized⁽⁹⁰⁾ that because of the high local velocities (about 50 centimeters per second) associated with high frequency (400 kilocycles per second), high intensity (above cavitation, or over 0.3 watt per square centimeter) sound energy, a substantially increased rate of diffusion may be expected at a mass transfer boundary. Results of this investigation partially substantiate the above hypothesis and are discussed in the following order: (1) effect of intensity of insonation; (2) effect of flow rate; and (3) effect of solvent-to-feed ratio.

Effect of Intensity of Insonation. Stage efficiency of the extractor increased as intensity of insonation increased, as shown in Figure 22, page 100. Insonation at maximum intensity investigated (200 milliamperes plate current) resulted in an

average stage efficiency of 99.1 per cent as compared to an average stage efficiency of 82.1 per cent for tests conducted without insonation. For further comparison, tests conducted at 150 milliamperes plate current averaged 94.9 per cent, while those tests insonated with 100 milliamperes plate current averaged only 83.6 per cent. Control tests were conducted at flow rates corresponding to the flow rates employed for insonation tests to obtain results on a comparable time basis.

Analysis of Insonation Tests. Insonation at minimum intensity investigated (100 milliamperes) was found to produce slightly lower values for stage efficiency than would be expected from a consideration of the extraction data for the two greater levels of insonation intensity. Intensities high enough to produce the disruptive action of cavitation⁽¹⁰⁹⁾ (0.3 watt per square centimeter) were evidenced only at the two higher levels of insonation intensity (150 and 200 milliamperes plate current). Mass transfer of the acetone from the carbon tetrachloride phase to the water phase was facilitated at these two higher intensities and this increased transfer was attributed⁽⁹⁰⁾ to selective microagitation at the interface

between these two phases. Absorption of ultrasonic energy increased proportionally as interfacial area was increased^(1,79). Liquid-liquid and liquid-gas interfaces were present in the system during, and increased by, insonation. Increased liquid-liquid interface was provided by dispersion of each phase within the other, and increased liquid-gas interface was provided by formation of cavities and degassing of the liquids. Visible cavitation was not noticed at minimum intensity insonation (100 milliamperes). An acoustic intensity of approximately 0.3 watt per square centimeter was necessary before cavitation occurred. Therefore, the system was not subjected to the disruptive forces accompanying cavitation⁽¹⁰⁹⁾ until the intensity had been increased from 100 to 150 milliamperes plate current, the critical intensity occurring between these two values.

Flow Rate Phenomenon. During the series of extraction tests conducted for this investigation, two values of stage efficiency were recorded that exceeded 100 per cent. Test No 12 and Test No 16 gave stage efficiencies of 102.8 and 100.5 per cent,

respectively, as shown in Table VII, page 96. It is recognized that stage efficiency, as defined, cannot exceed 100 per cent. Proceeding along this line of reasoning, attention is invited to Table VIII, page 97, where the material balance for these tests shows abnormally high deviations of 4.90 and 3.23 per cent as compared with the mean deviation of 1.60 per cent. In both tests, the discrepancy is positive, indicating more "acetone out" than "acetone in", which, of course, cannot be true. An interesting aspect for speculation is that both values for stage efficiency that exceeded 100 per cent occurred when the system was being insonated at maximum intensity investigated (200 milliamperes), which intensity of insonation produced cavitation that may have affected the volume of liquids in the reactor and also the flow rates to and from the reactor to such a degree that the graphical method used for calculating the theoretical maximum acetone concentration in the extract did not provide a correct answer. The true instantaneous solvent-to-feed ratio may have varied and the cumulative values recorded may not have reflected properly the instantaneous variations. The flowrator in the

solvent line was calibrated in the absence of insonation, and in the absence of contrary information, this calibration was assumed valid in the presence of ultrasonic energy; however, in retrospect, this assumption probably was invalid for high intensities.

Ultrasonic Absorption. Absorption of ultrasonic energy travelling through a solution is affected⁽⁷⁰⁾ by temperature, pressure, frequency, and concentration of the solute. When the acoustical waves must traverse a phase boundary, as is the case in liquid-liquid extraction, the additional consideration of ρ_c match is introduced. During this investigation, the temperature, pressure, and frequency were held constant, thereby eliminating these factors affecting absorption of the ultrasonic energy. The remaining influential factors, concentration and ρ_c match, become one complex variable since the ρ_c value of each phase changes as the concentrations change. Table X, page 113, presents the ρ_c values for the three components used in this investigation. To determine the relationship between the ρ_c values and the concentration, attention is invited to Figure 9, page 52, and Figure 8, page 51. The former figure indicates a sharp increase

TABLE X

Density and Acoustic Velocity of Carbon
Tetrachloride, Acetone, and Water

Chemical Component	Temperature, °C	Density, ρ gm/cm ³	Acoustic Velocity, c m/s	ρc Value gm/cm ² s
			x10 ³	x10 ⁵
Carbon tetra- chloride	20	1.594	0.943	1.50
Acetone	20	0.791	1.190	0.94
Water	25	0.997	1.497	1.49

Bergmann, L.: "Der Ultraschall und seine Anwendung in
Wissenschaft und Technik," pp. 175-9. VDI-Verlag,
Berlin, Germany, 1942. 3 ed.

(from 2.5 to $9 \alpha / f^2 \times 10, \text{ sec}^2$) in the absorption of ultrasonic energy as the concentration of acetone in benzene is decreased from 25 to 0 per cent. Since the absorption characteristics of benzene and carbon tetrachloride are similar⁽⁷⁰⁾, it may be assumed that the absorption trend evidenced with benzene would apply equally to carbon tetrachloride. Figure 8, page 51, shows the opposite trend of acoustical absorption when the system is acetone and water. As the concentration of acetone increases from 0 to 25 per cent, the ultrasonic absorption also increases markedly (from 5 to $15 \alpha / f^2 \times 10, \text{ sec}^2$). Application of these trends to the liquid-liquid system employed in this investigation indicates that as the mass transfer of acetone proceeds from the carbon tetrachloride phase to the water phase, the ultrasonic energy absorption increases and thus favors the desired direction of transfer. Maximum effects of an ultrasonic field are obtained when the acoustical waves are reflected, as by a phase boundary, or absorbed, because of a mismatch of ρc values.

Effect of Flow Rate on Ultrasonic Liquid-liquid

Extraction. Within the range of flow rates investigated, the ultrasonic energy applied to the system was sufficient to provide intimate contact of the two liquid phases.

Superficial examination of the data presented in Table IX, page 98, would lead one to attribute the increased stage efficiency to the increased flow rate as well as the intensity of ultrasonic insonation--such is not entirely the case. Maximum increase in stage efficiency, 21.8 per cent (from 75.1 to 96.9 per cent), occurred with maximum intensity of insonation, 200 milliamperes, as well as with maximum flow rate, 120 grams per minute; however, further examination of the circumstances is warranted. Discussion of these circumstances is divided into the time of contact and maximum limiting flow rate.

Time of Contact. With a total flow rate of 120 grams per minute, the solvent and feed were contacted in the mixing chamber, or reactor, for only 20 seconds. Insufficient time was allowed for the phases to approach equilibrium, so the resulting stage efficiency was exceptionally low, 75.1 per cent. As the flow rate is decreased from 120 to 32 grams per minute,

the stage efficiency of the extractor, without insonation, increased from 75.1 to 93.0 per cent. This trend suggests that at a critical minimum flow rate the time of mixing would be sufficient to eliminate the effect of the ultrasonic field. In this investigation, at the critical minimum flow rate of 32 grams per minute, no increase in stage efficiency resulted when the system was insonated at 100, 150, or 200 milliamperes plate current. Eight tests were conducted with a total flow rate of 32 grams per minute to check the reproducibility of the results. The calculated deviation from the mean of 1.55 per cent is illustrated in Figure 24, page 102.

Maximum Limiting Flow Rate. A maximum limiting flow rate, above which the time of insonation is insufficient to obtain any effects from the intensity employed in the ultrasonic field, should exist. This maximum critical flow rate was not observed during the investigation, so it was inferred that the ultrasonic energy applied to the system was sufficient to provide intimate contact of both phases throughout the flow rates employed.

Effect of Solvent-to-feed Ratio on Ultrasonic Liquid-liquid Extraction. Rate of extraction was increased by employment of ultrasonic insonation regardless of solvent-to-feed ratio. Figure 23, page 101, illustrates the independence of solvent-to-feed ratio on ultrasonic liquid-liquid extraction from data presented in Table VII, page 96.

Of more importance to this investigation was the variability of the solute concentration in the feed, which was 13.78 ± 2.72 weight per cent acetone. The effect of the solute concentration in the feed on the stage efficiency has received a great deal of speculation in the literature. Pyle, Colburn, and Duffy⁽⁶⁸⁾ stated that an increased solute concentration seemed to increase the stage efficiency. The other variables in their work were not constant enough, however, to state more than that there was an apparent trend. The effect of increased solute concentration has been commented on by Feick⁽³⁵⁾ and Sherwood⁽⁸⁰⁾. Both of these authors also point out that the stage efficiency is increased by using a system with high mutual solubility of the solvents. That is, better stage efficiencies would be expected for an extractor using

solvents such as water-methyl-ethyl-ketone and water-butanol than for solvents such as water-carbon tetrachloride and water-benzene.

Recommendations

Investigation of the effects of 400-kilocycle insonation on the extraction of acetone from carbon tetrachloride with water suggested a number of questions for which no answer was apparent, indicating possibilities for future investigations. Specific recommendations for future investigations are presented in this section.

Feed Composition. It is recommended that the feed composition be adjusted before each test to a predetermined value. This would eliminate one of the variables affecting the stage efficiency.

Flow Rates. It is recommended that positive-displacement, proportioning pumps be incorporated into the apparatus, with the flow rate instruments for constant indication and control. With the use of this type pump, accurate control of the feed and solvent rates would be possible.

Systems. It is recommended that systems other than carbon tetrachloride-acetone-water be used to fully determine the effect of ultrasonic energy on the rate of mass transfer. It is recommended that a system be used in which water is the heavy phase. An example of a system of this type that might be used is the system benzene-acetone-water.

Measurement of Ultrasonic Intensity. Ultrasonic intensity at various points within the extractor should be measured directly, either by using a probe incorporating a calibrated piezoelectric crystal or by using a probe incorporating a thermocouple. In the case of the former, the probe would give a direct indication of absolute pressure amplitude; in the case of the latter, the probe would give an indication of acoustical energy absorbed and converted to thermal energy.

Attenuation. Attenuation of ultrasonic energy in the carbon tetrachloride-acetone-water system for various intensities and times of insonation should be determined. Attenuation should be experimentally determined within the system for various concentrations of solute.

Extractor Design. Utilization of the transducer cavity as a reactor should be investigated. The direct

insonation of the system, without a separate mixing chamber, should result in greater usable insonation intensities because no coupling media are required that would absorb the ultrasonic energy.

Chemical Reaction. It is recommended that a study be made to determine the possibility of chemical reactions occurring in the extraction system when insonated at high intensities.

Localized Mechanical and Thermal Effects. The extent to which localized mechanical and thermal effects at the solvent-feed interface aid extraction should be investigated. A comprehensive investigation of localized mechanical and thermal effects produced by insonation will require the development of suitable equipment and instrumentation.

Extraction Operation. It is recommended that ultrasonic energy be incorporated in a countercurrent system and also a multi-stage column. The latter effect could be accomplished by using the extract from one stage as the solvent for the next in a series of single-contact stages.

Limitations

Limitations of the specific fields of work and the quantitative boundaries of the variables investigated are presented in this section.

Extractor. For this investigation a single-contact, continuous-flow extractor was employed. The reactor was designed with an acoustic window as the bottom to transmit a maximum amount of ultrasonic energy into the liquid-liquid extraction system. Constant head tanks were used as reservoirs for the feed and solvent.

System. The system used in this investigation was carbon tetrachloride-acetone-water. The direction of transfer of the solute was from the carbon tetrachloride phase into the water phase.

Flow Rates. The flow rates investigated were 32, 40, 72, 90, and 120 grams per minute.

Solvent-to-feed Ratio. Three solvent-to-feed ratios were studied in this investigation. On a weight basis, these ratios were 1:1, 1:2, and 1:3.

Intensity of Insonation. Measurement of compressional wave intensity was restricted to measurement of ultrasonic generator plate current. The ultrasonic plate potential

was automatically adjusted within the generator, but was not indicated externally. Plate current intensities used in this investigation were 100, 150, and 200 milliamperes.

Frequency of Insonation. Frequency of insonation was restricted to 400 kilocycles per second.

Reproducibility of Data. Eight reproducibility tests indicated an average deviation from the mean of ± 1.55 per cent.

Emulsification. Entrainment of one phase in the other would introduce an error in the determination of the refractive index because the refraction of light through an emulsion would necessarily be different from the refraction through a pure solution. No signs of emulsification were observed in this investigation when the extract and raffinate phases were compared with the solvent and feed by means of a Klett-Sommerson colorimeter.

Chemical Reaction. Liberation of chlorine has been reported by several investigators^(47,89,109). The formation of hydrochloric acid in the system was not detectable with indicating litmus paper.

Thermal Reaction. Localized temperatures as high as 200 °C have been reported⁽⁵⁷⁾ to occur in an ultrasonic field. Measurement of bulk temperatures of the system indicated a change of + 1 °C which would not affect the system appreciably.

V. CONCLUSIONS

Extraction using the system carbon tetrachloride-acetone-water, was performed in a single-contact extractor in a 400-kilocycle ultrasonic field. High-frequency electrical power, supplied by a Brush Hyper-sonic generator, was transferred to high-frequency vibrational mechanical power (ultrasonic energy) by a barium titanate, bowl-shaped transducer. This investigation led to the following conclusions:

1. Stage efficiencies of the extractor, without insonation, were 84.0, 87.3, and 75.1 per cent for total flow rates of 72, 90, and 120 grams per minute, respectively.

2. Insonation with 100 milliamperes plate current increased the stage efficiency of the extractor from 84.0 to 86.9 per cent, and from 87.3 to 89.0 per cent for total flow rates of 72 and 90 grams per minute, respectively.

3. No increase in stage efficiency resulted when the system was insonated at 100 milliamperes when the total flow rate was 120 grams per minute.

4. Insonation with 150 milliamperes plate current increased the stage efficiency of the extractor from 84.0 to 94.5 per cent, from 87.3 to 95.1 per cent, and

from 75.1 to 95.0 per cent with total flow rates of 72, 90, and 120 grams per minute, respectively.

5. Insonation with 200 milliamperes plate current increased the stage efficiency of the extractor from 84.0 to 100.5 per cent, from 87.3 to 99.9 per cent, and from 75.1 to 96.9 per cent with total flow rates of 72, 90, and 120 grams per minute, respectively.

6. A stage efficiency increase of 20.0 per cent, from 82.2 to 102.2, resulted with a total flow rate of 40 grams per minute when insonated with an intensity of 200 milliamperes plate current.

7. No stage efficiency increase resulted with a total flow rate of 32 grams per minute when the system was insonated with an intensity of 200 milliamperes plate current.

8. Reproducibility of tests conducted with a total flow rate of 32 grams per minute at insonation intensities of 100, 150, and 200 milliamperes plate current indicated a 1.55 per cent deviation from the mean.

VI. SUMMARY

Extraction of acetone from carbon tetrachloride with water was performed in a single-contact extractor in the presence of a 400-kilocycle ultrasonic field. High-frequency electrical power was transferred into high-frequency vibrational mechanical power by a barium titanate, bowl-shaped transducer. A summary of this investigation is presented as purpose of the investigation, plan of experimentation, and results and conclusions.

Purpose of Investigation. Application of ultrasonic energy to liquid-liquid extraction has not been previously reported; however, selective micro- and macroagitation at interfacial boundaries has been observed by several investigators. This investigation employed ultrasonic insonation to accomplish intimate solvent-to-feed contact. The purpose of the investigation was to evaluate a liquid-liquid extraction unit incorporating 400-kilocycle insonation and to study the effect of the ultrasonic field on the rate of mass transfer.

Plan of Experimentation. Acetone was extracted from a feed containing 13.78 ± 2.72 weight per cent acetone in carbon tetrachloride (saturated with water) using water as the solvent. A single-contact, continuous-flow extractor

was used for the investigation. Insonation extraction tests and control extraction tests were conducted, as were reproducibility tests. Variables investigated were: flow rate, solvent-to-feed ratio, and intensity of insonation.

Results and Conclusions. Rate of acetone extraction was increased by employment of ultrasonic insonation. An increase in stage efficiency of the extractor was observed when the system was insonated at 400 kilocycles with an intensity that exceeded 100 milliamperes plate current, regardless of the solvent-to-feed ratio. However, the increase was only apparent when the total flow rate of the extract and raffinate phases was greater than 32 grams per minute. Reproducibility of tests was ± 1.55 per cent stage efficiency.

Maximum increase in stage efficiency of 21.8 per cent, from 75.1 to 96.9 per cent, resulted with a solvent-to-feed ratio of 1:3 and a total flow rate of 120 grams per minute when the system was insonated at maximum intensity (200 milliamperes plate current).

An increase in stage efficiency of 12.3 per cent, from 87.3 to 99.9 per cent, resulted with a solvent-to-feed ratio

of 1:2 and a total flow rate of 90 grams per minute when the system was insonated at maximum intensity.

An increase in stage efficiency of 16.5 per cent, from 84.0 to 100.5 per cent, resulted with a solvent-to-feed ratio of 1:1 and a total flow rate of 72 grams per minute when the system was insonated at maximum intensity.

Significant increases in stage efficiency resulted only after discernible cavitation was observed, between 100 and 150 milliamperes plate current. Bulk agitation and selective microagitation at the solvent-feed interfacial boundary aided extraction by increasing the effective area available for mass transfer.

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