THE EFFECT OF INTERFACIAL TENSION ON THE RATE OF MASS TRANSFER IN TERNARY LIQUID-LIQUID EXTRACTION

by

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I. INTRODUCTION

The use of liquid-liquid extraction as a chemical engineering unit operation has become increasingly important during the past few years, because improved equipment design has allowed a wider, economical application of this process to many fields, heretofore unexplored. Included in these applications are the recovery of oils from agricultural products, the processing of petroleum oils, the separation of azeotropes, and the separation, concentration, and purification of metallic ions, vitamins, and antibiotics. Considerable interest has been shown in the use of liquid-liquid extraction in metallurgical separation processes, especially in recovery of the more valuable alloying constituents such as molybdenum, beryllium, germanium, tungsten, and zirconium. Liquid-liquid extraction methods have recently assumed important positions in metallurgical processes of interest in the atomic energy field. It is significant also to note that many of the extraction processes and techniques originally developed for the production of reactor grade uranium, separation of fission products, such as plutonium, from irradiated uranium, and the preparation of reactor moderator materials, such as hafnium, have now been released for commercial utilization in the metallurgical fields. Declassification of this atomic energy information may provide a valuable incentive for much deeper study of methods for inorganic extractive processing in the future.

Despite the rapid advances in the applications of liquid-liquid extraction techniques, the major shortcomings continue to be the lack of well correlated mass-transfer data, and the lack of understanding of the fundamental mechanisms that govern this mass-transfer operation. This is in part caused by the increased realization that these mechanisms are much more complex and interrelated than was first suspected, and in part, because of concentration on the development of the practical applications of the techniques. The overall addition to the collection of fundamental knowledge continues to be of the greatest importance. Ultimately, it is through the application of this knowledge that extraction techniques can be utilized fully in solving problems peculiar to any situation, and design practices can be elevated above trial and error procedures.

Usually, the mechanism of solute transfer from one liquid phase, through an interface, into a second liquid phase, and the relationship of the rate of extraction with physical and dynamic properties of the substances involved, are explained by the "two-film" theory of mass transfer. According to this concept, the resistance to mass transfer of a solute between two liquid phases is considered to lie in stagnant laminar films which are assumed to exist in either side of the interface. The mass-transfer coefficients of the individual films, which are a measure of this resistance, have been shown to be functions of film properties in the separate phases.

Some difficulty has been encountered by previous investigators in experimentally evaluating and correlating the effects of these physical properties, and as a result, the relationships obtained have been at best only an approximate indication of the actual mechanism taking place within the extractor. Previous work at the Virginia Polytechnic Institute has resulted in equations correlating mass-transfer coefficients of the individual films with physical properties of liquids for binary systems. In these correlations, the dynamic conditions existing in the column in regards to interfacial tension behavior were not considered, but instead it was assumed that the interfacial tension measured at static equilibrium could be used to represent the transient states encountered during extraction. It is believed that the fundamental mechanisms of mass transfer behavior would be better understood if dynamic interfacial-tension phenomena and their interaction with mass transfer were known.

Therefore, it was the purpose of this investigation to ascertain the qualitative nature of the interfacial tension equilibrium characteristics of the systems hexane-acetone-water and toluene-acetone-water by studying the effect of drop velocity on drop weight through use of the modified drop weight procedure, and comparing these results with those obtained from systems known to have time dependent interfacial tension relationships; to then evaluate the effect of interfacial tension on the rate of mass transfer by obtaining extraction data for the above systems in a horizontal, countercurrent, liquid-liquid extraction tube for a series of interfacial tension values achieved through variation of the total concentration of acetone in the system; and finally, to attempt to obtain an equation correlating the overall mass transfer coefficient based on the solvent film with the physical and operational variables of the systems and extractor.

II. LITERATURE REVIEW

This section includes a brief review of the results previously reported in the literature that discuss the nature of interfactial tension and its measurement, interfacial tension and time effects, two film theory of mass transfer, and effect of interfacial tension on mass transfer.

The Nature of Interfacial Tension

The region in which two phases meet is designated in general as an interface, and an interface between a gaseous and a liquid or solid phase is designated as a surface. Much time and scientific effort have been expended in an attempt to physically understand and correctly describe a surface or an interface, and to measure forces which constitute these surface and interfacial boundaries.

Interfacial Boundaries and Boundary Forces. Molecules within a liquid body are for the most part, completely surrounded by other molecules and on the average equally attracted in all directions. Molecules on or near the surface, however, are subjected to a net average attraction toward the center of the liquid, because of the unbalance of forces resulting from the smaller number of similar molecules in the opposite phase. From this standpoint(106), a liquid is under a so-called internal pressure acting perpendicularly to the boundary surface.

An extension of this boundary surface requires an expenditure of work, in order to bring the molecules from the bulk of the liquid to the surface against this attractive force; the work necessary to extend the surface one square centimeter is called free surface energy(35). The possession of this free surface energy by a liquid is characterized by the tendency of the surface to contract; a contraction thereby reducing the free energy and entropy of the system, lowering it to a more stable state.

Associated with the internal liquid force is a force acting parallel to the surface of the liquid; a consequence of the tendency of the surface to contract. The force is the same at every point and in all directions along the surface of the liquid.

Surface tension is the name given to this contraction tendency of a liquid surface, and is defined(35) as the force in dynes acting at right angles to any line one centimeter in length in the surface plane.

This surface plane, as used here, does not signify a rigorous sharp boundary, but rather one composed of a boundary layer of molecules in which a continuous density gradient exists. Across this gradient there is a gradual transition(106) from the characteristics of one phase to those of the opposite phase, either gas or liquid. This density gradient, although finite, is of molecular thicknesses, and hence appears as a sharp boundary. It is this density gradient in the surface layer that accounts for what is termed surface tension(106).

The existence of a surface presupposes a separation between two media; either liquid and gas, liquid and liquid, or liquid and solid. The surface energies are dependent, therefore, on the nature of both substances(35). By custom, the recorded values for interfacial tension between liquid and gas systems are referred to as surface tensions; those between liquid and liquid systems termed interfacial tension.

The phenomena present at the boundary of a liquid-vapor surface exist also at the boundary of a liquid-liquid surface. The work necessary to enlarge the surface of separation between two immiscible or partially miscible liquids is termed the interfacial surface energy, and is expressed as the interfacial tension in dynes per centimeter(106). Since the mutual attraction across the interfacial boundary between the molecules of the two liquids tends to reduce the inward pull of the molecules in the surface by those of its own kind, the magnitude of interfacial tension is generally less than the largest of the two surface tensions. Based on this generalization, Antonoff(35) proposed that interfacial tension between two liquids would be equal to the difference of the surface tensions, against vapor or air, of the two mutually saturated solutions. It has been pointed out(57) that this deduction is applicable only to very special cases, which in themselves cannot be predicted without experimental verification. Deviations up to 40 per cent were found for some of the simple liquid systems.

Static Methods of Measurement of Interfacial Tension

Interfacial tension has long been used as an identifying property for immiscible liquid systems, and many methods of measurement have been proposed(36,44,49,61,81) which were designed to give the best results with the least effort contingent on the degree of accuracy desirable. There is no single best method. An excellent review of the methods for surface tension as well as interfacial tension measurement is presented by Harkins(39). The more common procedures which are best adapted to interfacial tension measurement, are discussed in the following section.

Capillary Rise Method. The capillary rise, or capillary height method is generally accepted(39) as the most absolute or accurate method of all, but is used more extensively for surface rather than interfacial tension measurements. The principles for making determinations for both tensions are exactly alike, and constitute measuring the height or rise of the interface in a capillary tube of known and uniform diameter. Certain precautions which must be adhered to when using this method for interfacial tension work are discussed quite thoroughly by Harkins and Jordan(44), along with a detailed description of a suitable apparatus. Interfacial tension is calculated by use of the equation:

$$\sigma = 0.5hdgr/\cos\theta \qquad (1)$$

where:

σ = interfacial tension, dynes/cm

h = height of liquid rise in capillary, cm

d = upper liquid density in two phase system, gm/cm^3

g = gravitational constant, cm/sec^2

r = capillary radius, cm

θ = contact angle between liquid and capillary.

The time consuming nature of this method makes it rather unsuitable for most engineering purposes.

<u>Ring Detachment Method</u>. The ring detachment method, developed by du Nouy(35) in 1919 and standardized by Harkins and Jordan(45) in 1930, is

at present the most popular method for rapid, simple, and fairly accurate measurement of surface tension. Although not yet properly tested for accurate interfacial work, it has been used (57,111) to this end with good results. As now used, the method depends upon the determination, with a suitable balance, of the maximum pull necessary to force a horizontal circular platinum ring through the interface of the two liquids under examination. The force required to force the ring through the interface is proportional to the interfacial tension as follows:

$$\sigma = P/4\pi R \cdot F \qquad (2)$$

where:

σ = interfacial tension, dynes/cm
P = force on ring, dynes
$4, \pi$ = constants
R = mean radius of ring, cm
F = correction factor.

Harkins has suggested (39) that the ring method could be used even if time effects on interfacial tension were apparent, as long as they were of considerable magnitude.

Pendant Drop Method. Two very well known methods for interfacial tension measurement have been derived from consideration of the interaction of interfacial forces and shape of liquid drops which hang from a horizontal sharp-edged circular tip into a second liquid. These are the method of the hanging or pendant drop, and the drop weight method. The pendant drop is not one of the so-called absolute methods, yet largely due to the theory of Bashforth and Adams(4), Freud and Harkins(24), and the empirical correction factors of Andreas, Hauser, and Tucker(3) the method has been standardized for limited usefulness. Errors inherent and unavoidable in the process, however, still make it the least accurate(39) of the known methods of interfacial measurement. Use of the method involves forming a liquid drop from a tip immersed in a second liquid, and determining the shape of the drop by use of an enlarged photograph. The interfacial tension is then calculated from the curvature of the drop at the point of maximum diameter by the following equation:

$$\sigma = g(\rho_1 - \rho_2) d_e^2 \cdot F \qquad (3)$$

where:

σ = interfacial tension, dynes/cm

g = gravitational constant, cm/sec^2

ρ_1, ρ_2 = densities of heavy and light phases, respectively, gm/cm^3

d_e = equatorial diameter, cm

F = correction factor.

This method is useful in rapid work, especially if interfacial tension is changing with time, but considerable accuracy is sacrificed with its use.

Sessile Drop Method. The sessile drop or bubble method involves the same general considerations as the pendant drop; that is, this method is dependent on the relationship between the geometry of a liquid drop suspended within a second liquid and the interfacial tension forces between the two. The major difference is in the mechanism of suspension; in the pendant drop method the drop of liquid hangs from a tip immersed within the second liquid; the sessile drop method involves forming a drop on a horizontal plate resting well below the surface of the second liquid. The volume of any given drop is then constant with respect to time, and any changes in drop shape will be the direct result(77) of interfacial forces adjusting to a minimum value. The shape of such a drop will depend on the interfacial tension between the two liquids, the volume of the drop, and density differences of the two phases. Porter(70) published a method of calculating interfacial tension from the dimensions of a sessile drop:

$$\frac{\beta^2}{r^2} = 0.5\,\frac{h^2}{r^2} + \Delta \qquad (4)$$

$$\beta^2 = \frac{\sigma}{g(\rho_1 - \rho_2)} \qquad (5)$$

where:

β = correlation factor

r = radius of drop at maximum diameter, cm

h = height of drop from equator to vertex, cm

σ = interfacial tension, dynes/cm

g = gravitational constant, cm/sec^2

ρ_1, ρ_2 = densities of respective phases, gm/cm^3

Δ = correction factor.

Harkins(39) recommends this method as the best one available if extremely long time effects are in evidence, since it does not disturb the surface once the drop has been formed.

Drop Weight Method. The drop weight method, developed by Harkins and Brown(41), is recommended(39) as being the best general method for surface and interfacial tension determinations if both accuracy and speed are desirable. It is one of the two more generally used methods based on shapes of hanging drops, and has been employed to a much greater extent than has its counterpart, the pendant drop method.

The theory of the drop weight method was presented in a preliminary way by Lohnstein(60) but was too inaccurate to be of extensive value. Morgan(42) determined values for drop weights, but ignored any theoretical corrections for drop formation. Harkins and Humphery(43) attempted a preliminary standardization of the drop weight method in 1912. Their experiments were extended by Harkins and Brown(41) in 1918, and the combined work of the three authors was made a basis for the method of calculating surface and interfacial tension by drop-weight techniques. Although the theory has not yet been fully worked out (34), the semi-empirical equations developed by Harkins and Brown have proved to be extremely valid for the most accurate experimental demands.

An extensive development of the known theory of the drop weight method is given by Harkins (40) and will not be included here. In essence, the theory dictates that the weight of a drop of liquid falling from a tip immersed within a second, lighter, liquid depends on the radius of the dropping tip, the interfacial tension between the liquids, and the shape of the drop. From the measured weight of a drop, or series of drops, and the tip radius, the interfacial tension can be calculated as follows: The weight of a drop, (W), which falls from the tip is proportional to the interfacial tension

$$W = 2\pi r \sigma \cdot \phi(r/V^{1/3}) \qquad (6)$$

so, since

$$W = m_o g \qquad (7)$$

then it follows that

$$\sigma = m_o g/2\pi r \cdot \phi(r/V^{1/3}) \qquad (8)$$

where:

m = apparent mass of drop, gm

W = weight of drop, dynes

m_o = apparent mass of drop, = $m\frac{\rho_1-\rho_2}{\rho_1}$, gm

g = gravitational constant, cm/sec^2

V = drop volume, cm^3

$2, \pi$ = constants

r = radius of dropping tip, cm

ρ_1, ρ_2 = densities of heavy and light phase liquids, respectively, gm/cm^3.

The correction factor, $\phi(r/V^{1/3})$, was necessary to account for the non-sphericity of the drops falling from the tip, and was expressed as a function of the tip radius and the drop volume. These correction factors were determined in an extensive series of experiments(41) in which four pure liquids were dropped from 15 glass and 20 metal tips. In agreement with theory, the correction factors were found to depend only on tip radius; independent of material of construction of the dropping tip, or characteristics of the liquid systems under investigation.

In using this method, Harkins(39) cites the following precautions: (1) the drop must be made to detach itself as slowly as possible from the tip, and (2) presaturated solutions must be used to minimize disturbances of the interface by counterdiffusion. Harkins and Brown(41) made a series of tests to determine the allowable rate of drop formation below which a constant drop weight was obtained. They used a glass tip of 0.24456 centimeter radius, and water as the testing material. The results of the tests are given in Table I. They concluded from these tests that when the rate of formation of a drop is faster than one in three minutes on "ordinary" sized tips, some of the liquid streaming from the capillary seems to

TABLE I

Drop Weight as a Function of Drop Velocity for Water at 20 °C

Test No	Rate of Drop Formation, min	Drop Weight, gm
1	1.30	0.07191
2	1.75	0.07187
3	3.50	0.07179
4	6.00	0.07172
5	9.00	0.07174
6	11.00	0.07175
7	11.30	0.07173
8	slower than 11.30	0.07172

Harkins, W. D. and F. E. Brown: Surface Tension of Water and Benzene. J. Am. Chem. Soc., 41, 509 (1919).

force its way into the falling drop during the time of detachment, and thus, a drop formed rapidly is heavier than a drop formed slowly. They also reported(41), but did not show any data to substantiate, that the weight of the drops increased very rapidly at rates of drop formations slower than those in the table. On the basis of this one study, a time of drop formation of five minutes for small and medium sized drops, up to 12 and 15 minutes for larger drops, was recommended.

Interfacial Tension Equilibria

Of the many factors affecting interfacial tension equilibria, solute concentration and temperature(35) are two of the most influential. Time dependency of interfacial tension for certain liquid systems containing solutes of high molecular weight is a less obvious yet equally important factor to be considered in interfacial tension studies.

Effect of Temperature. It is generally believed(39) that surface and interfacial tension of liquids decrease with increasing temperature, although no rigorous mathematical relationships have been developed which allow direct linkage of interfacial tension and temperature.

The interfacial energy of a liquid system can also be defined(22) as the additional potential energy per unit surface because the particles of the surface layer lack neighbors on the external side. The surface energy is therefore(22) practically independent of temperature. The temperature dependence is thus represented by some function of surface entropy, the basis of which is the conception of a specific type of heat motion associated with the free surface of a liquid phase. A mathematical relationship between interfacial tension and temperature was developed by Eotvos(39), and modified later by Ramsey and Shields(39) and Frankel(23). It was shown later by Walden(39) and Jaeger(39), that the modified expression was not applicable, except for a very few isolated cases, even for normal liquids, and the association factor of Ramsey and Shields was quite unreliable. It would appear(39), in addition to molecular association, that something more fundamental, such as shape and orientation of molecules and molecular attraction, will have to be considered in the light of additional thermodynamic potentials before agreement on the mechanisms of temperature effect on interfacial and surface tensions will be reached.

Effect of Solute Concentrations. In the solution of a solute and solvent, the nature and concentration of the solute ultimately determine the effect on the interfacial tension at a given interface(33). If the solute has a lower surface energy than the solvent, it will tend to concentrate at the interface, thus lowering the interfacial tension of the system in keeping with the tendency of the free energy of the surface to seek a minimum. The net result will be a greater proportion of solute to solvent at the interface than in the bulk of the solution. This adsorption mechanism is termed positive adsorption, and substances exhibiting this behavior are called surface active substances(39). Conversely, if the solute possesses a lower surface energy than the solvent it will tend to concentrate in the bulk of the solution, thereby giving rise to so-called negative adsorption at the interface. In this type of solution, the interfacial tension of the solvent in general will be raised slightly, but will differ little from that of the pure solvent(106).

Most experimental work on the effect of solute nature and concentration on interfacial tension has been carried out using aqueous solutions as one of the phases, and some organic compound as the other. The results obtained have closely paralleled those obtained from surface tension studies using aqueous solutions, as would be expected, since the effects measured in both cases are due primarily to changes in behavior of the aqueous phase. There is evidence(57) that most solutes in organic solvents have little effect on the surface tension of the solvent; that is, negative adsorption is the general characteristic. Conclusions drawn from surface and interfacial tension studies, where aqueous solutions are used, generally indicate that long chain, highly complex solutes, such as fatty acids, alcohols, and urethanes, lower the interfacial tension, as well as exhibit a time dependency. Most dissolved non-electrolytes lower the interfacial tension, some do not change it appreciably, while others raise it slightly(106). The interfacial tension between salt solutions and organic oils show slight increases, as do strong basic solutions; however, ammonia, and nitric, hydrochloric, and hydrobromic acids lower it(106).

A detailed discussion of the theories of Gibbs and Freundlich on relating surface concentration and interfacial tension variations is given by Weiser(106). The extreme difficulty of experimentally verifying the equations proposed by the above theories has limited their use, but Weiser shows that for the most part the equations represent only simple approximations, and limiting boundary conditions, without considering such factors as presence of solvent in surface layers, and adsorption resulting from electrification of the surface.

Time Dependency of Interfacial and Surface Tensions

The factors attributing to time lags in surface and interfacial tension equilibrium attainment are discussed in this section. A brief mention of methods used to study time variations is also made.

Surface Tension-Time Variation. The variation of surface tension with time has long been the object of investigation, particularly in the field of colloid chemistry.

It has been pointed out by many authors(1,2,7,15, 64,65,69,83,103) that the surface tension of many dilute aqueous solutions undergoes very slow changes, either increases or decreases, depending on the nature of the solute, and may take days or even weeks to reach equilibrium. In still other cases, the final surface tension is attained very rapidly, sometimes immeasurably fast(8,63). Often the results have been confusing, and although a great deal of time and effort have been devoted to a study of these phenomena, no general prediction characteristics have been found; indeed, there is even no general agreement as to the mechanisms of such variations.

Variation of Interfacial Tensions with Time. Among the first to report variation of boundary tension with time were Reed and Tartar(75), who observed that the interfacial tension between benzene and solutions of long chain colloidal electrolytes required up to a week to reach an equilibrium value. This fact was observed in the course of an investigation to determine solubilities and other colloidal properties of the system, and was not considered important enough at the time to receive any explanation by the authors.

Evans(20), in 1937, investigated the effect of uni-univalent electrolytes on the interfacial tension between n-hexane and water, but reported no time effect studies. It was not until 1939 that Matthews(62), studying the effect of aqueous carbohydrate solutions on the interfacial tension between them and cyclohexane, reported the first systematic investigation on interfacial tension-time effects. Using the drop volume apparatus of Dedrick and Hanson(16), Matthews first determined the time necessary for a constant drop weight to be attained, and found it to be on the order of 2.5

minutes per drop. With this drop time as a minimum, he then established the equilibrium times for each carbohydrate compound, which he subsequently used as a basis in the rest of the investigation. The equilibrium times varied essentially from zero (immeasurable) for dextrose and sucrose, to five minutes for glycogen, and citrus and apple pectins, and were independent of concentration of the solute. Matthews then compared the equilibrium times with the diffusion coefficients and concluded that the extreme differences which were present did not support the diffusion theory(62). He then suggested that the values recorded were times required for molecular penetration and reorientation at the interface.

Ward and Tordai(104), experimenting with a precision drop weight apparatus, showed that time and interfacial tension between water and solutions in hexane of long chain amphipathic substances were related, and studied this variation by means of the pendant drop method which allowed continuous readings to be made without disturbing the interface. The interfacial tension was found to fall rapidly at first, gradually leveling off, and reaching equilibrium in approximately a week(104). They also reported that the decrease in interfacial tension was much slower than that predicted if diffusion was the controlling step. From this(104), it was concluded that the diffusion to the surface was followed by a process of high activation energy changes which produced the final state of the surface films. In confirmation of this, the rate at which the final interfacial tension reached equilibrium was found to increase sharply with increasing temperature.

In connection with a slight refinement in the drop weight method for studying interfacial tension variations with time, Subrahmanya et al(82) measured the variation of interfacial tension with time between benzene and aqueous solutions of rubin. They found the equilibrium time to be on the order of 10 to 25 minutes, and to vary with the concentration of the rubin. They suggested the theories of Doss(17) to explain the variation, and attributed the changes in interfacial tension to the fluctuations of zeta potential within the postulated electrical double layer existing at the interface.

In a recent article, Shotton(77) made a comparison of the drop volume and sessile drop methods for determining the variation of interfacial tension with time. He used aqueous solutions of arabic acid and benzene as a system, and concluded that for long time effects, the sessile drop method was preferred to the drop weight method since in the former, no disturbance of the interface over the time period in question took place. The change in interfacial tension with time showed the same general form with both methods, although the drop volume method at the slowest rate gave results greater than those attained by the sessile drop method. He attributed this discrepancy to the fact that the drops growing on the tip did not have time to reach equilibrium with the bulk of the solutions. The shape of the interfacial tension-time curve and interfacial tension-concentration curve was interpreted as being due to the formation of an adsorbed multilayer, containing a high concentration of arabic acid in the layer possessing gel-like properties.

Christiansen and Hixson(9) made a study attempting to characterize the effects of certain surface active solutes on liquid jet disruption in an immiscible liquid in terms of a non-equilibrium interfacial tension existing at the time of jet breakup. They developed equations from theoretical considerations of jet stability, and found that interfacial tension was an important factor in jet breakup. From pure two-component, two-phase studies, without solute, the correlation of critical flow producing maximum jet area with the ratio of jet velocity to wave celerity was remarkably constant for the system studied. It was possible from this correlation to predict not only optimum velocity for a jet of given diameter to give the maximum area but also, if critical velocity can be determined by direct area measurements, to predict the interfacial tension at jet breakup. The method is similar to the vibrating jet technique(39) of surface tension measurement.

An investigation of some 14 solutes in the toluene-water system indicated that interfacial tension at time of jet breakup was higher than when the interfacial tension for the same solute system was measured under static, equilibrium conditions for large molecular weight solutes. It was concluded that the interfacial tension depressing effect of the solute was only partially accomplished by the time of jet breakup, and that its subsequent alteration of jet flow rate at maximum area was due entirely to lack of interfacial equilibrium between the two phases. In the case of small molecular weight solutes, the effective interfacial tension behavior was quite different from that of the larger molecules. For example, the systems toluene-water with n-butyl alcohol, octyl alcohol, and actylamine acetate exhibited a lower, effective interfacial tension than when the tension was measured under static conditions; the reverse situation of the larger solutes, and from the results reported by Addison(9). In correlating this behavior, the concept of solute and solvent were interchanged. For these three systems in which the effective interfacial tension was lower than the equilibrium value, the interfacial tension of the binary system solute-water rather than toluene-water was considered the equilibrium value, and toluene was interpreted as raising the interfacial tension of the solute-water binary system.

Liquid-Liquid Extraction Definitions

The definitions and nomenclature used to describe liquid-liquid extraction operations are generally consistent in the literature. A discussion of the more pertinent terms that will be used throughout this discussion is included in this section.

Feed. The feed to a liquid-liquid extraction process is the solution(18) of components whose separation is desired. One or more components may be removed from the feed during the operation.

Extracting Solvent. The extracting solvent(18) is the liquid or liquid mixture agitated with the feed to remove one or more components from the feed.

Carrier Solvent. The carrier solvent(18) is the name sometimes given to the component or components of the feed that usually occur in the greater volume, and are not dissolved by the extracting solvent.

Solute. The solute(18) is that component, or components, removed from the feed by the extracting solvent.

Extract. The extract or extract layer(18) is the phase that contains the extracted solute; it is sometimes called the solvent-rich layer.

Raffinate. The raffinate or raffinate layer(18) contains the carrier solvent from which the solute has been extracted. Generally, some extracting solvent is also present in the raffinate, depending on the solubility of solvent and feed.

Theoretical Stage. The theoretical stage is a hypothetical concept used to indicate the maximum amount of extraction that could be achieved with a given method of contact(92). It represents the ideal case in which sufficient time is allowed for the extract and raffinate layers to reach equilibrium.

Actual or Extraction Stage. An actual stage(92) is defined as a mechanical device or series of devices wherein the feed and solvent are mixed, allowed to settle into two immiscible layers, and are then withdrawn.

Diffusion. Diffusion is a general term applied to the transfer of molecules from one point to another in a fluid without respect to fluid flow phenomena(54). Molecular diffusion is characterized by the transfer of molecules through a stagnant layer by Brownian movements; eddy diffusion represents the transfer of molecules by intermingling of fluid sections by means of eddies and turbulence. In both cases, the net amount of mass transfer is proportional to the differences in concentration of the diffusing material at the two points(54).

Height of a Transfer Unit. The height of tower, either for spray or packed towers, required to effect a differential change of concentration(90) per unit concentration difference causing the change is called the height of a transfer unit. It is a measure of the difficulty of extraction, and when multiplied by the number of transfer units gives the height of the tower. The height of a transfer unit is also related to the mass transfer coefficient through a mass velocity function.

Height Equivalent to a Theoretical Stage. A design method using the height equivalent to a theoretical stage concept was used extensively in the past for extractor design. Essentially, it consisted of determining the number of theoretical stages equivalent to a given amount of mass transfer, and then multiplying this quantity by an experimentally determined height equivalent to a theoretical stage. Subsequent experience has proved this method to be fundamentally unsound, since it applies a procedure involving stepwise changes in concentration to an operation where the concentration actually changes differentially with height(90).

Transfer Coefficient. The transfer coefficient is a number indicating the rate of mass transfer per unit interfacial area and unit driving force (concentration difference)(90). For certain cases where the interfacial area is not known, a capacity coefficient is used, representing the rate of transfer per unit volume of tower cross section(54).

Methods and Techniques of Liquid-Liquid Extraction

The separation of the components of a solution by extraction may be carried out in a number of ways, all dependent, mainly, on the nature of the solvent system and the physical arrangement of the desired process. Generally, the processes used in liquid-liquid extraction fall into two categories; stagewise contact, and continuous countercurrent contact.

Stagewise Contact. In this category are included those arrangements of equipment where solvent and feed are intimately contacted, allowed to approach equilibrium, and the two phases then separated(88). The simplest possible case would be a single batch contact of solvent and feed, but as this results in very poor separation efficiency, the more common arrangement involves successive extraction in several steps with portions of fresh feed being added at each step. Known as simple multiple batch or cocurrent contact, this arrangement gives any desired degree of stripping of the solute from the feed if a sufficient number of stages are used(88). Where large scale work is necessary, this process often becomes uneconomical.

A more efficient arrangement, and one used most universally of all of the extraction processes, is the countercurrent multistage contact unit. Here, the feed and solvent are fed into opposite ends of the extraction cascade, where repeated contact and separation of the phases occur in each stage in essentially cocurrent or batchwise fashion, but the streams flow from each stage in opposite directions within the cascade. It is characteristic of this process that no fresh solvent is added between stages. The outstanding advantage of this arrangement is that the maximum concentration of solute in the extract can be obtained with a given solvent to feed ratio(79).

Continuous Countercurrent Contact. Extraction processes wherein the two immiscible phases flow past each other in continuous contact in a single piece of equipment are characteristic of true continuous countercurrent differential contact. In most cases, the countercurrent flow is brought about by the density differences of the two phases, and commercial equipment usually takes the appearance of a vertical tower, either with or without internal baffles(92). The number of various designs which have been proposed is very large(92), and will not be dealt with here.

One type of design for continuous countercurrent contact equipment used with fair results for fundamental mass transfer studies has been the horizontal tube extractor, first introduced by Berglin, Lockhart, and Brown(6). The extraction tube consisted of a horizontal pyrex pipe through which two immiscible phases were forced countercurrently under pressure. Among the advantages of this extractor for fundamental research studies were the ability to maintain a definite and known interfacial area, and the ease with which a wide range of flow rates could be controlled. Although this tube has very poor extraction efficiencies compared with commercial extractors, it has helped to avoid many of the disadvantages encountered when commercial type extractors were adapted for fundamental extraction studies.

Theories of Extraction Mechanisms

When a mixture containing a solute is brought into contact with a suitable immiscible solvent, definite composition relationships for the distribution of the solute between the two phases are set up. These relationships are dependent primarily on the chemical nature of the compounds, the concentration of solute, and the temperature. The rate at which solute transfer will take place from the carrier solvent to the extracting solvent is a function of the area of contact of the two phases and to the degree of mixing to which the two phases are subjected(110). If mixing and contact time are insufficient to establish equilibrium distribution of solute between the two layers, then the actual compositions attained are governed by diffusion rates and degree of mixing(18).

The classical mechanisms of diffusion have been used to explain the transfer of mass between two phases, such as in liquid-liquid extraction. For the most part this approach has been an extension of the expressions developed for the treatment of diffusion in gases, although it is known(98) that the kinetic theory of gases is not readily applied to liquids. Also, knowledge of the variation of physical properties with concentration for liquids is less developed than for gases. As a result, the expressions developed are not reliable, and account for the wide variation in the theories reported in the literature for explaining liquid-liquid and liquid-gas mass transfer mechanisms.

However, since in every case one phase is brought into contact with another phase, a concentration gradient is established, and a transfer of matter from one phase to the other results(96), it may be assumed that a single theory, covering all cases, could be developed to explain these seemingly different mechanisms.

Molecular and Eddy Diffusion. Consider the extraction operation where moving immiscible liquids are brought into contact for the purpose of transferring a mutually soluble solute from one phase across the interfacial boundary into the other phase. One may assume that immediately adjacent to, and on both sides of, the interface, there is a thin film of fluid(96) in laminar or viscous flow, characterized by orderly movements of the fluid particles in streamlines parallel to the interface. In the outer regions of the fluids, however, flow is turbulent, characterized by irregular velocity distributions and considerable mixing. The transition between these two zones gives rise to an intermediate buffer zone, exhibiting first one type of flow and then the other(97). If the substance is to pass or diffuse through the various zones of such a moving system, it is clear that at least two(97) separate mechanisms are involved. Diffusion of solute across the so-called laminar zone is called molecular diffusion, and that across the turbulent zone, eddy diffusion(97).

Molecular diffusion characteristics and mechanisms are fairly well developed, with the most important contributions being those of Fick(85) and Maxwell-Stefan(85). The basic equations developed by these and other authors have been integrated for various situations, and an excellent review of their limitations and applications is given by Sherwood(86). Relatively little is known concerning the eddy diffusion and buffer zone diffusion processes(86), and as a result the entire mechanism of transfer is described by expressions similar to those for molecular diffusion. These expressions attempt to include the effects of all three zone characteristics by use of a fictitious layer film whose thickness, the "effective film thickness", accounts for the entire resistance to mass transfer(86). Thus:

$$N_A = \frac{D_A S C (C_{A1} - C_{A2})}{C_{BM} I} \qquad (9)$$

where:

N_A = rate of mass transfer, mol/hr

D_A = coefficient of diffusion of component (A), ft/hr

S = cross sectional area across which diffusion occurs, sq ft

C = total concentration of components (A) and (B), mol/cu ft

C_{A1}, C_{A2} = concentration of component (A) at points 1 and 2, mol/cu ft

C_{BM} = log mean of (C_{B1}) and (C_{B2}), mol/cu ft

I = effective film thickness for combined eddy and molecular diffusion, ft.

Equation 9, page 43, may be simplified by introducing a mass transfer coefficient, (k),

$$N_A = kS(C_{A1}-C_{A2}) \qquad (10)$$

where:

$$k = D_A C/C_{BM} I \qquad (11)$$

Equation 10 expresses what is known as a "local" coefficient(99), applying only to the particular situation existing at the point in question. The local mass transfer coefficient will vary from point to point in the system, and if an entire operation is to be described by one coefficient, then an averaging of conditions is necessary(99).

Two Film Theory. The oldest and most widely used theory of mass transfer is the Whitman two-film theory(86). The mechanism proposed by this theory has been more or less successful in interpreting the results of most two-phase mass transfer operations of industrial importance.

Consider the typical extraction process where two liquid phases are passing in continuous countercurrent contact to each other, and between which a steady state transfer of solute is taking place. If both liquids are assumed to be moving in a direction parallel to the interface, concentration gradients will be established in both phases which will act as driving forces for the solute transfer across the "effective" film thicknesses and the interface(86). Because of the complexity of the process, and in order to simplify the subsequent mathematics, certain qualifying assumptions are usually made(86):

(a) The rate of mass transfer within each phase is proportional to the difference in concentration of solute in the main body of the fluid and at the phase boundary or interface.

(b) Equilibrium distribution of solute exists at the interface, that is, the relationship between the concentrations given by the equilibrium curve for the system is set up.

(c) There is no resistance offered by the interface to diffusing solute; all resistance is accounted for by the films immediately adjacent to the interface.

(d) Steady state diffusion occurs to the extent of negligible holdup of diffusing solute in the region near the phase boundary.

A graphical representation(86) of the two film mass transfer mechanism is shown in Figure 1. The concentration of the diffusing solute is plotted as a function of the distance through the two-phase region. The two liquid phases are designated (E) and (R) (for extract and raffinate), while the subscripts on the concentration terms denote various positions in the system [(i) for the interface, (E) and (R) for the main portion of the respective phases]. In the (R) phase, (C_R) represents the bulk concentration of the diffusing solute, whereas (C_{Ri}) designates the interfacial concentration on the (R) side of the interface. The driving force causing transfer of solute through the equivalent film thickness, (L_R), in the (R) phase is ($C_R - C_{Ri}$). Because of the assumption of no diffusional resistance at the interface (C_{Ri}) and (C_{Ei}) are in equilibrium in accordance with the distribution coefficient for the system, and the solute passes through the interface into the (E) phase. The

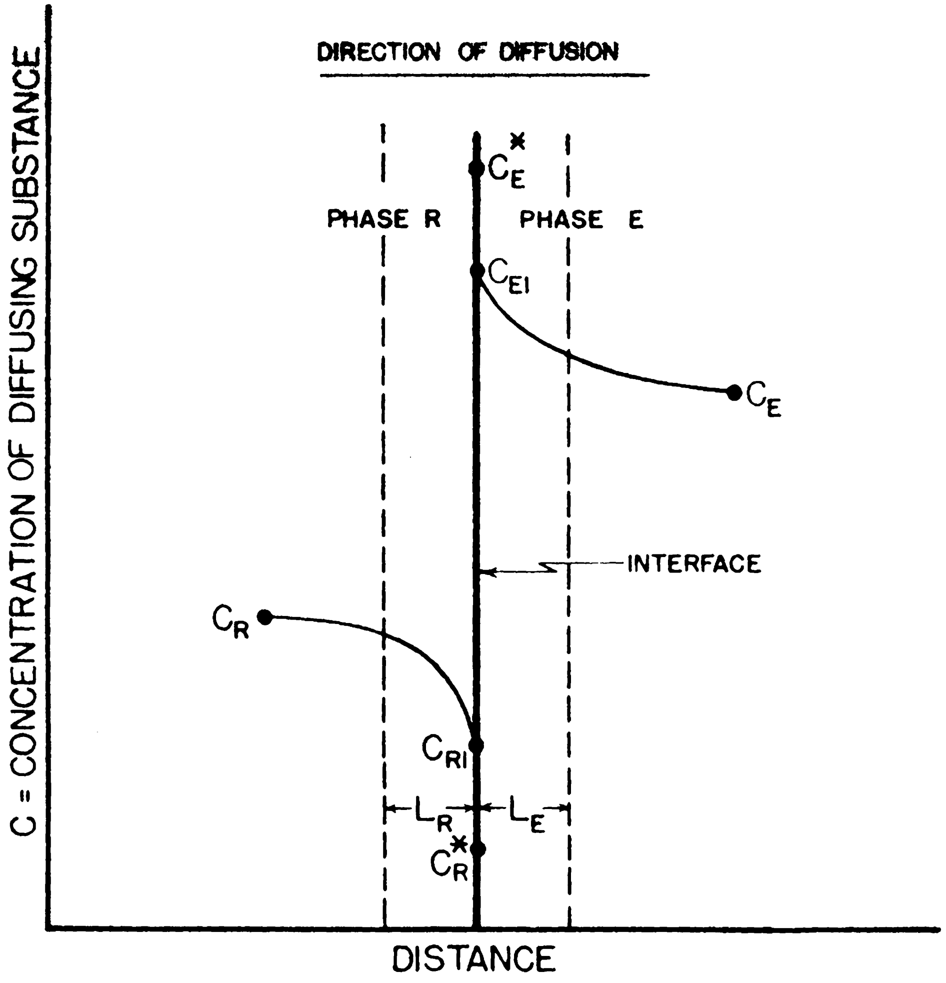


FIGURE I . CONCENTRATION GRADIENTS IN A LIQUID-LIQUID SYSTEM

TREYBAL, R.E. : "LIQUID EXTRACTION," P. 119. MCGRAW-HILL BOOK CO., INC., NEW YORK, N.Y., 1951. I ED.

concentration gradient $(C_{Ei} - C_E)$ then removes the solute from the interface through the effective film thickness (L_E) into the bulk of the (E) phase where the concentration is (C_E). For a differential rate of diffusion, (dN), across a differential element of interfacial area (dA), the rates of mass transfer may be expressed mathematically as

$$dN = k_R dS(C_R - C_{Ri}) = k_E dS(C_{Ei} - C_E) \qquad (12)$$

where:

k_R = individual film coefficient based on the (R) phase

k_E = individual film coefficient based on the (E) phase.

Overall Mass Transfer Coefficients. In most practical situations, the determination of (k_R) and (k_E) are ordinarily impossible. Routing sampling of liquids will give the coordinates (C_E) and (C_R) on Figure 2, but no sampling methods have been devised to date that will permit approach to the interface sufficiently close to determine (C_{Ei}) and (C_{Ri}) by physical methods. The true individual film driving forces (ΔC_E) and (ΔC_R) cannot then be determined.

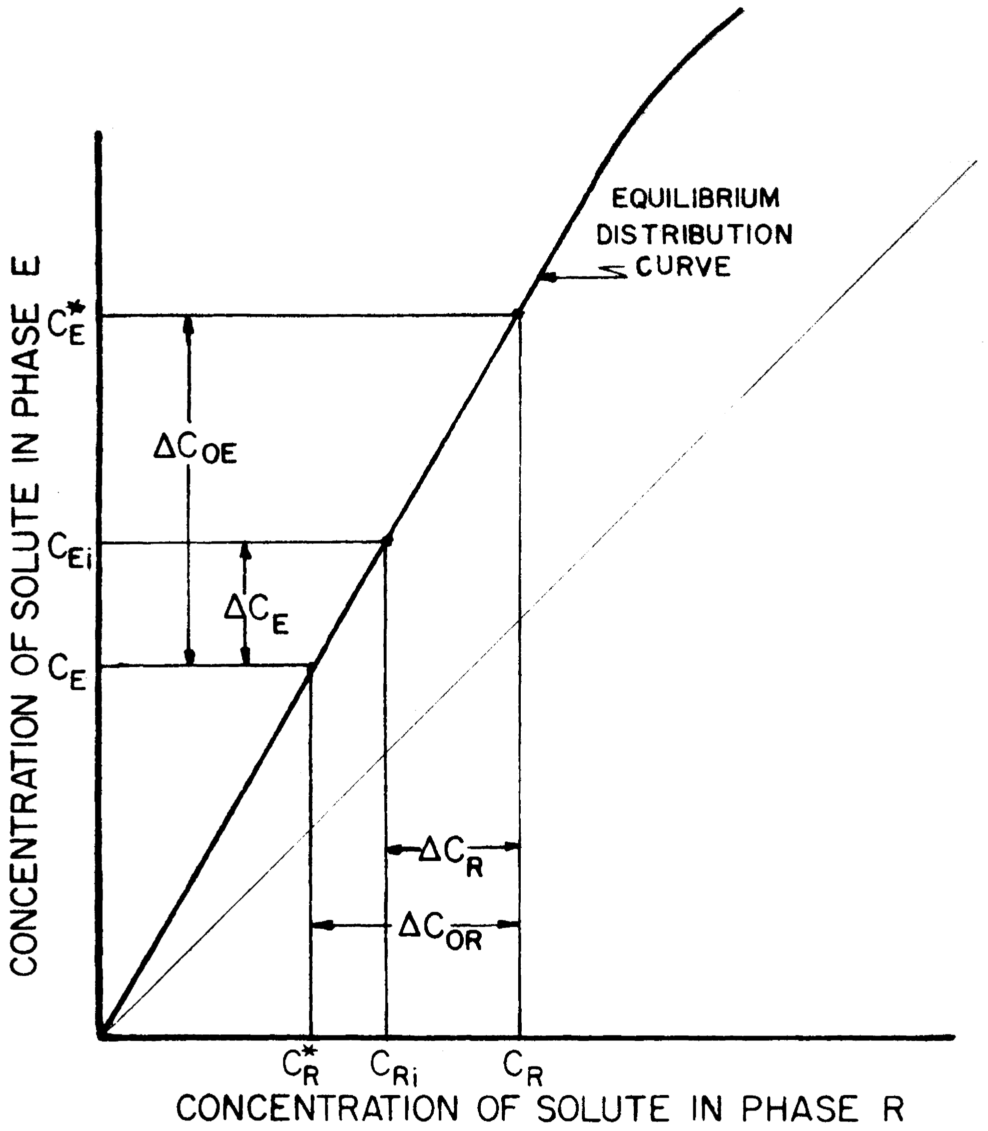


FIGURE 2 . OVER-ALL AND INDIVIDUAL FILM DRIVING FORCES

TREYBAL, R.E.: "LIQUID EXTRACTION", P.120. MCGRAW-HILL BOOK CO., INC., NEW YORK, N.Y. 1951. I ED.

If, however, the equilibrium distribution curve is sufficiently straight over the concentration ranges employed, then

$$C_{Ei} = mC_{Ri} \tag{13}$$

where:

m = equilibrium distribution constant of solute between the (E) and (R) phases.

It is impossible to define a concentration (C_E^*) which would be in equilibrium with the bulk concentration (C_R). Thus,

$$C_E^* = mC_R \tag{14}$$

This fictitious concentration, (C_E^*), represents the concentration of solute in the (E) phase that would be in equilibrium with the bulk concentration in the (R) phase(87). Similarly,

$$C_R^* = C_E/m \tag{15}$$

where (C_R^*) represents the concentration of solute in the (R) phase that would be in equilibrium with the bulk concentration in the (E) phase.

The gross, overall transfer process in both phases may then be expressed as

$$dN = K_E dS(C_E^* - C_E) = K_R dS(C_R - C_R^*) \qquad (16)$$

where:

K_E, K_R = overall mass transfer coefficient based on the overall concentration gradients (ΔC_{OQ}) and (ΔC_{OR}), respectively, lb mol/hr-sq ft-ΔC

dN = differential rate of mass transfer, lb mol/hr

dS = differential element of interfacial area, sq ft

$(C_E^* - C_E)$, $(C_R - C_R^*)$ = overall driving forces based on (E) and (R) phases, respectively, lb mol/cu ft.

The relationship between the overall and individual coefficients are given by(87):

$$1/K_E = 1/k_E + m/k_R \qquad (17)$$

$$1/K_R = 1/k_R + 1/mk_E \qquad (18)$$

$$K_R = mK_E \qquad (19)$$

where:

$1/K$ = total resistance to mass transfer

m = $C_E/C_E^* = C_E^*/C_R$ = equilibrium distribution coefficient expressed in terms of mol/unit volume

$m/K, 1/k, 1/mk$ = individual film resistances

E,R = subscript references to the (E) and (R) phases, respectively.

Characteristic behavior of certain liquid systems can be predicted from Equations 17 and 18. If the equilibrium distribution of solute strongly favors the (E) phase, (m) will be very large, provided (k_E) and (k_R) are of comparable order of magnitude, (K_R) will nearly equal (k_R) and the principal resistance to diffusion lies in the (R) phase. This condition is shown graphically in Figure 3a, where (ΔC_{OR}) is very nearly equal to (ΔC_R). By the same analogy, if

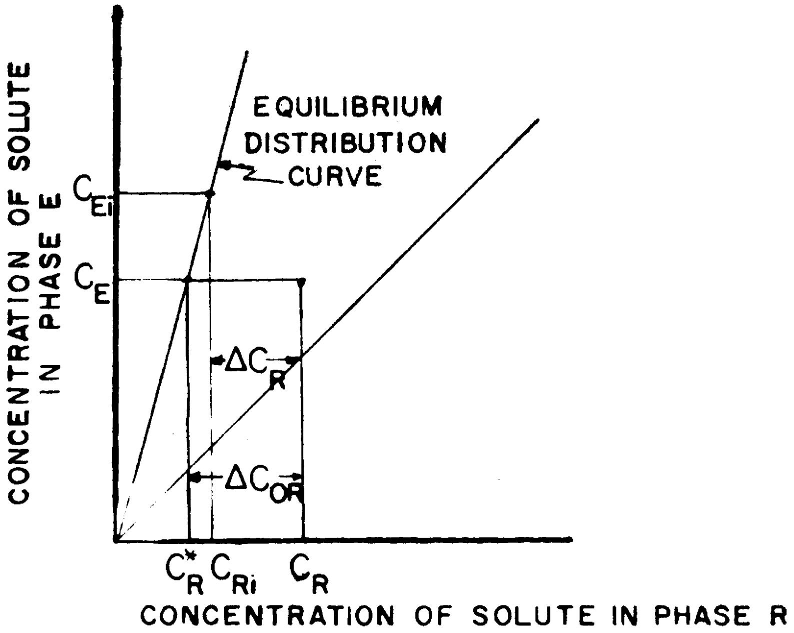


FIGURE 3a. PRINCIPAL DIFFUSIONAL RESISTANCE IN PHASE R

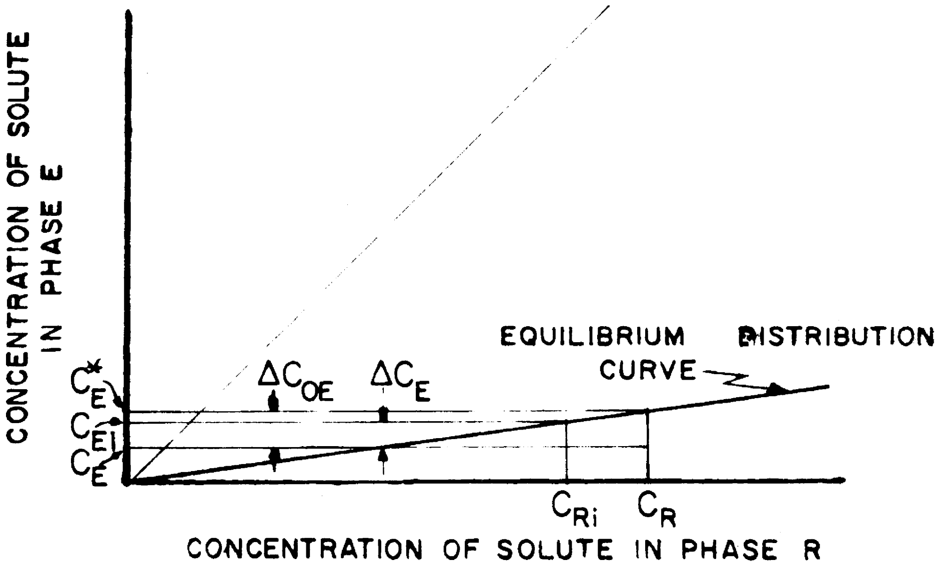


FIGURE 3b. PRINCIPAL DIFFUSIONAL RESISTANCE IN PHASE E

TREYBAL, R.E.: "LIQUID EXTRACTION," P. 121. MCGRAW-HILL BOOK CO., NEW YORK, N.Y., 1951. 1 ED.

(m) is very small and the distributed substance favors the (R) phase, (K_E) nearly equals (k_E), and the resistance in the (E) phase controls. Figure 3b, page 53, illustrates this situation.

In continuously operating extraction processes, each phase is subjected to changes in solute concentration as it flows through the equipment. The "point" conditions considered in the development of the previous equations represent only one position in the equipment. The rate equations, therefore, represent instantaneous conditions, and in applying them to actual operations, must be integrated over the concentration range which may exist in the liquids(87). In addition to the listed assumptions for the two-film theory, it is clear also that if the simple distribution law does not hold over the concentration ranges employed, (K_E) and (K_R) will vary widely with concentration, even if (k_E) and (k_R) do not change appreciably(87). Since factors affecting (k_E) and (k_R) are also likely to vary, the use of overall coefficients is definitely limited. Nevertheless, Treybal(90) says these equations are used under all conditions for lack of anything better.

The integration and extension of Equation 16, page 51, for the general case have been shown in detail by others(91), and will not be considered here. The final result, for an entire column, takes the form

$$N = KaSH\Delta C_{lm} = KA\Delta C_{lm} \qquad (20)$$

where:

N = rate of mass transfer, lb mol/hr

K = overall coefficient of mass transfer, lb mol/hr-sq ft-ΔC

a = constant area per unit tower volume, sq ft/cu ft

S = tower cross sectional area, sq ft

H = effective tower height, ft

A = total contact area, sq ft

ΔC_{lm} = log mean driving force, lb mol/cu ft.

<u>Transient Film Theory of Mass Transfer</u>. Higbie(48) has postulated, in an attempt to explain mass transfer phenomena in gas absorption, a transient film theory, built around the assumption

that as liquid flows across each piece of packing in a tower, it is partially or wholly mixed at the surface. Absorption of gas takes place only during a brief series of contacts between liquid and gas in which dissolved gas diffuses only a short distance into the liquid before the liquid is again mixed(102). If, then, (C_1) is defined as the concentration(102) of the interfacial liquid, the boundary conditions at the interface, where (t) is time, and (x) the distance into the liquid bulk measured perpendicular to the interface, are

$$\text{at} \quad x = 0, \quad t > 0, \quad C = C_1 \qquad (21)$$

Also, if (C_o) is the average concentration in the liquid, then at the instant just after mixing, at a finite distance from the interface,

$$t = 0, \quad x > 0, \quad C = C_o \qquad (22)$$

Finally, since the concentration undergoes no change at a distance infinitely far from the interface, even in a finite time,

$$x = \infty, \quad t \gg 0, \quad C = C_o \qquad (23)$$

Substituting these boundary conditions into the appropriate equations(102), and integrating, the total amount absorbed per unit area in each absorption period of time (t_e) is

$$2(C_i - C_o)\sqrt{Dt_e/\pi} \tag{24}$$

where:

C_i = interfacial concentration, mol/liter

C_o = average bulk concentration at start of absorption period, mol/liter

D = diffusion coefficient of solute in liquid, sq cm/sec

π = constant

t_e = time of exposure of liquid to gas, sec.

This equation is also equal to

$$k_L(C_i - C_o)t_e \tag{25}$$

where:

k_L = liquid side film coefficient of absorption, cm/min

from whence, the final equation is

$$k_L = 2\sqrt{D/\pi t_e} \tag{26}$$

In order to use Equation 26, page 57, the exposure time, (t_e), must be evaluated. Since this is the time during which an element of surface of liquid is exposed to the gas(102), it may be calculated from the interfacial velocity of the liquid and the length of column. If interfacial velocity, (v_i), is assumed uniform(102), then

$$t_e = h/v_i \tag{27}$$

where (h) is the height of the column in feet. Combining Equations 26 and 27, the final form is obtained:

$$k_L = 2 \sqrt{Dv_i/\pi h} \tag{28}$$

Here, (v_i) is some function of the liquid velocity.

<u>Surface Renewal Theory</u>. Recently, Danckwerts(14) proposed a surface renewal theory that was, in principle, similar to that of Higbie. His assumption was that the surface of contact was continuously being replaced with fresh liquid from the bulk of the solution. In other words, eddy diffusion was the controlling and only important contribution to mass

transfer(52). Accordingly, a new term, called "surface renewal rate", was proposed. Based on this postulate, the mass transfer equation takes the form(52)

$$N = \sqrt{D_s}\ (C_i - C)A \tag{29}$$

Now, since the rate of transfer through a single phase resistance is given by

$$N = k(C_i - C)A \tag{30}$$

then,

$$k = \sqrt{D_s} \tag{31}$$

where:

N = rate of mass transfer, gm/sec

D = solute diffusivity, sq cm/sec

s = fractional rate of surface renewal, sec^{-1}

C_i = interfacial concentration, gm/liter

C = concentration of bulk solution, gm/liter

A = interfacial area, sq cm.

Correlation of Mass Transfer Coefficients with Physical Variables

Considerable effort has been expended by a number of investigators in attempting to predict mass transfer coefficients, or their equivalent design expressions, height of a transfer unit and height equivalent to a theoretical stage, from empirically determined equations. Usually, these equations are correlated as a function of the physical and operational variables of the extraction system. The bulk of the data has been determined on spray or packed towers(25,26,27,28,31,32,73,74,76,84) and has been reported in terms of capacity coefficients and/or transfer units where contact area is unknown. Usually, the variables investigated have included temperature, viscosity, density, diffusivity, and interfacial tension, with the correlation taking the usual form of a product of various dimensionless arrangements of the variables.

Curiously conflicting results(94) have been obtained by various investigators working with wetted wall towers and studying transfer rates in ternary systems. These discrepancies have not been resolved fully. However, the correlations reported(12,19,67,101) are useful, since they are among the first to be obtained while an effort was made to control and measure interfacial area. This eliminated an unknown variable from the prediction equation.

Ideally, the most desirable correlations would involve the more fundamental individual film resistances, since these are far more sensitive to changes in fluid properties of the system than are the overall coefficients. The latter can always be calculated provided the film coefficients can be first determined. Only relatively little information is available(57) on the attempts to correlate film coefficients with physical variables, because of the limitations imposed on investigations of this type. The most severe restriction is that of having to work with only binary systems, and measuring the approach to saturation of the two phases during the extraction process. Attempts(58) have been made to predict ternary film coefficients using binary system correlations, but have been unsuccessful(95).

Some work has been done(6,57,80) using a horizontal tube extractor in an attempt to predict film coefficients from physical variables, but again the work was restricted to the use of binary systems in the absence of a diffusing solute. Although, as has been mentioned, the overall coefficients are less sensitive to physical variables than the individual film coefficients, a correlation of this nature might prove useful in ultimately aiding to explain mass transfer phenomena.

Effect of Interfacial Tension on Rate of Mass Transfer

Several conflicting investigations have been reported in the literature describing various effects of lowering interfacial tension on mass transfer rates. For instance, it has been shown that lowered interfacial tension reduces the resistances to flow in plate extractors(93) and, in general, increases operating efficiency. On the other hand, seemingly anomalous results have been reported for the effect of interfacial tension on mass transfer rates(59,66,78,107).

Unfortunately, most of the experimental results on interfacial tension effects have been obtained using surface active agents(29,30,46,59) to bring about variations in the boundary tensions. The addition of these agents actually results in a four-component(89) system, instead of three, and often true effects of interfacial tension phenomena are masked by the blocking effect of these molecules orientating at the interface. No results have been reported for ternary extraction systems wherein the interfacial tension was lowered by varying from test to test the amounts of the solute present. Johnston(53) found that a very small amount of surface active agent decreased the extraction of acetic acid from isopropyl ether droplets to approximately one-third of the value before addition. Chu et al(10) found that the extraction rates in a packed column increased linearly with a decrease in interfacial tension brought about by addition of a surface active agent, but the effect was ascribed to the increased area resulting from the decreased interfacial tension. With increasing concentration of a comparatively weak surface active agent, the extraction rates exhibited a maximum. From this they concluded that up to a maximum concentration, the net effect was an increase in transfer rate owing to the decreased area of the liquid droplets. At this maximum concentration, however, the diffusing resistance offered by the orientated molecules at the interface overbalanced the decreased area effects, and the transfer rate decreased. Farmer(21) also increased extraction by adding surface active agents to acetic acid-carbon tetrachloride-water system, but observed no maximum or minimum in the relationship. Gordon and Sherwood(38) performed tests on a stirred tank extractor, removing butyric acid from aqueous solutions with benzene. With the addition of small amounts of surface active agents, which gave approximately a five fold lowering of the interfacial tension, no change in extraction rates whatever were observed. Lewis(58), in a similar investigation employing a stirred tank extractor, also noted no change in extraction rates for the systems water-furfural and water-ethyl acetate upon the addition of small amounts of surface active agents. Since the interfacial tensions were reduced to very low values, Lewis concluded that this was further evidence of the non-dependence of transfer rates on interfacial tension.

Holm and Terjesen(50) observed the effect of the addition of surface active agents on rates of extraction of iodine from aqueous solution with carbon tetrachloride, and found that up to a certain concentration of agent, the extraction rate decreased, after which, as concentration increased, the rate increased far above the original value with no agent present. They concluded that the increased area of liquid droplets accounted for the increasing rates.

Because of the conflicts in these and other data, and the still rather insufficient data available on studies of this type, no definitive conclusions with regard to the nature of this effect can be drawn.

III. EXPERIMENTAL

The experimental section includes the purpose of the investigation, plan of investigation, materials and apparatus, methods of procedure, data and results, and a sample of the calculations used.

Purpose of Investigation

It was the purpose of this investigation to ascertain the qualitative nature of the interfacial tension equilibrium characteristics of the systems hexane-acetone-water and toluene-acetone-water by studying the effect of drop velocity on drop weight through use of the modified drop weight procedure, and comparing these results with those obtained from systems known to have time dependent interfacial tension relationships; to then evaluate the effect of interfacial tension on the rate of mass transfer by obtaining extraction data for the above systems in a horizontal, countercurrent, liquid-liquid extraction tube for a series of interfacial tension values achieved through variation of the total concentration of acetone in the system; and finally, to attempt to obtain an equation correlating the overall mass transfer coefficient based on the solvent film with the physical and operational variables of the systems and extractor.

Plan of Investigation

The investigation was carried out using the following general plan.

Literature Review. A survey of recent literature was made to obtain information on procedures and results of other investigators studying interfacial tension equilibria. Special consideration was given to the experimental methods used in these investigations in an effort to find a simple, inexpensive, yet accurate apparatus for qualitative studies on the variation of interfacial tension with time. Careful attention was given to the theories underlying each method in exploring the possibility of extending and simplifying one of the accepted methods of interfacial tension determination. In particular, emphasis was placed on finding and utilizing a method for dynamic interfacial tension studies that was theoretically sound, and yet simple and accurate.

Also, a search of the literature was made to review the usefulness, limitations, and assumptions characterizing the two-film theory of mass transfer. Various theories explaining the mechanism of mass transfer across a liquid-liquid interface were compared, with special attention being given to the effect of physical variables on the rate of mass transfer. Methods for correlating extraction data with physical and operational variables of the systems and extractor assembly were reviewed. Consideration was given to several investigations concerned with measurement and interpretation of interfacial resistances.

Apparatus Employed. After selecting the drop weight method for interfacial tension equilibrium studies, effort were directed at securing a suitable, drop weight apparatus. Various precision stalagmometers were tried, but proved unsuccessful. So, a satisfactory dropping tip was constructed which had the advantages of optimum tip diameter and adequate liquid capacity.

The horizontal tube extractor used for the extraction tests was essentially the same assembly as that used by Lastovica(57), with only slight modifications made for improvement of operational characteristics.

Selection of Liquid Systems. The two systems chosen from the literature to use in studying mass transfer rates were hexane-acetone-water(100), and toluene-acetone-water(51,68).

The interfacial tension equilibrium characteristics of the two systems were determined by modification of the drop weight method. Since this modification resulted in semi-qualitative results, it was desirable to compare the interfacial tension-time effects of a system known to have a definite time dependency on interfacial tension with the results obtained from the systems used in this investigation. The systems cyclohexane-arabic acid-water and benzene-arabic acid-water were selected as being representation of the time-dependent systems reported in the literature.

Equilibrium and Physical Property Data. Equilibrium and distribution data for the ternary systems were obtained from the literature. Refractive indexes of the conjugate phases of the two systems were measured as a function of acetone concentration at 25 and 30 °C. In addition, densities and viscosities of the saturated phases were determined for both systems at 27 °C.

Dynamic Interfacial Tension Studies. To ascertain whether or not attainment of interfacial tension equilibrium for the systems studied in this investigation required time, tests were made using the systems toluene-water, cyclohexane-water, and benzene-water with acetone and arabic acid as solutes in each system. The apparatus used permitted determination of the variation of drop weight with different rates of drop formation.

Three Component Extraction Tests. In an effort to extend correlation equations for predicting transfer coefficients from physical properties of the systems involved and to determine the effect of interfacial tension on the rate of mass transfer, 56 tests were made in the horizontal tube extractor using the systems toluene-acetone-water, and hexane-acetone-water.

Treatment of Data. Overall mass transfer coefficients were calculated from the data obtained on the two ternary systems. Plots to show the variation of transfer coefficients with phase flow rates were prepared to show the significance of flow conditions on extraction variables. Also, the variation of transfer coefficients with interfacial tension were shown graphically. An equation, derived from dimensional analysis, relating the overall mass transfer coefficient based on the solvent film with physical properties of the systems, was fitted to the data from the extraction tests, and the exponents evaluated by the method of least squares. The equation was then statistically evaluated to determine whether or not the variables included in the equation satisfactorily accounted for the variations in the overall transfer coefficient.

Materials

The materials used in the extraction tests and drop weight studies are presented in this section.

Acetone. Reagent grade, code No 1004, lot No K110. Obtained from General Chemicals Division, Allied Chemical and Dye Corp., New York, N. Y. Used as solute in extraction tests, and in drop weight studies.

Acid, Arabic. Gum arabic, USP, white powder, lot No 760246, catalog No G-85. Manufactured by Fisher Scientific Co., Silver Spring, Md. Used as solute in drop weight studies.

Benzene. Purified, 99-100 per cent quality, code No 1444, lot No H086. Manufactured and distributed by General Chemicals Division, Allied Chemical and Dye Corp., New York, N. Y. Used as solvent in drop weight studies.

Cyclohexane. Practical grade, boiling point 79-81 °C at 760 mm Hg. Manufactured by Distillation Products Industries, Rochester 3, N. Y. Used as solvent in drop weight studies.

Hexane. Commercial grade, from petroleum; boiling range maximum, 1.8 °C. Obtained from

Hercules Powder Co., Radford Ordnance Works, Radford, Va. Used as solvent in extraction tests.

Sodium Chloride. Granular, USP, lot No 43213. Manufactured by Merck and Co., Inc., Rahway, N. J. Used as standardization solution in refractometer calibration.

Toluene. ACS, reagent grade, "Baker Analyzed", lot No 1-110. Obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. Used as solvent in extraction tests.

Water. V. P. I. tap water was used in all experimental extraction tests without further treatment. Used as carrier solvent in extraction tests.

TABLE II

Physical Properties of Solvents Used in Drop Weight Studies and Extraction Tests

Material	Normal Boiling Point		Specific Gravity		Refractive Index	
	Experimental, °C	Literature, °C	Experimental, d_{27}^{27}	Literature, d_4^t	Experimental, n_d^{25}	Literature, n_d^{25}
Acetone	56.0-56.4	56.3 (e)	0.7824	0.7844 d_4^{25} (d)	1.3563	1.3555 (b)
Benzene	80-82	80.1 (f)	0.8706	0.8788 d_4^{20} (d)	----	----
Cyclohexane	78-81	80.7 (g)	0.7705	0.7790 d_4^{20} (d)	----	----
Hexane (a)	67.7-69.3	68.3-69.0	0.6771	0.6550-0.6574 d_4^{25}	1.3824	1.3779-1.3840
Toluene	110-111	110.3 (h)	0.8601	0.8658 d_4^{20} (d)	1.4943	1.4955 (c)

(a) Egloff, Guston: "Physical Constants of Hydrocarbons," p. 36. Reinhold Publishing Corp., New York, N. Y., 1939.

(b) Lange, N. A.: "Handbook of Chemistry," p. 1307. Handbook Publishers, Inc., Sandusky, Ohio, 1952. 8 ed.

(c) ibid, p. 388.

(d) International Critical Tables, Vol III, p. 33. McGraw-Hill Book Co., Inc., New York, N. Y., 1928.

(e) ibid, p. 218.

(f) ibid, p. 221.

(g) ibid, p. 222.

(h) ibid, p. 223.

Apparatus

The extraction apparatus and all analytical equipment used in this investigation are presented in this section.

Balance, Analytical. Capacity, 100 grams, complete with weights; beam graduated in tenths of a gram, chair pulley graduated in hundredths of a gram, with vernier reading to ten-thousandths of a gram. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in making up two phase samples for physical property and refractive index determinations, and for weighing samples in drop weight studies.

Balance, Beam. Triple beam type construction; capacity, 610 grams; sensitivity, 0.05 gram; catalog No 3-3423. Obtained from Phipps and Bird, Inc., Richmond, Va. Used for determining the weight rate of flow of extractor streams.

Bath, Constant Temperature. Fisher Unitized, cooled as required by tap water circulating through a 5-ft coil of 1/4-inch copper tubing. Catalog No 15-445. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to maintain samples at 27 °C for viscosity and density determinations.

Bath, Constant Temperature. Metal construction, equipped with frosted glass plate in bottom and adjustable metal reflector to direct light up through samples. Two metal shelves are provided to support the sampling beakers, each shelf capacity, six beakers. The bath is also provided with a rack for supporting the refractometer, and inlet and outlet base connections for water circulation. Catalog No 13-971. Manufactured by Bausch and Lomb; obtained from Fisher Scientific Co., Silver Spring, Md. Used to maintain extractor samples at 30 °C for analysis with refractometer.

Bottles, Sample. Capsule type, screw cap containing vinyl chloride liner; 30-ml capacity. Obtained from Wilkens-Anderson Co., Chicago, Ill. Used as sample receivers for extraction tests.

Bottles, Weighing. Metric shelf bottles, narrow mouth, 60-ml capacity, reagent glass construction. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as sample bottles in drop weight studies.

Drop Weight Apparatus. A picture of the drop weight assembly is shown in Figure 4. The dropping tip was constructed on the stem of a 125-ml

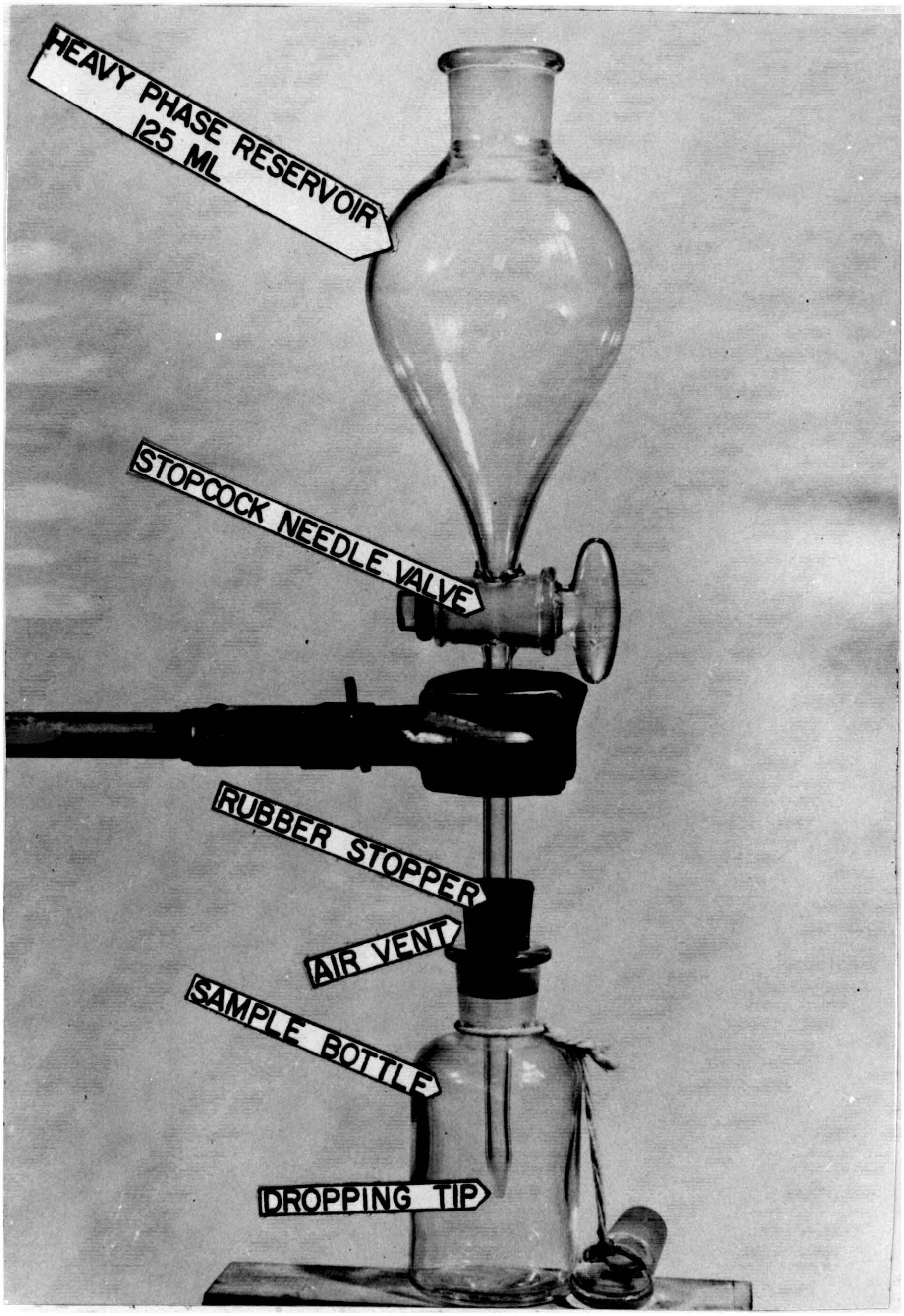
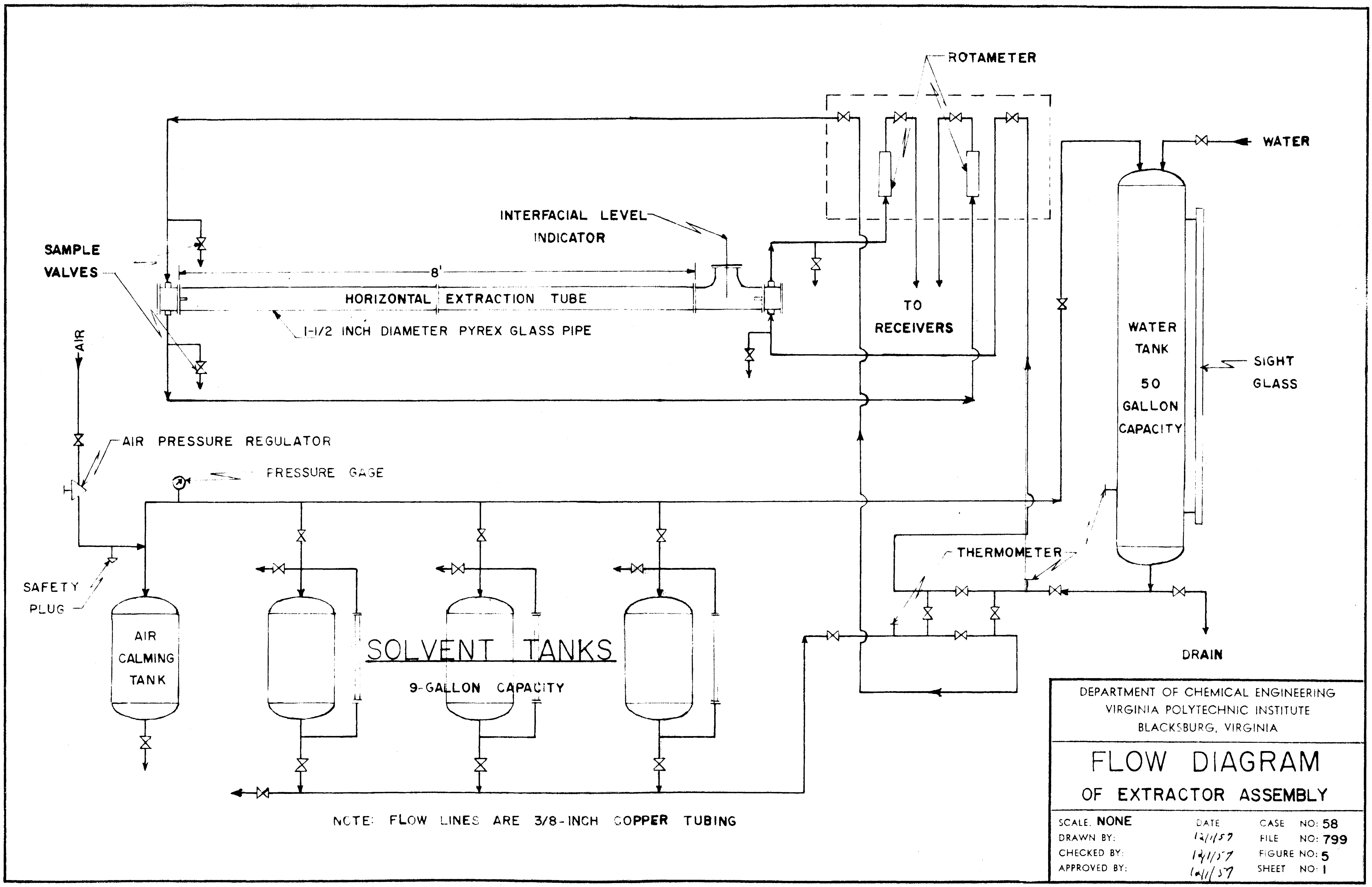


Figure 4. Modified Drop Weight Apparatus

separatory funnel. The component parts of the assembly include a size 00 rubber stopper used to minimize evaporation losses; a size 4 rubber stopper used as a cushion between clamp and funnel; sample bottle for liquids; and wooden support.

Extractor, Horizontal Tube. The extractor used in this investigation is shown in the flow sheet of the extractor assembly, Figure 5. A picture of the overall assembly is shown in Figure 6. Minor modifications to the extractor and accessories include: installation of 1/4-inch stainless steel needle valves for more accurate flow rate and interfacial level control; use of 1-1/2 inch diameter copper end boxes, with removable flanges, to facilitate and allow cleaning of the extractor after each test; and equipment and supports for eventual incorporation of automatic interfacial level control. A detailed description of materials of construction for the extractor and extractor support and their source is given by Lastovica(57).

Funnel, Separatory. Globe-shaped, Kimble brand resistance glass, 125-ml capacity, with standard taper stopper and stopcock; catalog No 10-420. Obtained



NOTE: FLOW LINES ARE 3/8-INCH COPPER TUBING

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

FLOW DIAGRAM
OF EXTRACTOR ASSEMBLY

SCALE. NONE	DATE	CASE NO: 58
DRAWN BY:	12/1/57	FILE NO: 799
CHECKED BY:	12/1/57	FIGURE NO: 5
APPROVED BY:	12/1/57	SHEET NO: 1

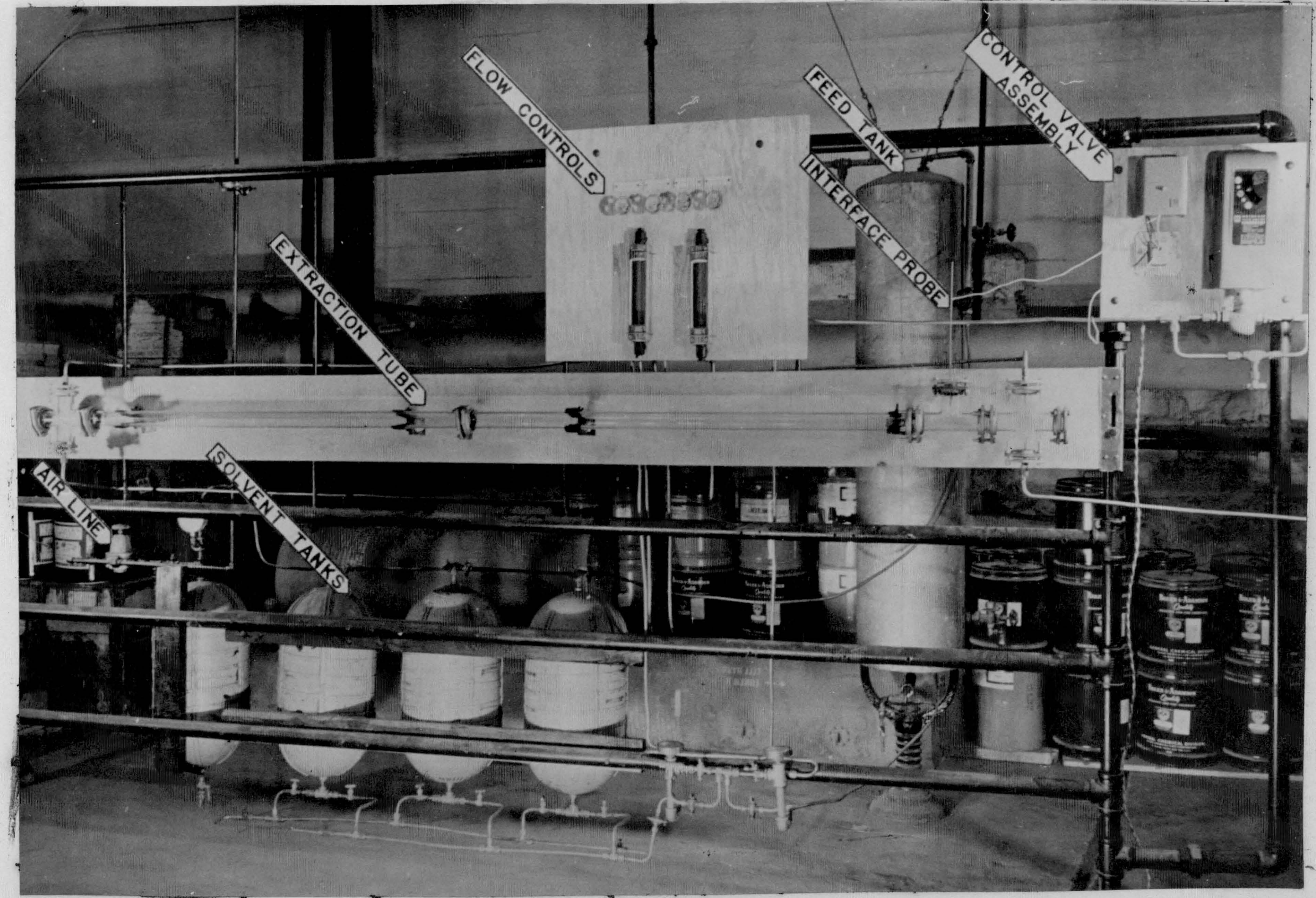


Figure 6. Over-all View of Horizontal Extractor and Accessories

from Fisher Scientific Co., Silver Spring, Md. Used to construct apparatus with dropping tip for drop weight studies.

Glassware, Miscellaneous. Various sized pipets, beakers, flasks, burets, and other general laboratory glassware. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in preparation of test samples, transferring liquids, cleaning purposes, etc.

Lamp, Sodium Vapor. Adjustable, self contained unit including housing and support base. At full power, lamp supplies 650 lumens of monochromatic light, largely concentrated in the 5889-5895 Angstrom wave length band; catalog No 11-985. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as light source for analysis of extractor samples by refractive index.

Motor, Modutrol. Type M6046, electric valve actuator motor; floating control valve type, motor No M604C54084, 24 v, 60 cy, ac, 114 watts. Obtained from Minneapolis-Honeywell Regulator Co., Minneapolis, Minn. Used as driving mechanism for control valve.

Pycnometers. Unadjusted, for laboratory calibration; made of lamp blown glass with ground-in perforated glass stoppers hollowed at the base to allow escape of vapor bubbles; 12 used; 10-ml capacity each. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to determine specific gravity of test samples.

Refractometer, Dipping. Immersion type, Bausch and Lomb, improved model, focusable eyepiece, equidivision scale on dial, compensator prisms with scale for dispersion comparisons included with precision-ground prisms A, B, C, D, E, and F, covering refractive indexes from 1.32 to 1.51. Tables for each prism for converting scale readings to N^d refractive indexes; catalog No 13-966. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to determine refractive indexes of samples from extraction tests.

Relay, Transistor. Model 30 transistor relay, suitable for use with non-inductive load of 4 amp or less; sensitivity, 12 microamperes input, 115 v, 50-60 cy, ac, catalog No 13-991-75. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as intermediate step-up relay to actuate relay for control valve drive motor.

Relay. Low voltage, intermediate relay, catalog No R182B; relay No R182B1CGOA2. Obtained from Minneapolis-Honeywell Regulator Co., Minneapolis, Minn. Used as low voltage control on modutrol motor.

Solvent Purification Apparatus. The distillation apparatus, used for purification of test samples, consisted of a 3-neck, 5000-ml, round bottom, distillation flask; a 2-ft, unpacked, 27 mm OD glass tube, reflux column, fitted to the distillation flask with 29/42 standard taper joints; and a 7-bulb, allihn condenser. The distillation apparatus was clamped to a standard, laboratory apparatus support stand having a rectangular base. Heat was supplied to the distillation flask by an electrical heating mantle.

Stalagmometer Set, Traube. Set consists of three calibrated capillary tubes, the ends of which are flattened to give a large dropping surface, and are ground and polished. Each tube has an enlarged center reservoir, and 10 divisions are etched above and below the reservoir to facilitate drop volume determinations. Catalog No 5-944. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure surface and interfacial tensions in preliminary drop weight studies.

Still. Water, electrically heated, 750 watts, 230 v, ac. Obtained from war surplus. Manufacturer unknown. Used as a source of distilled water.

Tanks, Storage. Aluminum, 50-gal drop tanks, designed for use on model airplane SC-1, USN. Obtained from war surplus. Manufacturer unknown. Used for storing solvents and as collection tanks during extraction tests.

Thermometers, Precision. Without certificate, range from -1 to 101 °C, in 0.1 °C graduations, catalog No 15-040. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in controlling tamperature of constant temperature bath during physical property determinations.

Thermoregulator. Mercury type, adjustable, with sealed-in platinum electrodes and a guard. Sensitivity, ± 0.05 °C. Catalog No 15-445-35. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for controlling temperature in constant temperature bath during physical property determinations.

Timer. Kodak interval timer, spring-actuated, small hand from 0 to 60 minutes in 1-minute intervals; second hand from 0 to 60 seconds, in 1-second intervals; catalog No 6-658. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for determining flow rates of extractor streams, and for timing tests.

Timer, Electric. Precision, Time-it, direct reading from 0 to 9999.9 minutes, 0.1 second divisions, 115 v, 60 cy, ac, catalog No 69230. Obtained from Precision Scientific Co., Chicago, Ill. Used in viscosity determinations, and to time drop velocity in drop weight studies.

Valve, Control. Stainless steel, series 340 needle valves. Four 1/4-inch valves, v-point type, equipped with teflon packing below spindle threads. Manufactured by Hoke, Inc., Englewood, N. J.; obtained from Fisher Scientific Co., Silver Spring, Md. Used to control flow rates of terminal extractor streams.

Valve, Control. One-half inch, with 1/8-inch bushing, bronze construction, modified to give coefficient of discharge of 0.63. Obtained from Minneapolis-Honeywell Regulator Co., Minneapolis, Minn. Used in attempt to automatically control interfacial level in extractor.

Valve, Motorized Linkage. Type Q601D, No Q601D2x1. Especially adapted for use with 1/2-inch control valve. Obtained from Minneapolis-Honeywell Regulator Co., Minneapolis, Minn. Used to link modutrol motor to control valve stem.

Viscosimeter. Standard, Ostwald-Fenske, ASTM, uncalibrated, catalog No 13-695. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to determine viscosities of solvents.

Methods of Procedure

The methods of procedure followed in this investigation are presented in this section.

Preliminary Attempts to Make Dynamic Interfacial Tension Studies. With the discovery that some systems required a finite amount of time to establish interfacial tension equilibrium, several experimental methods were proposed to study this phenomenon. For the most part, the methods involved prohibitively expensive, custom made equipment, elaborate timing mechanisms, and the like.

The primary purpose in this investigation was not to measure such equilibrium time, but simply to learn whether or not the systems used in this investigation exhibited such behavior. In other words, what was desired was a quick and fairly simple test that would indicate if interfacial tension between the liquids in the systems under study was time dependent. No such method was available prior to this investigation.

In attempting to devise such a method, a study was made of the more common static methods for measuring interfacial and surface tensions, namely, the bubble point, pendant drop, capillary rise, ring tensiometer, and drop weight methods, to see if any of them could be adapted for use as a dynamic method. The drop weight method appeared to be the logical one to choose, as this method allowed the formation of a completely new surface with each drop, and also permitted the rate of formation of the drops to be varied. In their refinement of this method, Harkins and Brown(41) showed that the drop volume, and hence drop weight, was a function of the rate of flow of liquid into the drop at the instant of detachment of the drop. They gave no further consideration to this effect of drop rate, other than to recommend a rate of less than one drop in 2.5 minutes when using this method to determine interfacial and surface tensions.

Construction of Drop Weight Apparatus. After selecting the drop weight method for investigating interfacial tension equilibrium, an attempt was made to secure suitable drop weight pipets. A set of biological stalagmometers was ordered and tested, but were found to be unsuitable because the large diameters of the dropping tips did not allow significant variation in either drop velocity or drop weight. Also, insufficient pipet capacity indicated that a larger reservoir would be needed for the heavy phase liquid.

To overcome these two problems, it was decided to construct a dropping tip from the stem of a 125-ml separatory funnel; thereby obtaining both the desired tip diameter, and the additional capacity. The tip was constructed in the following manner. The stem of a separatory funnel was heated approximately six inches from the stopcock, and then carefully drawn until the inside orifice of the funnel was reduced to a fine capillary. The heating process also produced a marked thickening of the stem walls at the heated area, while reducing the outside diameter of the stem. The lower half of the stem was broken off, and the remaining tip carefully hand ground and polished with emery paper and sharpening stone until smooth and symmetrical. Several attempts had to be made before a successful tip was formed, and the polishing and grinding required three days. Trial and error tests using toluene and water, and various tip diameters established the optimum diameter that allowed duplication of experimental results. The final tip had an outside diameter of 0.204 centimeter. The diameter of the capillary tube, although of no importance in the drop weight tests or results, was on the order of 0.027 centimeter.

Procedure for Drop Weight Studies. After securing a satisfactory dropping tip, various kinds of sample bottles were tried in an effort to determine what type of sample bottles to use for the drop weight experiments. The bottles containing the light phase liquid samples should be of a convenient size for weighing on an analytical balance, and should be so constructed as to allow minimum evaporation losses.

Seven tests were made with the dropping apparatus. A toluene-10 weight per cent acetone-water system was tested first and the results from this study compared with results obtained from testing the systems benzene-1.025 weight per cent arabic acid-water, and cyclohexane-2.785 weight per cent arabic acid-water. In addition, results were reported for the systems toluene-2.785 weight per cent arabic acid-water, benzene-2 weight per cent acetone-water, cyclohexane-2 weight per cent acetone-water, and cyclohexane-10 weight per cent acetone-water.

A ternary mixture for each test was made up gravimetrically. All components were weighed into the same bottle, the bottle was capped, shaken vigorously, and placed in a constant temperature bath at 27 °C for 24 hours. Forty milliliters of the light phase were pipetted into each of twenty 60-milliliter, narrow-mouth sample bottles, the bottles capped and weighed on an analytical balance. The separatory funnel was filled with approximately 80 milliliters of the heavy phase to a mark etched on the funnel reservoir. As the test progressed, additional liquid was added to the funnel from time to time, to maintain the constant level in the reservoir at ± 0.1 centimeter. The stem of the funnel was filled also, to maintain an unbroken column of liquid between the funnel reservoir and the dropping tip.

Each of the sample bottles was then placed in turn under the dropping tip, and the height adjusted until the tip was approximately one centimeter below the surface of the light phase. The funnel stopcock was opened slightly, and the drops counted and timed to the nearest one-tenth of a second from the detachment of the first drop. Variation in drop velocity was controlled by stopcock opening.

Velocities ranged from approximately one drop per minute to the maximum velocity at which kinetic energy and momentum effects caused streaming of the liquid from the dropping tip.

Since there was no direct way to measure drop velocity during a test, the velocity changes from one test to the next had to be approximated by guess. It was found that satisfactory variation in velocities could be obtained easier if the drop velocities were increased successively over the desired range.

After a sufficient number of drops had detached from the tip--20 to 30 in the case of high interfacial tension samples; 50 to 70 in the case of low--the stopcock was closed, the sample bottles recapped and weighed. Drop velocity was calculated from the elapsed time and number of drops; drop weight from the weight and number of drops.

Correlation of Drop Weight Results. Drop weight results were correlated by means of Equation 36, page 180, the derivation of which is given in the discussion. Seven experiments were made to test the validity of this equation. Three systems were tested with arabic acid as the solute; cyclohexane-water, benzene-water, and toluene-water, the first two having been previously cited in the literature as having interfacial tensions dependent on time. The results from these tests were then compared with results obtained using the same respective pairs of immiscible liquids with acetone as the solute.

Viscosity Determinations. Viscosity as a function of acetone concentration was determined for the conjugate phases for the systems toluene-acetone-water, and hexane-acetone-water using an ostwald viscosimeter. Twelve samples were made up for both systems on an analytical balance, covering a range of compositions from zero per cent acetone to almost that at the plait point, agitated thoroughly, and allowed to stand 24 hours. The two phases of each sample were then separated into glass stoppered bottles, and placed in a constant temperature bath at 27 °C for two hours. Then, a portion of the sample was transferred to the viscosimeter, also immersed in the bath, and the time required for the flow between etched calibration marks on the instrument was measured with a stopwatch. Distilled water was used as a reference liquid to determine the orifice constant for the viscosimeter.

Efflux time for each sample was converted to viscosity by the equation:

$$\frac{\mu_1}{\mu_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \qquad (32)$$

where:

μ = viscosity, cp

ρ = density, gm/cc

t = efflux time, sec

1,2 = test sample and distilled water, respectively.

Specific Gravity Determinations. Ten-milliliter pycnometers, calibrated with distilled water at 27 °C, were used to measure specific gravities of the two ternary systems used in this investigation. Ten samples of each system covering a range from zero to almost plait point acetone compositions, were weighed on an analytical balance, mixed thoroughly, and allowed to stand for 24 hours. The two phases of each sample were then separated into sample bottles, and placed into a constant temperature bath, at 27 °C, with the tared pycnometers, for two hours. The samples were then transferred to the pycnometers, kept at 27 °C for an additional half hour, removed from the bath, dried, and weighed.

Refractive Index Calibration Curves. No data for refractive indexes as a function of acetone concentration were available from the literature for the system toluene-acetone-water, so these were obtained in the following manner: ten samples of acetone concentrations, varying from zero to 55.0 per cent, were weighed on an analytical balance, shaken vigorously, and allowed to stand 24 hours. The two phases of each sample were then separated into glass stoppered bottles, and placed in a constant temperature bath at 25 °C for two hours. The refractive index of each sample was then measured with a dipping refractometer, and large scale plots constructed from the data. Refractive indexes of known compositions of solutions for the system hexane-acetone-water at 25 °C were available from the literature, and are given in the data section of this dissertation.

After two extraction tests had been made, it was observed that the solvent samples tended to separate into two phases when cooled in the constant temperature bath from a room temperature of 28 to 30 °C to the

25 °C analysis temperature. Accordingly, new refractive index-acetone concentration curves were obtained for both systems at 30 °C employing the same procedure as outlined above.

Installation and Test of Interfacial Level Control. To overcome difficulties in interfacial level control experienced by previous investigators using the horizontal extraction tube, a reversible modutrol motorized valve with a 60-second delay from open to closed was installed on the inlet water feed line to the extractor. The valve was actuated by fluctuations in interfacial level transmitted to the control valve through an electrical make or break contact probe. When the probe was set at the desired interfacial level, contact between it and the conducting water phase completed an electrical circuit, causing the valve to close. When, on the other hand, contact between the probe and water phase was broken, the floating valve mechanism reversed, and the valve opened. The 60-second floating delay, theoretically, would allow ultimate stabilization of the interfacial level, with only slight cycling about the control point.

Several tests were made to evaluate the control valve, and recommendations for improvement of the control system were outlined.

Operation of the Horizontal Tube Extractor. The ternary systems toluene-acetone-water, and hexane-acetone-water were used in this investigation to test the effect of interfacial tension on mass transfer rates, expressed in terms of overall mass transfer coefficients in keeping with the philosophy of the two film theory of mass transfer. Both systems were chosen because of the wide ranges of interfacial tensions that could be obtained by varying the acetone concentration. In the toluene system, the interfacial tension may be varied from 27.2 to zero dynes per centimeter, and in the hexane system, from 50.2 to zero dynes per centimeter, by increasing the acetone concentration from zero per cent to that corresponding to the concentration at the plait point for the respective systems.

The procedures followed in operating the horizontal tube extractor (Figure 5, page 79) closely paralleled those recommended by Lastovica(57). Except for a few minor changes in the location and type of control valves, end box construction, and tubing arrangements, the extractor assembly remained essentially unchanged. The most important change worthy of mention was in the sampling procedure.

Instead of waiting for equilibrium conditions to be established, that is, six changes of the slowest moving phase, before taking samples of the terminal extractor streams, a sampling procedure was so arranged that four samples of the extract and raffinate phases were taken at equal intervals over the final one-third of the time required to reach steady-state conditions. Also, two samples were taken of each of the feed streams; one half way through the steady-state period, and one at the end. The length of the steady-state period depended, of course, on the flow rate of the slowest moving phase. This procedure was found to be advantageous not only because it provided a check on steady-state conditions, but also minimized errors that may have been introduced by taking only a single sample at the end of the steady-state period. The samples were all taken from sample taps installed in the flow lines adjacent to the extractor. After steady-state conditions were reached, the exact flow rate of each phase was determined by collecting and weighing the outlet streams for a given time interval.

In all, a total of 21 separate tests were made using the horizontal extractor; 14 on the system toluene-acetone-water, and 7 on the system hexane-acetone-water. For the first system, concentration ranges of zero to 20 weight per cent acetone in toluene and 5 to 35 weight per cent acetone in water were used. Flow rates ranged from 1,000 to 10,000 pounds per hour per square foot for each phase. For the hexane-acetone-water system, acetone concentration in the hexane phase ranged from zero to 2 weight per cent and in the water phase from 15 to 45 weight per cent. Flow rates for the latter system were also varied between 1,000 and 10,000 pounds per hour per square foot. An attempt was made to vary the direction of acetone transfer, with success only in the direction water to solvent. An average of four velocity combinations, varying both stream flow rates, were attained with each test, making a total of approximately 85 separate runs on the extractor.

Transfer Under Static Conditions. To show that transfer of material from solvent to water would take place if sufficient time of contact were allowed, six samples, three containing 10 and three containing 30 weight per cent acetone in toluene, were placed in contact with pure water in separatory funnels. The samples were allowed to stand undisturbed for 24, 48, and 72 hours, respectively. At the end of each assigned time period, one sample of each concentration was separated into the toluene and water layers, and analyzed for acetone concentration.

Measurement of Solute Concentration. The concentration of acetone in the extractor streams was determined by measuring the refractive indexes of the samples taken during operation. A dipping refractometer, accurate to the fifth place of decimals, was used in making the measurements. Although distilled water was the basis for the refractive index calibration curves, it was found that the refractive index of tap water used in the extractor tests was not significantly different from that of distilled water, and the calibration curves thus developed could be used interchangeably.

In using the dipping refractometer to analyze extractor samples, it was noticed that an appreciable period of time was necessary for the refractive index of the samples once placed in the metal sample holder and attached to the refractometer to reach a constant value. The time interval was usually on the order of 8 to 10 minutes for the hydrocarbon phase, and 6 to 8 minutes for the water phase. The refractive index would drift as much as 0.00060 unit while the temperatures were reaching equilibrium.

Preliminary Attempt to Use Two Component Film Correlation Equation to Predict Overall Transfer Coefficients. An attempt was made to extend the equation developed by Lastovica(57) for two component extraction systems to predict overall mass transfer coefficients from physical and operational variables obtained from the ternary systems studied in this investigation. His more accurate solvent film equation(57) was modified slightly in the following manner: exponents on the viscosity, Reynolds number, and Schmidt number were assumed to be satisfactory and, using the data from this investigation, the equation was re-evaluated by the method of least squares to give a new constant of proportionality and a new exponent for the interfacial tension group. A statistical analysis of the resulting equation indicated very poor correlation. It was then decided to refit the exponents on all of the groups to see if better correlation could be obtained.

Preliminary Attempts to Correlate Overall Coefficients with Phase Flow Rates. An attempt was made in this investigation to check the results of Bergelin, Lockhart, and Brown(9), Skrzec(80), and Lastovica(57) on the relation between (K_s) and the flow properties, but no confirmation could be produced. Rectangular plots of (K_s) versus (G_w) showed no reproducible or sensible correlation, possibly because of the comparatively narrow range of water phase flow rates employed. As a comparison, however, a log-log plot was constructed showing the variation of (K_s) with (G_w), and was found to be more consistent than the previous plots. Plots were also attempted for (K_s) versus (G_s), and (K_w) versus both (G_s) and (G_w) but in these cases, correlation was considerably poorer than with the (K_s) - (G_w)

plot, and it was felt that nothing was added to the investigation by their inclusion.

Correlation of Overall Mass Transfer Coefficients with Physical Variables. Because of the present inability to determine interfacial concentrations in three component extraction systems, and thereby to calculate individual film coefficients, an attempt was made to correlate the gross, overall transfer coefficients with the physical properties of the systems. Although this correlation is not as desirable as one employing the more fundamental film coefficients, as previously discussed in the literature review, nevertheless, a prediction equation of any sort, however poor, is generally better than none at all.

The development used in this investigation was similar to the one originally employed by Skrzec(80), and later used also by Lastovica(57). The relationship between the overall transfer coefficient based on the solvent phase and the density, viscosity, diffusivity, interfacial tension, and the phase flow rates was evolved by means of dimensional analysis. The equation took the form of six dimensionless groups, and included five unknown exponents and an unknown constant factor of proportionality. Of the six groups, the one containing the transfer coefficient was the dependent variable. Data for a total of 75 extraction tests were used to calculate the unknown constants of the equation. Only one equation was developed, that based on the solvent film, since experience has shown(57) that it is much more accurate than the water film equation. For this solvent film basis, then, the equation took the final form:

$$\frac{K_s d}{D_s} = A_s\left(\frac{d\sigma}{\mu_s D_s}\right)^a \left(\frac{\mu_w}{\mu_s}\right)^b \left(\frac{\mu_s}{\rho_s D_s}\right)^c \left(\frac{dG_s}{\mu_s}\right)^e \left(\frac{dG_w}{\mu_w}\right)^f \qquad (33)$$

where:

K_s = overall mass transfer coefficient, lb/hr-sq ft-(lb/cu ft)

d = diameter of horizontal extraction tube, ft

D_s = diffusivity of solute in the solvent phase, sq ft/hr

σ = interfacial tension, lb/hr^2

μ_s, μ_w = viscosity of solvent and water phase, respectively, lb/ft-hr

G_s, G_w = mass velocity of solvent and water phase, respectively, lb/hr-sq ft

A_s = proportionality constant.

The procedure used to evaluate these unknown constants consisted of calculating values for all of the dimensionless groups for each of the 75 tests, setting these results up in specific forms by standard computational techniques(5,55), and then solving for the constants by use of the abbreviated Doolittle method for matrix inversion.

An analysis of variance test was made to determine the accuracy of the correlation for predicting values of the film coefficients. In addition, the multiple regression coefficient was calculated to see how well the dependent variable correlated with the independent variables included in the equation.

Data and Results

The data and results obtained during the course of this investigation are presented in this section.

Preliminary Attempts to Make Dynamic Interfacial Tension Studies. After consideration of various methods of determining the interfacial tensions, under conditions such that at the interface the molecules had no time for equilibrium orientation, the measurement of drop weight as a function of rate of drop formation was chosen as best suited to show the qualitative variation of interfacial tension with time.

Dynamic Interfacial Tension Studies. The data and results for the interfacial tension equilibrium studies are presented in Tables III, IV, and V. Benzene-water data, with acetone and arabic acid as solutes, are presented in Table III. Table IV contains the data for the systems cyclohexane-water with acetone and arabic acid as solutes; and the data for toluene-water, also with acetone and arabic acid as solutes, are given in Table V. The relationship between drop velocity and drop weight are shown graphically in Figures 7 to 13.

TABLE III

Drop Weight and Drop Velocity Data for the Systems Benzene-Acetone-Water and Benzene-Arabic Acid-Water

Test No	Number of Drops	Time, min	Drop Weight, gm	Drop Velocity, drop/min	Drop Velocity, (drop/min)^2
System Benzene-2 wt % Acetone-Water					
2	20	10.51	0.1098	1.81	3.27
4	20	7.86	0.1106	2.41	5.81
6	20	5.20	0.1087	3.66	13.37
7	20	6.98	0.1104	2.72	7.40
8	20	2.49	0.1097	7.65	58.46
9	20	3.07	0.1096	6.20	38.43
11	20	1.84	0.1040	10.33	106.63
12	20	1.14	0.0916	16.67	277.78
13	30	1.52	0.0881	19.12	365.59
14	35	2.82	0.1030	12.08	145.88
15	25	1.81	0.1006	13.30	176.79
16	20	2.92	0.1074	6.52	42.48
17	25	2.12	0.1017	11.34	128.56
18	20	1.20	0.0946	15.90	252.79
19	20	1.79	0.1031	10.60	112.25
21	20	2.34	0.1065	8.13	66.12
22	25	1.42	0.0998	14.09	198.58
System Benzene 1.025 wt % Arabic Acid-Water					
7	15	6.07	0.1596	2.31	5.33
8	16	3.38	0.1589	4.44	19.73
10	16	3.95	0.1572	3.80	14.43
11	16	3.25	0.1579	4.62	21.32
13	16	1.65	0.1483	9.10	82.81
14	16	1.29	0.1391	11.63	135.21
15	21	1.17	0.1268	16.22	262.97
16	16	1.14	0.1334	13.12	172.13
17	16	2.98	0.1528	7.59	57.59
18	15	6.22	0.1589	2.25	5.07
19	16	3.35	0.1574	4.48	20.07
20	15	4.69	0.1584	2.78	7.70
21	16	3.65	0.1593	4.11	16.86
22	15	8.07	0.1591	1.74	3.01

TABLE IV

Drop Weight and Drop Velocity Data for the Systems Cyclohexane-Acetone-Water and Cyclohexane-Arabic Acid-Water

Test No	Number of Drops	Time, min	Drop Weight, gm	Drop Velocity, drop/min	Drop Velocity, (drop/min)^2
System Cyclohexane-2 wt % Acetone-Water					
2	10	8.52	0.0778	1.06	1.12
8	20	2.84	0.0758	6.70	44.92
9	20	1.73	0.0746	10.96	120.20
10	20	2.59	0.0754	7.36	54.10
11	25	2.15	0.0745	11.15	124.41
12	25	1.23	0.0669	19.59	383.89
13	30	0.81	0.0501	34.71	1204.74
14	30	0.93	0.0518	30.05	903.22
15	30	1.35	0.0655	21.46	460.31
17	40	0.93	0.0504	37.84	1431.70
20	25	1.03	0.0626	23.26	541.18
21	25	1.54	0.0709	15.58	242.87
22	30	1.17	0.0606	24.86	617.84
System Cyclohexane-10 wt % Acetone-Water					
1	50	3.91	0.0370	12.27	150.45
3	25	12.86	0.0372	1.95	3.49
5	35	8.81	0.0373	3.86	14.89
6	35	8.57	0.0372	3.97	15.73
8	40	4.48	0.0373	8.71	75.78
10	50	1.90	0.0346	25.79	665.09
11	50	1.40	0.0319	35.08	1230.32
12	50	0.88	0.0250	55.10	3035.99
13	50	1.15	0.0305	39.30	1544.59
14	70	1.42	0.0281	45.78	2095.32
15	50	1.56	0.0334	31.48	990.79
16	50	2.56	0.0362	19.17	367.31
17	50	3.21	0.0369	14.96	223.83
19	50	4.20	0.0369	11.68	136.32
21	50	1.50	0.0327	32.04	1026.74
System Cyclohexane-2.785 wt % Arabic Acid-Water					
9	23	6.04	0.1017	3.64	13.25
10	20	3.85	0.1006	4.93	24.31
13	20	2.20	0.1031	8.63	74.48
14	20	2.32	0.1029	8.18	66.97
15	20	2.38	0.1027	7.98	63.64
16	20	0.87	0.0939	21.76	473.31
17	20	0.70	0.0883	27.34	747.37
18	23	0.57	0.0850	35.09	1231.15
19	42	1.17	0.0850	34.34	1178.88
20	20	1.09	0.0981	17.51	306.65
21	20	3.65	0.1023	5.20	27.07
22	20	3.53	0.1026	5.38	28.94

TABLE V

Drop Weight and Drop Velocity Data for the Systems Toluene-Arabic Acid-Water and Toluene-Acetone-Water

Test No	Number of Drops	Time, min	Drop Weight, gm	Drop Velocity, drop/min	Drop Velocity, $(\text{drop/min})^2$
System Toluene-2.785 wt % Arabic Acid-Water					
1	15	4.30	0.1208	3.26	10.60
6	18	4.91	0.1210	3.47	12.01
7	18	4.68	0.1212	3.65	13.34
8	18	4.56	0.1215	3.73	13.88
9	20	2.14	0.1216	8.89	78.95
11	20	1.32	0.1162	14.41	207.72
12	20	1.08	0.1110	17.65	311.42
14	25	0.90	0.0922	25.60	655.56
15	30	1.37	0.1085	18.27	333.82
16	25	0.91	0.0910	21.90	479.55
19	25	0.85	0.0953	23.67	560.20
20	25	1.82	0.1187	13.21	174.53
21	20	1.51	0.1196	12.57	157.98
System Toluene-10 wt % Acetone-Water					
3	40	3.58	0.0723	10.88	118.37
4	52	2.33	0.0609	21.43	459.25
5	50	3.00	0.0684	16.33	266.67
6	40	4.47	0.0744	9.64	92.93
7	20	8.90	0.0764	2.13	4.54
8	35	6.97	0.0772	4.88	23.81
9	40	4.28	0.0742	9.11	82.99
10	51	3.93	0.0714	12.71	161.54
11	61	3.92	0.0683	15.32	234.70
12	61	3.65	0.0658	16.44	270.27
13	61	3.33	0.0642	18.00	324.00
14	41	4.83	0.0752	8.28	68.56
15	41	5.23	0.0769	7.64	58.37
16	31	7.58	0.0762	3.96	15.69
17	21	9.13	0.0749	2.19	4.80
18	61	6.40	0.0739	9.38	87.98
19	65	3.32	0.0642	18.09	327.25

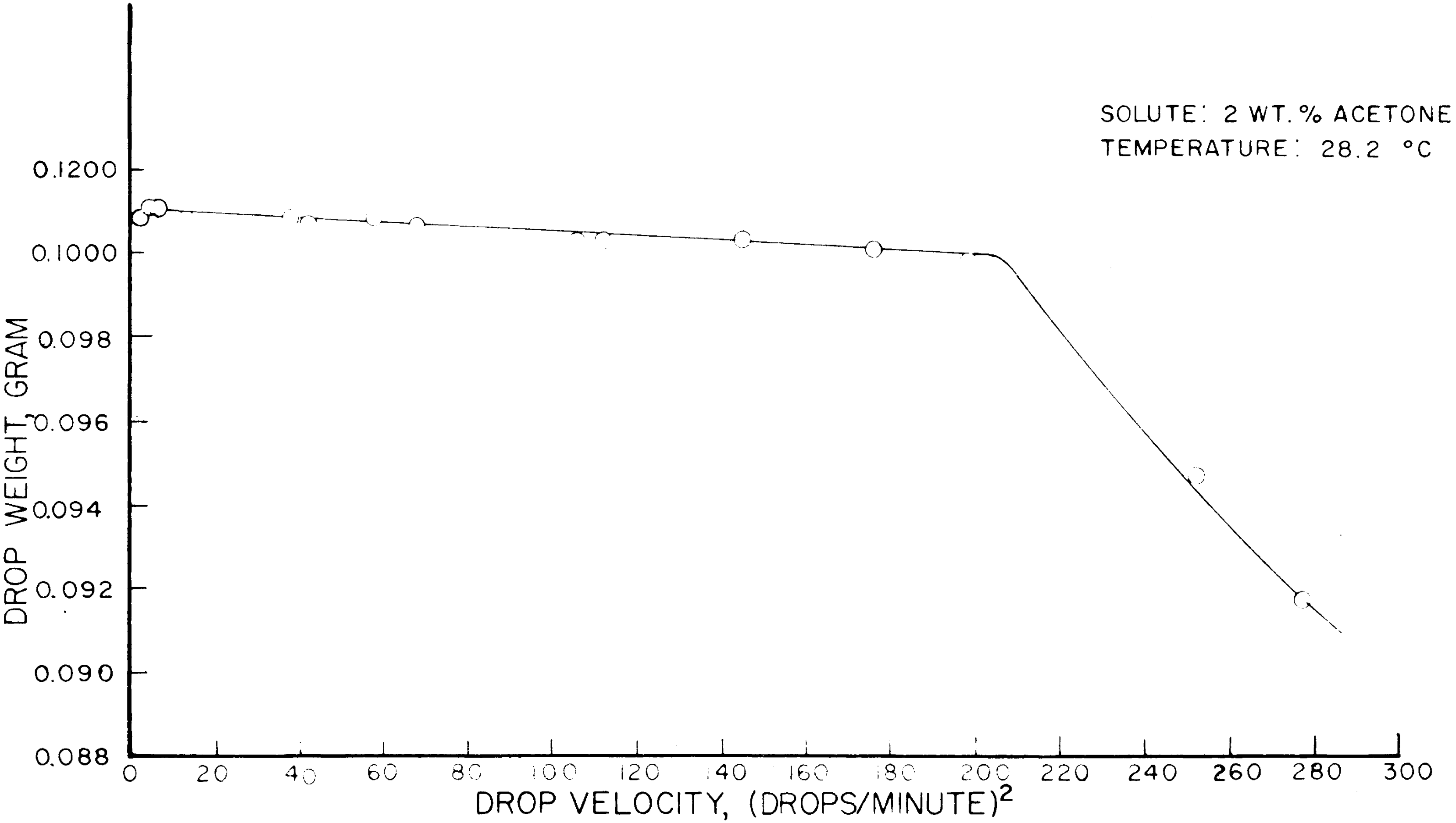


FIGURE 7. VARIATION OF DROP WEIGHT WITH DROP VELOCITY FOR THE SYSTEM BENZENE-ACETONE-WATER

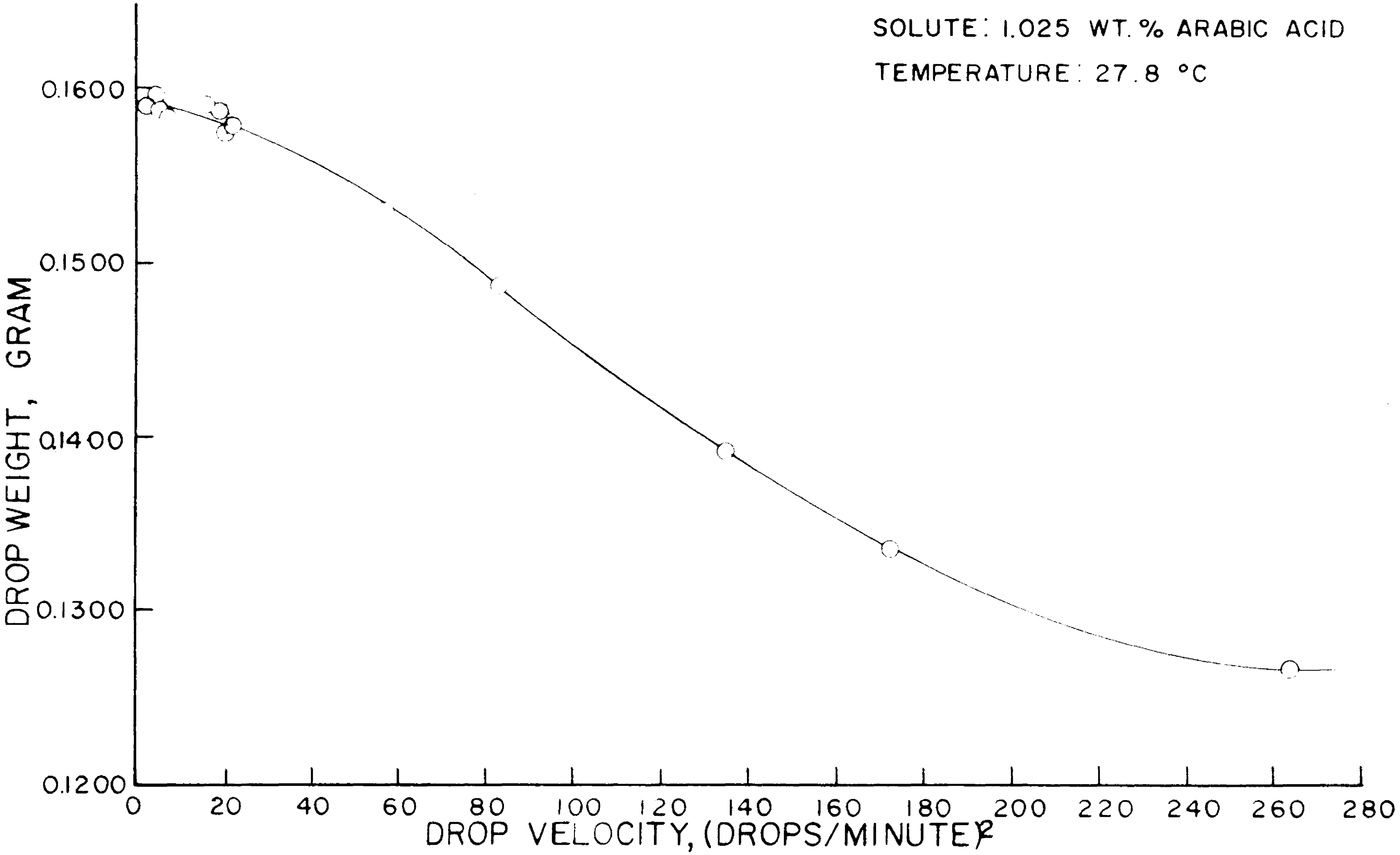


FIGURE 8. VARIATION OF DROP WEIGHT WITH DROP VELOCITY FOR THE SYSTEM BENZENE-ARABIC ACID-WATER

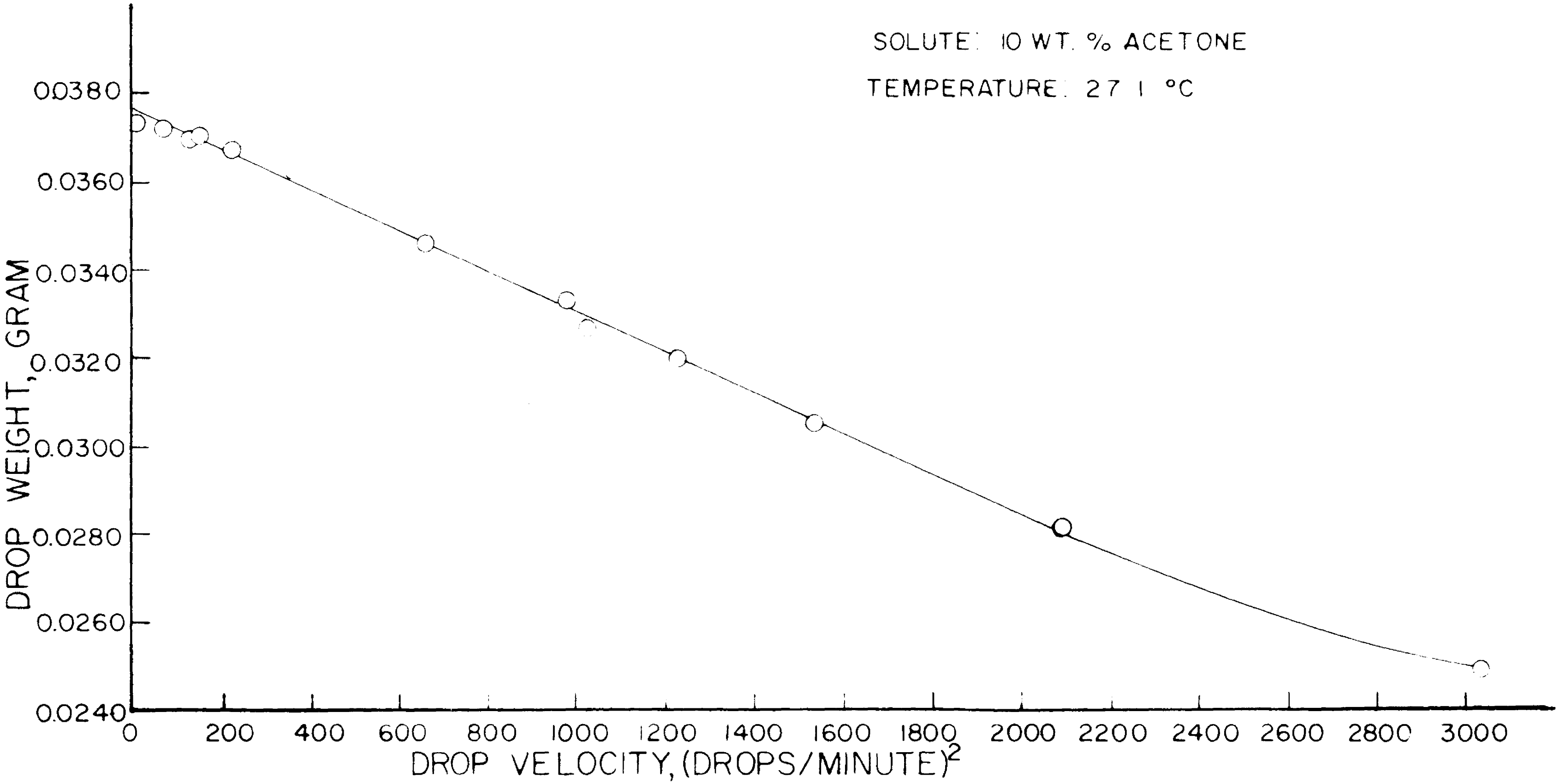


FIGURE 9. VARIATION OF DROP WEIGHT WITH DROP VELOCITY FOR THE SYSTEM CYCLOHEXANE-ACETONE-WATER

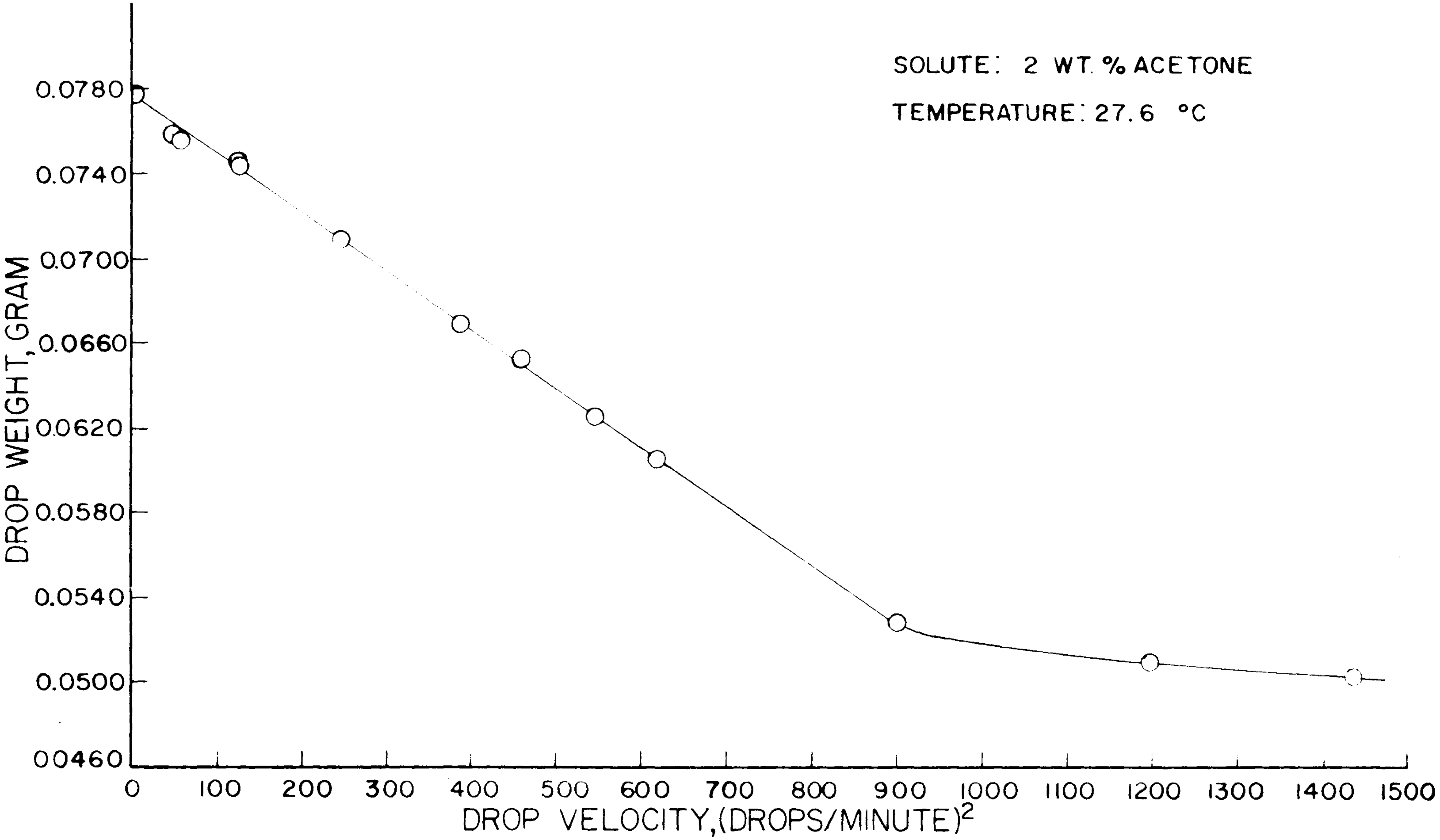
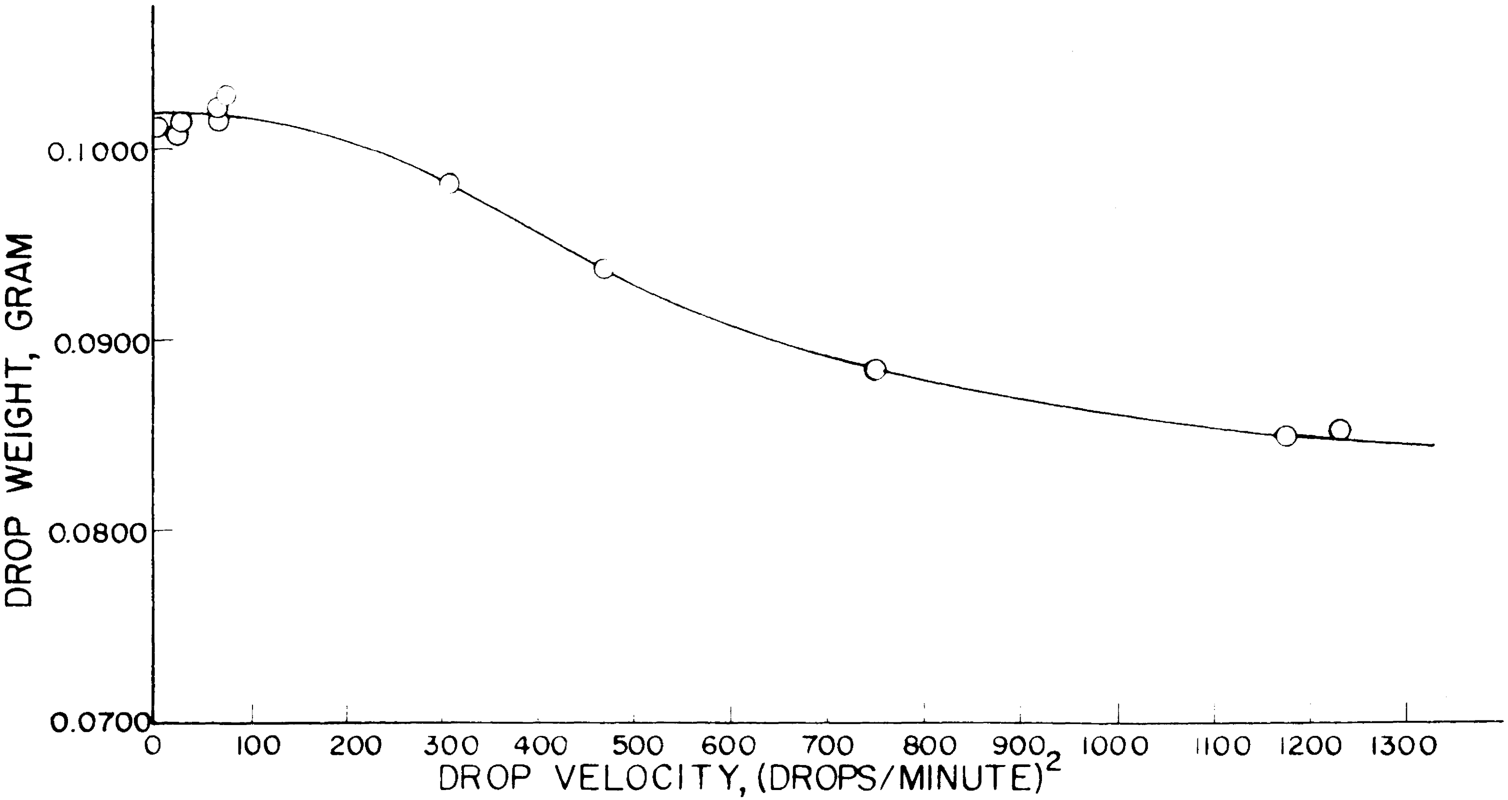


FIGURE 10. VARIATION OF DROP WEIGHT WITH DROP VELOCITY FOR THE SYSTEM CYCLOHEXANE-ACETONE-WATER



SOLUTE: 2.785 WT. % ARABIC ACID

TEMPERATURE: 27.0 °C

FIGURE 11. VARIATION OF DROP WEIGHT WITH DROP VELOCITY FOR THE SYSTEM CYCLOHEXANE-ARABIC ACID-WATER

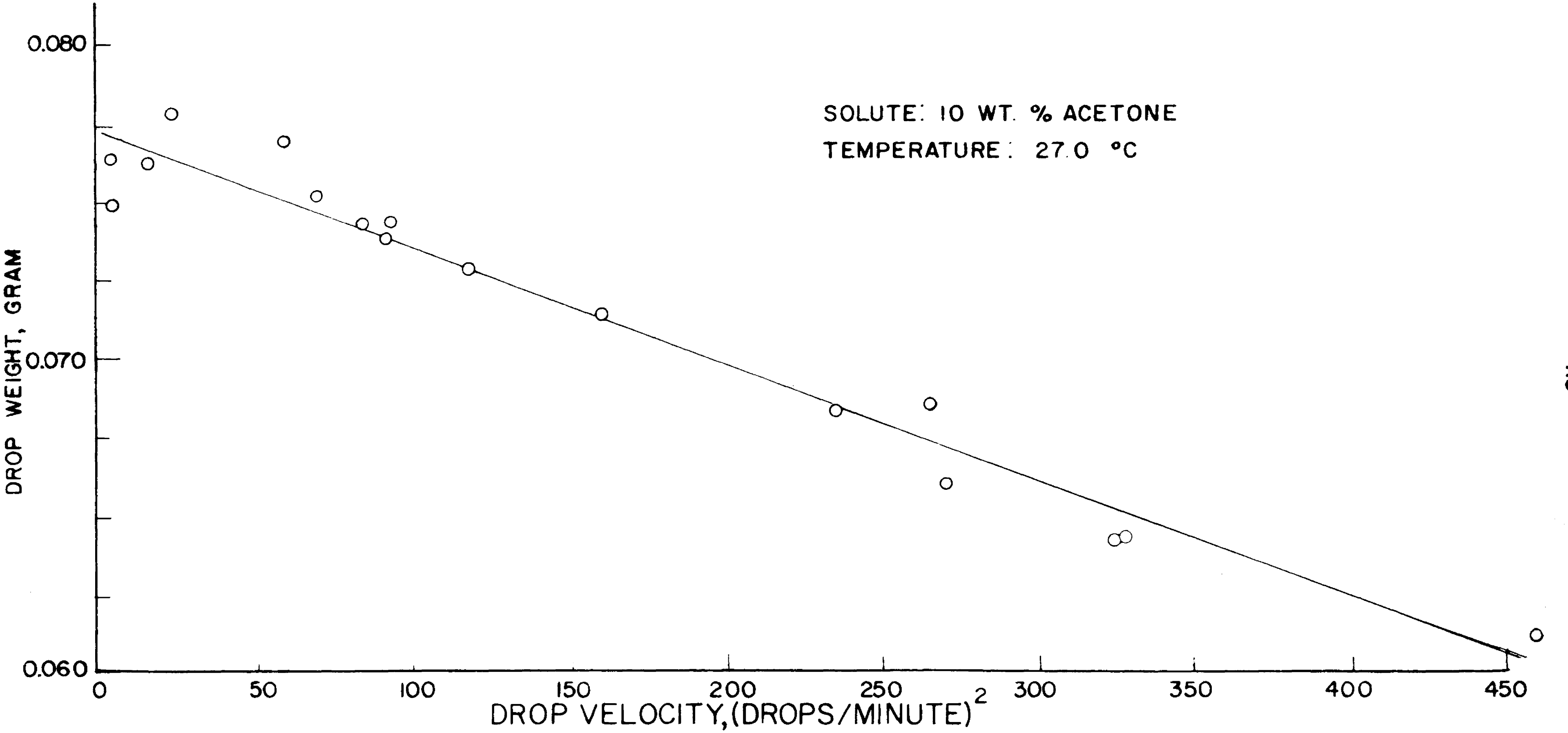


FIGURE 12. VARIATION OF DROP WEIGHT WITH DROP VELOCITY FOR THE SYSTEM TOLUENE-ACETONE-WATER

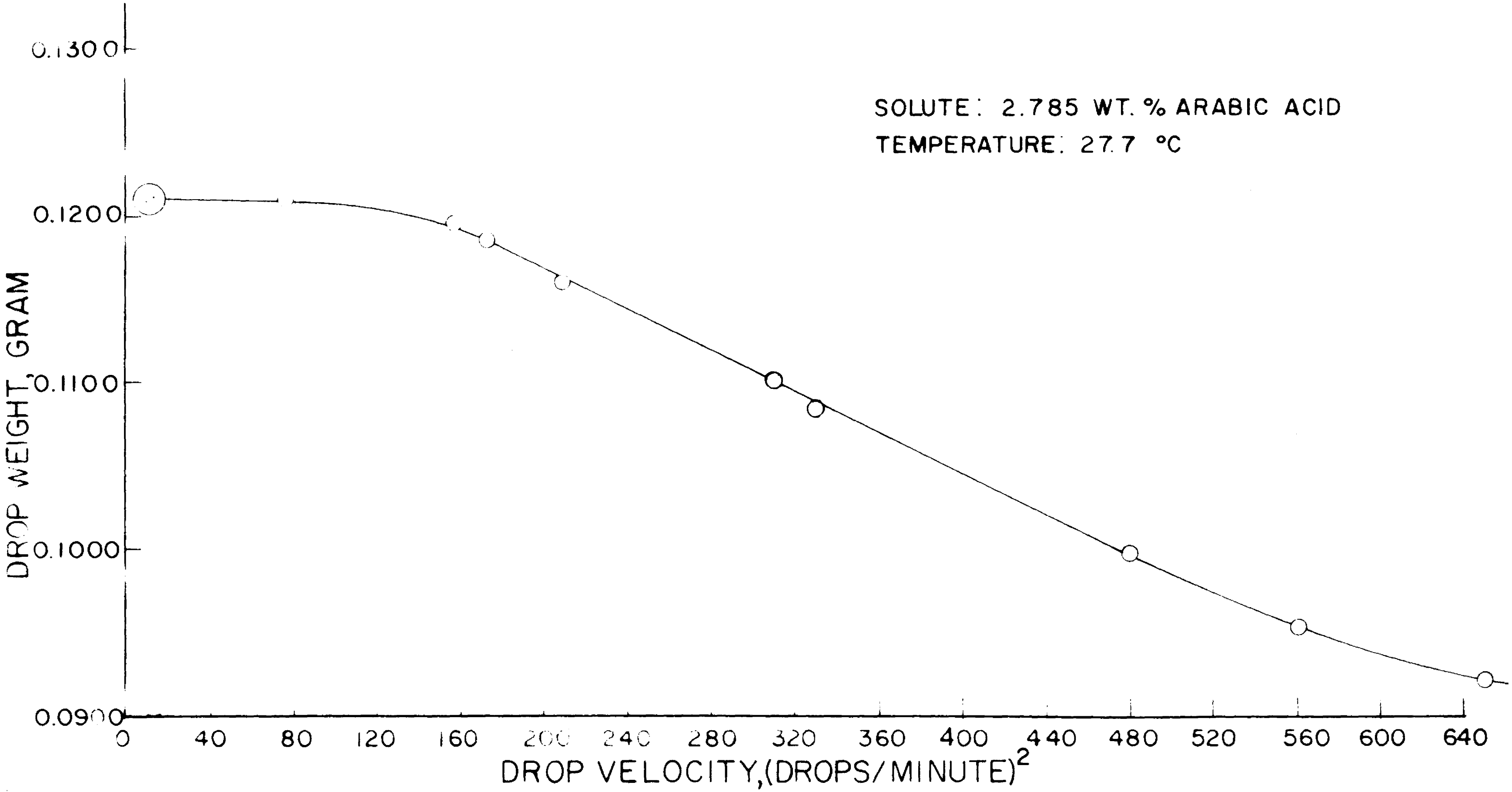


FIGURE 13. VARIATION OF DROP WEIGHT WITH DROP VELOCITY FOR THE SYSTEM TOLUENE-ARABIC ACID-WATER

Specific Gravities and Viscosities. The specific gravities and viscosities of the conjugate phases of the ternary systems used in this investigation were determined at 27 °C. These data, for hexane-acetone-water and toluene-acetone-water, are presented in Tables VI and VII, and are shown graphically in Figures 14, 15, 16; and Figures 17 and 18, respectively.

Refractive Index Curves. The refractive indexes of the conjugate phases of the system hexane-acetone-water and the system toluene-acetone-water at 25 and 30 °C are presented in Table VIII. Plots of these data are shown in Figures 19 and 20. These curves were used for determining the concentration of acetone in samples from the terminal streams of the extractor.

Interfacial Level Controller. Attempts to make the interfacial level control automatic were inconclusive, and require further study. Manual control was found to be sufficient for the purposes of this study.

Mutual Solubility and Tie Line Data. Mutual solubility and tie line data, all of which were obtained from the literature, for the ternary systems

TABLE VI

Specific Gravities of the Conjugate Phases of the Systems Hexane-Acetone-Water at 25 and 27 °C and Toluene-Acetone-Water at 27 °C

		Hexane-Acetone-Water at 27 °C			
	Water Phase			Hexane Phase	
Sample No	Specific Gravity, d_{27}^{27}	Acetone, wt %	Sample No	Specific Gravity, d_{27}^{27}	Acetone, wt %
H-0-W	0.9882	0.00	H-0-H	0.6771	0.00
H-1-W	0.9750	15.72	H-1-H	0.6792	2.28
H-2-W	0.9660	21.75	H-2-H	0.6810	4.34
H-3-W	0.9588	26.00	H-3-H	0.6818	7.25
H-4-W	0.9441	33.79	H-4-H	0.6863	13.29
H-5-W	0.9371	37.32	H-5-H	0.6887	16.18
H-6-W	0.9186	46.00	H-6-H	0.6970	24.95
H-7-W	0.9028	52.51	H-7-H	0.7040	32.52
H-8-W	0.8932	56.48	H-8-H	0.7106	38.38
H-9-W	0.8842	60.30	H-9-H	0.7173	42.98
		Hexane-Acetone-Water at 25 °C (a)			
	Water Phase			Hexane Phase	
	0.9781	13.57		0.6901	19.25
	0.9564	28.18		0.7043	33.72
	0.9260	44.48		0.7144	40.96
	0.9241	45.26		0.7291	50.80
	0.8893	59.08		0.7531	61.27
	0.8791	62.70		0.7914	71.04
	0.8773	63.18		0.8292	73.37
	0.8446	71.84			
		Toluene-Acetone-Water at 27 °C			
	Water Phase			Toluene Phase	
T-0-W	0.9963	0.00	T-0-T	0.8601	0.00
T-1-W	0.9897	4.21	T-1-T	0.8570	2.88
T-2-W	0.9861	7.00	T-2-T	0.8550	6.38
T-3-W	0.9806	10.83	T-3-T	0.8517	11.00
T-4-W	0.9729	16.45	T-4-T	0.8489	14.40
T-5-W	0.9705	18.23	T-5-T	0.8465	18.00
T-6-W	0.9673	20.12	T-6-T	0.8445	20.52
T-7-W	0.9652	21.63	T-7-T	0.8422	24.25
T-8-W	0.9515	30.06	T-8-T	0.8406	26.22
T-9-W	0.9430	34.84	T-9-T	0.8333	38.53
T-10-W	0.9342	38.66	T-10-T	0.8287	45.77
T-11-W	0.9228	43.47	T-11-T	0.8267	52.11
			T-12-T	0.8260	58.43

(a) Treybal, R. E. and O. J. Vondrak: Distribution of Ketones in Water-Hydrocarbon Systems. Ind. Eng. Chem., 41, No 8, 1763 (1949).

TABLE VII

Viscosities of the Conjugate Phases of the Systems Hexane-Acetone-Water and Toluene-Acetone-Water at 27 °C

Sample No	Viscosity, cp	Acetone, wt %	Sample No	Viscosity, cp	Acetone, wt %
		System Hexane-Acetone-Water			
	Water Phase			Hexane Phase	
H-0-W	0.8561	0.00	H-1-H	0.3117	2.28
H-1-W	0.9777	6.23	H-2-H	0.3079	3.11
H-2-W	1.1147	15.72	H-3-H	0.3067	4.34
H-3-W	1.2070	21.77	H-4-H	0.3032	5.49
H-4-W	1.2442	24.76	H-5-H	0.3040	10.00
H-5-W	1.2713	26.00	H-6-H	0.3024	16.18
H-6-W	1.2803	29.91	H-7-H	0.2977	32.52
H-7-W	1.2954	33.79	H-8-H	0.3069	42.98
H-8-W	1.2754	35.48			
H-9-W	1.2843	37.32			
H-10-W	1.1971	46.00			
H-11-W	1.1047	52.51			
H-12-W	1.0211	56.48			
H-13-W	1.9640	60.30			
		System Toluene-Acetone-Water			
	Water Phase			Toluene Phase	
T-0-W	0.8521	0.00	T-0-T	0.5348	0.00
T-1-W	0.9566	4.21	T-1-T	0.5196	2.92
T-2-W	0.9974	7.00	T-2-T	0.5089	6.42
T-3-W	1.0823	10.83	T-3-T	0.4891	11.23
T-4-W	1.1243	14.26	T-4-T	0.4844	14.50
T-5-W	1.1482	16.45	T-5-T	0.4667	18.00
T-6-W	1.1714	18.23	T-6-T	0.4647	20.52
T-7-W	1.2044	20.12	T-7-T	0.4496	24.25
T-8-W	1.2141	21.63	T-8-T	0.4521	26.22
T-9-W	1.2802	30.06	T-9-T	0.4291	38.53
T-10-W	1.2721	34.84	T-10-T	0.4140	45.77
T-11-W	1.2877	38.66	T-11-T	0.4197	58.43
T-12-W	1.2199	43.47			

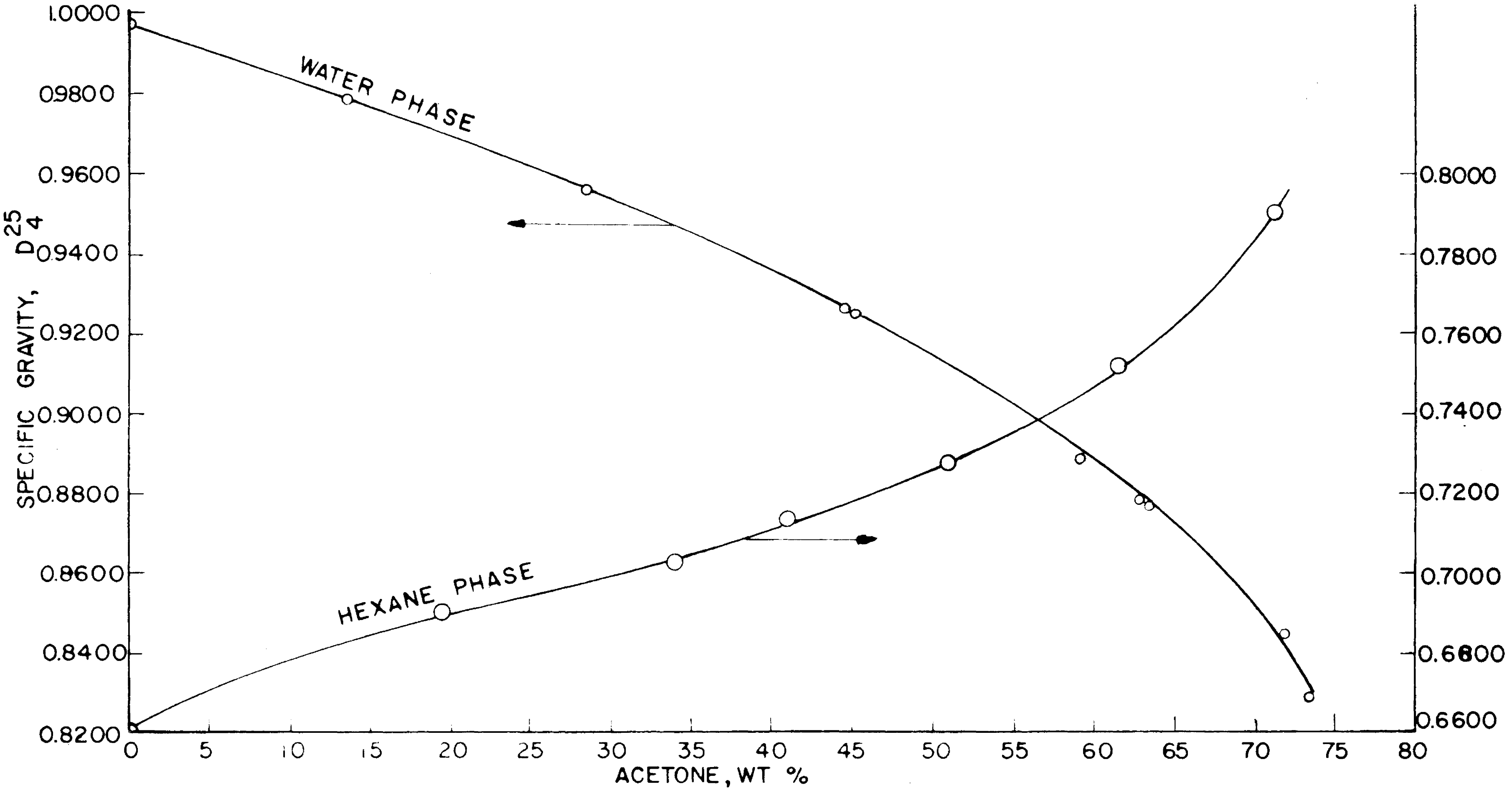


FIGURE 14. SPECIFIC GRAVITIES OF THE CONJUGATE PHASES OF THE SYSTEM HEXANE-ACETONE-WATER AT 25 °C

TREYBAL, R.E. AND O.J. VONDRAK: DISTRIBUTION OF KETONES IN WATER—HYDROCARBON SYSTEMS IND. ENG. CHEM., 41, 1761 (1949)

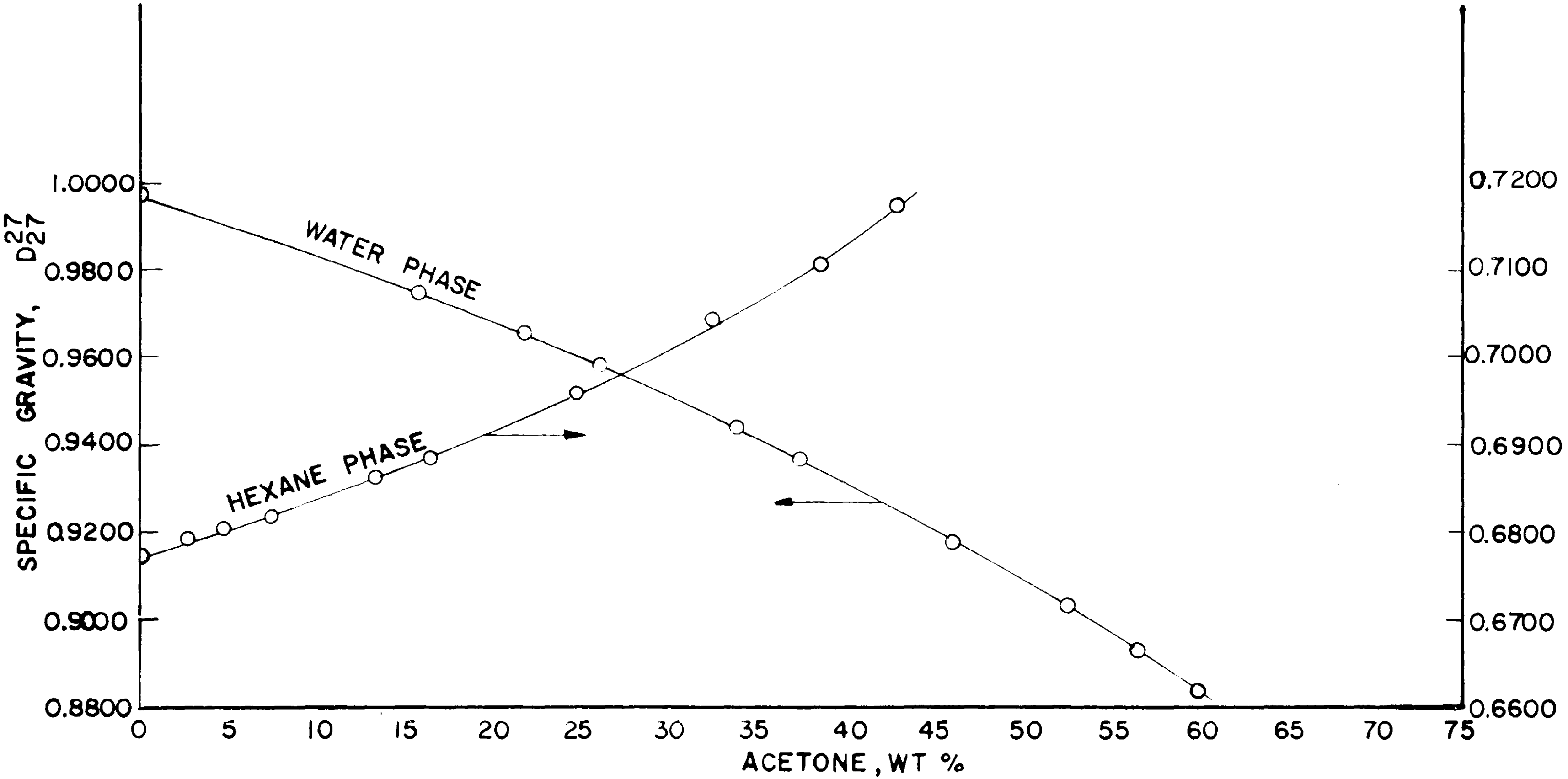


FIGURE 15. SPECIFIC GRAVITIES OF THE CONJUGATE PHASES OF THE SYSTEM HEXANE-ACETONE-WATER AT 27 °C

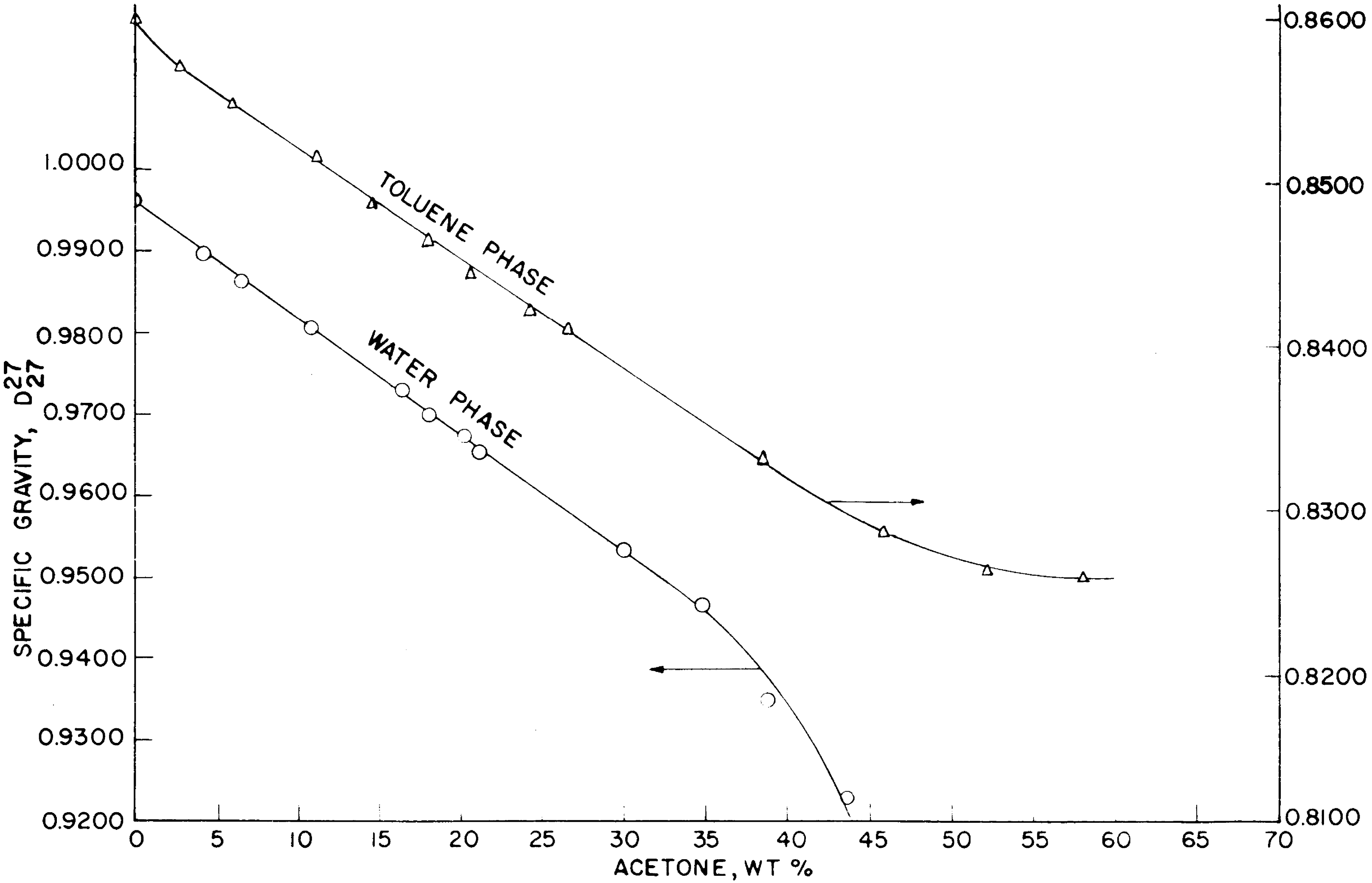


FIGURE 16. SPECIFIC GRAVITIES OF THE CONJUGATE PHASES OF THE SYSTEM TOLUENE-ACETONE-WATER AT 27 °C

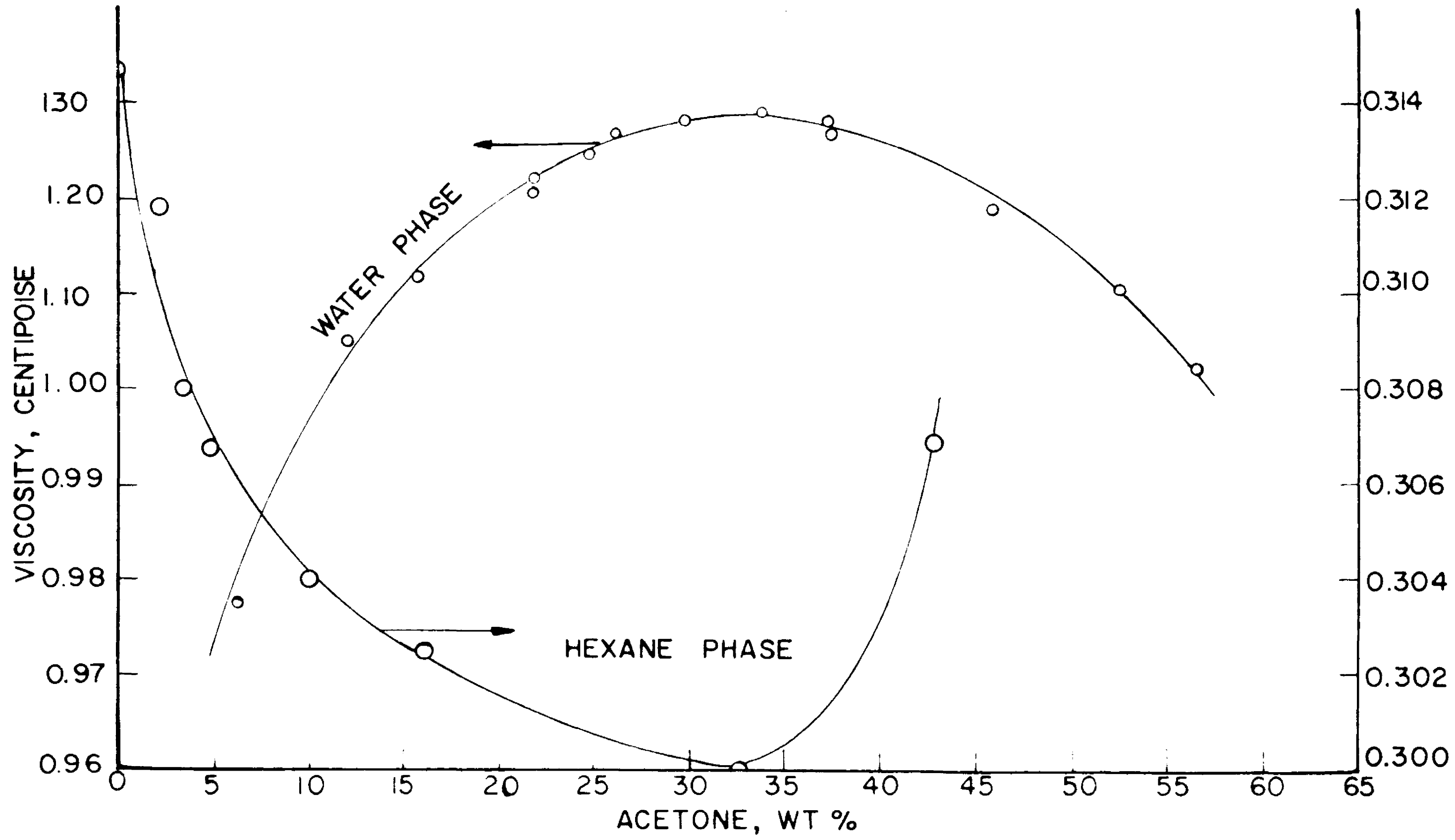


FIGURE 17. VISCOSITIES OF THE CONJUGATE PHASES OF THE SYSTEM HEXANE-ACETONE-WATER AT 27 °C

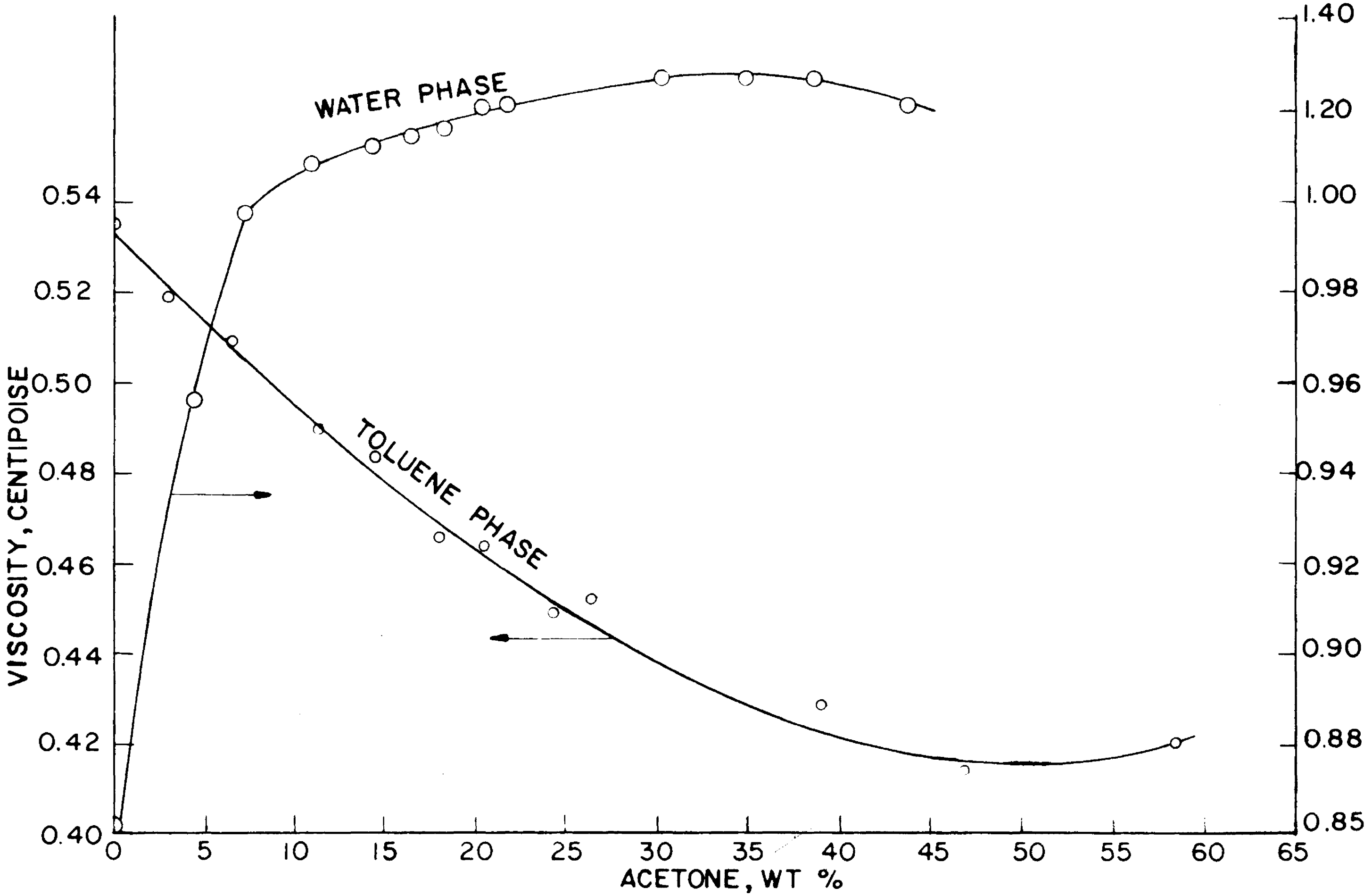


FIGURE 18. VISCOSITIES OF THE CONJUGATE PHASES OF THE SYSTEM TOLUENE-ACETONE-WATER AT 27 °C

TABLE VIII

Refractive Indexes of the Conjugate Phases of the Systems Hexane-Acetone-Water and Toluene-Acetone-Water at 25 and 30 °C

Sample No	Refractive Index, N_D^{25}	Acetone, wt %	Sample No	Refractive Index, N_D^{25}	Acetone, wt %
System Hexane-Acetone-Water at 30 °C					
Water Phase			Hexane Phase		
H-0-W	1.33185	0.00	H-0-H	1.37934	0.00
H-1-W	1.34018	12.21	H-1-H	1.37833	2.87
H-2-W	1.34603	20.30	H-2-H	1.37700	6.83
H-3-W	1.34866	25.31	H-3-H	1.37615	8.50
H-4-W	1.35021	28.29	H-4-H	1.37565	9.71
H-5-W	1.35308	33.70	H-5-H	1.37434	13.42
H-6-W	1.35745	44.68	H-6-H	1.37169	21.10
H-7-W	1.35837	46.92	H-7-H	1.37135	21.85
H-8-W	1.35980	53.62	H-8-H	1.36850	30.62
H-9-W	1.36052	56.75	H-9-H	1.33695	35.72
H-10-W	1.36099	60.48	H-10-H	1.36564	39.35
H-11-W	1.36113	63.14	H-11-H	1.36435	44.25
System Hexane-Acetone-Water at 25 °C (a)					
Water Phase			Hexane Phase		
	1.3422	86.31		1.3631	73.37
	1.3519	71.67		1.3629	74.01
	1.3568	62.06		1.3628	71.04
	1.3590	55.21		1.3642	61.27
	1.3594	54.37		1.3661	50.80
	1.3629	39.33		1.3686	40.96
	1.3631	35.41		1.3704	33.72
	1.3631	34.92		1.3746	19.25
	1.3632	23.74			
H-0-W	1.33254	0.00	H-0-H	1.38235	0.00
H-1-W	1.35010	26.00	H-1-H	1.37869	8.11
H-2-W	1.36214	54.51	H-2-H	1.37096	32.00
H-3-W	1.36364	67.83	H-3-H	1.36583	51.13
H-4-W	1.36349	63.68	H-4-H	1.36740	44.98
System Toluene-Acetone-Water at 30 °C					
Water Phase			Toluene Phase		
T-1-W	1.34022	11.95	T-1-T	1.47384	11.28
T-2-W	1.34533	18.18	T-2-T	1.45774	22.91
T-3-W	1.35060	28.48	T-3-T	1.43912	23.54
T-4-W	1.35485	35.34	T-4-T	1.42146	46.49
T-5-W	1.35913	42.78	T-5-T	1.40446	57.73
T-6-W	1.36193	48.52			
System Toluene-Acetone-Water at 25 °C					
Water Phase			Toluene Phase		
T-0-W	1.33272	0.00	T-0-T	1.49365	0.00
T-1-W	1.33751	7.30	T-1-T	1.48488	6.11
T-2-W	1.34079	10.39	T-2-T	1.47852	10.05
T-3-W	1.34423	15.75	T-3-T	1.47018	15.83
T-4-W	1.34996	23.97	T-4-T	1.46133	23.55
T-5-W	1.35410	31.28	T-5-T	1.45184	28.63
T-6-W	1.35610	34.10	T-6-T	1.44366	33.76
T-7-W	1.35836	38.43	T-7-T	1.43616	38.86
T-8-W	1.36025	42.08	T-8-T	1.42824	44.47
T-9-W	1.36208	44.94	T-9-T	1.41909	51.08
			T-10-T	1.41163	55.67
			T-11-T	1.40364	60.05

(a) Treybal, R. E. and O. J. Vondrak: Distribution of Ketones in Water Hydrocarbon Systems. Ind. Eng. Chem., 41, No 8, 1763 (1949).

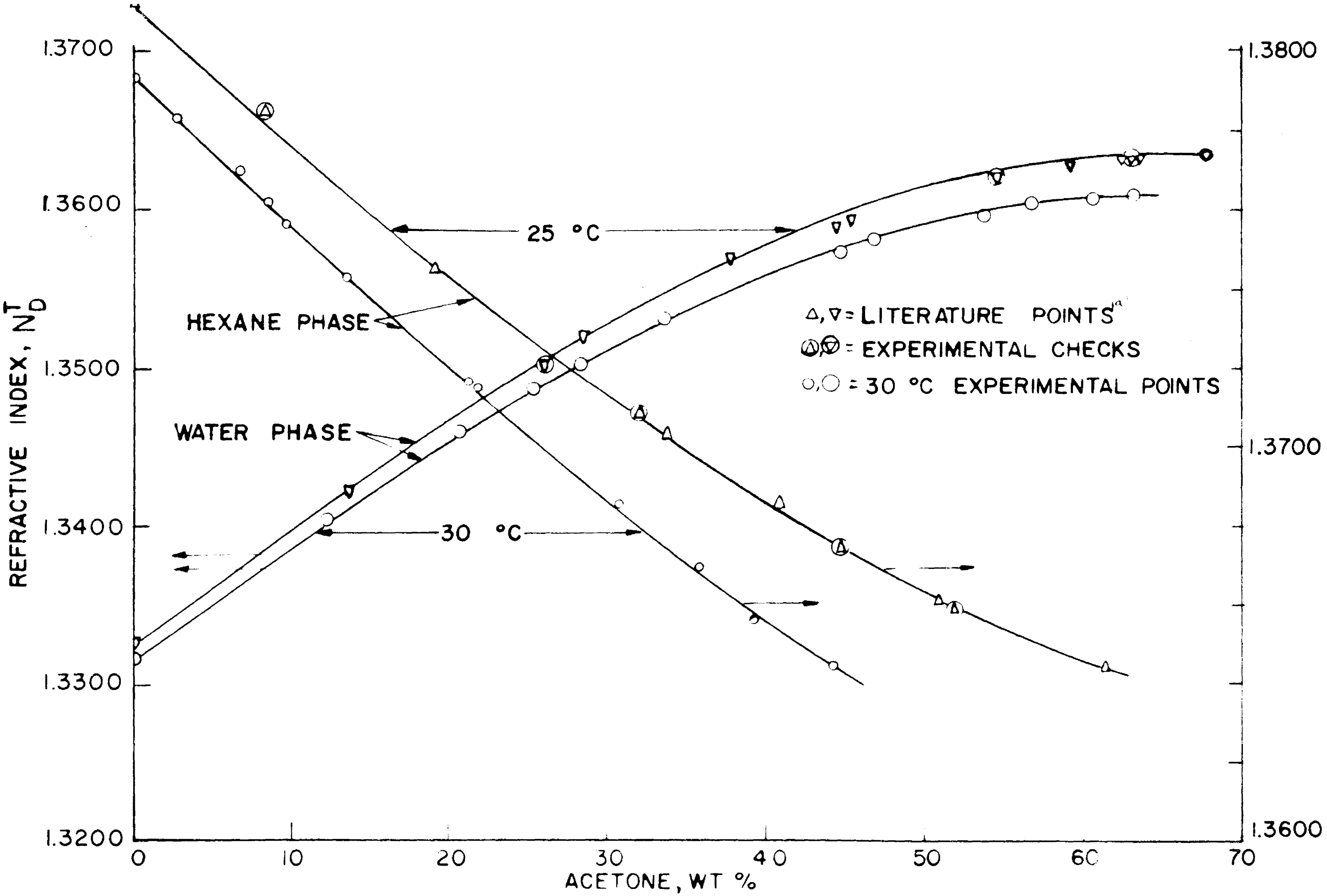


FIGURE 19. REFRACTIVE INDEXES OF THE CONJUGATE PHASES OF THE SYSTEM HEXANE-ACETONE-WATER AT 25 AND 30 °C

[a] TREYBAL, R.E. AND O.J. VONDRAK: DISTRIBUTION OF KETONES IN WATER-HYDROCARBON SYSTEMS, IND.ENG. CHEM., 41, 1761 (1949)

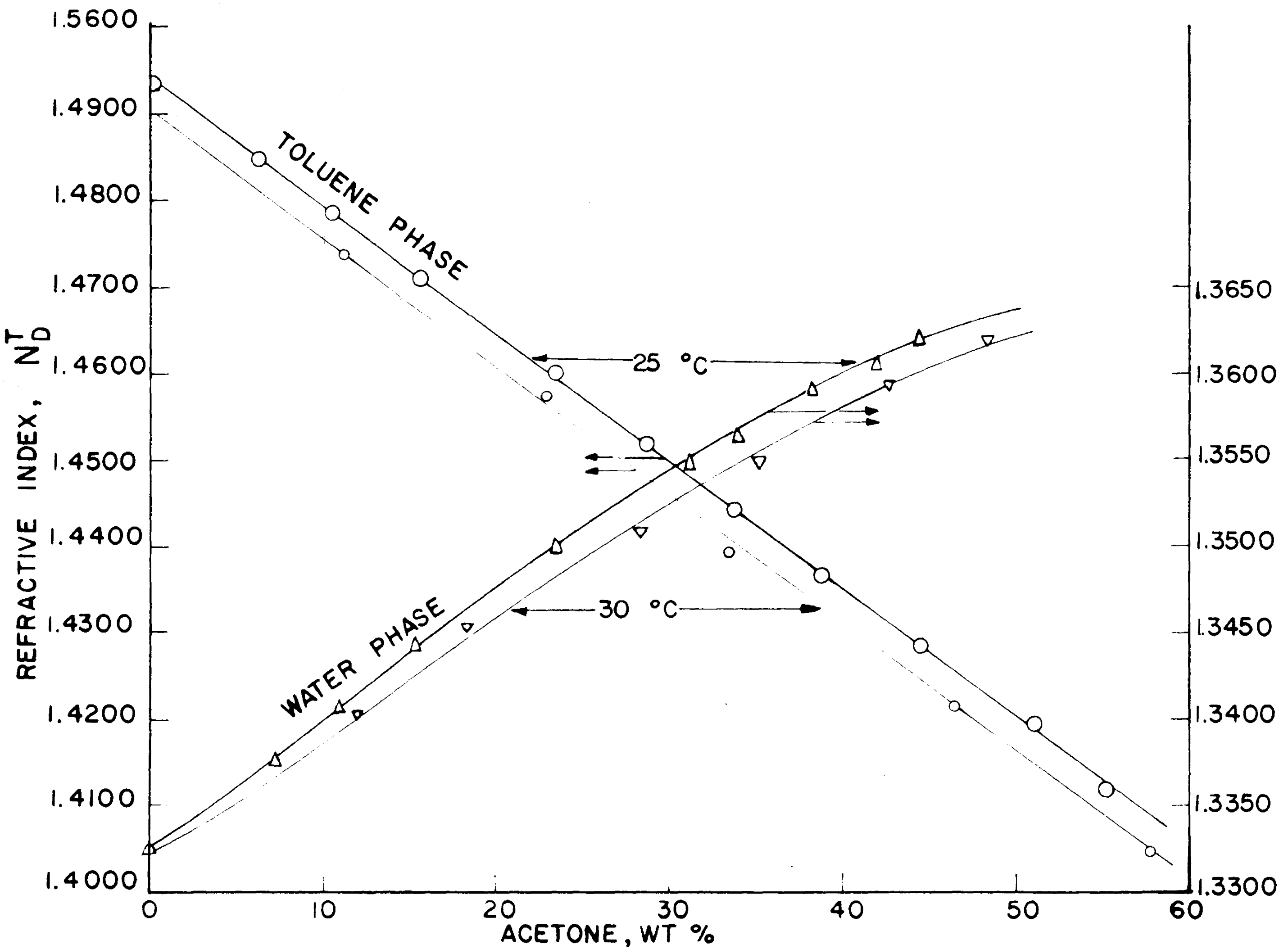


FIGURE 20. REFRACTIVE INDEXES OF THE CONJUGATE PHASES OF THE SYSTEM TOLUENE-ACETONE-WATER AT 25&30°C

hexane-acetone-water at 25 °C and toluene-acetone-water at 30 °C are presented in Tables IX and X. Plots of these data are shown in Figures 21 and 22.

Distribution Coefficients. Distribution coefficients used in calculating overall mass transfer rates were defined as the equilibrium concentration of solute in the water phase divided by the concentration of solute in the solvent phase, these concentrations being expressed as pounds of solute per cubic foot of solution. Table XI contains the distribution coefficients for the systems hexane-acetone-water at 25 °C and toluene-acetone-water at 30 °C. The distribution coefficients are plotted against the solute concentrations in the solvent phase for the systems in Figures 23 and 24.

Ternary Extraction Data. Ternary extraction data and values of experimentally determined overall mass transfer coefficients for the systems hexane-acetone-water and toluene-acetone-water at 27 ± 2 °C are presented in Tables XII and XIII. These systems were studied in a horizontal tube extractor 1-1/2 inches in diameter, eight feet long. Interfacial tension values for the systems used in this

TABLE IX

Mutual Solubility and Tie-Line Data for the System Toluene-Acetone-Water at 30 °C

Limiting Solubilities (a)

Toluene, wt %	Acetone, wt %	Water, wt %
61.5	37.0	1.5
56.1	41.9	2.0
51.6	45.9	2.5
48.5	48.5	3.0
43.1	52.9	4.0
38.6	56.4	5.0
32.3	60.7	7.0
26.0	64.0	10.0
19.7	65.3	15.0
15.5	64.5	20.0
12.2	62.8	25.0
10.0	61.3	28.7
7.0	58.7	34.3
5.0	56.0	38.0
4.0	53.9	42.1
3.0	51.0	46.0
2.0	47.2	50.8
1.5	44.1	54.4
1.0	39.6	59.4
0.5	31.2	68.3
0.4	28.1	71.5
	Estimated Plait Point	
9.5	61.0	29.5

Tie-Line Data (b)

Acetone in Toluene Layer, wt %	Acetone in Water Layer, wt %
8.14	9.75
17.33	17.07
25.30	21.30
34.00	29.20
41.30	32.50
48.50	36.95
52.72	39.52
54.46	40.86
59.69	44.68
62.00	47.87
64.39	51.34
66.09	54.48

(a) International Critical Tables, Vol III, p. 406. McGraw-Hill Book Co., Inc., New York, N. Y., 1928.

(b) Othmer, D. F., R. E. White, and E. Trueger: Liquid-Liquid Extraction Data. Ind. Eng. Chem., 33, 1241 (1941).

TABLE X

Mutual Solubility and Tie-Line Data for the System N-Hexane-Acetone-Water at 25 °C

	Mutual Solubility	
Acetone, wt %	N-Hexane, wt %	Water, wt %
13.57	0.12	86.31
28.18	0.15	71.67
37.73	0.21	62.06
44.48	0.31	55.21
45.26	0.37	54.37
59.08	1.59	39.33
62.70	1.89	35.41
63.18	1.90	34.92
71.84	4.42	23.74
73.37	6.92	19.71
74.01	10.09	15.90
71.04	17.22	11.74
61.27	33.42	5.31
50.80	46.64	2.56
40.96	58.07	0.97
33.72	65.89	0.39
19.25	80.61	0.14
	Estimated Plait Point	
71.1	17.1	11.8

Tie-Line Data	
Acetone in Water Layer, wt %	Acetone in Hexane Layer, wt %
18.02	4.95
25.89	8.67
27.01	9.28
33.30	13.02
41.08	18.66
43.55	21.10
47.15	24.22
52.61	29.28
56.10	33.85
57.64	36.21
63.00	44.20
68.52	52.18

Treybal, R. E. and O. J. Vondrak: Distribution of Ketones in Water-Hydrocarbon Systems. Ind. Eng. Chem., 41, No 8, 1763 (1949).

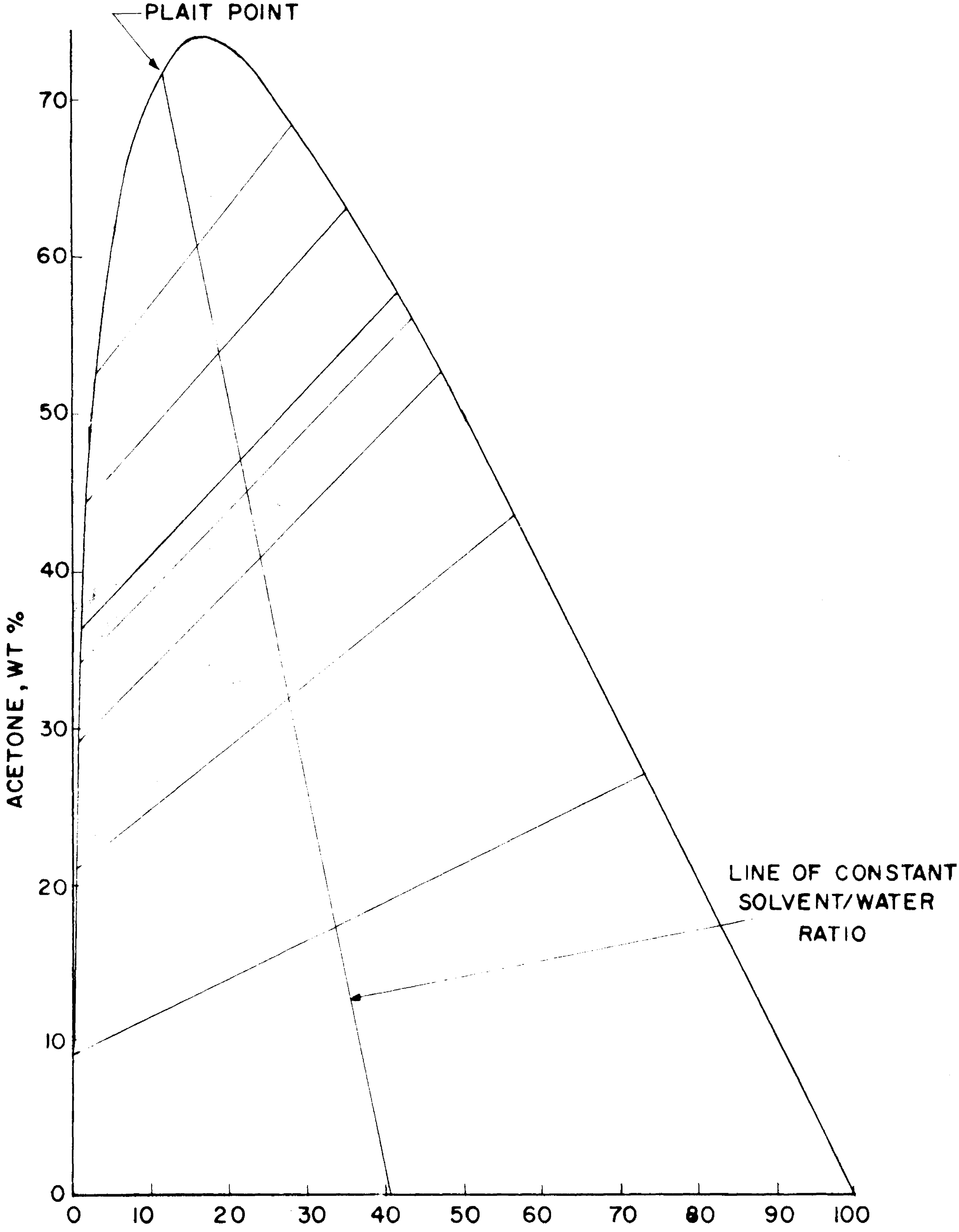


FIGURE 21. TERNARY PHASE DIAGRAM FOR THE SYSTEM N-HEXANE-ACETONE- WATER AT 25 °C

TREYBAL, R.E., AND O.J. VONDRAK: DISTRIBUTION OF KETONES IN WATER-HYDROCARBON SYSTEMS, IND. ENG. CHEM., 41, 1761 (1949)

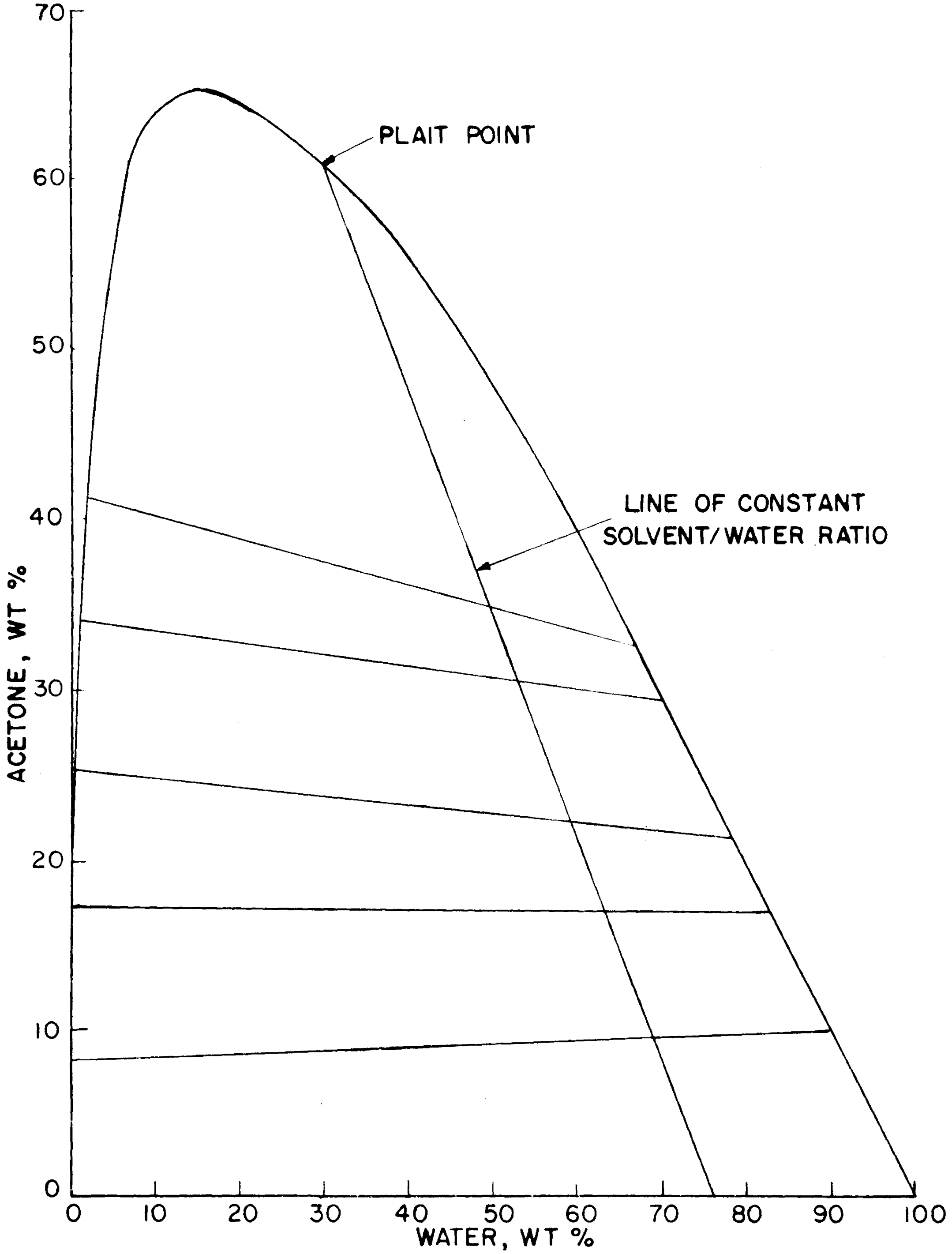


FIGURE 22. TERNARY PHASE DIAGRAM FOR THE SYSTEM TOLUENE–ACETONE–WATER AT 30 °C

INTERNATIONAL CRITICAL TABLES, VOL. 3, P. 406, MCGRAW-HILL BOOK CO., INC. NEW YORK, N.Y., 1928

TABLE XI

Distribution Coefficients for the Systems Hexane-Acetone-Water and Toluene-Acetone-Water

System Hexane-Acetone-Water at 25 °C (a)

Equilibrium Concentration of Acetone in Hexane Phase,		Distribution Coefficient, C_w/C_s
wt %	lb/cu ft	dimensionless
2.28	0.96	9.900
4.34	1.84	7.110
7.25	3.08	5.043
13.29	5.67	3.498
16.18	6.93	3.141
24.95	10.82	2.433
32.52	14.24	2.087
38.38	16.97	1.854
42.98	19.18	1.734

System Toluene-Acetone-Water at 30 °C (b)

Equilibrium Concentration of Acetone in Toluene Phase,		Distribution Coefficient, C_w/C_s,
wt %	lb/cu ft	Dimensionless
1.52	1.00	1.850
5.49	3.00	1.560
9.50	5.00	1.322
10.38	5.50	1.273
16.19	8.50	1.118
25.41	13.00	1.008
28.50	14.50	0.983
30.00	15.50	0.968
38.67	20.00	0.915
46.71	24.00	0.875
58.50	30.00	0.837

(a) Treybal, R. E. and O. J. Vondrak: Distribution of Ketones in Water-Hydrocarbon Systems. Ind. Eng. Chem., 41, No 8, 1763 (1948).

(b) Othmer, D. F., R. E. White, and E. Trueger: Liquid-Liquid Extraction Data. Ind. Eng. Chem., 33, 1241 (1941).

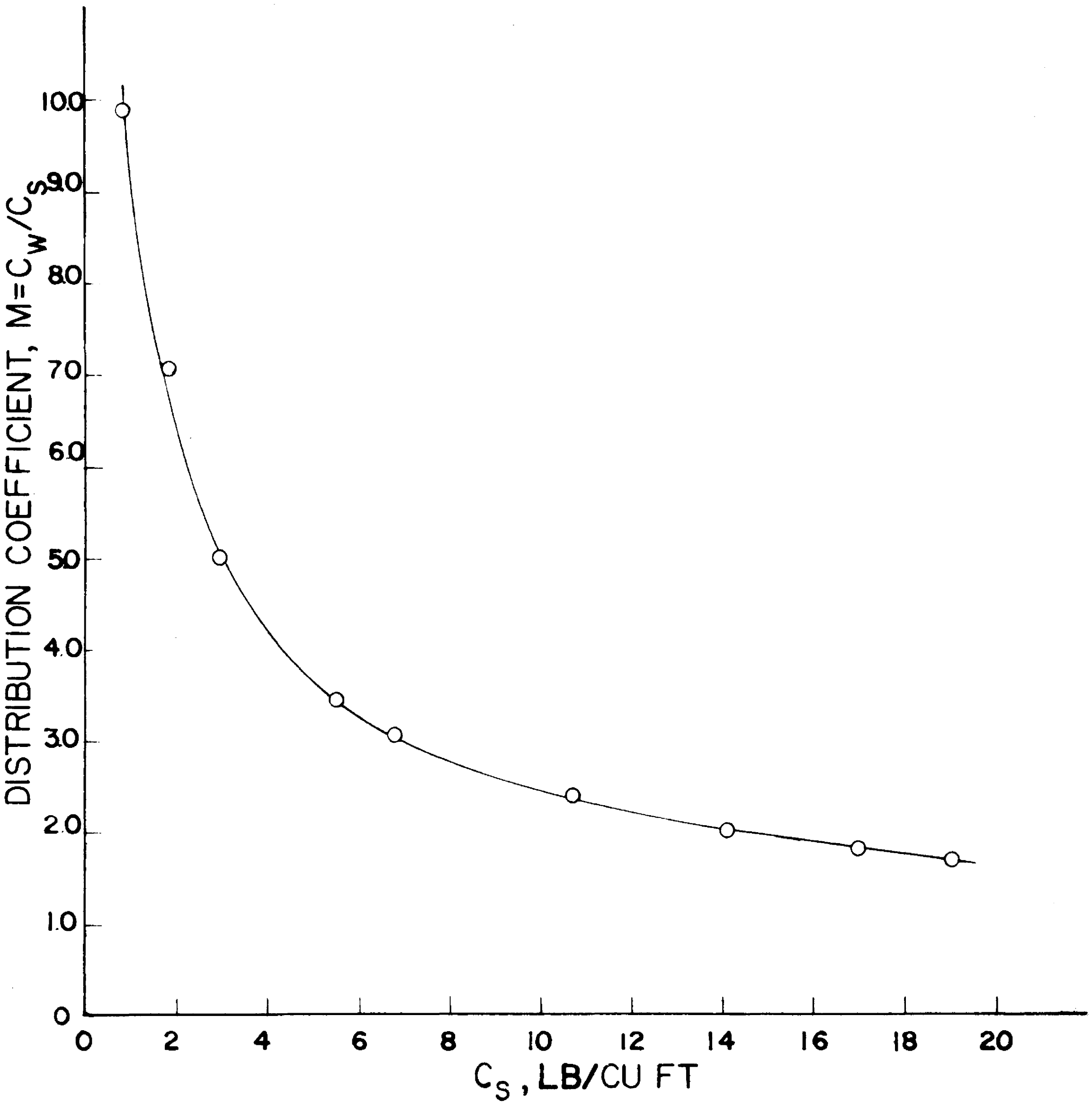


FIGURE 23. DISTRIBUTION OF ACETONE BETWEEN HEXANE AND WATER

TREYBAL, R.E. AND O.J. VONDRAK: DISTRIBUTION OF KETONES IN WATER-HYDROCARBON SYSTEMS, IND. ENG. CHEM., 41, 1761 (1949)

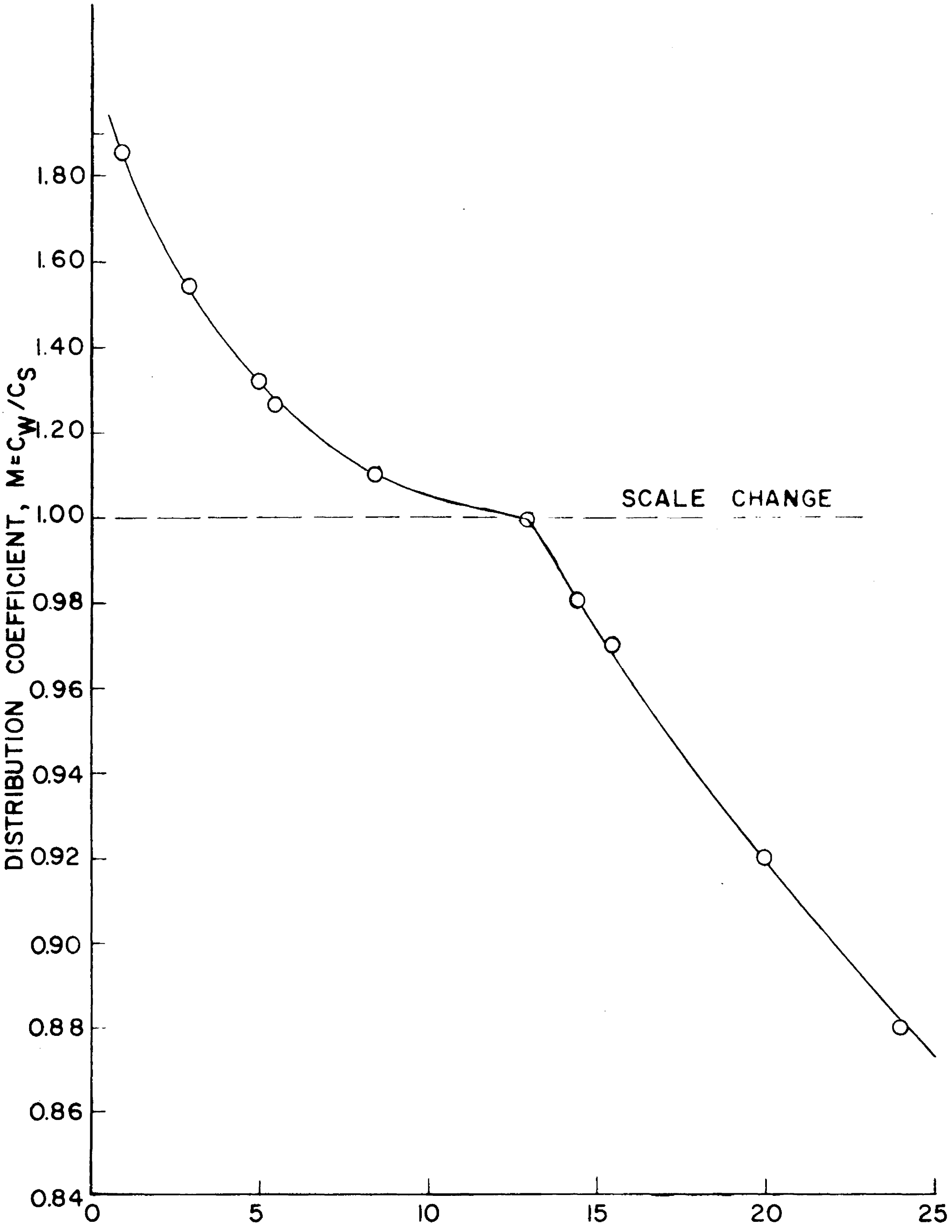


FIGURE 24. DISTRIBUTION OF ACETONE BETWEEN TOLUENE AND WATER

OTHMER, D.F., R.E.WHITE, AND E.TRUEGER: LIQUID–LIQUID EXTRACTION DATA, IND. ENG. CHEM., 33, 1241 (1941)

TABLE XII

Extraction Data for the Systems Hexane-Acetone-Water and Toluene-Acetone-Water Tested in a Horizontal Tube Extractor at 27 °C

Test No	Average Phase Flow Rates		Average Phase Densities		Concentrations of Acetone						C_{pp} (a)	Interfacial Tension
	Water Phase	Solvent Phase	Water Phase	Solvent Phase	Water Phase			Solvent Phase				
					Inlet	Exit	Average	Inlet	Exit	Average		
	lb/hr	lb/hr	lb/cu ft	lb/cu ft	wt %	wt %	lb/cu ft	wt %	wt %	lb/cu ft	wt %	dynes/cm
System Hexane-Acetone-Water												
1	28.98	20.79	57.29	42.14	44.746	44.391	25.535	0.000	0.503	0.106	25.75	7.63
2	14.31	20.79	57.31	42.15	44.746	43.822	25.380	0.000	0.625	0.132	21.63	9.91
3	36.79	15.56	57.26	42.15	44.746	44.492	25.550	0.000	0.589	0.124	31.67	5.24
4	29.49	20.94	58.12	42.18	38.499	38.131	22.269	0.504	0.998	0.317	22.31	9.46
5	40.35	20.73	58.11	42.17	38.499	38.250	22.299	0.504	0.909	0.298	29.91	9.13
6	17.95	21.11	58.13	42.17	38.499	38.003	22.236	0.504	0.930	0.302	19.39	11.42
7	28.77	31.56	58.10	42.16	38.499	38.294	22.307	0.504	0.696	0.253	19.43	11.39
8	28.15	21.03	58.23	42.20	37.819	37.454	21.915	0.901	1.397	0.485	21.29	10.13
9	21.31	20.90	58.21	42.19	37.819	37.500	21.921	0.901	1.197	0.443	19.99	11.00
10	10.42	20.82	58.24	42.20	37.819	36.977	21.743	0.901	1.297	0.464	16.61	13.63
11	42.10	21.06	58.17	42.21	37.819	37.604	21.937	0.901	1.350	0.475	22.59	9.32
12	30.33	20.93	59.39	42.18	28.583	28.311	16.895	0.692	1.061	0.370	15.64	14.50
13	21.07	14.63	59.40	42.19	28.583	28.250	16.880	0.692	1.161	0.391	15.60	14.54
14	20.48	30.31	59.41	42.18	28.583	28.096	16.838	0.692	0.998	0.356	13.51	16.60
15	29.49	43.61	59.41	42.18	28.583	28.197	16.866	0.692	1.000	0.357	13.49	16.63
16	29.72	20.91	60.10	42.20	22.201	21.930	13.261	0.931	1.316	0.474	11.79	18.52
17	20.41	43.00	60.73	42.19	22.201	21.678	13.325	0.931	1.130	0.435	9.60	21.28
18	10.45	30.34	60.74	42.19	22.201	21.587	13.298	0.931	1.130	0.434	9.79	21.03
19	46.30	30.19	60.10	42.20	22.201	21.905	13.254	0.931	1.231	0.456	12.00	18.27
20	29.80	21.01	60.14	42.20	21.793	21.663	13.068	1.068	1.250	0.490	11.70	18.62
21	9.18	21.43	60.15	42.20	21.793	21.250	12.945	1.068	1.289	0.497	9.60	21.28
22	49.00	21.07	60.14	42.20	21.793	21.675	13.071	1.068	1.332	0.506	12.41	17.80
23	30.07	20.86	60.62	42.19	16.247	16.129	9.812	0.846	1.014	0.392	8.52	22.80
24	46.14	13.64	60.60	42.19	16.247	16.176	9.825	0.846	1.123	0.415	9.28	21.72
25	46.34	45.48	60.60	42.18	16.247	16.179	9.826	0.846	0.913	0.371	8.31	23.10
26	13.66	45.27	60.63	42.18	16.247	16.901	9.746	0.846	0.944	0.376	6.51	25.90
System Toluene-Acetone-Water												
1	28.81	21.28	55.42	52.45	34.002	29.434	18.961	18.954	25.559	11.669	26.80	6.33
2	37.30	33.99	59.11	52.48	34.002	30.794	19.147	18.954	24.023	11.275	26.00	6.69
3	36.64	26.46	59.10	52.47	34.002	30.895	19.174	18.954	24.948	11.513	26.40	6.55
4	30.42	20.50	59.97	52.80	23.877	21.487	13.555	10.357	15.270	6.774	18.28	10.15
5	21.96	45.64	59.96	52.98	23.877	21.662	13.650	10.357	11.906	5.895	18.31	10.13
6	42.06	44.97	59.94	52.95	23.877	21.943	13.650	10.357	12.926	6.162	16.89	10.94
7	31.08	20.37	60.70	53.15	14.888	13.781	8.690	5.173	7.244	3.310	11.24	14.83
8	23.41	20.90	60.71	53.19	14.888	13.685	8.679	5.173	6.701	3.146	10.88	15.12
9	38.76	20.64	60.70	53.19	14.888	13.781	8.666	5.173	7.102	3.260	11.92	14.31
10	19.05	23.68	60.71	53.20	14.888	13.603	8.645	5.173	6.327	3.053	10.01	15.84
11	18.65	32.41	60.70	53.21	14.888	13.726	8.670	5.173	6.021	2.983	9.47	16.31
12	18.92	37.43	60.71	53.22	14.888	13.548	8.629	5.173	5.946	2.931	9.18	16.56
13	19.18	49.07	60.77	53.18	13.849	13.096	8.169	6.412	6.782	3.501	8.98	16.75
14	46.56	20.77	60.75	53.18	13.849	13.555	8.338	6.412	7.870	3.797	11.98	14.25
15	8.33	20.64	60.72	53.15	15.158	13.151	8.664	6.537	7.557	3.747	9.47	16.31
16	12.17	20.77	60.70	53.15	15.158	13.685	8.743	6.537	7.577	3.722	9.67	16.13
17	15.74	20.77	60.69	53.15	15.158	13.740	8.743	6.537	7.605	3.756	9.87	15.96
18	19.05	20.64	60.67	53.15	15.158	14.206	8.902	6.537	7.577	3.761	10.00	15.85
19	18.92	11.24	60.67	53.10	15.158	14.247	8.913	6.537	8.651	3.964	11.93	14.28
20	18.92	14.68	60.67	53.12	15.158	14.288	8.930	6.537	7.822	3.800	11.50	14.62
21	19.05	17.86	60.67	53.15	15.158	14.247	8.918	6.537	7.618	3.754	11.00	15.02
22	30.70	21.05	61.15	53.48	9.616	8.836	5.642	0.000	0.985	0.263	6.14	19.51
23	38.68	14.82	61.14	53.45	9.616	8.986	5.692	0.000	1.631	0.436	7.16	18.47
24	23.60	29.00	61.16	53.49	9.616	8.630	5.581	0.000	0.803	0.215	5.00	20.75
25	31.79	21.11	61.55	53.44	4.959	4.671	2.963	0.822	1.278	0.561	3.67	22.28
26	20.56	18.16	61.55	53.44	4.959	4.548	2.926	0.822	1.287	0.564	3.70	22.25
27	35.76	25.27	61.54	53.44	4.959	4.753	2.988	0.822	1.149	0.527	3.73	22.22
28 (b)	31.27	20.08	61.55	52.16	4.534	5.027	2.942	30.038	29.352	15.662	14.37	12.52
29 (b)	18.66	11.70	61.55	52.16	4.534	4.932	2.913	30.038	29.425	15.506	14.49	12.44
30	8.80	16.65	60.59	53.15	17.055	14.192	9.435	6.058	8.036	3.442	10.67	15.29
31	15.85	16.44	60.53	53.15	17.055	15.390	9.788	6.058	8.121	3.765	11.91	14.30
32	22.77	16.75	60.52	53.14	17.055	15.753	9.895	6.058	8.520	3.871	12.33	13.98
33	29.76	16.64	60.51	53.15	17.055	16.041	9.980	6.058	8.573	3.885	12.73	13.68
34	12.34	16.88	60.56	53.15	17.055	14.877	9.636	6.058	8.148	3.773	11.45	14.66
35	29.99	20.73	60.28	53.07	19.794	18.459	11.524	7.478	10.049	4.648	14.97	12.13
36	19.34	21.17	60.30	53.08	19.794	18.055	11.406	7.478	9.552	4.517	14.12	12.69
37	8.77	21.06	60.37	53.07	19.794	16.440	10.992	7.478	9.002	4.372	11.98	14.25
38	29.72	20.85	59.92	53.00	24.212	22.195	13.902	9.713	13.576	6.155	18.00	10.30
39	42.46	21.03	59.88	52.79	24.274	22.993	14.132	9.713	13.325	6.089	18.84	9.84
40	20.09	21.10	59.91	52.95	24.335	22.309	13.935	9.713	12.278	5.817	15.11	12.03
41	8.51	21.10	59.98	52.95	24.381	20.753	13.482	9.713	11.944	5.172	17.46	10.60
42	8.18	18.24	59.92	52.85	25.305	21.082	13.891	12.325	15.020	7.483	17.24	10.73
43	15.54	18.42	59.87	52.80	25.305	22.243	14.227	12.325	15.891	7.450	18.00	10.30
44	27.53	18.37	59.80	52.80	25.305	23.777	14.669	12.325	15.726	7.407	19.24	9.63
45	37.73	18.33	59.77	52.82	25.305	24.412	14.852	12.325	15.509	7.350	21.01	8.76
46	30.20	21.17	60.64	53.20	15.460	14.721	9.146	5.347	6.711	3.205	11.50	14.62
47	20.52	20.94	60.65	53.21	15.460	14.386	9.047	5.347	6.653	3.190	11.00	15.02
48	8.74	21.02	60.70	53.20	15.460	13.350	8.739	5.347	6.422	3.129	10.50	15.43
49	38.64	20.91	60.63	53.20	15.460	14.923	9.206	5.347	6.659	3.191	12.98	13.50
50 (b)	32.96	21.09			0.000	0.067		5.144	5.143			
51 (b)	21.51	18.19			0.000	0.010		5.144	5.144			
52 (b)	45.03	37.38			0.000	0.011		5.144	5.090			
53 (b)	32.13	21.07			0.000	0.179		10.364	10.316			
54 (b)	29.02	18.32			0.000	0.178		10.364	10.269			
55 (b)	21.19	14.79			0.000	0.178		10.364	10.241			
56 (b)	17.66	11.07			0.000	0.203		10.364	10.201			

(a) C_{pp} = overall concentration of toluene at constant, plait point ratio of solvent to water; located where a tie line through the overall composition point intersects the line of constant solvent to water ratio (solvent to water ratio at the plait point).

(b) Direction of mass transfer from toluene to water. In all other tests, direction of mass transfer from water to toluene.

TABLE XIII

Extraction Rates, Compositions, and Overall Mass Transfer Coefficients for the Systems Hexane-Acetone-Water and Toluene-Acetone-Water Tested in a Horizontal Tube Extractor

Test No	Average Rate of Solute Transfer,	Concentrations in Equilibrium with Bulk-Phase Compositions,				Overall Mass Transfer Coefficients	
	N	C_w^*	C_s^*	$(C_w-C_w^*)_{lm}$	$(C_s^*-C_s)_{lm}$	K_w	K_s
	lb/hr	lb/cu ft	lb/cu ft	lb/cu ft	lb/cu ft	ft/hr	ft/hr
System Hexane-Acetone-Water at 27 ± 2 °C							
1	0.1037	0.698	10.296	24.8369	10.1343	0.0042	0.0102
2	0.1311	0.898	10.152	24.4818	10.0200	0.0054	0.0131
3	0.0924	0.800	10.327	24.7496	10.2029	0.0037	0.0091
4	0.1060	2.003	7.478	20.2657	7.1610	0.0052	0.0148
5	0.0922	1.811	7.523	20.4879	4.5419	0.0045	0.0203
6	0.0895	1.898	7.457	20.3384	7.1545	0.0044	0.0125
7	0.0596	1.578	7.531	20.7289	7.2781	0.0029	0.0082
8	0.1035	3.130	7.206	18.7846	6.7215	0.0054	0.0154
9	0.0649	2.872	7.213	19.0486	6.7705	0.0034	0.0096
10	0.0903	3.005	7.092	18.7376	6.6278	0.0048	0.0136
11	0.0925	3.094	7.226	18.8431	6.7507	0.0049	0.0137
12	0.0809	2.370	3.875	14.5245	3.5052	0.0056	0.0231
13	0.0694	2.490	3.870	14.3902	3.4787	0.0048	0.0200
14	0.0973	2.302	3.818	14.5357	3.4617	0.0067	0.0281
15	0.1241	2.305	3.853	15.5609	3.4964	0.0085	0.0355
16	0.0806	3.091	1.910	10.1704	1.4357	0.0080	0.0561
17	0.0983	2.893	1.926	10.4316	1.4907	0.0094	0.0660
18	0.0638	2.894	1.918	10.4043	1.4836	0.0061	0.0430
19	0.0904	2.901	1.908	10.3526	1.4514	0.0087	0.0623
20	0.0395	3.145	1.834	9.9237	1.3450	0.0040	0.0294
21	0.0486	3.220	1.803	9.7252	1.3052	0.0050	0.0372
22	0.0567	3.290	1.835	9.7813	1.3287	0.0058	0.0427
23	0.0349	2.484	1.001	7.3284	0.6090	0.0048	0.0572
24	0.0353	2.691	1.003	7.1336	0.5877	0.0049	0.0600
25	0.0310	2.352	1.004	7.4735	0.6330	0.0042	0.0489
26	0.0458	2.384	0.988	7.3623	0.6090	0.0048	0.0572
System Toluene-Acetone-Water at 27 ± 2 °C							
1	1.3609	12.043	20.697	29.2037	9.0192	0.0466	0.1509
2	1.4600	11.724	21.279	7.4787	9.9454	0.1952	0.1468
3	1.3621	11.893	21.333	7.1300	9.8101	0.1910	0.1389
4	0.8683	7.921	13.631	5.6711	6.8423	0.1531	0.1270
5	0.5967	7.178	13.675	6.4719	7.7724	0.0922	0.0768
6	0.9848	7.436	13.769	5.5103	7.6173	0.1787	0.1293
7	0.3303	4.902	7.671	2.0676	4.3672	0.1597	0.0756
8	0.3193	4.773	7.628	3.9030	4.4589	0.0818	0.0716
9	0.4136	4.884	7.671	3.8114	4.4032	0.1085	0.0939
10	0.2590	4.662	7.594	3.9805	4.5332	0.0651	0.0571
11	0.2458	4.610	7.647	4.0750	4.6636	0.0603	0.0527
12	0.2715	4.604	7.559	4.0265	4.5926	0.0674	0.0591
13	0.1631	5.144	7.019	3.0433	2.7700	0.0536	0.0589
14	0.1370	5.426	7.174	2.8867	3.3675	0.0475	0.0407
15	0.1889	5.366	7.509	3.2151	3.7441	0.0588	0.0505
16	0.1977	5.369	7.723	3.3847	3.9663	0.0584	0.0498
17	0.2225	5.371	7.750	3.3951	3.9859	0.0655	0.0558
18	0.1981	5.369	7.903	3.5361	4.1532	0.0560	0.0477
19	0.2050	5.626	7.924	3.2871	3.8875	0.0624	0.0527
20	0.1767	5.435	7.952	3.5039	4.1353	0.0504	0.0427
21	0.1833	5.368	7.924	3.5688	4.1629	0.0514	0.0440
22	0.2240	0.621	4.005	5.0096	3.7490	0.0446	0.0596
23	0.2430	0.919	4.049	4.7259	3.9620	0.0514	0.0613
24	0.2330	0.526	3.949	5.0494	3.7332	0.0461	0.0624
25	0.0938	1.315	1.527	1.6548	0.9639	0.0567	0.0973
26	0.0845	1.321	1.509	1.6013	0.9440	0.0527	0.0895
27	0.0779	1.297	1.550	1.6853	1.0223	0.0463	0.0762
28 (a)	0.1460	15.231	1.519	12.2951	13.9689	0.0019	0.0011
29 (a)	0.0729	15.025	1.507	12.1126	13.9996	0.0006	0.0005
30	0.2904	5.327	8.633	6.2883	4.8654	0.0462	0.0597
31	0.3056	5.347	9.099	4.4471	5.7060	0.0687	0.0536
32	0.3542	5.456	9.232	4.5607	5.3581	0.0777	0.0661
33	0.3601	5.470	9.339	4.5335	5.4458	0.0794	0.0661
34	0.3108	5.346	8.887	4.3185	5.1052	0.0720	0.0609
35	0.4666	6.104	11.219	5.4197	6.5669	0.0861	0.0711
36	0.3877	6.070	11.089	5.9120	6.5562	0.0656	0.0591
37	0.3075	5.904	10.467	5.0009	6.0564	0.0615	0.0508
38	0.7025	7.473	13.953	6.4208	7.7859	0.1094	0.0902
39	0.6518	7.467	14.184	6.6519	8.0748	0.0980	0.0807
40	0.4690	7.186	13.987	6.7148	8.1542	0.0698	0.0575
41	0.3898	7.104	13.472	6.3604	7.7256	0.0613	0.0505
42	0.4184	8.256	13.951	5.6102	6.7009	0.0746	0.0624
43	0.5664	8.432	14.338	5.7964	6.8668	0.0977	0.0825
44	0.5226	8.413	14.790	6.2541	7.3767	0.0836	0.0709
45	0.4603	8.394	15.024	6.7094	7.6566	0.0686	0.0601
46	0.2559	4.823	8.246	6.2291	5.0370	0.0411	0.0508
47	0.2469	4.820	8.229	4.2344	4.8812	0.0583	0.0506
48	0.2052	4.747	7.704	3.9860	4.5524	0.0515	0.0451
49	0.2410	4.814	8.303	4.3904	5.1102	0.0549	0.0472

(a) Direction of transfer from toluene to water; for all other tests, direction of transfer from water to toluene.

investigation were calculated from the correlations of interfacial tension with acetone concentration presented by Lastovica(57). The values of interfacial tension for each test on hexane-acetone-water and toluene-acetone-water are also presented in Table XII. Changes in composition with time for transfer of acetone from toluene to water for the static system toluene-acetone-water are presented in Table XIV. Plots showing the variation of (K_s) with mass velocity of the water phase for the toluene-acetone-water system, the relation between (K_s) and (K_w) and interfacial tension for both systems, and the concentration changes for the diffusion study are shown in Figures 25 to 28.

Values of Dimensionless Groups. The values of the dimensionless groups used in evaluating the constants of the prediction of the overall mass transfer coefficient are presented in Table XV.

Evaluation of Constants in Prediction Equation. The data from 75 tests on two ternary systems in a horizontal tube at 27 ± 2 °C, and at flow rates varying between 1,000 and 10,000 pounds per hour per square foot for each phase, were used in

TABLE XIV

Change in Composition with Time for the Transfer of Acetone from Toluene to Water Under Static Conditions

Sample No	Time	Concentration of Acetone	
		Water Phase,	Toluene Phase,
	hr	wt %	wt %
initial-10	0	0.00	10.36
1-10	24	2.40	7.20
2-10	48	3.19	6.27
3-10	72	3.59	5.66
initial-30	0	0.00	29.44
1-30	24	7.58	23.04
2-30	48	8.33	20.88
3-30	72	9.44	19.12

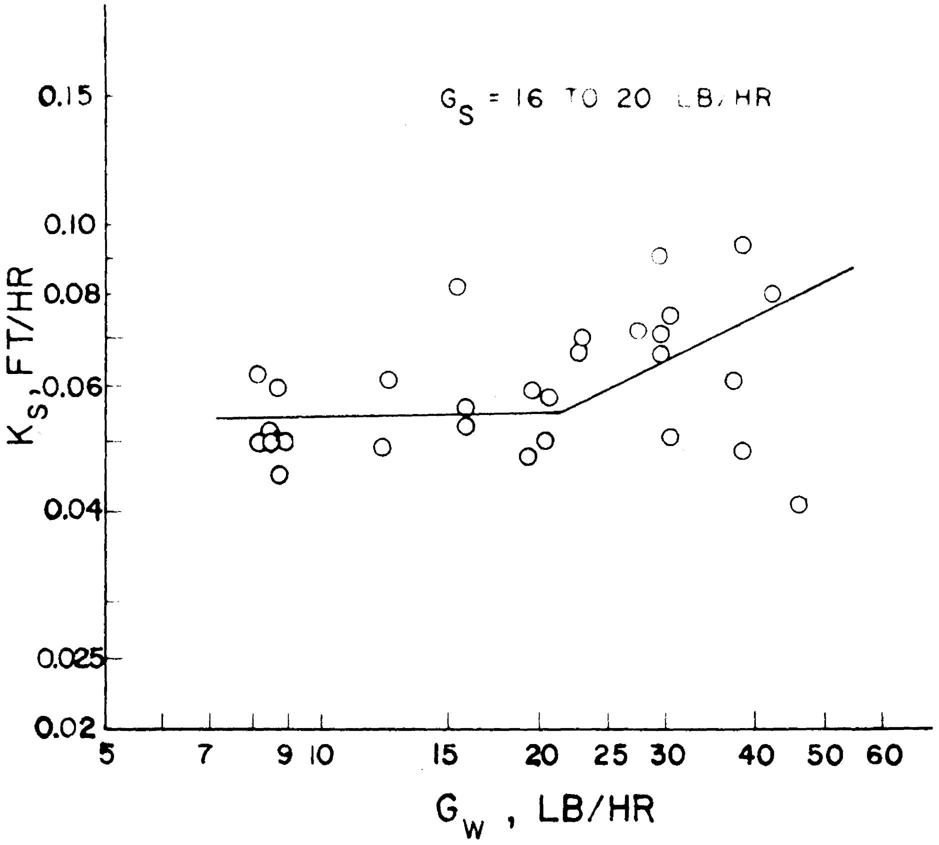


FIGURE 25. VARIATION OF K_S WITH MASS VELOCITY OF WATER PHASE FOR THE SYSTEM TOLUENE-ACETONE-WATER AT 27.0 ± 2.0 °C

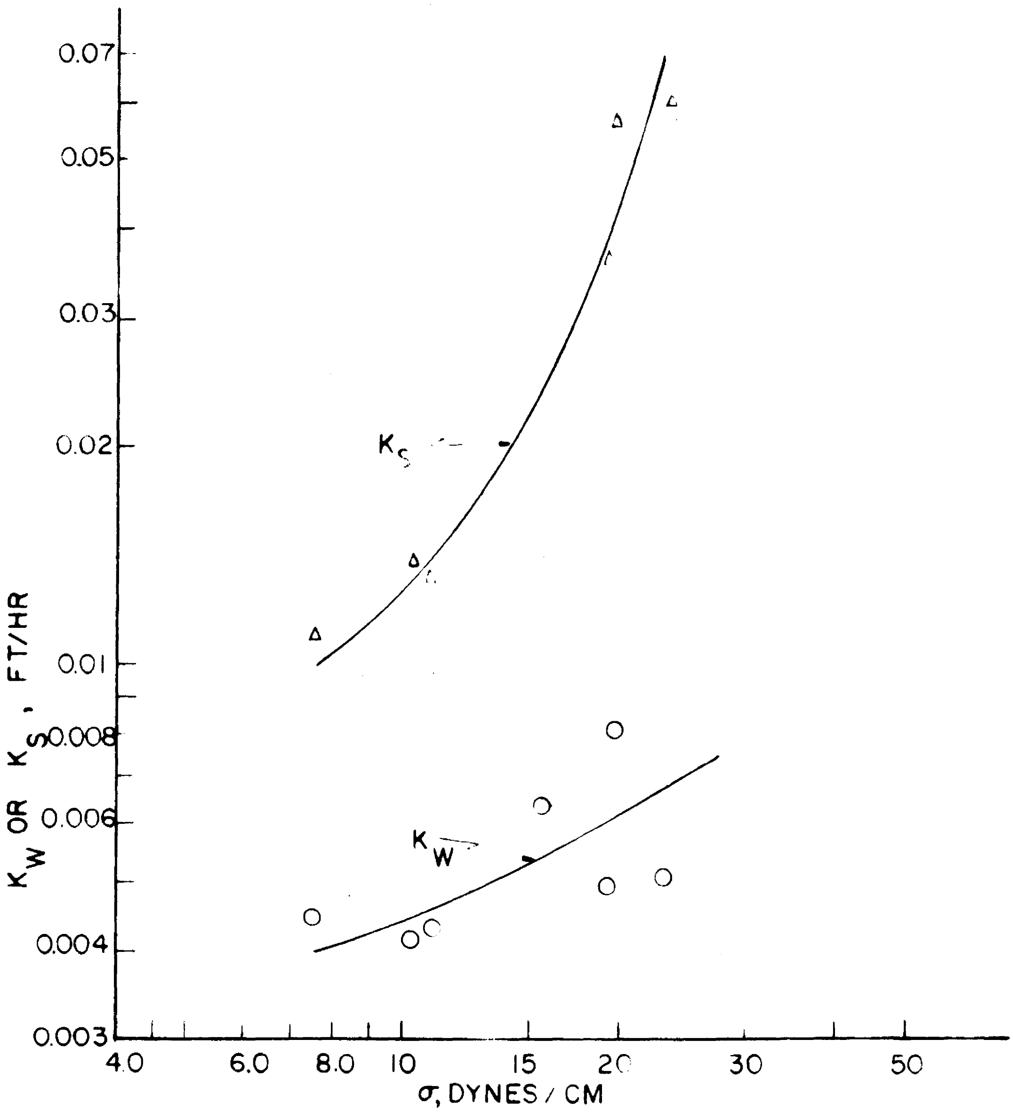


FIGURE 26. RELATION BETWEEN K_W AND K_S AND INTERFACIAL TENSION FOR THE SYSTEM HEXANE-ACETONE-WATER

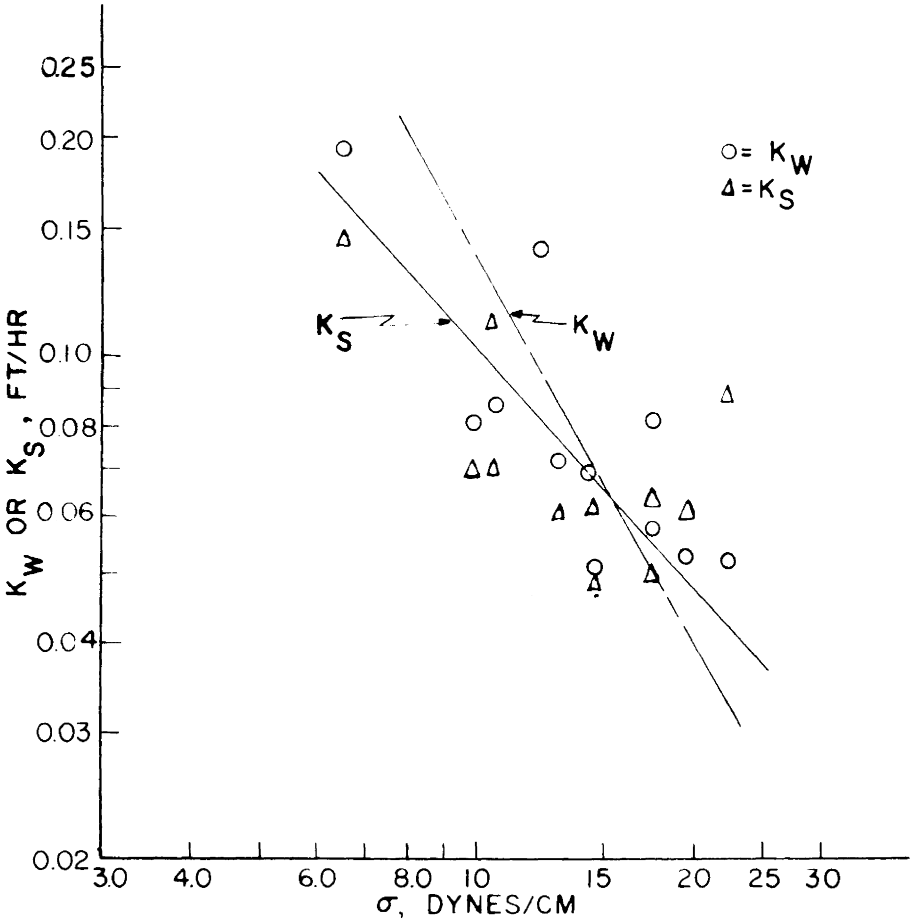


FIGURE 27. RELATION BETWEEN K_W AND K_S AND INTERFACIAL TENSION FOR THE SYSTEM TOLUENE-ACETONE-WATER

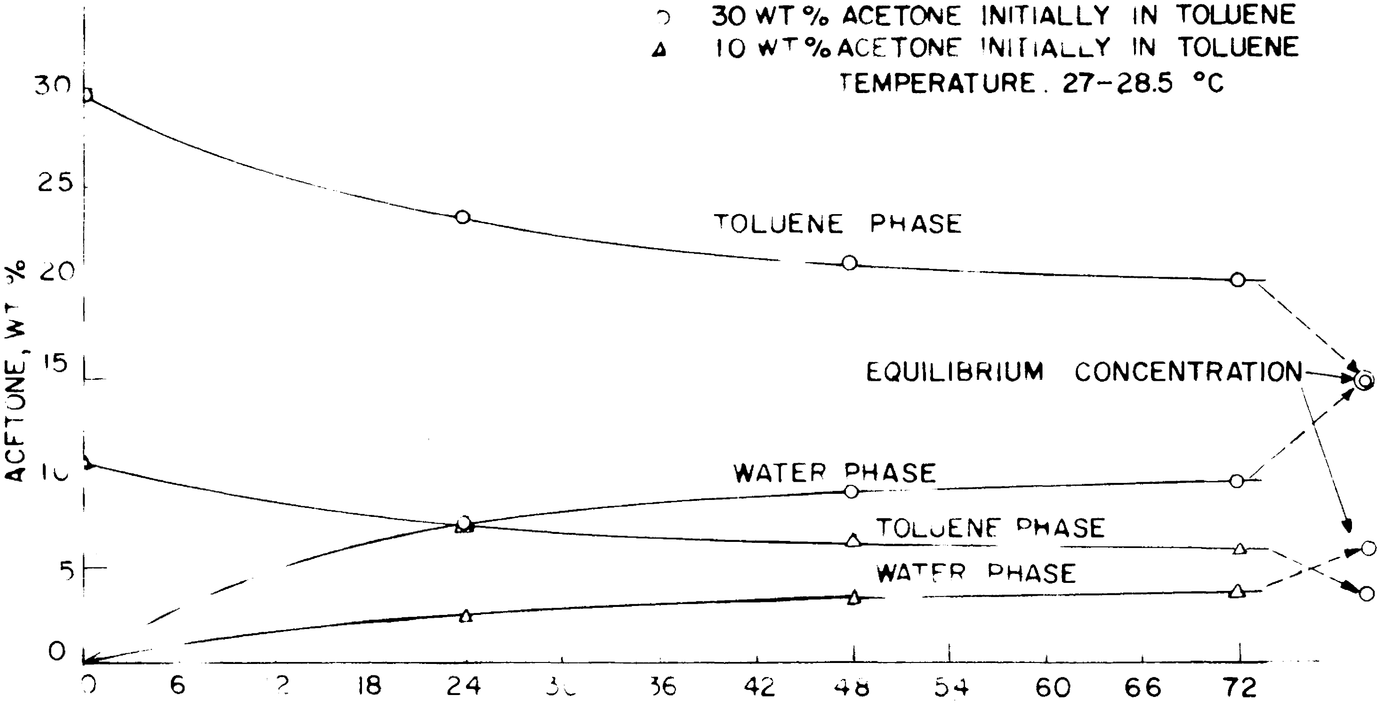


FIGURE 28 CHANGE IN COMPOSITION WITH TIME FOR TRANSFER OF ACETONE FROM TOLUENE TO WATER UNDER STATIC CONDITIONS

TABLE XV

Values of Dimensionless Groups for Evaluating Constants in the Correlation Equation for the Systems Hexane-Acetone-Water and Toluene-Acetone-Water at 27 °C

Test No	$\frac{K_s d}{D_s}$		$\frac{d\sigma}{\mu_s D_s}$		$\frac{\mu_w}{\mu_s}$		$\frac{\mu_s}{\rho_s D_s}$		$\frac{dG_s}{\mu_s}$		$\frac{dG_w}{\mu_w}$	
	Number	Log	Number x 10^8	Log	Number	Log	Number	Log	Number	Log	Number	Log
					System Hexane-Acetone-Water							
1	8.351	0.92174	2.348	8.37070	3.866	0.58726	117.28	2.06930	558.910	2.74733	201.503	2.30428
2	10.674	1.02816	3.051	8.48444	3.863	0.58692	117.25	2.06930	558.910	2.74733	99.581	1.99817
3	7.386	0.86835	1.612	8.20737	3.856	0.58726	117.27	2.06930	418.151	2.62138	256.376	2.40892
4	12.064	1.08135	2.912	8.46419	4.067	0.60927	117.18	2.06893	562.706	2.75028	194.823	2.28959
5	16.565	1.21932	2.813	8.44917	4.061	0.60863	117.20	2.06893	557.096	2.74593	267.027	2.42651
6	10.204	1.00860	3.516	8.54605	4.054	0.60788	117.15	2.06893	567.327	2.75381	119.017	2.07555
7	6.681	0.82484	3.507	8.54494	4.058	0.60831	117.21	2.06893	848.185	2.92850	190.612	2.28012
8	12.559	1.09899	3.119	8.49402	4.080	0.61066	117.11	2.06856	565.182	2.75220	185.437	2.26811
9	7.816	0.89298	3.387	8.52982	4.080	0.61045	117.11	2.06856	561.716	2.74950	140.413	2.14737
10	11.117	1.04610	4.197	8.62294	4.090	0.61162	117.10	2.06856	559.571	2.74788	68.512	1.83575
11	11.183	1.04844	2.871	8.45803	4.074	0.61002	117.10	2.06856	565.842	2.75266	277.746	2.44373
12	18.823	1.27462	4.465	8.64982	4.090	0.61162	117.16	2.06893	562.376	2.75005	199.322	2.29951
13	16.272	1.21139	4.477	8.64099	4.086	0.61130	117.16	2.06893	393.234	2.59461	138.611	2.14176
14	23.563	1.37218	5.112	8.70859	4.080	0.61055	117.16	2.06893	814.521	2.91089	134.911	2.13001
15	28.942	1.46150	5.121	8.70935	4.086	0.61130	117.16	2.06893	1172.112	3.06893	193.942	2.28758
16	45.761	1.65049	5.704	8.75618	3.914	0.59262	117.12	2.06856	562.046	2.74981	204.089	2.30984
17	53.793	1.73070	6.553	8.81644	3.898	0.59084	117.12	2.06856	1155.776	3.06258	140.752	2.14860
18	35.061	1.54481	6.476	8.81131	3.888	0.58973	117.12	2.06856	815.512	2.91142	72.241	1.85879
19	50.765	1.70561	5.626	8.75020	3.911	0.59229	117.12	2.06856	811.221	2.90913	318.282	2.50284
20	23.951	1.37566	5.734	8.75864	3.898	0.58084	117.15	2.06893	564.522	2.75166	205.539	2.31281
21	30.377	1.48259	6.558	8.81677	3.888	0.58973	117.15	2.06893	575.908	2.76035	63.455	1.80250
22	34.814	1.54170	5.481	8.73866	3.898	0.59084	117.15	2.06893	566.337	2.75305	337.907	2.52879
23	46.668	1.66904	7.021	8.84640	3.575	0.55328	117.15	2.06893	560.726	2.74873	226.043	2.35411
24	48.939	1.68966	6.688	8.82530	3.582	0.55413	117.15	2.06893	366.502	2.56407	346.203	2.53933
25	39.870	1.60065	7.113	8.85205	3.585	0.55449	117.15	2.06893	1222.277	3.08707	347.468	2.54096
26	61.119	1.78618	7.975	8.90173	3.562	0.55169	117.15	2.06893	1216.502	3.08529	103.086	2.01326
					System Toluene-Acetone-Water							
1	179.578	2.25431	1.946	8.28914	2.782	0.44436	200.69	2.30233	391.791	2.59306	190.670	2.28035
2	175.212	2.24353	2.061	8.31408	2.785	0.44483	201.69	2.30471	624.324	2.79539	245.912	2.39076
3	165.670	2.21932	2.017	8.30471	2.790	0.44560	201.67	2.30471	485.992	2.68655	241.189	2.38238
4	160.390	2.17725	3.125	8.49485	2.514	0.40037	224.54	2.35122	355.818	2.55121	210.029	2.32222
5	98.028	1.99136	3.119	8.49402	2.489	0.39602	228.68	2.35927	783.305	2.89393	151.423	2.18013
6	164.750	2.21696	3.369	8.52750	2.501	0.39794	227.96	2.35774	773.332	2.88835	289.414	2.46149
7	100.095	2.00004	4.567	8.65963	2.242	0.35064	244.85	2.38899	337.469	2.52827	229.635	2.35097
8	95.082	1.97809	4.656	8.66801	2.231	0.34850	246.24	2.39129	345.093	2.53794	173.192	2.23855
9	124.417	2.09482	4.406	8.64404	2.233	0.34889	245.07	2.38934	341.362	2.53326	287.224	2.45818
10	75.949	1.88053	4.878	8.68824	2.221	0.34655	246.63	2.39199	390.599	2.59173	114.411	2.05843
11	70.175	1.84621	5.022	8.70088	2.225	0.34733	247.62	2.39375	533.347	2.72705	137.991	2.13956
12	78.743	1.89620	5.099	8.70749	2.212	0.34479	247.69	2.39393	616.108	2.78965	140.711	2.14829
13	77.853	1.89126	5.158	8.71248	2.251	0.35238	244.25	2.38792	813.619	2.90041	141.281	2.15014
14	53.547	1.72876	4.388	8.64227	2.276	0.35717	241.83	2.38346	345.949	2.53895	340.839	2.53250
15	66.442	1.82243	5.022	8.70088	2.251	0.35238	242.44	2.38453	343.520	2.53593	61.592	1.78951
16	65.641	1.81717	4.967	8.69609	2.257	0.35353	242.44	2.38453	345.666	2.53870	89.732	1.95294
17	73.468	1.86611	4.915	8.69152	2.259	0.35392	242.07	2.38399	345.949	2.53895	116.081	2.06483
18	62.747	1.79761	4.881	8.68851	2.261	0.35430	242.01	2.38382	343.801	2.53631	140.286	2.14675
19	72.337	1.85938	4.397	8.64316	2.290	0.35984	236.68	2.37420	189.466	2.27761	139.235	2.14364
20	56.188	1.74966	4.502	8.65341	2.270	0.35583	242.10	2.38399	244.579	2.38846	138.884	2.13270
21	58.002	1.76343	4.625	8.66511	2.263	0.35468	242.44	2.38453	297.220	2.47319	140.033	2.14613
22	82.611	1.91703	6.008	8.77873	1.956	0.29137	266.71	2.42602	332.945	2.52231	248.311	2.39498
23	84.611	1.92742	5.687	8.75488	1.970	0.29425	265.18	2.42357	235.191	2.37144	311.585	2.49359
24	86.418	1.93661	6.389	8.80543	1.952	0.29048	266.77	2.42619	458.625	2.66143	191.282	2.28172
25	134.261	2.12808	6.861	8.83639	0.817	0.25935	264.87	2.42308	335.218	2.52530	277.855	2.44389
26	123.277	2.09096	6.851	8.83575	1.819	0.25983	263.60	2.42095	288.867	2.46075	179.768	2.25479
27	105.316	2.02243	6.842	8.85318	1.818	0.25959	270.37	2.43007	400.916	2.60304	311.991	2.49402
28	12.037	1.08063	3.855	8.58602	2.219	0.34616	186.97	2.27161	384.164	2.58456	273.229	2.43648
29	5.986	0.77714	3.831	8.58331	2.219	0.34616	186.98	2.27161	223.684	2.34967	163.090	2.21245
30	78.513	1.89492	4.708	8.67284	2.290	0.35965	242.36	2.38453	277.187	2.44279	63.996	1.80618
31	70.474	1.84800	4.403	8.64375	2.301	0.36173	242.04	2.38382	273.936	2.43759	114.625	2.05919
32	86.889	1.93897	4.305	8.63397	2.312	0.36399	241.58	2.38310	279.177	2.44592	164.245	2.21537
33	86.837	1.93872	4.212	8.62449	2.319	0.36530	240.94	2.38184	277.892	2.44389	214.166	2.21564
34	79.887	1.90249	4.514	8.65456	2.301	0.36192	240.78	2.38166	281.891	2.45010	89.570	1.95216
35	92.339	1.96539	3.735	8.57229	2.400	0.35021	236.42	2.37365	349.627	2.54357	210.735	2.32367
36	76.955	1.88627	3.808	8.58070	2.382	0.37694	237.24	2.37511	356.389	2.55194	136.766	2.13609
37	66.270	1.82132	4.389	8.64237	2.356	0.37218	238.42	2.37731	353.651	2.54864	62.347	1.79477
38	114.973	2.06032	3.172	8.50133	2.499	0.39777	227.51	2.35698	358.728	2.55473	204.642	2.31091
39	102.886	2.01242	3.031	8.48159	2.514	0.40037	227.84	2.35755	361.592	2.55823	290.393	2.46299
40	73.630	1.86705	3.704	8.56867	2.495	0.39707	229.96	2.36154	361.228	2.55775	137.849	2.13956
41	64.744	1.81124	3.264	8.51375	2.494	0.39690	231.06	2.36380	360.319	2.55666	58.294	1.76559
42	78.105	1.89271	3.304	8.51904	2.547	0.40603	220.02	2.34242	319.600	2.50461	106.919	2.02898
43	103.265	2.01410	3.172	8.50133	2.560	0.40807	220.62	2.34361	322.442	2.50840	55.929	1.74765
44	88.791	1.94836	2.867	8.45743	2.572	0.41027	221.03	2.34439	321.306	2.50691	187.166	2.27231
45	75.459	1.87772	2.698	8.43104	2.574	0.41061	220.61	2.34361	320.111	2.50529	256.000	2.40824
46	67.399	1.82860	4.502	8.65341	2.257	0.35353	245.76	2.39058	349.736	2.54370	221.054	2.34459
47	67.109	1.82679	4.625	8.66511	2.245	0.35122	245.77	2.39058	345.982	2.53895	150.985	2.17869
48	59.902	1.77743	4.753	8.67669	2.231	0.34850	246.58	2.39199	346.738	2.53995	64.633	1.81043
49	62.549	1.79623	4.150	8.61805	2.261	0.35430	245.76	2.38058	345.576	2.53857	282.451	2.45102

developing a prediction equation in the following manner. The constant of proportionality, (A), and the exponent on the interfacial tension group, (a), in the equation for the solvent film overall mass transfer coefficient developed from the two-component film coefficient equation of Lastovica(57), were determined by the method listed in Table XVI. The value of the proportionality constant, (A), changed from 2.663×10^{17} to 9.972×10^{20}, and the value of the exponent of the interfacial tension group, (a), changed from -1.0116 to -0.7952. Table XVII shows that using these re-evaluated constants, a very poor correlation resulted. Failure of this equation led to a re-determination of all of the constants in the equation by the method given in Table XVIII.

Table XVI, page 146, contains the calculated values used in the least squares method of calculation. This equation was shown, Table XVII, page 147, to permit a satisfactory degree of prediction of the overall mass transfer coefficients from the physical properties of the systems for the transfer of acetone from water to

TABLE XVI

Evaluation of Constants in the Equation for Correlating the Solvent Phase Overall Mass Transfer Coefficients

Logarithmic Form of Correlation Equation Obtained by Dimensional Analysis [a]

$$\log(K_s d/D_s) = \log A_s + a \log(d\sigma/\mu_s D_s) + b \log(\mu_w/\mu_s) + c \log(\mu_s/\rho_s D_s) + e \log(dG_s/\mu_s) + f \log(dG_w/\mu_w)$$

Equation Written in Abbreviated Form in the Order Given Above

$$Y' = C_o' + aX_1' + bX_2' + cX_3' + eX_4' + fX_5'$$

For simplicity of calculation, the values of the dimensionless groups were adjusted by the following coding scheme:

$$Y = (Y'-0.5);\ X_1 = (X_1'-8);\ X_2 = (X_2');\ X_3 = (X_3'-2);\ X_4 = (X_4'-2);\ X_5 = (X_5'-1.5)$$

Least Squares Equations in Synthetic Form

$N = 75$	$SX_1 = 46.91$	$SX_2 = 33.10$	$SX_3 = 20.02$	$SX_4 = 48.17$	$SX_5 = 53.71$	$SY = 89.52$
	$SX_1^2 = 30.91$	$SX_1X_2 = 20.52$	$SX_1X_3 = 12.55$	$SX_1X_4 = 30.38$	$SX_1X_5 = 33.45$	$SX_1Y = 56.63$
		$SX_2^2 = 15.62$	$SX_2X_3 = 7.59$	$SX_2X_4 = 22.30$	$SX_2X_5 = 23.87$	$SX_2Y = 37.19$
			$SX_3^2 = 6.95$	$SX_3X_4 = 11.55$	$SX_3X_5 = 13.99$	$SX_3Y = 27.02$
				$SX_4^2 = 33.35$	$SX_4X_5 = 34.91$	$SX_4Y = 55.94$
					$SX_5^2 = 42.49$	$SX_5Y = 64.18$
						$SY^2 = 117.84$

The functional relationships with the coefficients as determined by the abbreviated Doolittle reduction of the above matrix

$$Y = -3.0194 + 0.7227X_1 + 4.0592X_2 + 5.4361X_3 + 0.4701X_4 + 0.3027X_5$$

$$C_o = -3.0194$$

Because of coding technique

$$C_o' = 0.5 + C_o - 8a - 2c - 2e - 1.5f$$

$$C_o' = 0.5 - 3.0194 - 5.7816 - 10.8722 - 0.9402 - 0.4541$$

$$C_o' = -20.5674$$

Now, since

$$\log A_s = C_o'$$

$$A_s = 2.708 \times 10^{-21}$$

$$\frac{K_s d}{D_s} = (2.708 \times 10^{-21})\left(\frac{d\sigma}{\mu_s D_s}\right)^{0.7227}\left(\frac{\mu_w}{\mu_s}\right)^{4.0592}\left(\frac{\mu_s}{\rho_s D_s}\right)^{5.4361}\left(\frac{dG_s}{\mu_s}\right)^{0.4701}\left(\frac{dG_w}{\mu_w}\right)^{0.3027}$$

(a) Skrzec, A. E.: Mass-Transfer Studies in Countercurrent Liquid-Liquid Extraction Systems. Unpublished Ph. D. Thesis in Chem. Eng., Library, Va. Poly. Inst., Blacksburg, Va., 1952.

TABLE XVII

Statistical Analysis of Overall Transfer Coefficient Equation

Source of Estimate	dF	SS	V	F-Statistic	Conclusions
For Re-evaluation of Interfacial Tension Exponent and Constant					
Regression	1	10,042	10,042	6.40	Regression variance is highly significant compared to error variance; R = 0.284; 8% of total sum of squares accounted for by regression. F is significant above 3.97 with 95% certainty; not significant above 7.0 with 99% certainty [a].
Residual (error)	73	114,517	1,569		
Total	74	124,559			
For Re-evaluated Equation					
Regression	5	7.5429	1.51	30.816	Regression variance is highly significant compared to error variance; R = 0.828; 67% of total sum of squares accounted for by regression. F is significant above 2.36 with 95% certainty; significant above 3.33 with 99% certainty [a].
Residual (error)	69	3.4488	0.049		
Total	74	10.9917			

SS = sum of squares of the derivations about the experimental mean of the dependent variable

dF = degrees of freedom
R = multiple regression coefficient
V = variance = SS/dF

[a] Davies, O. L.: "Statistical Methods in Research and Production," p. 272. Oliver and Boyd, London, England, 1949. 2 ed.

TABLE XVIII

Abbreviated Doolittle Method for Solving for Six Unknowns in Six Simultaneous Equations

	Column Designation							
Definitions[(a)]	1	2	3	4	5	6	Y	Row Sums
	a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	a_{16}	a_{1y}	S_1
		a_{22}	a_{23}	a_{24}	a_{25}	a_{26}	a_{2y}	S_2
			a_{33}	a_{34}	a_{35}	a_{36}	a_{3y}	S_3
				a_{44}	a_{45}	a_{46}	a_{4y}	S_4
					a_{55}	a_{56}	a_{5y}	S_5
						a_{66}	a_{6y}	S_6
$A_{1j} = a_{1j}$	A_{11}	A_{12}	A_{13}	A_{14}	A_{15}	A_{16}	A_{1y}	S_1
$B_{1j} = A_{1j}/A_{11}$	B_{11}	B_{12}	B_{13}	B_{14}	B_{15}	B_{16}	B_{1y}	S_1/A_{11}
$A_{2j} = a_{2j} - A_{12}B_{1j}$		A_{22}	A_{23}	A_{24}	A_{25}	A_{26}	A_{2y}	S_2
$B_{2j} = A_{2j}/A_{22}$		B_{22}	B_{23}	B_{24}	B_{25}	B_{26}	B_{2y}	S_2/A_{22}
$A_{3j} = a_{3j} - A_{13}B_{1j} - A_{23}B_{2j}$			A_{33}	A_{34}	A_{35}	A_{36}	A_{3y}	S_3
$B_{3j} = A_{3j}/A_{23}$			B_{33}	B_{34}	B_{35}	B_{36}	B_{3y}	S_3/A_{33}
$A_{4j} = a_{4j} - A_{14}B_{1j} - A_{24}B_{2j} - A_{34}B_{3j}$				A_{44}	A_{45}	A_{46}	A_{4y}	S_4
$B_{4j} = A_{4j}/A_{44}$				B_{44}	B_{45}	B_{46}	B_{4y}	S_4/A_{44}
$A_{5j} = a_{5j} - A_{15}B_{1j} - A_{25}B_{2j} - A_{35}B_{3j} - A_{45}B_{4j}$					A_{55}	A_{56}	A_{5y}	S_5
$B_{5j} = A_{5j}/A_{55}$					B_{55}	B_{56}	B_{5y}	S_5/A_{55}
$A_{6j} = a_{6j} - A_{16}B_{1j} - A_{26}B_{2j} - A_{36}B_{3j} - A_{46}B_{4j} - A_{56}B_{5j}$						A_{66}	A_{6y}	S_6
$B_{6j} = A_{6j}/A_{66}$						B_{66}	B_{6y}	S_6/A_{66}

Subscript: (j) refers to column designation

Exponents of Overall Mass Transfer Equation:

$f = B_{6y}$ $e = B_{5y} - fB_{56}$ $c = B_{4y} - eB_{45} - fB_{46}$ $b = B_{3y} - cB_{34} - eB_{35} - fB_{36}$

$a = B_{2y} - bB_{23} - cB_{24} - eB_{25} - fB_{26}$ $A = B_{1y} - aB_{12} - bB_{13} - cB_{14} - eB_{15} - fB_{16}$

The "row sums" column was included as a computational check.

Substitution of the numerical values of the six least-squares equations for the solvent-film coefficient correlation into the tabular scheme above, yielded the following results.

Column Designations							
1	2	3	4	5	6	Y	Row Sums
75	46.91	33.10	20.02	48.17	53.71	89.52	366.43
	30.9123	20.5153	12.5537	30.3832	33.4481	56.6284	184.4410
		15.6204	7.5941	22.3017	23.3743	37.1932	106.5837
			6.9504	11.5486	13.9891	27.0173	59.5054
				33.3537	34.9059	55.9426	124.2022
					42.4847	64.1776	106.6623
75	46.91	33.10	20.02	48.17	53.71	89.52	366.43
1	0.6255	0.4413	0.2669	0.6423	0.7161	1.1936	4.8857
	1.5701	-0.1861	0.0334	0.2529	-0.1442	0.6366	2.1627
	1	-0.1185	0.0213	0.1611	-0.0918	0.4054	1.3775
		0.9913	-1.2363	1.0716	0.1543	-2.2395	-1.2586
		1	-1.2471	1.0810	0.1556	-2.2591	-1.2696
			0.0646	0.0208	-0.1518	0.3150	0.2486
			1	0.3220	-2.3498	4.8762	3.8484
				1.2083	0.3167	0.6638	2.1888
				1	0.2621	0.5494	1.8115
					3.5460	1.0733	4.6193
					1	0.3027	1.3027

Values of Exponents for Re-evaluated Equation

$C_o = -3.0194$ ($C_o' = -20.5674$; $\log A = C_o'$; $A = 2.708 \times 10^{-21}$); $a = +0.7227$

$b = +4.0592$; $c = +5.4361$; $e = +0.4701$; $f = +0.3027$

Values of exponents for re-evaluation of constant of proportionality and interfacial tension group exponent by similar procedure.

Lastovica's Constant and Exponents[(b)]	Re-evaluated
$A = 2.663 \times 10^{17}$	$A = 9.972 \times 10^{20}$
$a = -1.0116$	$a = -0.7952$
$b = -10.0508$	
$c = -4.1715$	
$e = +0.9271$	

(a) Personal Communications, Statistics Department, Va. Poly. Inst., Blacksburg, Va.

(b) Lastovica, J. E.: Correlation of Mass Transfer Coefficients with Physical Variables on Liquid-Liquid Extraction, p. 279a. Unpublished Ph. D. Thesis in Chem. Eng., Library, Va. Poly. Inst., Blacksburg, Va., June 1955.

hexane or toluene. The equation took the following form:

$$\left(\frac{K_s d}{D_s}\right) = 2.078\text{x}10^{-21}\left(\frac{d\sigma}{\mu_s D_s}\right)^{0.7227}\left(\frac{\mu_w}{\mu_s}\right)^{4.0592}\left(\frac{\mu_s}{\rho_s D_s}\right)^{5.4361}\left(\frac{dG_s}{\mu_s}\right)^{0.4701}\left(\frac{dG_w}{\mu_w}\right)^{0.3027}$$

Sample Calculations

A sample of each of the more complex calculations made in this investigation is presented in this section.

Drop Weight-Drop Velocity Calculations. Since the calculations involved in obtaining the results for the drop weight studies were elementary, no detailed procedure was felt necessary. Sufficient information is included in the tables for each test to make them self-explanatory.

Concentration Conversions. Concentrations expressed in weight percentages of acetone were converted to pounds per cubic foot for use in calculating mass transfer coefficients. As an illustration, the inlet concentration in the water stream for test 22, Table XII, page 136, for the system toluene-acetone-water was 9.616 per cent by weight, and 8.836 per cent by weight in the exit stream, for an average value of 9.226 per cent by weight acetone. From Figure 16, page 122, the specific gravity of a 9.226 per cent aqueous solution of acetone has a density of 0.9828 times 62.219, or 61.15 pounds per cubic foot, where 62.219 pounds per cubic foot is the density of pure water at 27 °C. The average composition of the water stream was reported as 61.15 times 9.226, or 5.642 pounds per cubic foot, where 61.15 is the average phase density and 9.226 the average phase composition.

Distribution Coefficients. Distribution coefficients were calculated from tie-line concentration data for the ternary systems studied, Table XI, page 133, as

$$m = \frac{C_w}{C_s}$$

where:

m = distribution coefficient, dimensionless

C_w, C_s = equilibrium concentrations of acetone in the water and solvent layers, respectively, lb/cu ft

$$m = \frac{0.540}{0.960} = 9.900$$

Conversion of Interfacial Tension. The values of the interfacial tensions used in the correlation equation and in evaluating the effect of interfacial tension on mass transfer coefficients were calculated from equations suggested by Lastovica(57). For the hexane-acetone-water system, the variation of interfacial tension with acetone concentration was expressed by

$$\log(\sigma_i) = 1.593 - 0.0276\ C_{pp}$$

and for the toluene-acetone-water system

$$\log(\sigma_i) = 1.434 - 0.0234\ C_{pp}$$

where:

σ_i = interfacial tension, dynes/cm

C_{pp} = overall concentration of toluene at constant, plait-point ratio of solvent to water; located where a tie line through the overall composition point intersects the line of constant solvent to water ratio (solvent to water ratio at the plait point)

The overall composition point for each test was located on the equilibrium diagram by use of the phase flow rates and terminal stream compositions. The intersection of a tie line extrapolated through this point and the line of constant solvent to water ratio gave the value of (C_{pp}). These values are tabulated in Table XII, page 136. For test 1 for the system toluene-acetone-water, (C_{pp}) is 26.80 weight per cent acetone. Therefore,

$$\log(\sigma_i) = 1.434 - 0.0234\ C_{pp}$$

$$\log(\sigma_i) = 1.434 - 0.0234(26.80)$$

$$\log(\sigma_i) = 0.8069$$

$$\sigma_i = 6.32 \text{ dynes/cm}$$

Since interfacial tension values used in the correlation equation were expressed in units of pounds per hour^2, each experimental value expressed in dynes per centimeter was multiplied by the conversion factor, $0.286 \times 10^5, \dfrac{\text{lb/hr}^2}{\text{dynes/cm}}$. Thus

$$6.32 \times 0.286 \times 10^5 = 0.544 \times 10^5 \text{ lb/hr}^2$$

Viscosity Conversions. The experimental values of viscosity were obtained using an ostwald viscosimeter, and are summarized in Table VII, page 119. Effluent times were converted to centipoise and then to pounds per foot, hour, for use in the correlation equation. Thus for sample T-O-W, Table VII, page 119

$$\mu = (\mu_r \times \rho \times t)/(\rho_r \times t_r)$$

where:

μ = viscosity of water saturated with toluene at 27 °C, cp

μ_r = viscosity of pure water at 27 °C

ρ_r = specific gravity of distilled water at 27/27 °C

ρ = specific gravity of water saturated with toluene at 27/27 °C

t_r, t = effluent times for distilled water and of water saturated with toluene, respectively, see

$$\mu = \frac{(0.8545 \times 272.7 \times 0.9963)}{(0.9965 \times 273.4}$$

$$\mu = 0.8521 \text{ cp}$$

Also

$$\mu = 0.8521 \times 2.42 = 2.062 \text{ lb/ft, hr.}$$

Diffusion Coefficients. Diffusion coefficients were determined from the method of Wilke(108). His method utilizes the molal volume of the solute, and a diffusion factor that is peculiar to the solute in question. Using a value of 0.9(108) for the solvent factor, and 74.0 cubic centimeters(57) for the molal volume of acetone, the diffusion factor, (F), was calculated from plots offered by Wilke. The diffusivity was then calculated from the relation

$$D_s = \frac{T}{F \times \mu_s} \times 3.87$$

where:

D_s = diffusivity for acetone in water, sq ft/hr

T = absolute temperature, °K

F = diffusion factor, sec-°K/sq cm-cp

μ_s = viscosity of solution, cp

3.87 = conversion to change (D_s) from sq cm/sec to sq ft/hr

For test 1, Table XII, page 136, for the system toluene-acetone-water,

$$D_s = \frac{300}{2.42 \times 10^7 \times 0.4568} \times 3.87$$

$$= 10.5024 \times 10^{-5} \text{ sq ft/hr}$$

Rate of Solute Transfer. The rate of solute transfer was calculated from the phase flow rates and the change in solute concentration between inlet and outlet streams of the extractor. The amount of solute leaving one phase must equal the amount of solute entering the second phase. In calculating the overall mass transfer coefficients, the average of rates based on the water and solvent phase flow rates was used. For test 22, Table XII, page 136, for the system toluene-acetone-water, the average rate of transfer was calculated as follows:

$$N_w = G_w(C_{inlet} - C_{exit})_w/100$$

$$N_s = G_s(C_{exit} - C_{inlet})_s/100$$

$$N_{avg} = (N_w + N_s)/2$$

where:

N_w, N_s = rate of solute transfer based on the flow rates of the water and solvent phases, respectively, lb/hr

G_w, G_s = weight rate of flow of the water and solvent phases, respectively, lb/hr

C = solute concentration, wt %

$$N_w = 30.7017(9.6164-8.8356)/100 = 0.2397 \text{ lb/hr}$$

$$N_s = 21.0454(0.9854-0.0000)/100 = 0.2073 \text{ lb/hr}$$

$$N_{avg} = (0.2397+0.2073)/2 = 0.2236 \text{ lb/hr}$$

The average transfer rate for each test is listed in Table XIII, page 137.

Calculation of Overall Mass Transfer Coefficients. The calculation of the overall mass transfer coefficients, based on the solvent film, is illustrated for test 22, Table XIII, page 137, for the system toluene-acetone-water. The following equation was used:

$$K_s = \frac{N}{A(C_s^* - C_s)_{lm}}$$

where:

K_s = overall mass transfer coefficient based on the solvent phase, $\frac{\text{lb}}{\text{hr-sq ft-(lb/cu ft)}}$

N = average rate of mass transfer, lb/hr

A = total interfacial contact area, sq ft

$$(C_s^* - C_s)_{lm} = \frac{(C_s^* - C_s)_{inlet} - (C_s^* - C_s)_{exit}}{2.303 \log \frac{(C_s^* - C_s)_{inlet}}{(C_s^* - C_s)_{exit}}}$$

= log mean concentrational driving force, lb/cu ft

Also,

$$C_s^* = C_w/m$$

where:

C_s^* = concentration in the solvent phase that would exist in equilibrium with the concentration in the water phase, lb/cu ft

C_w = concentration in the water phase, lb/cu ft

m = equilibrium distribution coefficient, based on concentrations expressed as lb/cu ft; equal to ratio of solute concentration in the water to the solute concentration in the solvent.

From Figure 24, page 135, (m) corresponding to:

$C_{w\ inlet}$ of 5.8769 lb/cu ft = 1.39; and,

$C_{w\ exit}$ of 5.4063 lb/cu ft = 1.43; therefore

$$C^*_{s\ inlet} = \frac{5.4063}{1.43} = 3.7779 \text{ lb/cu ft}$$

$$C^*_{s\ exit} = \frac{5.8769}{1.39} = 4.23103 \text{ lb/cu ft}$$

From Table XII, page 136,

C_s inlet = 0.0000 lb/cu ft

C_s exit = 0.5266 lb/cu ft

ΔC inlet = $(C_s^* - C_s)$ = (3.7779-0.0000)

= 3.7779 lb/cu ft

ΔC exit = $(C_s^* - C_s)$ = (4.23103-0.5266)

$$(C_s^* - C_s)_{lm} = \frac{3.7779-3.7144}{2.303 \log \dfrac{3.7779}{3.7144}}$$

$$= 3.7490 \text{ lb/cu ft}$$

From Table XII, page 136, N = 0.2236 lb/hr

$$K_s = \frac{0.2236}{1.0(3.7490)}$$

$$= 0.0596 \frac{\text{lb}}{\text{hr-sq ft(lb/cu ft)}}$$

Evaluation of Constants in Correlation Equation for Overall Mass Transfer Coefficient. The constants in the overall mass transfer coefficient equation were calculated from the mass transfer data obtained on the systems hexane-acetone-water and toluene-acetone-water. The procedure for calculating the value of each dimensionless group in the equation for each test is shown for test 22, for toluene-acetone-water.

(1) $$\frac{K_s d}{D_s}$$

where:

K_s = overall mass transfer coefficient based on solvent film, ft/hr

d = inside diameter of horizontal tube extractor, ft

D_s = diffusivity of acetone in toluene, sq ft/hr

$$\frac{K_s d}{D_s} = \frac{0.05963 \times 0.125}{9.023 \times 10^{-5}} = 82.611$$

$$\log \frac{K_s d}{D_s} = \log 82.611 = 1.91703$$

(2) $$\frac{d\sigma}{\mu_s D_s}$$

where:

σ = interfacial tension, lb/hr^2

μ_s = viscosity of solvent phase at concentration in question, lb/ft-hr

$$\frac{d\sigma}{\mu_s D_s} = \frac{0.125 \times 5.5799 \times 10^5}{1.287 \times 9.023 \times 10^{-5}} = 6.008 \times 10^8$$

$$\log \frac{d\sigma}{\mu_s D_s} = \log 6.008 \times 10^8 = 8.77873$$

(3) $$\frac{\mu_w}{\mu_s}$$

where:

μ_w, μ_s = viscosity of water and solvent phases, respectively, lb/ft-hr

$$\frac{\mu_w}{\mu_s} = \frac{2.517}{1.287} = 1.956$$

$$\log \frac{\mu_w}{\mu_s} = \log 1.956 = 0.29137$$

(4) $$\frac{\mu_s}{\rho_s D_s}$$

where:

ρ_s = density of solvent phase, lb/cu ft

$$\frac{\mu_s}{\rho_s D_s} = \frac{1.287}{53.48 \times 9.023 \times 10^{-5}} = 266.71$$

$$\log \frac{\mu_s}{\rho_s D_s} = \log 266.71 = 2.42602$$

(5) $$\frac{dG_s}{\mu_s}$$

where:

G_s = mass velocity of solvent phase, lb/hr-sq ft

$$\frac{dG_s}{\mu_s} = \frac{0.125 \times 3428}{1.287} = 332.945$$

$$\log \frac{dG_s}{\mu_s} = \log 332.945 = 2.52231$$

(6) $\dfrac{dG_w}{\mu_w}$

where:

G_w = mass velocity of water phase, lb/hr-sq ft

$$\frac{dG_w}{\mu_w} = \frac{0.125 \times 5000}{2.517} = 248.311$$

$$\log \frac{dG_w}{\mu_w} = \log 248.311 = 2.39498$$

These values, along with those for the remaining tests, are listed in Table XV, page 144.

A stepwise procedure is presented for evaluating the constants in the correlation equation from the dimensionless group values. The method of least squares was used to combine the data into a set of six simultaneous equations, and the abbreviated Doolittle method(5) was used to solve the matrix.

To simplify the mathematics and manual problems in handling the data on an electrical computating machine, the data were coded according to the scheme listed in Table XVI, page 146, and the logarithms of the groups were abbreviated to (X_1), (X_2), (X_3), (X_4), and (X_5), for the independent variables, and (Y) for the dependent group containing the overall coefficient. The equations were written in tabular form for convenience, and the exponents and constant of proportionality calculated according to the scheme listed in Table XVIII, page 148.

Statistical Analysis of Overall Mass Transfer Coefficient Equation. The results of the statistical analysis of the prediction equation and the re-evaluated binary system equation are presented in Table XVII, page 147. As an illustration, the calculation for the statistical analysis are presented in detail in this section.

The total "sum of squares" of the dependent variable about its mean value was calculated as follows:

$$SS_{total} = S(Y)^2 - (SY)^2/N$$

where:

SS_{total} = sum of squares of dependent variable about mean value

$Y = \left(\frac{K_s d}{D_s}\right)$ = the dependent variable of the equation

N = total number of tests, 75

$$SS_{total} = 117.8428 - 106.8511$$

$$SS_{total} = 10.9917$$

The sum of squares of the contributions of all independent variables about the mean contribution, the sum of squares due to regression, was calculated by the relation,

$$SS_{reg} = A_{1y}B_{1y}+A_{2y}B_{2y}+A_{3y}B_{3y}+A_{4y}B_{4y}+A_{5y}B_{5y}$$

where:

SS_{reg} = sum of squares due to regression

(A_y) and (B_y) are defined in Table XVIII, page 148.

$$SS_{reg} = (0.6366)(0.4054)+(-2.2395)(-2.2591)+ (0.3150)(4.8762)+(0.6638)(0.5494)+ (1.0733)(0.3027)$$

$$SS_{reg} = 7.5429$$

The error sum of squares, or the residual sum of squares, was obtained by subtracting (SS_{reg}) from the total sum of squares, (SS_{total}). Thus,

$$SS_{res} = SS_{total} - SS_{reg}$$

$$SS_{res} = 10.9917 - 7.5429$$

$$SS_{res} = 3.4488$$

Variances based on the regression sum of squares and the residual sum of squares were calculated by dividing the sum of squares by the degrees of freedom, which is the effective number of samples upon which the variances depend. Thus, for the variance due to regression

$$V_{reg} = SS_{reg}/dF$$

where:

V_{reg} = variance due to regression

dF = number of degrees of freedom, here equal to the number of independent variables

$$V_{reg} = \frac{7.5429}{5}$$

$$V_{reg} = 1.51$$

Also, for the variance due to residual error,

$$V_{res} = SS_{res}/dF$$

where:

V_{res} = residual variance

dF = number of degrees of freedom, here equal to number of total tests minus and for the grand mean minus the number of independent variables

$$V_{res} = \frac{3.4488}{69}$$

$$V_{res} = 0.049$$

The F-statistic was used to compare the variance due to regression with the residual variance. Numerically, (F) is equal to the larger variance over the smaller. The hypothesis in the F-test is that the two variances are estimates of the same population. If the F-value is less than that obtained from probability, on some assigned level, the calculated value of (F) is considered insignificant, which means the hypothesis is false within the certainty of the selected probability level.

$$F = V_{reg}/V_{res}$$

where:

F = the F-statistic

V_{reg} = variance due to regression

V_{res} = residual variance

$$F = \frac{1.51}{0.049} = 30.816$$

From tables(5), for 5 and 69 degrees of freedom, the F-statistic is highly significant above 2.36, with 95.0 per cent certainty.

The multiple regression coefficient is a measure of how well the regression equation fits the data. For a perfect correlation, the multiple regression coefficient has a value equal to one. Thus

$$R = (SS_{reg}/SS_{total})^{1/2}$$

where:

R = multiple regression coefficient

$$R = \left(\frac{7.5429}{10.9917}\right)^{0.5}$$

$$R = 0.828$$

IV. DISCUSSION

A discussion of the results obtained in this investigation is presented in this section. It includes a discussion of interfacial level control problems, interfacial tension equilibrium studies, and mass transfer results. The limitations under which the investigation was carried out are enumerated, and recommendations for future studies are included and discussed.

Attempted Automation of Interfacial Level Control

An attempt was made during the modification of the extractor assembly to install an automatic interfacial level control in the system. A control valve was installed in the inlet water line, which was operated by a reversible modutrol motor, actuated by changes in interfacial level within the extraction tube transmitted through a make-or-break probe circuit. Upon contact of the conducting water phase with the probe, the circuit through the motor was closed, resulting in a closure of the valve. When contact was broken between the water phase and probe, the open circuit caused the motor to reverse direction, opening the valve and allowing increased flow into the tube. The characteristics of the valve were such that there was a 60-second delay between full open and full close; it was hoped that, ideally, this delay would be sufficient to permit readjustment of inlet flows to the tube, thereby stabilizing the interfacial level about the probe set point with a minimum of cycling.

Because of the interaction of pressure within the tube, however, this did not occur. Since the pressure under which the water and solvent phases were forced into the extraction tube originated from a common, equal-pressure supply, any change in valve setting of either phase flow rate automatically and instantaneously affected the pressure drop, and hence flow rate, across the other valves. Thus, if adjustments of flow rate were required, it was necessary to adjust the valves simultaneously in order to maintain constant interfacial level within the extraction tube. As the flow control system had provision for only one flow rate adjustment, satisfactory operation was not obtained.

Not only did pressure interaction complicate the control picture, but the response time of the modutrol motor was much too rapid for the low flow rates and holdup of the apparatus. Liquid-level change in response to a change in flow rates was extremely slow; although the pressure drop responses across each inlet valve for even a slight change in setting of the other was immediate. The time for the change in liquid level to become noticeable was, of course, dependent on the magnitude of the original upset in pressure, and the flow rates during the time of upset.

Because of these difficulties, automatic control of interfacial level was then abandoned for the remainder of tests on the extractor. By this time, however, considerable experience had been gained in observing operational characteristics of the horizontal tube, and it was found that with the new needle valves in the flow lines, the more accurate liquid flowrators, and the central grouping of the control valves, excellent control of the interfacial level was possible through manual adjustment and regulation of flow rates. So sensitive was pressure and flow rate adjustment for each combination of flow rates, that it was possible to quickly and easily balance inlet and outlet pressures, and stabilize flow rates and interfacial level. Usually, steady-state flow conditions could be established within ten minutes of original attempts, and thereafter only periodic, minor adjustments were necessary to maintain interfacial level to within a maximum deviation of ± 0.15 centimeter from the center of the extraction tube. This deviation corresponds to an approximate error in interfacial area of 3 per cent.

It is obvious, however, that if manual control of the interfacial level is possible, a control system could be designed to do the job better. From observations and experience gained through operation of the horizontal tube, this design would be a difficult one to devise. Severe complications arise in setting up a mathematical analysis of the system, because of the tremendous high gain and interaction of pressure, and the extremely slow response of liquid level change to flow rate adjustment. Such an analysis is felt to be essential if even an approximate knowledge of response characteristics is desired. Such necessary assumptions as linearity of control valve performance with flow rate, which breaks down especially at low flow rates, would lead to mathematical simplifications that ultimately reduce to response rates and time constants for the system. Because of these assumptions, however, the results would give a very unrealistic picture of actual response mechanisms. Since adequate interfacial level control is now possible with a minimum of effort, the only thing to be gained would be increased ease of operation, without significantly decreasing interfacial level fluctuations.

Interfacial Tension Equilibrium Studies

Results of the interfacial tension equilibrium studies, conducted with the modified drop weight method, are discussed in this section.

Static Versus Dynamic Interfacial Tension Measurement.

Until recently(80), the effect of interfacial tension as a physical variable on the rate of mass transfer was not considered by most investigators interested in predicting transfer coefficients from physical properties of the systems studied. As the importance of interfacial tension slowly became known, it was included definitely as a physical property effect, but its measurement was conducted on the systems under investigation by accepted standard procedures(39) involving static determinations which were wholly divorced from the dynamic conditions actually existing between the phases in contact in the extraction columns.

During the more extensive investigations of interfacial tension phenomena that evolved out of the need to understand the relations existing between surface energies and colloidal properties, it was learned that certain high molecular weight compounds, primarily surface active agents, when dissolved in a liquid system of two immiscible phases, created transient interfacial equilibrium conditions. Varying lengths of time were required for the interfacial tension between the two phases to reach a constant value, either higher or lower than the value obtained after equilibrium was reached. The limitations of investigation of interfacial tension-time effects have thus far been centered around experimental equipment. Since the equilibrium times for most of the studies reported have been on the order of from a few hours to several days, the static methods of measurement can be used, since the time required to make an interfacial tension determination by these methods is negligible when compared to the total equilibrium time. As a result of these experimental limitations, relatively little information has been reported on time effects for low molecular weight solutes. From this information, it has been concluded that for the most part, these compounds would exhibit negligible time effects.

Ternary extraction studies, involving transfer of solute between two immiscible phases, have followed the philosophy of these conclusions, assuming that interfacial tension-time effects were negligible compared to time of contact of the phases, and have proceeded to report interfacial tension values obtained through static measurements. An attempt was made in this investigation to determine whether or not the systems used obeyed the assumptions of negligible interfacial equilibrium time effects. Since the primary interest was not to measure such time dependency, but to learn whether or not the systems used exhibited such behavior, the use of prohibitively expensive and elaborate custom made equipment and timing mechanisms to secure such actual measurements was not required. What was desired was a quick and fairly simple test that would be theoretically sound and yet indicate time dependency of interfacial tension if present in the systems studied. Since no direct measurements were sought, qualitative methods would suffice.

In attempting to devise such a method, the more common techniques for interfacial tension measurement, such as bubble point, pendant drop, capillary rise, ring tensiometer, and drop weight were considered. All but the latter of these were rejected on the basis that none could be adapted for extremely short time effect determinations, because of the inherent limitations in each method. The drop weight method appeared as the logical choice, since this method allowed the formation of a completely new surface with each drop, and had the additional advantage of presenting an easy way to vary rate of formation of the drops.

Modification of the Drop Weight Method. In attempting to extend the drop weight method to dynamic equilibrium studies, consideration had to be given to limitations involved. The largest and most serious of these limitations which was imposed in static measurements was the necessary use of a correction factor to account for the non-sphericity of the drops as they fall from the dropping tip. The correction factors were evaluated under equilibrium conditions; that is, for each dropping tip, the liquid being used in the correction factor determination was allowed to form and drop from the tip well within the recommended static drop rate. This procedure resulted in a correction factor that was a function of tip radius only, independent of material and system. Since any rate study would involve drop formations at a rate exceeding those for equilibrium conditions, the subsequent use of these correction factors would be meaningless. Any attempt to determine new correction factors for use with dynamic methods in order to calculate actual values of interfacial tension would be impossible. The correction factor under dynamic conditions might be a complicated function of many variables, including drop rate as well as tip radius. Results obtained with the dynamic method, then, must be of a qualitative nature only, indicating time dependency, without providing an accurate value of the interfacial tension at a given time.

On the basis of a consideration of the forces acting on a drop at the instant of detachment from a dropping tip, an equation was derived expressing the relationship between drop velocity and drop weight.

The forces acting on a drop falling from a tip at the instant of detachment are composed of (1) the force due to gravitational acceleration, (mg), and (2) the force resulting from the change in momentum of the fluid particles flowing from the capillary tube into the drop, ($A\rho v^2$). The sum of these forces is counterbalanced at the instant of drop detachment by the interfacial tension, $2\pi r\sigma\phi$, acting at the circumference of the tip. This is the contact point of the tip and the two immiscible liquid phases. Summing and equating forces:

$$2\pi r\sigma\phi = mg + A\rho v^2 \quad (34)$$

$$mg = 2\pi r\sigma\phi - A\rho v^2 \quad (35)$$

$$m = \frac{2\pi r\sigma\phi}{g} - \frac{A\ v^2}{g} \quad (36)$$

where:

σ = interfacial tension, dynes/cm

m = mass of drop, gm

2, π = constants

r = radius of dropping tip, cm

g = gravitational acceleration, cm/sec^2

A = cross sectional area of capillary, sq cm

ρ = density of fluid in capillary, gm/cu cm

v = linear velocity of fluid in capillary, cm/sec

ϕ = correction factor for non-ideality of drop detachment from tip.

Since the linear velocity of fluid in the capillary is directly proportional to the rate of drop formation, no discrepancy or loss of continuity is experienced by using drop velocity instead of linear velocity in expressing the final results. By assuming a constant correction factor for each system, a plot of (m) versus (v^2) should be a straight line with a constant slope and intercept, provided interfacial tension can adjust itself sufficiently rapidly for the rate of drop formation. The assumption of a constant correction factor would appear perhaps a gross oversimplification of a complicated process, since, intuitively, one would expect the fraction of a drop that detached from the tip to be dependent somewhat on drop rate. Recognizing the limitations this assumption then places on the method, and having no way of evaluating the magnitude of the change in the correction factor, the following experimental results are presented as only of qualitative value.

Drop Weight-Drop Velocity Results. An inspection of Figures 7 through 13, pages 110 through 116, indicates that the results obtained agree very well with those anticipated from Equation 36, page 180. The system toluene-ten weight per cent acetone-water was the first one investigated, and the constant intercept of the curve indicates the interfacial tension remained essentially constant over the drop velocities studied. In each test, the limiting velocity was that at which the heavier phase falling from the dropping tip ceased to form individual drops, and streamed from the tip in a continuous thin filament of liquid. The curve through the points in Figure 12, page 115, was determined by first dividing the data into two groups, one consisting of those above and one of those below 10 drops per minute, and determining, by the least squares method, the line for each group. The two straight lines thus obtained were then statistically tested and no significant difference was found. Accordingly, the least squares line for the entire group of data was then determined, and this is the line shown in Figure 12.

To show that the method used here would indicate a time-dependent interfacial tension as a curve, two systems known to have time dependent interfacial tension values(62,77) were then tested using the same procedure and apparatus. The drop velocity-drop weight results for the systems benzene-1.025 weight per cent arabic acid-water are shown in Figure 8, page 111, and for cyclohexane-2.785 weight per cent arabic acid-water in Figure 11, page 114. A comparison of these curves with the results obtained for the toluene system, Figure 12, page 115, very clearly indicates the differences of behavior between systems with and without time dependent interfacial tension phenomena. Using the results for the cyclohexane system, Figure 11, as an example, the shape of the curves for these time dependent systems is explained as follows: Up to a drop velocity of approximately 10 to 12 drops per minute, the relationship between drop weight and drop velocity is the same as that indicated by Equation 36, page 180. As the rate of drop formation increases, the molecules of arabic acid do not have sufficient time to orient themselves in the interfacial layer, with the result that interfacial energies are higher than if equilibrium conditions were present. At these higher drop velocities, the transient effects cause a non-linear relationship between drop velocities of 12 and 18 drops per minute. Tangents drawn to the curve between these velocity limits would intersect the drop weight axis at higher values than the equilibrium drop weight, indicating that the value of the interfacial tension is greater than that between liquids at equilibrium. The slope of the curve is constant between drop velocities of 18 to 22 drops per minute. At rates above 22 drops per minute, the curve exhibits another point of inflection, and the drop weight approaches a constant value at the streaming velocity. This last inflection point is attributed to a nozzle effect which causes complications in the drop weight-drop velocity relationship. The velocities at this extreme end of the curve are approaching the "streaming" velocity; that is, the velocity at which the liquid no longer forms separate drops before being forced from the dropping tip. It is logical to assume that at these extreme velocities, the drop weight-drop velocity relationship would not obey the simple fundtion derived above.

The same comments also explain the relationship obtained for the benzene-1.025 weight per cent arabic acid-water system, and the toluene-2.785 weight per cent arabic acid-water system, Figures 8 and 13, pages 111 and 116. Although the equilibrium times for the benzene and cyclohexane systems were quite different, one and one-half days, and one minute, respectively, a comparison of Figures 8, 11, and 13, pages 111, 114, and 116, shows that the same defining characteristics were present for all three time dependent systems. Each curve shows an initial range of velocities in which the drop weigh remains essentially a linear function of drop velocity, a second velocity range in which the relationship is a polynomial function, indicating changing interfacial tension phenomena and transient interfacial conditions, a central velocity range in which the relationship between drop weight and drop velocity is again essentially linear, and finally, a second point of inflection after which the drop weight approaches a constant value up to the streaming velocity. Although the equilibrium time has not been determined for the system toluene-arabic acid-water, the results obtained in this investigation indicate a time dependent interfacial tension, as would be expected from the behavior of the benzene system.

The systems benzene-2 weight per cent acetone-water, and cyclohexane-water with 2 and 10 weight per cent acetone were also investigated; Figures 7, 9, and 10, pages 110, 112, and 113, show the drop weight-drop velocity relationship for these systems. A comparison of the above figures indicates that all systems apparently followed the relationship of Equation 36, page 180, indicating, as was the case with toluene-10 weight per cent acetone-water, that interfacial tension adjustment was practically instantaneous.

Two different concentrations of acetone were used with the cyclohexane-water system in an attempt to obtain an indication of the effect of interfacial tension on the onset of velocity disturbances as the critical streaming velocity was approached. The onset of the disturbances causing departure from the linear drop weight-drop velocity relationship occurred at a velocity which was approximately 80 per cent of the streaming velocity in the case of the 2 weight per cent acetone test, and at approximately 87 per cent of the streaming velocity for the test of the solution containing 10 weight per cent acetone. It would appear, then, that since the same dropping tip was used for both studies, the interfacial tension between the liquids influences to some extent the onset of these disturbances. The nature of this influence, which may be, in part, because of the smaller resulting drop sizes for the lower interfacial tension, is not exactly known.

The results for the benzene-acetone-water system, Figure 7, page 110, show rather large average drop weight values, 0.1 of a gram compared to 0.05 of a gram for the cyclohexane system, indicative of high interfacial tension. For this system, the departure from Equation 36, page 180, occurs very abruptly at a velocity approximately 75 per cent of the streaming velocity. This is a value somewhat smaller than the 80 and 87 per cent obtained for the cyclohexane systems. The large drop weight and earlier departure of the drop weight-drop velocity relationship from linearity would again indicate the influence of interfacial tension on flow characteristics near the critical streaming velocity. The reason for the sharp break in Figure 7 is not completely understood. It is possible that in high interfacial tension, non-time-dependent systems, such as this one, the disturbances are much more pronounced, and result in more severe departures from Equation 36.

Comparison of Results with Other Investigations. Harkins and Brown(41), in standardizing the drop weight method, made only a few tests to indicate the effect of velocity, per se, on drop weight. These results are shown in Table I, page 20. It will be noticed from an examination of this table that the larger drop weights occurred at the higher drop velocities. In explaining these variations in drop weight, the authors postulated that when the rate of drop formation exceeded three drops per minute, some of the liquid streaming from the drop weight apparatus forced its way into the falling drop at time of detachment. Thus, a drop formed rapidly was heavier than a drop formed slowly. The claim was then made that when the rate of drop formation was reduced below that given in the table, the drop weight increased considerably over those values shown, although no data were included to substantiate this claim. The two conclusions seem to be contradictive, since in one instance they indicate an increase in drop weight with an increase in drop velocity, and in the other, an increase in drop weight with a decrease in drop velocity. The latter result is the one indicated by the results of this investigation. It is possible that Harkins and Brown(41) did not investigate these variations sufficiently to enable them to detect any significant trends. If the variation in drop weight of the last five determinations is attributed to experimental error, as suggested by the authors, then it is doubtful whether much significance can be placed in the variation of the drop weights for the first three runs, either. The maximum drop weight that was obtained, for the first test, showed a deviation from the mean drop weight for all the tests, of only 0.18 per cent. This deviation was of the same order of magnitude as was the experimental error, and thus indicates that the conclusions based on this one study are open to question.

The results of this investigation agree in principle with those reported by Addison(9); that is, solutes of smaller molecular weight in ternary systems have an interfactial tension that is essentially independent of time. The time required for solute orientation in the interfacial boundary increases with molecular weight, becoming appreciable with very large molecular weight compounds.

The results of the investigation by Christiansen and Hixon(9) on the influence of interfacial tension jet breakup in liquid-liquid systems show somewhat anomalous results. The effective interfacial tension values calculated by them from theoretical relationships derived from fluid dynamics principles were higher for the high molecular weight solutes, such as the surface active agents, than the interfacial tension measured under equilibrium conditions, which is in agreement with other findings(2,50,77,83). For the low molecular weight solutes, such as n-butyl alcohol, they found that the calculated "effective" interfacial tension was lower than the equilibrium interfacial tension value. Such behavior cannot be explained by classical liquid theory. Addison(9), also using n-butyl alcohol in his investigation, found that the equilibrium time was extremely short, approximately 0.01 second, but the initial interfacial tension was higher than the equilibrium value, as would be expected.

Extraction Studies

The results of the extraction tests are discussed in this section. Effects of such variables as phase flow rates, interfacial tension, direction of mass transfer, and correlation of overall mass transfer coefficients with physical variables are included.

Variation of Transfer Coefficients with Phase Velocities. The major portion of the basic data which has been reported on liquid-liquid extraction equipment has been concerned with the performance of small-scale experimental units with particular emphasis being placed upon the effects of the operational parameters; that is, phase flow rates on the mass transfer coefficients. Performance data have been reported for such equipment as packed towers(11,12,32), spray columns(28,30,31), and wetted-wall columns(12,67,101), but because of difficulties in separating effects of velocity on both area and overall coefficients, and restriction to a narrow range of flow rates, agreement between correlations relating these effects has been poor.

In an effort to obtain more reliable data on the effect of velocity on transfer coefficients, for a known interfacial area, Bergelin, Lockhart, and Brown(6) studied the transfer of isopropyl alcohol from tetrachloroethylene to water in a two-inch diameter, 10-foot long horizontal tube extractor. They were able to evaluate the interfacial area, and vary the velocities of both countercurrently-flowing phases over wide ranges; the water phase velocity was varied between 5,000 and 85,000 pounds per hour per square foot while the tetrachloroethylene phase was held constant either at 17,500, 35,000, or 50,000 pounds per hour per square foot. The same concentration of alcohol in tetrachloroethylene was used in each test, so any variations in the overall transfer coefficients would be caused by effects of flow rates. Plots of the overall mass transfer coefficients based on the solvent phase, (K_t), versus the mass velocity of the water phase exhibited a minimum, while a point of inflection was observed in plots of (K_t) versus the tetrachloroethylene phase velocity.

Their explanation of these phenomena was based on the movement of the so-called "plane of zero velocity" from one phase, through the interface, into the other phase. When the mass velocities of the two phases are equal in magnitude, "the velocity at the interface is either zero or at a minimum value"(16). When the mass velocities of the two phases are not equal in magnitude, the interface moves with the faster phase, and the greater the difference in magnitude of the two phase's flow rates, the faster the interface will be dragged along. Under any set conditions of phase flow rates, there will be some point, in either phase or at the interface, in which the velocity will be zero. This is called the plane of zero velocity. Displacement of this plane into either phase by differences in flow rates results in increased turbulence at the interface, thereby increasing the rate of mass transfer. Lastovica(57) confirmed these results in similar studies using dye injections to show not only displacement of the zero velocity plane, but also an actual reversal when the differences in flow rates were appreciable.

Skrzec(80) measured the transfer of acetic acid from methyl ethyl ketone, butanol, and cyclohexanol to water using a 1-1/2 inch diameter, eight-foot long horizontal tube extractor. In one series of tests, the water phase flow rates were varied between 1,000 to 15,000 pounds per hour per square foot, and solvent phase flow rates were held constant at approximately 5,000 or 10,000 pounds per hour per square foot. In a second series of tests, the solvent phase flow rates were varied between 1,000 to 15,000 pounds per hour per square foot, and the water phase kept constant at 5,000 or 8,000 pounds per hour per square foot. Plots of these data showed the following interesting results.

In the first series of tests, with the solvent phase flow rates constant at 5,000 or 10,000 pounds per hour per square foot, the plots showed that (K_s) gradually increased with water phase flow rates up to 10,000 to 12,000, when a sharp increase occurred. No minima were observed, which was in conflict with the results of Bergelin, Lockhart, and Brown(6). A second series of plots showing the variation of (K_s) with solvent phase flow rates, at constant water phase rates of approximately 5,000 and 8,000 pounds per hour per square foot, exhibited a minimum value of (K_s) at approximately equal mass velocities in all cases. This, also, was in conflict with the results of Bergelin, Lockhart, and Brown. The minimum was more pronounced in the cyclohexanol-acetic acid-water system, than in the butanol- or methyl ethyl ketone-acetic acid-water systems. These minima did not consistently occur at equal mass velocities. Since the direction of transfer and concentration of material was the same for each investigation, it is curious to note that plots of (K_s) versus (G_w) or (G_s) for both investigations showed exactly opposite results.

Acetone was transferred from water to hexane and toluene, in this investigation, using a 1-1/2 inch diameter, 8-foot long horizontal tube extractor, and effects were made to correlate (K_s) with (G_w) and (G_s), but were unsuccessful. No realistic or consistent relationship resulted from these plots. A log-log plot of (K_s) versus (G_w) at constant (G_s) was then tried for the system toluene-acetone-water, and the resulting correlation is shown in Figure 25, page 140. The break in the curve occurs at approximately equal mass velocities, since the solvent phase flow rate was held constant at 3,300 pounds per hour per square foot. A possible explanation for the failure of the overall coefficient to correlate any better than it did with the phase flow rates was the fact that flow rate variation might not have been sufficient to show significant trends. The water phase flow rate was varied from 1,300 to approximately 8,000 pounds per hour per square foot, while the solvent phase flow rate was held constant at 3,300 pounds per hour per square foot. This range was considerably smaller than the range used by Bergelin, Lockhart, and Brown(6), or Skrzec(80).

It might be mentioned here that Bergelin, Lockhart, and Brown(6) passed over the use of mass velocities as a basis of comparing the various positions of the plane of zero velocity in the extractor without any discussion. In explaining the transfer coefficient variation with water phase velocity, they treat the plane of zero velocity as a definite plane of zero velocity in the extraction tube, the position of which is only a function of the relative velocities of the two phases moving in countercurrent direction to one another. Since the mass velocity is simple the weight rate of flow divided by the cross sectional area of the phase, it seems that even as a crude first approximation, the linear velocities of the respective phases would be a better comparison than mass velocities. It is obvious that, because of differences in density of the two phases, the mass velocity and linear velocity would not be the same. However, the latter quantity, from just a velocity consideration, would seem to be a better basis for comparison than mass velocity, since at least with equal and opposite linear velocities, the velocity effects would tend to cancel. In systems where the difference in densities of the two phases are not appreciable, this factor would not be as important. A much more realistic basis might be achieved if a quantity such as kinetic flow, or momentum were used. To evaluate these, however, some knowledge will have to be gained concerning the velocity profiles existing throughout the two immiscible phases flowing countercurrently in a horizontal tube. Some work on co-current flow has been previously reported(71), which might serve as a starting point.

Effect of Interfacial Tension on Overall Mass Transfer Coefficients. In most work reported(10,29, 30,38,50), the method used to vary the interfacial tension has involved the addition of surface active agents to a ternary extraction system. The amount of agent added has generally been small, and as such has probably affected the physical properties of the system, excluding interfacial tension, very little. Since such agents have a lower surface energy in water than in the solvent of the systems in which they are used, they accumulate at the water-side interface. This concentration in the interfacial films, where the major resistance to mass transfer exists, may be high, resulting in a quatenary extraction system at the interface. The results obtained in these investigations have been anomalous, with the result that many different conclusions concerning the mechanism of interfacial tension lowering by these solutes have been offered. Often, the same mechanism has been used to explain entirely divergent results.

Three main factors thus far have been prevalent in limiting the conclusions drawn from results obtained with use of these commercial wetting agents. First, such agents may contain substantial quantities of inorganic compounds added to improve solution and, thus, may vary widely in composition and nature. It is possible that these differences are due to the nature of the systems used with the solutes, as well as the solute itself. Second, the ionic properties of the molecules are mostly unknown, isomers are present, and wide ranges of molecular weights are common. Instead, then, of having a quatenary system, and attempting to predict results on the assumption of a ternary system, the picture is considerably more complicated. In fact, no firmly based conclusions can be drawn with regard to the nature of this effect. Third, and perhaps most important, the use of the two film theory to interpret the results is not adequate in view of the presence of these solute molecules at the interface.

Even if increased transfer rates are the ultimate result, the interfacial picture under these conditions is not one of simple equilibrium and no resistance, as postulated by the above theory. There is still considerable need to discriminate between a change in interfacial properties produced by the presence of the solute undergoing transfer, and that resulting from the addition of specifically surface active agents. The former is the more desirable in attempting to evaluate the nature of the effect of interfacial tension on mass transfer.

An attempt was made in this investigation to study the effect of interfacial tension on the overall mass transfer coefficient for ternary systems by varying the concentration of the solute being transferred from one phase to the other. It was recognized that this method is not ideal, either, because again variation in interfacial tension is being accomplished by changing the concentration of acetone. Although not the ideal method, it is considered to be at least a one step improvement over the use of surface active agents, since no material is introduced that is foreign to the ternary system.

Unfortunately, variation in acetone concentration also brings about variation in other physical properties of the systems, besides just interfacial tension. Among these are density, viscosity, and diffusivity. To study the effect of interfacial tension on mass transfer rates, these other variables also had to be included. To accomplish this, the overall mass transfer coefficients were related to the physical properties of the systems by means of dimensional analysis. The equation derived and the function evaluated from the data taken during experiments with the systems toluene-acetone-water and hexane-acetone-water is shown in Table XVI, page 146.

In this equation, since the value of the interfacial tension (σ) appears in only one of the dimensionless groups, the exponent of that group, 0.7227, indicates the effect which interfacial tension had on the value of the transfer coefficient. Unfortunately, there are equations for ternary systems reported in the literature where interfacial tension was a variable, so comparison of this coefficient with other results it not possible. Lastovica(57) and Skrzec(80) found the exponent on the interfacial tension group for their individual film coefficient correlation (k_s) with physical properties of the system to be -1.0116.

A log-log plot of the overall transfer coefficient (K_s) versus the interfacial tension, (σ), at constant solvent and water velocities, is shown for the system hexane-acetone-water in Figure 26, page 141, and toluene-acetone-water in Figure 27, page 142. The correlation for the toluene system indicates a decreasing value of (K_s) for increasing (σ); however, the data are considerably scattered, and the least squares equations through the points indicate the general trend only. This scatter of data may result from changes in other variables, as well as experimental error. For the hexane system, on the other hand, the plot shows an increasing value of (K_s) for an increase in (σ). Obviously, the latter effect is more pronounced, since the interfacial tension exponent is a positive value. The curved lines drawn through the points are probably not justified, on the basis of experimental accuracy, since the correlation equation represents the best average net effect as a straight line with a positive slope of 0.7227. The lines are merely included as a general indication of variation.

Since the two ternary systems used were not overly different in physical properties, the reason for the apparent discrepancy between the effects of interfacial tension on transfer coefficients for the two systems is not understood. It is possible that interaction between the other physical variables and interfacial tension might account for part of the anomalous results but, of course, this assumption will have to be substantiated by additional experimental work.

Effect of Direction of Transfer. Considerable data have been reported in the literature(28,58,96) on the variation of direction of solute transfer between immiscible phases in ternary extraction systems. For the most part, this experimental work has been confined to spray towers, with some general disagreement as to the best transfer direction; dispersed phase to continuous phase, or vice versa. Results on this point are still rather inconclusive. It has been suggested(58) that direction of transfer is quite specific, depending not only on the equipment, but also on the nature of the solute and solvents.

An attempt was made in this investigation to vary the direction of acetone transfer between toluene and water. It was found that practically no transfer would take place in the direction from toluene to water, even under very large driving forces. Table XII, page 136, contains the data for the eight tests in which transfer was attempted from toluene to water. It will be noted that even with an acetone concentration in toluene of approximately 30 weight per cent, and approximately 4 weight per cent in water, the overall transfer coefficients for tests 28 and 29, Table XIII, page 137, were on the order of 0.1 to 0.025 times that of the overall coefficients for transfer from water to toluene. The overall coefficients for tests 50 and 56 were not calculated, because of the extremely low transfer rate of acetone magnified the experimental error considerably, and the results were meaningless. The data are included for comparison, however.

To show that the transfer of acetone from toluene to water actually would take place if sufficient time of contact were allowed, a study was made of the changes of concentration with time under conditions approaching those of diffusion. Samples of toluene containing 10 and 30 weight per cent acetone were placed in contact with water containing no acetone initially, and analyses of both phases were made after 24, 48, and 72 hours. The results of this study are shown in Figure 28, page 143. It will be noticed that a definite transfer of material does take place, at a greater initial rate for the 30 weight per cent sample than for the 10 weight per cent. After approximately 48 hours, the concentrations for both systems had leveled off, and diffusion proceeded at a very slow rate.

Various theories have been offered to explain the apparently different resistances that are offered by the same system to transfer of solute in both directions. Lewis(58) found in his stirred tank extractor using toluene-acetone-water that the rate of transfer was faster in the direction water to toluene than vice versa. He postulated that this effect was because of the energy and entropy changes arising from the different type of solvation in the two phases. This was further substantiated by the evidence of a marked temperature coefficient for the distribution of acetone between water and toluene, while the distribution coefficient of other systems with acetone as solute are rather temperature independent. The retardation in transfer from toluene to water then was probably due to a solvation effect. The results for the spray towers have been inconclusive; the effect of transfer direction seems to depend more on the dispersed phase than on the transfer direction.

Another possible explanation of the differences in transfer rates for transfer from water to toluene and vice versa, is the positive and negative adsorption characteristics of acetone in the two phases. In the water phase, acetone molecules are positively adsorbed in the interface, signifying that acetone has a lower surface energy than water. On the other hand, acetone molecules tend to concentrate in the bulk of the toluene solution, away from the interface, thus signifying that acetone has a higher surface energy than toluene. Because of the difference in transfer rates in going from toluene to water than in the reverse direction, it would appear at first to be an irreversible process. Since there is no reason to suspect that transfer in one direction is harder or easier than in the other; a more probable indication is that the two film theory is inadequate in expressing the proper relationships, in that the true driving force may be considerably different from that expressed by the two film equations. In the approach of an acetone molecule to the interface from both directions, different energy levels must be encountered; the same energy levels that are originally responsible for the positive and negative adsorption phenomena of the acetone molecules with regard to interfacial tension. Whether these differences are manifested in actual interfacial reaction such as the solvation mechanism of Lewis(58), or simply as a lower effective driving force for mass transfer, is not known. An answer to this question would be a major breakthrough in the understanding of the basic mechanisms of mass transfer.

Correlation of Overall Transfer Coefficients with Variables. One of the aims of fundamental studies of mass transfer is to provide a basis for correlating and predicting coefficients for design of commercial units. Many empirical equations have been developed using the principle of the two film additivity of resistances(13,37,56,72,105,109) as the first step in attempting to predict design coefficients. Because of the extreme complexity of liquid-liquid extraction processes, the wide variation in extraction mechanisms encountered between different kinds of contacting equipment, and the continued lack of a realistic, fundamental theory have continued to render these correlations specific, and greatly restrict their use to special cases.

Considerable effort has been expended at the Virginia Polytechnic Institute in an attempt to achieve a correlation equation that will allow prediction of mass transfer coefficients by studying mass transfer rates and effects as a function of the physical properties of the system in a horizontal tube extractor. The basis for the resulting correlation equation has been the two film theory, and as a result, the limitations imposed by its use has again restricted development of a more general equation of wide spread utility. From the mass transfer relationships discussed in the literature review, it is obvious that an equation derived on the basis of the more fundamental film coefficients would be preferred, for greater sensitivity to changes in physical variables can be achieved with their use than with the use of the overall coefficients. Again, however, the limitations of the two film theory confine such an equation to two component systems, in order for certain restrictive assumptions about interfacial compositions to be valid. Although of considerable interest, two component, or binary system extraction, is of little practical use. Correlation of the transfer coefficients for three component extraction systems is obviously the next step, but here no qualifying assumptions can be made concerning the concentration of solute at the interface. The final result, if any work is to be done on ternary systems, is that the correlation equation must relate overall mass transfer coefficients with physical variables instead of the individual film coefficients.

Skrzec(80) was the first investigator to use the horizontal tube extractor at Virginia Polytechnic Institute for extraction studies. Measuring transfer rates for five binary systems, he arrived at an equation for relating the individual film coefficients for the systems to such physical variables as density, viscosity, interfacial tension, and diffusivity. The interfacial tension values used by Skrzec were obtained through the application of Antonoff's rule(33), which Lastovica(57) later showed to be considerably in error. Re-evaluating Skrzec's data on the basis of experimentally determined interfacial tension values, Lastovica derived a more accurate equation for correlating film coefficients with physical variables.

Lastovica(57) then attempted to use the correlation equation developed on the basis of the binary extraction data to predict ternary film coefficients from physical variables of the systems. To do this, he used what he thought to be a method for calculating the interfacial concentrations of the ternary systems from the gross operating parameters of the system. The method was incorrect primarily because of the assumption that continuous countercurrent differential contact could be treated as stagewise cocurrent contact (for which the method will not apply, either). Secondly, the method was incorrect because he overlooked one of the fundamental assumptions of the two film theory; that the interfacial compositions do not have to obey a material balance, because of a negligible amount of solute assumed to be in the interface and in the interfacial films. The only stipulation that the two film theory places on the interface is that the solute concentration in one phase must be in equilibrium with the solute concentration in the other as given by the distribution coefficient for the systems. The interfacial concentrations are determined not only by the bulk-concentrations, phase-flow rates, and distribution curves, but also by the relative sizes of the film coefficients themselves. It is quite possible to vary the latter, independently of the chemical system and rates of flow of the respective phases merely by changing conditions of turbulence through use of various contacting devices.

Attempts to predict ternary film coefficients from binary extraction equations were also made by Gordon and Sherwood(38). They found that the individual film coefficient for mutual saturation of two solvents differed considerably from experimentally measured mass transfer rates of a solute from one phase to the other(95). Certainly, the mechanisms for binary transfer and ternary transfer are different, but they should be comparable by some suitable theory.

Further evidence was obtained in this investigation supporting the fallacy of using two components correlation equations for predicting ternary transfer coefficients. The equation re-developed by Lastovica(57) using experimentally determined interfacial tension values was used in the following manner: Exponents on only the interfacial tension group and the constant of proportionality were refitted using the ternary extraction data obtained in this investigation. Exponents on the remaining physical property groups were assumed to apply to ternary extraction systems, and were thus used in the re-evaluation of the equation. The largest source for the discrepancy between the two systems probably occurred in the variation of interfacial tension. The interfacial tension of the five binary systems varied from one to approximately five dynes per centimeter. For the present investigation the interfacial tension varied from 2 to 30 dynes per centimeter. The final result of the re-evaluation of the binary equation is

$$\frac{K_s d}{D_s} = 9.972\text{x}10^{20}\left(\frac{d\sigma}{\mu_s D_s}\right)^{-0.7952}\left(\frac{\mu_w}{\mu_s}\right)^{-10.0508}\left(\frac{\mu_s}{\rho_s D_s}\right)^{-4.1715}\left(\frac{dG_s}{\mu_s}\right)^{0.9271} \qquad (37)$$

A statistical analysis of Equation 37 is summarized in Table XVIII, page 148. Two statistical tests were performed in order to obtain a better evaluation of the equation. An F-test was performed to determine if the variance of the dependent variable (overall mass transfer group) was accounted for by the regression equation, and the variance of the experimental points about the regression line due to errors, were an estimate of the same population. If so, then the equation was not satisfactory in predicting overall transfer coefficients from experimental data. The criterion for selection or rejection of the hypothesis is an F-value calculated from statistical theory. For the number of samples tested and the number of independent variables studied, an F-value of 3.97 could have been obtained as the value of the ratio of the two variances purely by chance with 95 per cent certainty. Values above this number are considered not obtainable by chance, therefore significant. The F-value for the equation was 6.40, indicating that the hypothesis (the variances were an estimate of the same population) was false within 95 per cent certainty. That is, the variance due to regression and the error variance are not estimates of the same population. The F-value of the equation was just significant, however, and because of this, it is well to examine the equation further. One would suspect that perhaps some doubt could be placed on the correlation reliability of the equation because of the low significance value.

A second test frequently resorted to in statistical analysis procedures is the comparison of the sum of squares of the deviations of the values of the dependent variable calculated from the regression equation about its mean value, to the total sum of squares of the variations of the experimental values of the dependent variable about its mean value. This value is frequently expressed as a ratio; indicating the per cent of the total sum of squares accounted for by the regression equation. For the re-evaluated equation, this ratio was 10,042/124,559 or 0.0805; 8.04 per cent of the total sum of squares was accounted for by the regression equation. Since this ratio can vary from essentially zero for the case in which there is absolutely no correlation, to 100 per cent for perfect correlation, it was obvious that the equation developed from binary extraction data could not be used to predict satisfactorily overall transfer coefficients from physical variables. The multiple correlation coefficient, simply the square root of the above ratio, was 0.284. For a maximum value of 1, this again indicates a very poor correlation.

Because of these poor results, it was decided to refit the data for all of the dimensionless groups, and in this way obtain new values for all of the exponents and the constant of proportionality. The overall mass transfer coefficient based on the solvent film was related to the physical properties of the system by the following equation:

$$\frac{K_s d}{D_s} = 2.708\text{x}10^{-21}\left(\frac{d\sigma}{\mu_s D_s}\right)^{0.7227}\left(\frac{\mu_w}{\mu_s}\right)^{4.0592}\left(\frac{\mu_s}{\rho_s D_s}\right)^{5.4361}\left(\frac{dG_s}{\mu_s}\right)^{0.4701}\left(\frac{dG_w}{\mu_w}\right)^{0.3027} \qquad (38)$$

An analysis of the equation resulted in an F-value based on the variance due to regression to the error variance, of 30.816. The value of (F) is significant above a chance value of 3.33 with 95 per cent certainty. Again, the regression variance and the error variance were not estimates of the same population. With Equation 38, however, the ratio of the sum of squares due to regression to the total sum of squares was 0.67, indicating that 67 per cent of the total sum of squares was accounted for by the regression equation. The multiple correlation coefficient (R) had a value of 0.828, indicating that the regression equation was satisfactory for predicting overall mass transfer coefficients from physical properties.

A comparison of Equations 37 and 38, pages 212 and 215, will show immediately that correlations based on binary extraction data cannot be extended to predict ternary transfer coefficients. It is interesting to note that the Reynolds number for the water phase which had an insignificant effect on transfer in the binary system, has a significant effect on transfer in the ternary system. In many cases, the effect on the coefficient of overall mass transfer of the dimensionless groups is just the opposite to the effect on the film coefficients. Possibly, further study will clarify this behavior.

Recommendations

Many questions resulted from this investigation, the answers to which would contribute significantly to the knowledge of fundamental mechanisms present in liquid-liquid extraction.

Automation of Interfacial Level Control. If installation of an automatic interfacial level controller becomes necessary and desirable, it is first recommended that dynamic control stability studies be made on the extraction tube before attempting to redesign the control system. The characteristics of response for the system observed in this investigation are quite complex because of the rapid gain and low reaction responses. The process can be expressed mathematically, and the differential response equations either solved directly, if not too complex, or analyzed by means of frequency response or time response techniques. A control system could then be designed to fit the conditions specified by the mathematical analysis.

Influence of Interfacial Tension on Flow Characteristics. An examination of Figures 7, 9, 10, and 12, pages 110, 112, 113, and 115, will show that as the drop velocity approached the critical streaming velocity for the system, the linear relationship between drop weight and drop velocity did not hold. Thus, the departure of the curve from linearity was attributed to complications resulting from nozzle effects and the high velocities. This effect was more pronounced with higher interfacial tension systems, as Figure 7, page 110, indicates. It is recommended that more extensive studies be made on the effect of drop velocity on drop weight at or near the critical streaming velocity. An apparatus similar to the one used in this investigation would be suitable for the investigation, as would any of the systems used in these studies.

Variation of Overall Transfer Coefficient with Phase Flow Rates. Because of the inconclusive and conflicting evidence cited in the literature, and the inconsistent results obtained in this investigation, on the effect of flow rate on the overall mass transfer coefficient, it is recommended that further study be undertaken on this topic. If the present apparatus is employed, it is cautioned that tests should be made to determine the maximum capacity of the tube, as measured by the onset of interfacial turbulence. In the actual velocity tests, the flow rates employed must cover the maximum possible range to attain significant variation in overall coefficient values, in order to evaluate clearly the velocity effects.

Instead of using mass velocities as a comparison basis for the position of the plane of zero velocity in the tube, it is recommended that some term more fundamental to fluid dynamics, such as kinetic velocity, or momentum, be used.

Velocity Profile Studies. In order to accurately compare velocities of the two phases in the countercurrent horizontal extraction tube, knowledge will have to be gained concerning velocity profiles in the tube. Because of the complications arising from countercurrent flow of the two immiscible phases within the tube, these profiles are difficult to predict theoretically. Not only does the tube wall exhibit drag effects, but the interface also acts as an additional boundary or wall, further confusing the analysis. Because of its potential importance, it is recommended that such velocity profile studies be undertaken.

Since velocity profiles will be measured, the apparatus could simply consist of a short section of pipe, that could be mounted as part of the present apparatus. Suitable devices, such as pitot tubes, could be installed into the apparatus simply and easily. Binary systems of different densities could be chosen from those of this investigation, or from those studied by Lastovica(57).

Interfacial Tension and Mass Transfer. The results obtained in the course of this investigation on the effects of interfacial tension on the rate of mass transfer for ternary systems were rather inconclusive, and much more work of this nature is necessary. It is recommended that further studies be made following the same procedures of this investigation, using the horizontal tube extractor to clarify these effects.

It is recommended that systems used for the study have interfacial tension values of at least 25 dynes per centimeter. Several systems(57) that would be suitable for such studies include benzene-acetone-water, carbon tetrachloride-acetone-water, 1,1,2-trichloroethane-acetone-water, and toluene-acetic acid-water.

Correlation of Mass Transfer Coefficients with Physical Properties. The correlation equation proposed in this investigation, page 215, was derived from only 75 ternary extraction tests, using two systems, toluene-acetone-water and hexane-acetone-water. In order to extend its general utility, it is recommended that ternary extraction data of Lastovica(57) and Skrzec(60) be incorporated with the data from this investigation, and a new correlation equation derived.

It is further recommended that with any ternary extraction studies performed on the horizontal tube extractor in the future, sufficient data be taken along with that required for the primary study, so that eventually the results may also be included in the correlation equation.

Limitations

This investigation was performed under the following limiting conditions.

Drop Weight Apparatus. Only one dropping tip was used in the dynamic interfacial tension studies. The tip was constructed on the stem of a 125-milliliter separatory funnel, and was 0.204 centimeter in diameter. The capillary tube in the tip was approximately 0.027 centimeter in diameter.

Horizontal Tube Extractor. A horizontal tube extractor, constructed of two 4-foot pieces of pyrex pipe, 1-1/2 inches in diameter, and eight feet long, was used for the extraction studies. Teflon baffle plates, in copper end boxes, 1-1/2 inches long, 1-1/2 inches in diameter, prevented intermixing of incoming streams with the opposite phase.

Systems Studied. Six systems were used to study the effect of drop rate on drop velocity in the dynamic interfacial tension studies. Each of the following immiscible liquid pairs was tested with both acetone and arabic acid as solutes: benzene-water, cyclohexane-water, and toluene-water. For the benzene-water system, the concentration of acetone and arabic acid were, respectively, 2 and 1.025 weight per cent; for the cyclohexane-water system, the concentrations of acetone were 2 and 10 weight per cent, and 2.785 weight per cent arabic acid; for toluene-water, the concentrations were 10 and 2.785 weight per cent, respectively.

Extraction data were obtained for the systems toluene-acetone-water and hexane-acetone-water. In the first system, concentrations varied from 35 to 5 weight per cent acetone in water, and 20 to zero per cent acetone in toluene. For hexane-acetone-water tests, the concentrations were varied from 45 to 15 per cent acetone in water, and from 5 to zero per cent acetone in hexane.

Phase Flow Rates. The phase flow rates for the two ternary systems studied in the extraction tests were varied from 1,000 to 10,000 pounds per hour per square foot for each phase. In evaluating the effect of interfacial tension on mass transfer, the water phase was varied from 1,300 to 8,000 pounds per hour per square foot, while the solvent phase flow rate was held constant at approximately 3,300 pounds per hour per square foot.

Analytical Methods. The drop velocities in the drop weight tests were timed with an electrical timer, accurate to ± 0.1 second. Drop weights were determined by means of an analytical balance, accurate to ± 0.0002 gram.

Specific gravities of the conjugate phases for the two ternary systems were determined by means of pycnometers, calibrated against distilled water. The accuracy of the measurements was estimated to be ± 0.0005.

Viscosities of the conjugate phases of the ternary systems were determined by use of an ostwald viscosimeter, accurate to ± 0.5 per cent.

Concentrations of acetone in all of the samples taken during extraction operations were determined by use of an immersion refractometer, accurate to ± 0.00003.

Temperature. Drop weight tests were carried out between 27.0 to 28.2 °C.

Viscosity and specific gravity determinations were made at 27 ± 0.05 °C.

Refractive indexes were determined for both systems at 25 and 30 ± 0.05 °C.

Extraction tests were carried out between 25 and 29 °C.

V. CONCLUSIONS

The conclusions drawn from the results of this investigation are presented in two sections; interfacial tension studies, and extraction studies.

Interfacial Tension Studies

Study of the effect of rate of drop formation on drop weight using the modified drop weight procedure led to the following conclusions:

1. Adjustment of interfacial tension for the systems acetone in toluene, benzene, or cyclohexane with water was so rapid that equilibrium was reached as quickly as the drops could be formed.

2. The interfacial tension values of systems containing solutes having a molecular weight on the order of 50 to 60 measured by static equilibrium methods will be representative of the interfacial tension values for the systems under extracting conditions.

3. Equilibrium methods are not suitable for evaluating interfacial tension under extracting

conditions for solutes having a molecular weight on the same order of magnitude as that for arabic acid.

4. The experimental method used in this investigation failed to show any transient values of interfacial tension less than the equilibrium values as postulated by Christiansen and Hixon.

Ternary Extraction Studies

Experimental investigation of two ternary extraction systems in a horizontal tube extractor, 1-1/2 inches in diameter, and eight feet long, for phase flow rates of both phases varying from 1,000 to 10,000 pounds per hour per square foot, at temperatures of 25 °C to 27 °C led to the following conclusions:

1. The overall mass transfer coefficient for acetone from water to hexane based on the hexane film, increased from 0.012 to 0.060 with an increase in interfacial tension from 7.6 to 24 dynes per centimeter, as controlled by decreasing acetone concentration.

2. The overall mass transfer coefficient for acetone from water to toluene based on the toluene film, decreased from 0.145 to 0.048 with an increase in interfacial tension from 6.6 to 22.5 dynes per centimeter, as controlled by decreasing acetone concentration.

3. Because of the opposite effect of interfacial tension on transfer of acetone from water to hexane and to toluene, no generalisation as to the effect of interfacial tension on the overall mass transfer coefficient can be made.

4. The mass transfer coefficient for acetone from toluene to water was 0.1 to 0.025 of the transfer coefficient for acetone from water to toluene.

5. The overall mass transfer coefficient based on the solvent phase concentrations can be correlated with 67 per cent accuracy with the physical properties of the system by the equation:

$$\frac{K_s d}{D_s} = 2.708 \times 10^{-21} \left(\frac{d\sigma}{\mu_s D_s}\right)^{0.7227} \left(\frac{\mu_w}{\mu_s}\right)^{4.0592} \left(\frac{\mu_s}{\rho_s D_s}\right)^{5.4361} \left(\frac{dG_s}{\mu_s}\right)^{0.4701} \left(\frac{dG_w}{\mu_w}\right)^{0.3027}$$

6. Equations correlating the individual film coefficients with physical properties of the system derived from binary extraction studies cannot be used to predict ternary overall mass transfer coefficients.

VI. SUMMARY

It was the purpose of this investigation to ascertain the qualitative nature of the interfacial tension equilibrium characteristics of the systems hexane-acetone-water and toluene-acetone-water by studying the effect of drop velocity on drop weight through use of the modified drop weight procedure, and comparing these results with those obtained from systems known to have time dependent interfacial tension relationships; to then evaluate the effect of interfacial tension on the rate of mass transfer by obtaining extraction data for the above systems in a horizontal, countercurrent liquid-liquid extraction tube for a series of interfacial tension values achieved through variation of the total acetone concentration in the system; and finally, to attempt to obtain an equation correlating the overall mass transfer coefficient based on the solvent film with the physical and operational variables of the systems and extractor.

The observation that some three component, ternary systems containing high molecular weight solutes required time to reach interfacial tension equilibrium, prompted a more careful consideration of the assumption that determinations of this property obtained under static conditions represented the values existing under extracting conditions. The drop weight method was selected for comparison studies. An equation relating drop weight to drop velocity was derived, and took the form:

$$m = \frac{2\pi r r \phi}{g} - \frac{A \rho v^2}{g}$$

where:

m = drop weight, gm

$2, \pi$ = constants

r = tip radius, cm

σ = interfacial tension, dynes/cm

g = acceleration due to gravity, cm

A = cross sectional area of capillary tube, sq cm

ρ = density of fluid flowing in capillary, gm/cu cm

v = drop velocity, drops/min

ϕ = correction factor for non-ideal drop detachment from tip.

The equation predicted that if (σ) and (ϕ) were constants, a plot of drop weight (m) versus the square of the drop velocity (v^2) would result in a straight line. The systems used to test the validity of the above equation were arabic acid and acetone as solutes with each of the following liquid pairs: benzene-water, cyclohexane-water, and toluene-water.

From this study, it was concluded that

1. Adjustment of interfacial tension for the systems acetone in toluene, benzene, or cyclohexane with water was so rapid that equilibrium was reached as quickly as the drops could be formed.
2. The interfacial tension values of systems containing solutes having a molecular weight of 50 to 60 measured by equilibrium methods will be representative of the interfacial tension values for the systems under extracting conditions.
3. Equilibrium methods are not suitable for evaluating interfacial tension under extracting conditions for solutes having a

molecular weight on the same order of magnitude as that for arabic acid.

4. The experimental method used in this investigation failed to show any transient values of interfacial tension less than the equilibrium values as postulated by Christiansen and Hixon.

Extraction tests were made on the systems toluene-acetone-water and hexane-acetone-water at 25 to 29 °C, in an effort to determine the effect of interfacial tension on the overall mass transfer coefficient. Phase flow rates covered a range of 1,000 to 10,000 pounds per hour per square foot for both phases. Concentration ranged from 35 to 5 weight per cent acetone in the inlet water stream, and 20 to zero weight per cent acetone in the inlet toluene stream. For the hexane system, the concentrations varied from 45 to 15 weight per cent in acetone in the inlet water phase, and 5 to zero per cent acetone in the inlet hexane phase. The results of this study led to the following conclusions:

1. The overall mass transfer coefficient for acetone from water to hexane based on the hexane film, increased from 0.012 to 0.060 with

an increase in interfacial tension from 7.6 to 24.0 dynes per centimeter, as controlled by decreasing acetone concentration.

2. The overall mass transfer coefficient for acetone from water to toluene based on the toluene film, decreased from 0.0145 to 0.048 with an increase in interfacial tension from 6.6 to 22.5 dynes per centimeter, as controlled by decreasing acetone concentration.

3. Because of the opposite effect of interfacial tension on transfer of acetone from water to hexane and to toluene, no generalization as to the effect of interfacial tension on the overall mass transfer coefficient could be made.

4. The mass transfer coefficient for acetone to toluene was 0.1 to 0.025 of the transfer coefficient for acetone from water to toluene.

5. The overall mass transfer coefficient based on the solvent phase concentrations can be correlated with 67 per cent accuracy with

the physical properties of the system by the equation:

$$\frac{K_s d}{D_s} = 2.708\times10^{-21}\left(\frac{d\sigma}{\mu_s D_s}\right)^{0.7227}\left(\frac{\mu_w}{\mu_s}\right)^{4.0592}\left(\frac{\mu_s}{\rho_s D_s}\right)^{5.4361}\left(\frac{dG_s}{\mu_s}\right)^{0.4701}\left(\frac{dG_w}{\mu_w}\right)^{0.3027}$$

where:

K_s = overall mass transfer coefficient based on solvent phase, lb/hr-sq ft-ΔC

d = diameter of horizontal extraction tube, ft

D_s = diffusivity of solute in solvent, sq ft/hr

σ = interfacial tension, lb/hr^2

ρ_s = density of solvent phase, lb/cu ft

μ_w, μ_s = viscosity of water and solvent phases, respectively, lb/ft-hr

G_w, G_s = mass velocity of water and solvent phases, respectively, lb/hr-sq ft.

6. Equations correlating the individual film coefficients with physical properties of the system derived from binary extraction studies could not be used to predict ternary overall mass transfer coefficients.

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ABSTRACT

THE EFFECT OF INTERFACIAL TENSION ON THE RATE OF MASS TRANSFER IN TERNARY LIQUID-LIQUID EXTRACTION

by

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ABSTRACT

It was the purpose of this investigation to ascertain the qualitative nature of the interfacial tension equilibrium characteristics of the systems hexane-acetone-water and toluene-acetone-water by studying the effect of drop velocity on drop weight through use of the modified drop weight procedure, and comparing these results with those obtained from systems known to have time dependent interfacial tension relationships; to then evaluate the effect of interfacial tension on the rate of mass transfer by obtaining extraction data for the above systems in a horizontal, countercurrent liquid-liquid extraction tube for a series of interfacial tension values achieved through variation of the total acetone concentration in the system; and finally, to attempt to obtain an equation correlating the overall mass transfer coefficient based on the solvent film with the physical and operational variables of the systems and extractor.

The observation that some three component, ternary systems containing high molecular weight solutes required time to reach interfacial tension

equilibrium, prompted a more careful consideration of the assumption that determinations of this property obtained under static conditions represented the values existing under extracting conditions. The drop weight method was selected for comparison studies. An equation relating drop weight to drop velocity was derived, and took the form:

$$m = \frac{2\pi r\sigma\phi}{g} - \frac{A\rho v^2}{g}$$

where:

m = drop weight, gm

$2, \pi$ = constants

r = tip radius, cm

σ = interfacial tension, dynes/cm

g = acceleration due to gravity, cm

A = cross sectional area of capillary tube, sq cm

ρ = density of fluid flowing in capillary, gm/cu cm

v = drop velocity, drops/min

ϕ = correction factor for non-ideal drop detachment from tip.

The equation predicted that if (σ) and (ϕ) were constants, a plot of drop weight (m) versus the square of the drop velocity (v^2) would result in a straight line. The systems used to test the validity of the above equation were arabic acid and acetone as solutes with each of the following liquid pairs: benzene-water, cyclohexane-water, and toluene-water.

From this study, it was concluded that

1. Adjustment of interfacial tension for the systems acetone in toluene, benzene, or cyclohexane with water was so rapid that equilibrium was reached as quickly as the drops could be formed.

2. The interfacial tension values of systems containing solutes having a molecular weight of 50 to 60 measured by equilibrium methods will be representative of the interfacial tension values for the systems under extracting conditions.

3. Equilibrium methods are not suitable for evaluating interfacial tension under extracting conditions for solutes having a molecular weight on the same order of magnitude as that for arabic acid.

4. The experimental method used in this investigation failed to show any transient values of interfacial tension less than the equilibrium values as postulated by Christiansen and Hixon.

Extraction tests were made on the systems toluene-acetone-water and hexane-acetone-water at 25 to 29 °C, in an effort to determine the effect of interfacial tension on the overall mass transfer coefficient. Phase flow rates covered a range of 1,000 to 10,000 pounds per hour per square foot for both phases. Concentration ranged from 35 to 5 weight per cent acetone in the inlet water stream, and 20 to zero weight per cent acetone in the inlet toluene stream. For the hexane system, the concentrations varied from 45 to 15 weight per cent in acetone in the inlet water phase, and 5 to zero per cent acetone in the inlet hexane phase. The results of this study led to the following conclusions:

1. The overall mass transfer coefficient for acetone from water to hexane based on the hexane film, increased from 0.012 to 0.060 with an increase in interfacial tension from 7.6 to 24.0 dynes per centimeter, as controlled by decreasing acetone concentration.

2. The overall mass transfer coefficient for acetone from water to toluene based on the toluene film, decreased from 0.0145 to 0.048 with an increase in interfacial tension from 6.6 to 22.5 dynes per centimeter, as controlled by decreasing acetone concentration.

3. Because of the opposite effect of interfacial tension on transfer of acetone from water to hexane and to toluene, no generalization as to the effect of interfacial tension on the overall mass transfer coefficient could be made.

4. The mass transfer coefficient for acetone to toluene was 0.1 to 0.025 of the transfer coefficient for acetone from water to toluene.

5. The overall mass transfer coefficient based on the solvent phase concentrations can be correlated with 67 per cent accuracy with the physical properties of the system by the equation:

$$\frac{K_s d}{D_s} = 2.708 \times 10^{-21} \left(\frac{d\sigma}{\mu_s D_s}\right)^{0.7227} \left(\frac{\mu_w}{\mu_s}\right)^{4.0592} \left(\frac{\mu_s}{\rho_s D_s}\right)^{5.4361} \left(\frac{dG_s}{\mu_s}\right)^{0.4701} \left(\frac{dG_w}{\mu_w}\right)^{0.3027}$$

where:

K_s = overall mass transfer coefficient based on solvent phase, lb/hr-sq ft-ΔC

d = diameter of horizontal extraction tube, ft

D_s = diffisuvity of solute in solvent, sq ft/hr

σ = interfacial tension, lb/hr^2

ρ_s = density of solvent phase, lb/cu ft

μ_w, μ_s = viscosity of water and solvent phases, respectively, lb/ft-hr

G_w, G_s = mass velocity of water and solvent phases, respectively, lb/hr-sq ft.

6. Equations correlating the individual film coefficients with physical properties of the system derived from binary extraction studies could not be used to predict ternary overall mass transfer coefficients.