Mechanisms by Which Ultrasonic Energy Affects Transfer Rates in Liquid-Liquid Extraction

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Concurrent and spray-tower studies have been accomplished that illustrate the effects of ultrasonic insonation on transfer rates in liquid-liquid extraction. Stage efficiencies and over-all transfer rates in the system toluene-methyl alcohol-water were determined with and without insonation of the system at frequencies of 40 and 800 kc.

Insonation was shown to have a positive effect on mass transfer in both concurrent and spray-tower operations. Insonation of the system provides for increased interfacial area between the two phases, removal of relatively stagnant liquid layers at the interface, and increased circulation currents within a single liquid phase. Low-frequency insonation favors local agitation and mixing of the phases, and high-frequency insonation favors induced circulation currents.

The majority of the proved industrial uses of ultrasonics are of the nature of nondestructive testing and thickness measurement (*4, 13*), degassing of liquids (*8*), improved cleaning methods for finely-machined parts (*14, 23*), and formation of emulsions and homogenized mixtures (*5, 7, 17*). A field that is gradually becoming interesting commercially is the utilization of high frequency sound waves in extraction operations (*8, 17*).

In this investigation, in addition to the obvious purpose of comparing extraction rates obtained in the presence of ultrasonic waves with rates obtained without insonation, a secondary objective was that of presenting a picture more complete than formerly available of the mechanisms by which insonation affects mass transfer rates in a two-phase, three-component liquid system.

DIFFUSION OF ALKALI THROUGH A CELLOPHANE MEMBRANE

Rees (*18*) reports an increase of 30% for the dialysis constant in the transport of alkali through a cellophane membrane when subjected to insonation. A similar investigation by Bakhshi (*2*) indicated that insonation was responsible for increases of up to 80% in the over-all mass transfer coefficient for the system. Baumgartl (*3*) found that the diffusion of 5% sodium chloride was increased by a factor of 2 under the influence of ultrasonics.

Liquid-Solid Extraction

Grove (*11*) has reported increased extraction of protein from brewer's yeast with a 5% sodium chloride solution in the presence of audible sound waves. A patent (*20*) was granted for a process whereby audible and inaudible insonation was applied to the extraction of oil from fish materials. Increased extraction of flavor from hops in the brewery industry through application of ultrasonic vibrations has been reported in several instances (*5, 6*). Thompson and Sutherland (*21*) found that insonation of the system *n*-hexane and peanuts increased extraction of the peanut oil 2.76 times that of control samples.

Liquid-Liquid Extraction

With insonation at a frequency of 570 kc. Haul, Rust, and Lutzow (*12*) reported an increase of 76% in the extraction of phenanthrene from methanol by gasoline in a small spray tower.

Murray (*15*) investigated the effects of 400 kc. insonation on the extraction of acetone from carbon tetrachloride with water, finding an increase in stage efficiency of approximately 20% when the system was insonated at high power levels. In subsequent work (*16*) Murray studied the system benzene–acetic acid–water at the same frequency as before and found that with insonation at high power levels the stage efficiency increased approximately 30% over control tests.

Aeroprojects, Incorporated (*1*) has reported stage efficiencies of 90 ± 10% when working with frequencies from 15 to 30 kc. The particular extractor employed consisted of an ultrasonic device for emulsifying the two phases and a separate chamber for breaking the emulsion with a standing wave pattern.

The postulation has been made that ultrasonic energy may affect mass transfer in a liquid-liquid extraction system in a positive direction by at least three mechanisms, simultaneously occurring but separate in nature (*21*): increasing conductance of the interface by decreasing interfacial resistance to mass transfer, increasing interfacial area between two liquid phases by reducing size and increasing number of dispersed-phase particles, and increasing concentration gradients across the interface by decreasing the concentration gradient within a single phase.

EXPERIMENTAL

Two-Phase, Three-Component Liquid System

The system toluene–methyl alcohol–water was used because of component

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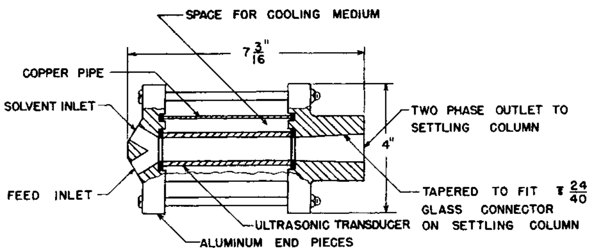

Fig. 1. Concurrent extractor used in extraction studies.

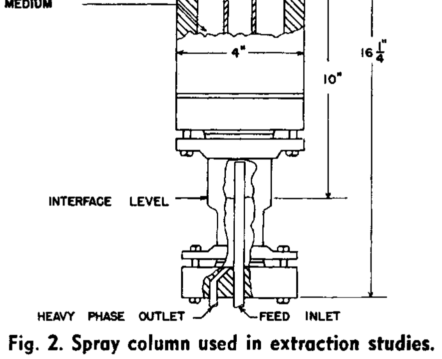

Fig. 2. Spray column used in extraction studies.

availability, noncorrosive nature, and ease of composition analysis. Methyl alcohol was considered as the solute, being extracted from the toluene with distilled water. A.C.S. reagent-grade toluene and methyl alcohol were used to prepare the feed mixture, and distilled water was used as solvent. All feed mixtures were in the concentration range of 14.4 to 14.8 weight % methyl alcohol in toluene, with the mixture saturated with distilled water. Composition analysis of samples was accomplished by refractive-index measurements.

Ultrasonic Equipment

Two cylindrical barium-titanate transducers, one 40-kc. radial frequency and one 800-kc. radial frequency, were utilized for this study. Both transducers were 4 in. long. The outside diameter of the 40-kc. transducer was 1½ in., and of the 800-kc. transducer 1 in. The 40-kc. transducer, powered by a Rich-Roth 400 generator, was used only in the spray column. The 800-kc. transducer was powered by a Brush Hypersonic generator but was used in both the concurrent extractor and the spray column. General construction features of the extractors are shown in Figures 1 and 2.

Procedure

The approximate power delivered to the liquid system from a transducer for any given generator setting was measured through a thermal calibration of each transducer and generator arrangement. The temperature rise of a known flow rate of distilled water going through the transducer was measured for various generator settings. Power output of the transducer was calculated from this data.

A solvent-to-feed ratio of 1.23:1.00 by weight was used for all concurrent tests, and a ratio of 1.00:7.00 was used for the spray-column tests. Feed rates of 40, 52, 85, and 122 g./min. were used for the concurrent tests. Time of contact was taken as the time required for a given cross-sectional plane of the two liquid phases to pass from one end of the transducer to the other, with plug flow conditions assumed. A single feed rate of 105 g./min. was used for the spray-column tests, in which solvent was the dispersed phase. Temperature of the solvent and feed was maintained between 25° and 27°C. by constant–temperature-circulation.

In all cases final samples of extract and raffinate streams were taken only after steady state conditions had been reached in the extractor, as indicated by continual analysis of the exit streams. Stage efficiency was used for comparison of tests with the concurrent extractor, and the over-all transfer rate of methyl alcohol was used for comparison of tests conducted with the spray column. A strong beam of light was directed through interfacial regions and dispersed drops to aid in observation of concentration gradients and liquid currents.

Data and Results

A summation of data and results for the concurrent tests is presented in Figure 3. Figure 4 represents a summation for the spray-column tests. Observations of the physical conditions occurring at a liquid-liquid interface both with and without insonation are represented in Figure 5.

DISCUSSION

Stage efficiencies resulting from concurrent tests at various contact times without insonation varied only slightly over the range of contact times studied (Figure 3, zero insonation power). From this result it can be reasoned that the stage efficiencies resulting from tests with insonation are truly indicative of the effect of insonation, with little or no interaction effect from the various contact times.

As illustrated by Figure 3, for a threefold increase in contact time at a constant insonation power, 5.9 to 18 sec. at 20 w., the increase in stage efficiency obtained was about three times, 15 to 45%. For a threefold increase in insonation intensity at a constant contact time, 20 to 60 w. at 18 sec., the maximum increase in stage efficiency was about 1.3 times, 45 to 59%. These results bear out the general opinion that, in cavitation processing, an insonation power level sufficiently high to produce cavitation generally serves the same purpose as a much more intense field and is often more economical to produce.

Three major effects of insonation that contribute to extraction increases were observed in this two-phase system: agitation or mixing of opposite phases, induced-circulation currents within a single liquid phase, and removal of stagnant liquid areas in vicinity of the interface between the two liquid phases. All three effects probably occur concurrently at high levels of insonation power, although intense mixing of the two phases makes observation of any circulation currents or stagnant areas difficult. As temperature rise of a liquid during insonation is an inherent characteristic of such treatment, no effort was made to separate this thermal effect from the mechanical effects that led to increased extraction rates.

At levels of 55- to 70-w. insonation power the two liquid phases in the insonation zone were thoroughly mixed by the sound waves, leaving no truly single interface between the two phases. The increase in extraction observed at these power levels may have resulted primarily from increased interfacial area and improved mixing of the two phases. With mild insonation at 5- to 10-w. power there was no apparent bulk mixing or dispersion of one phase in another; there was a slight increase in interfacial area as a result of ripples in the interface. Observation and rough measurement of the depth of these ripples led to an estimate of a maximum increase of about 10%, not nearly a sufficient increase to account for the extraction increase observed.

Observations of interfacial conditions

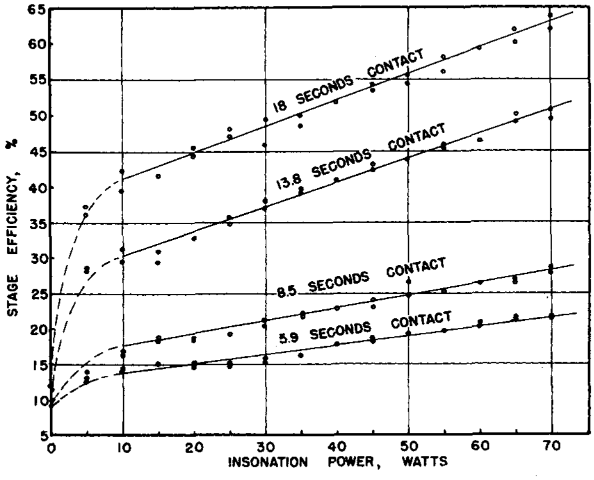

Fig. 3. Relationship between stage efficiency and insonation power at various contact times for concurrent extraction with an 800-kc. transducer.

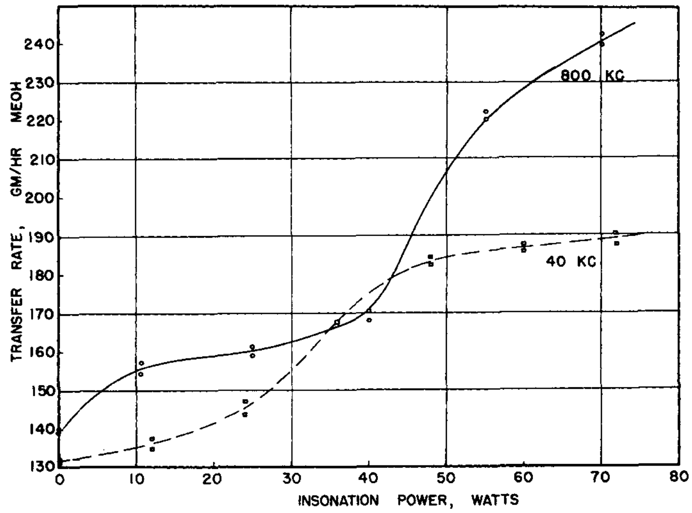

Fig. 4. Relationship between transfer rate and insonation power for spray-column extraction with 40- and 800-kc. transducers.

during concurrent extraction tests both with and without insonation are presented in Figure 5. In case A the two phases were observed to be in viscous flow. Liquid at the extreme top of the light phase and bottom of the heavy phase was not disturbed nor brought into contact with the opposite phase, and for all practical purposes these liquid portions were not a part of the extraction operation. The zone of high methyl alcohol concentration in the solvent was clearly distinguishable, with no noticeable turbulence. Over an observed travel distance of about 2 in. this high-concentration region increased in thickness from approximately $1/8$ to 3/16 in. Molecular diffusion was apparently responsible for all solute transfer between the different liquid regions under these conditions.

Case B (Figure 5) shows the effects of ultrasonic waves on a liquid-liquid interface. The high-concentration region of methyl alcohol in the solvent was considerably decreased in thickness to about 1/16 in. and was relatively constant at this value over the 2 in. of observed travel. Circulation currents immediately within this small zone were also observed. Interfacial agitation and mixing encompassing a liquid layer about 1/32 in. thick was observed through use of a hand magnifying glass. Fresh portions of feed and solvent were continually presented to the interface by circulation currents created in the bulk phases by the ultrasonic waves.

Over the range of 10- to 35-w. insonation power for the spray-column tests (Figure 4) the increased transfer rates were probably a result of internal circulation currents in the dispersed-solvent drops and a pronounced prolate-oblate oscillation of the falling drops, both effects produced by the insonation. Circulation currents in the drop interior gave the same effect of "cleaning" the solvent side of the interface as was noticed in the concurrent tests. Minor internal circulation currents were observed in tests without insonation. (Circulation currents inside the drops were observed with the aid of a beam of light directed through the area in question, the regions of different solute concentration showing up clearly.) It has been demonstrated in other studies that these two actions, internal-circulation currents (*10, 19*) and prolate-oblate oscillation of drops (*9*), enhance transfer rates in a dispersed-phase system.

Data have been accumulated to show that a large portion of the over-all extraction accomplished in a spray tower occurs as the dispersed phase is formed in drops at the nozzle tip (*22*). In the spray-column tests formation time for drops in the 800-kc. tests was approximately 0.8 sec. and for the 40-kc. tests 0.3 sec. This formation time did not vary significantly between insonated and noninsonated tests, and the longer formation time in the 800-kc. test (800-kc. column had only 36% of the cross-sectional area in the 40-kc. column) probably accounts for the slightly higher transfer rate at zero insonation power as illustrated in Figure 4. Circulation currents in the drops as a result of insonation were very prominent during this formation period and unquestionably affected mass transfer rates in a positive manner during this time.

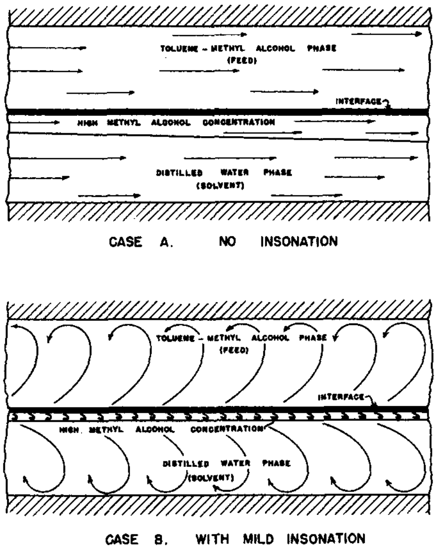

Fig. 5. Physical conditions at liquid-liquid interface with and without insonation.

At insonation powers of 35 to 55 w. single drops formed at the nozzle tip were dispersed further into numerous small drops, increased transfer rates being a consequence of this increased interfacial area. Circulation currents were still evident at this point and should receive partial credit for the high transfer rates.

At the highest insonation powers studied, approximately 70 w., single drops released from the nozzle were dispersed into fifty or seventy-five smaller drops. (The number of drops was estimated from the relation between diameter of the small drops and the diameter of the original one drop.) Internal circulation currents probably had less effect in these smaller drops than in the larger ones. Apparently the increase in interfacial area was sufficient to maintain the higher transfer rates.

CONCLUSIONS

Insonation of a two-phase, three-component liquid system with ultrasonic waves in the frequency range of 40 to 800-kc./sec. effects an increase in mass transfer rates in such a system.

Basically the same mechanisms are responsible for the mass transfer increases in a concurrent system and in a dispersed-phase system. The mechanical actions or results of insonation that have been shown to increase mass transfer rates are increase in interfacial area between phases through agitation and mixing, removal of minute stagnant liquid layers at the interface through cavitation-induced microagitation and circulation currents, and a continual supply of fresh material from both phases to the interface through bulk phase circulation currents. Local agitation and mixing appear to be favored by low-frequency insonation, and circulation currents appear to be favored by high-frequency insonation.

ACKNOWLEDGMENT

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