1812 *Ind. Eng. Chem. Res.* **2004**, *43*, 1812–1819

Gas–Liquid Mass Transfer Studies in Sonochemical Reactors

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In the present work, quantification of the overall gas–liquid mass-transfer coefficient (K_La) in the sonochemical reactors (two different types viz. ultrasonic horn and ultrasonic bath) has been done using the dynamic method. The effect of operating parameters such as the power density into the system, gas flow rate, position of the sparger relative to the ultrasound source, and the presence of sodium chloride (as an electrolyte) on the mass-transfer coefficient has been investigated. Correlations have been developed for the prediction of the volumetric mass-transfer coefficient for liquids in both types of ultrasonic reactors. The information obtained in the present work should be useful in understanding the role of gas–liquid mass transfer in a gas–liquid reaction system using ultrasound as a source of the supply of the energy and should be a breakthrough in the design procedure as no studies of this kind are currently available in the open literature.

Introduction

Application of ultrasound for the intensification of the chemical synthesis operation is a common practice at least on a laboratory scale.[1] In such operations, often gases are used either for intensification of the cavitational activity[2] or as one of the reactants.[3] The availability of the gas either as a reactant or as nuclei for the generation of cavitation events dictates the overall rate of synthesis and its intensification. Also the new and emerging area of sonophotocatalytic oxidation,[4,5] which results in the intensification of the rates of sonochemical as well as photocatalytic processes, requires a continuous supply of oxygen. The efficiency of the process is known to depend on the dissolved gas concentration in the liquid in addition to the cleaning action of the catalyst surface due to the ultrasonic irradiation. In large-scale reactors, the transfer rate of the gas into the liquid medium will be a crucial factor in determining the overall efficacy of the process. Thus, it appears necessary to have knowledge about the transfer of gas into the solution in the presence of ultrasound for efficient design of these large-scale sonoreactors.

Many studies have been reported in the literature[3,6–9] where researchers have tried to determine the role of the gaseous atmosphere (type of gas, mono-atomic, diatomic, etc.) on the cavity dynamics and the cavitational yields. The majority of this work does not take into account the gas dissolution process either through the surface or from the bubbles and only qualitatively discusses the thermal effects and degassing effects without taking into account the actual dissolved gas content. Since both degassing and the absorption phenomenon occur simultaneously during ultrasonic irradiation, these two effects should result in some net mass transfer in the presence of ultrasound (for chemical reactions, the aim will always be to have more absorption as compared to the degassing), which could also be significantly different from the conventional reactors. Gondrexon et al.[10] recently reported the dissolved oxygen concentration profiles in a liquid irradiated with ultrasound ($f = 500$ kHz, $P = 0-100$ W). They quantified the degassing effect and clearly indicated that the effect of degassing can be insignificant if the external gassing rates are sufficiently high and the final saturation value of the oxygen concentration is almost the same (or sometimes only marginally lower) as that in the absence of ultrasonic irradiation. Still no quantification of the transfer rates has been reported either by Gondrexon et al.[10] or any other researchers, and hence, this all-important information in the design procedure about gas–liquid mass transfer is still lacking.

In this study, our attempt has been to measure the overall volumetric mass-transfer coefficient (K_La) in two specific geometries of the sonochemical equipment, namely, ultrasonic horn and ultrasonic bath, which are most commonly used by the researchers in the area. The aim is also to investigate the dependency of the extent of intensification obtained in the mass transfer if any, due to the ultrasound as a function of the operating parameters.

It should also be noted here that the present work forms a base case (investigation of transfer of oxygen into pure water) for the desired design information. The exact study of the dissolution of gas into the sonochemical reaction systems might reveal some more interesting/realistic facts, though the quantum of chemical changes occurring over the time period as studied in the work (<10 min) will be minimal for the majority of the sonochemical reactions (normally the total reaction time to get significant conversion is of the order of few hours). Thus, these chemical changes will affect neither the energy balance nor the physicochemical properties of the system, and hence, the magnitude of the mass-transfer coefficient will not be much different as compared to the present work.

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10.1021/ie0341146 CCC: $27.50
Published on Web 03/11/2004

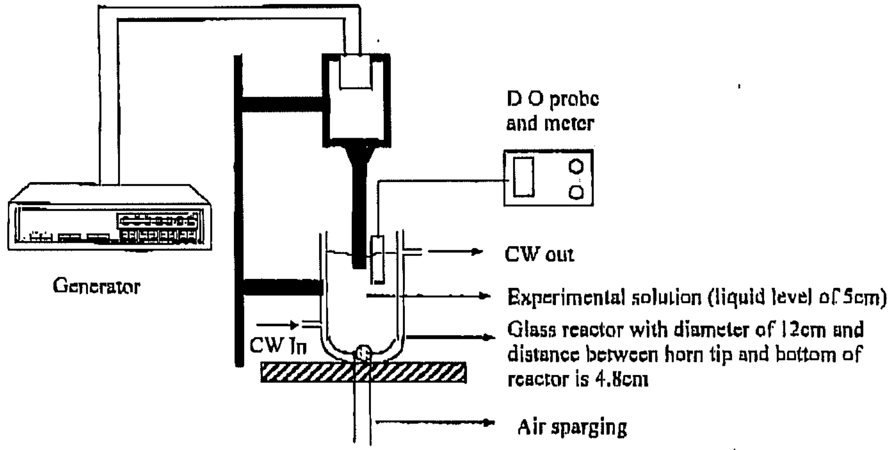

Figure 1. Schematic representation of an experimental setup for the ultrasonic horn.

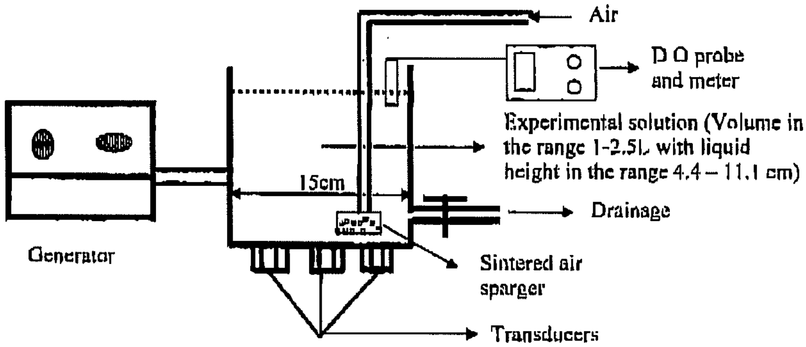

Figure 2. Schematic representation of an experimental setup for the ultrasonic bath.

Experimental Section

Experiments have been performed using an ultrasonic horn (M/s Vibracell, France) with variable amplitude/intensity (in the present work power dissipation into the solution was varied in the range of 0−65 W; actual power dissipation into the system has been quantified by using a calorimetric method[11] for all the systems) and fixed frequency of 20 kHz. Schematic representation of the experimental setup used for the study has been given in Figure 1. The reactor used in the work has a diameter of 12 cm, and the position of the horn was adjusted in such a way that the distance of the horn tip from the bottom of the reactor is 4.8 cm. The volume of the liquid was fixed at 500 mL (liquid level is 5 cm so that the horn is dipped 2 mm inside the liquid) whereas the operating temperature was maintained constant at 20 ± 1 °C by circulating a coolant through the jacket of the reactor (Initial studies indicated that there is no temperature gradient in the vessel; i.e., the difference in temperature measured at eight different locations in the reactor is always less than 2%.). Air was sparged into the reactor using a sintered glass sparger located at the bottom of the reactor (No information is available on the exact pore size of the sparger though the pore size might affect the distribution of the gas in the reactor and hence the values of the gas holdup and the mass-transfer coefficient as discussed later. In the present work, similar sparger has been used for all the cases so that there is no dependency on the pore size.), and the flow rate was varied in the range 7.38×10^{-6}–33.33×10^{-6} m^3/s (corresponding superficial velocities of 6.53×10^{-4}–29.5×10^{-4} m/s). Some experiments were also repeated using sodium chloride solution (concentration as 1 M) to check the dependence of the mass-transfer coefficient on the presence of salt (Sodium chloride has also been used in the past to intensify the rates of sonochemical reactions by concentrating the reactants at the cavity implosion sites and is also known to inhibit coalescence and give high interfacial area in gas-liquid contractors.[12,13]). The effect of position of the air sparger was investigated by varying the distance of the sparger in the range 1−5.7 cm from the ultrasound source (horn) whereas preliminary investigation into the effect of frequency was done by performing experiments in a high-frequency reactor (Nexus P 198-R ultrasonic module operating at 590 kHz, M/s Sinaptec, SA Lezennes, France) at similar levels of power dissipation.

To check the dependency of the extent of intensification in the mass-transfer coefficient using ultrasound on the type of sonochemical reactor, experiments were also done in an ultrasonic bath (Dakshin, Mumbai, India, capacity of 3.3 L with 15-cm diameter) equipped with three transducers attached at the bottom of the reactor in a triangular pitch for an air−water system. The ultrasonic bath operates at a fixed frequency of 20 kHz and also at a fixed power input of 120 W (actual power dissipation as measured by calorimetric method is 43 W for all the liquid volumes). Thus, in this case, the effect of power density into the system was investigated by varying the volume of the liquid (in the range 1−2.5 L thereby enabling a liquid level of 4.4−11.1 cm). Schematic representation of the experimental setup in this case has been given in Figure 2.

Although a number of techniques have been developed to measure the volumetric gas−liquid mass-transfer coefficient, the dynamic methods are preferably used, as they are fast, experimentally simple, and applicable to various systems.[14] In this method, a fast-responding

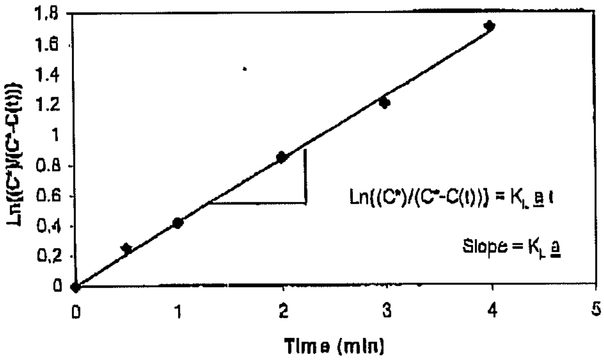

Figure 3. Estimation of mass-transfer coefficient from data of dissolved oxygen concentration and time (ultrasonic bath reactor with 120-W power input, volume of 680 mL, and gas flow rate of 24.31 cm^3/s).

(time constant (τ_s) ~5 s) oxygen electrode is employed to follow the oxygen uptake rate in the liquid phase following a step change in the oxygen concentration in the aerated gas. Initially the dissolved oxygen concentration in the liquid is brought to zero by the addition of sodium sulfite, which acts as an oxygen scavenger. After a gap of few minutes for stabilization of the system, the ultrasonic horn was switched on and the variation of dissolved oxygen concentration with time was recorded. Aeration was continued until the liquid was saturated with respect to dissolved oxygen at the operating conditions. A number of experiments have been repeated at any one particular operating condition, and the location of the horn and the observed variations have been quantified. A similar operating procedure was followed in ultrasonic bath type of reactor except for the fact that nitrogen gas was used for the scavenging of the oxygen and the system was kept stationary after this for some time so that all the nitrogen bubbles disengaged completely. It should be noted here that there is no effect with the type of scavenging medium used before the dynamic aeration on the magnitude of the mass-transfer coefficient.

For the estimation of the actual value of the gas–liquid mass-transfer coefficient from the data of dissolved oxygen concentration and time of irradiation, the following procedure has been adopted.

Dissolved oxygen mass balance in transient state in the reactor can be written as

$$K_L a V(C^*_{O_2} - C_{O_2}) = V\, d(C_{O_2})/dt \qquad (1)$$

where K_La is the volumetric mass transfer coefficient, V is the volume of the liquid in the reactor (m^3), $C^*_{O_2}$ is the dissolved oxygen saturation concentration measured for the highest values of time (mmol/m^3), and C_{O_2} is the dissolved oxygen concentration (mmol/m^3) in the reactor at any time t. Equation 1 after integration with the initial condition of C_{O_2} (at $t = 0$) = 0 gives

$$\mathrm{Ln}\{(C^*_{O_2})/(C^*_{O_2} - C_{O_2}(\text{at } t))\} = K_L a t \qquad (2)$$

A graph of $\mathrm{Ln}\{(C^*_{O_2})/(C^*_{O_2} - C_{O_2}(\text{at } t))\}$ versus time (t) gives a straight line with a slope as K_La (Figure 3 shows one such sample graph for the operating conditions of an ultrasonic bath reactor with 120 W power input, a volume of 680 mL, and a gas flow rate of 24.31 cm^3/s). A similar procedure has been adopted for all the cases and for all the equipment configurations studied in this work.

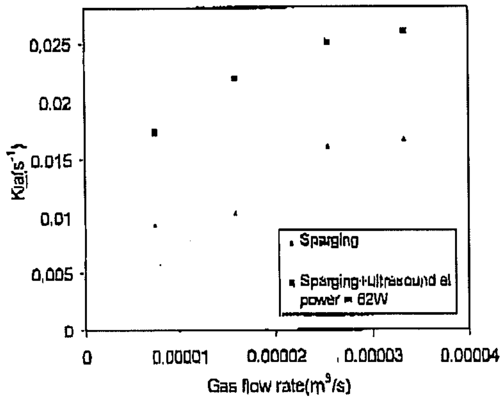

Figure 4. Dependency of mass-transfer coefficient on the gas flow rate in the presence and absence of ultrasound in the ultrasonic horn.

Mass-Transfer Studies with Ultrasonic Horn

Effect of Gas Flow Rate. The variation in the mass-transfer coefficient with gas flow rate for the two conditions of aeration alone and aeration in the presence of ultrasonic irradiation has been depicted in Figure 4. It can be seen from the figure that the mass-transfer coefficient increases with an increase in the gas flow rate, a trend very similar to that reported in the case of mechanically agitated gas–liquid contactors.[15] Further it can be observed that the presence of ultrasound (power dissipation of 62 W) results in an increase in the mass-transfer coefficient at the same gas flow rate (about 50–110% depending on the gas flow rate). The observed effect can be attributed to the additional interfacial turbulence created by the ultrasonic irradiation.[16] The bubbles are broken into smaller bubbles, which spend more time in the reactor (increasing the gas hold-up) and also increasing the interfacial area available for mass transfer. Visual observation of the system in the presence and absence of ultrasound confirmed this trend of decreasing bubble size. The dependency of the extent of increase in the mass-transfer coefficient due to ultrasonic action on the flow rate can be attributed to the fact that, at lower gas flow rate, the energy associated with the gas is much less and hence the supplementary action of ultrasound results in more favorable effects. Also, the gas remains in the active zone of cavitation for a longer time resulting in a better distribution of the gas and also larger reduction in the bubble size. One more factor affecting the intensification is the attenuation of ultrasonic energy due to the presence of gas. At higher flow rates, the extent of attenuation will be more[17] (also, decoupling action will be there) leading to lower availability of the ultrasonic energy for dispersion and breakage of gas bubbles or creation of the interfacial turbulence.

Thus, it can be said that the same transfer efficiency can be achieved at lower gas flow rates in the presence of ultrasound and also the extent of intensification obtained due to ultrasound depends on the gas flow rate. This information must be used in the design of reactors and in the selection of the operating parameters to achieve the expected yields of the reactions. To further understand the role of ultrasonic irradiation in the intensification of the mass-transfer coefficient, ultrasonic power dissipation into the system was varied at a constant gas flow rate.

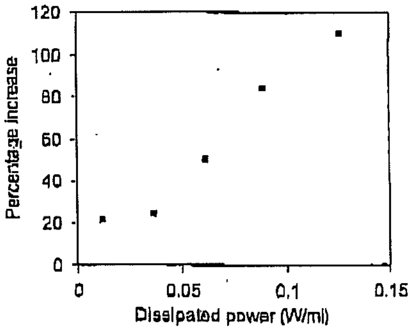

Figure 5. Dependency of extent of intensification obtained due to the use of ultrasound on ultrasonic power dissipation into the system at constant gas flow rate of 1.6 × 10^{-5}m^3/s.

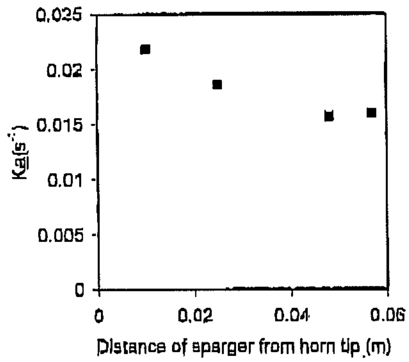

Figure 6. Dependency of gas–liquid mass-transfer coefficient on the distance of sparger from the horn type in the presence of ultrasound (power 30 W) and at constant gas flow rate of 1.6 × 10^{-5}m^3/s.

Effect of Ultrasonic Power Dissipation. Figure 5 shows the variation of the extent of intensification (depicted as percentage increase in the mass-transfer coefficient in the presence of ultrasound over and above that in the absence of ultrasound) with the ultrasonic power dissipation into the system as measured calorimetrically. It can be seen from the figure that dissipating more and more power into the system is favorable for the mass transfer process. In a certain range of dissipated power the percentage increase in the mass transfer coefficient is almost linear with the ultrasonic power over the range of power dissipation as studied in the work and can be expressed mathematically as (with a R^2 value of 0.95)

$$\text{percentage increase} = 889.1(\text{power density}) \quad (3)$$

where power density is expressed in watts per milliliter. It should be noted here that the above equation is valid for the operating power density in the range 0.01–0.125 W/mL, above which the beneficial effects may or may not be observed. Earlier studies with chemical reactions have indicated that an optimum power density exists above which the beneficial effects due to an increase in the power dissipation are not observed.[18–20]

The observed results of an increase in the mass-transfer coefficient with the increase in power dissipation can be attributed to higher cavitational activity (more will be the extent of turbulence created due to ultrasonic action and hence more breakage of the gas bubbles) and higher rates of liquid circulation (more dispersion of the bubbled gas resulting in increased residence time in the reactor) at higher power dissipation into the system. Though there is no direct measure of the higher cavitational activity at higher power dissipation, indirect confirmation of this hypothesis can be obtained from results in chemical processing applications. Sivakumar and Pandit[18] and Gogate et al.[19] have reported that the rates of degradation of pollutants are higher at higher power dissipation into the system (below the optimum power density above which the rate of degradation is lower; the value of optimum power density will also be dependent on the system) due to higher number of cavitating bubbles and hence free radicals. Also, Vichare et al.[16] have reported that the liquid circulation velocity due to acoustic streaming increases with an increase in the extent of power dissipation. Thus, dissipating more power seems to be beneficial for the mass-transfer operations. In the large-scale applications and for higher rates of chemical processing, usually higher power dissipation is desired, and hence, it seems that there will not be any mass-transfer limitations for the transfer of gaseous reactants. The extent of intensification obtained due to ultrasonic irradiation at large-scale application must be considered in the design procedure to avoid overdesign of the system, i.e., overprediction of the cavitational yields.

Effect of Distance of Sparger from the Horn Tip. The dependency of the mass-transfer coefficient on the position of the sparger is shown in Figure 6. It can be seen from the figure that the value of the mass-transfer coefficient is maximum when the sparger is located very near to the horn tip and K_La decreases as the sparger is moved away from the horn tip except for a marginal increase obtained at the position corresponding to a distance of 0.057 m. The observed trend is exactly identical to the variation of cavitational activity with distance from the horn tip. Previous studies[20–25] have indicated that the ultrasonic activity is maximum very near to the horn tip and it decreases with an increase in the distance away from the horn tip with marginal increase in the activity at distances corresponding to multiples of half the wavelength or where the activity of standing waves is maximum. A marginal increase observed at a position of 0.057 m could be attributed to higher cavitational activity due to the formation of a standing wave pattern. Thus, if the gas is introduced very near to the horn tip or at location of higher cavitational activity, the extent of dispersion and breaking of the gas bubbles will be more, leading to an enhancement in the mass-transfer coefficient mainly due to the increase in the interfacial area. The situation is exactly identical to a classical gas–liquid mechanically agitated contactor where maximum effects in terms of gas holdup or mass-transfer coefficient are obtained when the gas is introduced at the eye of the impeller, i.e., energy dissipating device. In the case of a sonochemical reactor, the horn tip is the point of the energy dissipation into the system and hence one can expect a maximum velocity effect on K_L and a.

Presence of Sodium Chloride. Sodium chloride has been used in the past for intensification of the chemical reactions due to ultrasound,[12,13] and also, the presence of sodium chloride has been reported to give higher gas-phase holdup and mass-transfer coefficient in the classical gas–liquid reactors due to noncoalescing action of the electrolyte.[26] Thus, it was thought desirable to investigate the dependency of the mass-transfer coefficient in sonochemical reactors on the presence of sodium chloride. The dependency of K_La on the gas flow rate in this system was exactly identical to that ob-

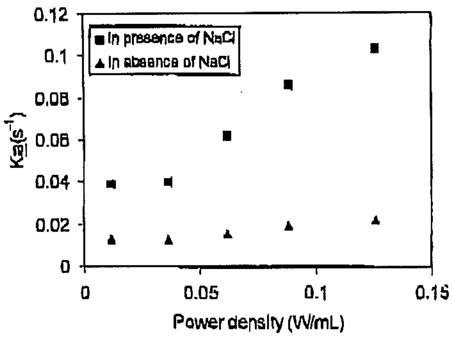

Figure 7. Dependency of gas—liquid mass-transfer coefficient on the ultrasonic power dissipation in the presence and absence of 1 M NaCl at constant gas flow rate of $1.6 \times 10^{-5} m^3/s$.

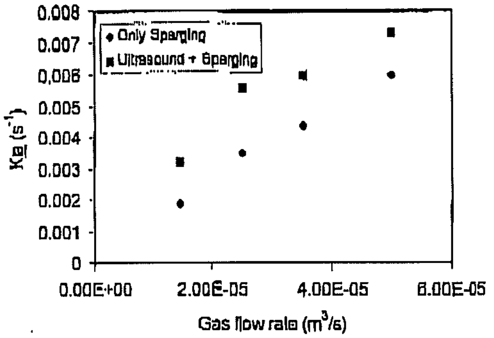

Figure 8. Dependency of mass-transfer coefficient on the gas flow rate in the presence and absence of ultrasound in ultrasonic bath.

served in an air—water system in sonochemical reactors as well as in conventional mechanically agitated contactors, i.e., an increasing trend with an increase in the gas flow rate. The variation of K_La with ultrasonic power dissipation in the presence and absence of 1 M NaCl solution is shown in Figure 7. It can be seen from the figure that the presence of sodium chloride is highly beneficial to the mass-transfer phenomena and K_La is about 3—5 times more (depending on the ultrasonic power dissipation) in the presence of NaCl as compared to that obtained in the absence of NaCl. The observed increase in the K_La due to the presence of NaCl can be attributed to the fact that aqueous sodium chloride is a noncoalescing system, which leads to generation of many small bubbles in the system, which subsequently increases the available gas—liquid interfacial area and hence the magnitude of K_La. The presence of NaCl might also lead to a decrease in the gas solubility, but it appears that the extent of increase in the interfacial area is perhaps substantially more as compared to the decrease in the gas solubility, thereby leading to an increase in the net effect, i.e., an increase in the mass-transfer coefficient.

It can be also seen from the figure that, at higher ultrasonic power dissipation, the extent of increase obtained in the presence of NaCl is also higher (5 times more K_La at power of 62 W and 3 times more K_La at power dissipation of 6 W). At higher powers, the formation of smaller bubbles due to the presence of NaCl is further augmented by the higher cavitational activity or fluid turbulence leading to a substantial enhancement in the magnitude of K_La. Thus, it can be said that intensification obtained due to the addition of sodium chloride is more pronounced at higher power dissipation and hence its use in a large-scale operation is indeed feasible considering the mass-transfer aspects; also, the presence of sodium chloride will lead to localization of the reactants at the cavitation spots, enhancing the intrinsic rates of sonochemical reactions.

It should also be noted here that the aim of using NaCl for the investigation of mass-transfer phenomena was just to explain the intensification observed in the sonochemical reactions studied earlier. A detailed investigation using different ionic strength solutions (type as well as concentration) will indeed reveal more design information but is beyond the scope of the present work. The effect will indeed be the same, as the mechanism of intensification, i.e., noncoalescing action, will remain the same.

Effect of the Frequency of Irradiation. Some preliminary investigation into the effect of frequency of irradiation on the mass-transfer phenomena was made using a high-frequency ultrasonic horn operating at 500-kHz frequency and 30-W power dissipation. The magnitude of K_La at a gas flow rate of 7.4×10^{-6} m^3/s was found to be 0.01 s^{-1} in the presence of ultrasound whereas in the absence of ultrasound the value was observed to be 0.0099 s^{-1}, indicating only a marginal effect. An increase in the power dissipation to 60 W also did not have any effect on the magnitude of the mass-transfer coefficient. The observed results can be attributed to the fact that at higher frequency of operation the degassing effect is significant (as discussed later) and hence the enhancement obtained due to the presence of ultrasound is nullified by the higher rates of degassing (~5 times higher) obtained in the high-frequency reactor as compared to the low-frequency reactor. Precise quantification of the degassing rates in the two reactors indicated that the initial degassing rate in the high-frequency reactor (500 kHz) is 0.4 ppm/min at 30-W power dissipation whereas it is ~0.08 ppm/min at 62-W power dissipation in the case of the horn with irradiating frequency as 20 kHz (no data were available at 30-W power dissipation in this reactor but at lower power dissipation it will be still lower as the extent of degassing is directly proportional to the ultrasonic power dissipation). Another reason for the observed results is that the active zone of cavitation is at the liquid surface in the case of high-frequency irradiation[27] 27
whereas it is at the horn tip in the case of low-frequency operation and also the mechanical effects of cavitation are much reduced when frequency is increased. This leads to a higher equilibrium gas content under the influence of ultrasound in the low-frequency reactor and hence the intensification is observed. Thus, these results have helped in disseminating the dependency of the intensification of mass transfer on the frequency of irradiation though more quantitative experiments need to be performed.

Mass-Transfer Studies in Ultrasonic Bath

The results of the experiments in an ultrasonic bath have been shown in Figure 8 and Figure 9. Figure 8 depicts the variation in the mass-transfer coefficient with the gas flow rate for the two cases viz. only air sparging and combination of ultrasonic irradiation and sparging. Figure 9 depicts the variation in K_La with the power density into the system (logic for performing such experiments have been already described earlier). It can be seen from the figures that the observed trends in the variation are identical to that obtained in the case of the ultrasonic horn though the absolute values of the

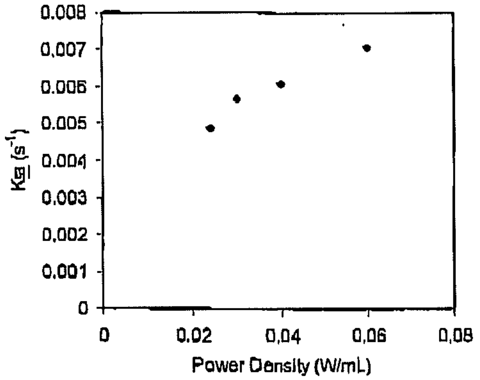

Figure 9. Dependency of mass-transfer coefficient on the ultrasonic power density in the case of the ultrasonic bath at constant gas flow rate of 5×10^{-5} m^3/s.

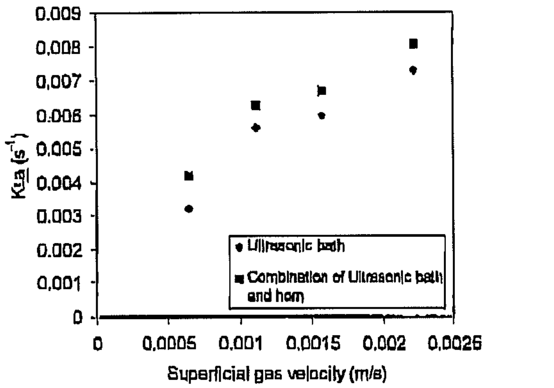

Figure 10. Investigating the efficacy of the combination of the ultrasonic bath and ultrasonic horn for mass-transfer operation.

mass-transfer coefficients and of the mass transfer improvement are different in both cases. At the same magnitude of power density (W/m^3) and gas flow rate (m^3/s), the mass-transfer coefficient in the case of the ultrasonic bath is 1 order of magnitude lower as compared to the ultrasonic horn. This can be attributed to the fact that in the case of the ultrasonic horn the cavitational activity is much higher as compared to that obtained in the case of ultrasonic bath, and hence, it helps in higher intensification of the mass-transfer phenomena. Also due to the location of the sparger in the case of the ultrasonic horn (sparger is located exactly below the transducer), all the introduced gas bubbles come under the cavitationally active zone (the natural tendency of the gas bubbles is to rise upward and come in contact with the cavitationally active or turbulent liquid) and hence get dispersed and broken into smaller bubbles to raise the mass-transfer coefficient. With the ultrasonic bath, the location of the sparger is between the two transducers (and the third transducer is far away from the sparger) so only a small percentage of the introduced gas comes under the influence of the cavitational zone. Also, in this case, the natural tendency of the gas will be to go away from the transducer surface and hence the zone of maximum cavitational activity. Due to a more homogeneous distribution of the cavitational activity in the case of the ultrasonic bath as compared to the horn,[25] and due to a higher value of free surface divided by the liquid volume the degassing rates with the ultrasonic bath could be higher as compared to the ultrasonic horn (Exact quantification of the degassing rates is currently being done in the department.). The combination of all these effects leads to a lower intensification of the mass-transfer process with the ultrasonic bath. Thus, the position of the sparger along with the distribution of the cavitational activity plays a crucial role in deciding the rates of mass transfer.

To further investigate the role of gas distribution in deciding the extent of intensification, additional experiments were performed using a combination of ultrasonic horn and ultrasonic bath. Such an arrangement has been used in the past[8] and was found to be beneficial for the degradation of formic acid. The logic of using such an arrangement that results in acoustic streaming generated by the horn, which is positioned at the surface of the liquid, i.e., above the sparger, more gas bubbles will be subjected to the cavitational activity by reintroduction of the bubbles in the system possiblly leading to more intensification in the mass-transfer process.

Figure 10 shows the results obtained for the combination of ultrasonic horn and ultrasonic bath in comparison to those obtained for only ultrasonic bath. It can be seen from the figure that the presence of the ultrasonic horn at the top indeed increases the rate of the mass-transfer process. A careful analysis of the obtained results indicates that the extent of enhancement obtained due to the presence of the ultrasonic horn also depends on the gas superficial velocity (the more the velocity, the less is the obtained extent of enhancement). This can be attributed to the fact that, at lower gas velocity, the convective currents generated by the ultrasonic horn are able to distribute the rising gas back into the system whereas at higher gas velocities, energy associated with the gas takes it out of the system. Thus, it can be said that distribution of the gas bubbles at the cavitationally active zone plays a crucial role in deciding the intensification obtained due to the presence of ultrasound.

Correlations for the Prediction of Mass-Transfer Coefficient

The volumetric mass-transfer coefficient from the bubble population is known to depend on the liquid-phase turbulence (power input into the system and gas flow rate will have significant effect on the turbulence). Liquid-phase turbulence is also known to affect the bubble size distribution and hence the gas–liquid interfacial area, affecting the overall mass-transfer coefficient. Thus, the overall observed rate of gas dissolution (gas transfer) is expected to be a complex function of the operating parameters and the geometric variables of the system. Generally, correlations depicting the dependency of the mass-transfer coefficient on the power dissipation per unit volume and gas superficial velocity are used in the case of conventional stirred reactors.[15,36] Correlations of a similar nature were also fitted for the prediction of the mass-transfer coefficient in the present case. Equations 4–6 give the correlations obtained for the air–water system in the ultrasonic horn/ultrasonic bath based on the results obtained in this work and mechanically agitated contactor (MAC), respectively.[15]

Ultrasonic horn $$K_La = 0.029(P/V)^{0.17}(V_g)^{0.37} \quad (4)$$

Ultrasonic bath $$K_La = 0.0039(P/V)^{0.4}(V_g)^{0.6} \quad (5)$$

MAC $$K_La = 0.0049(P/V)^{0.6}(V_g)^{0.4} \quad (6)$$

where K_La is in reciprocal seceonds, P/V is in watts per cubic meter, and V_g is in meters per second.

It should be noted here that eqs 4 and 5 are developed for the case of transfer of oxygen gas from air into water whereas eq 6 is valid for transfer of pure oxygen and also the geometries of the reactors used in the work are different. As the gases are sparingly soluble (of the order of few ppm), the gas side resistance is negligible and hence liquid side resistance will be the controlling factor. Hence, gas mixtures will not have much effect on the mass transfer of a single gas. Also Linek et al.[15] showed that the mass-transfer coefficient is strongly dependent on the P/V and gas flow rate and less dependence is observed for the geometry of the reactor. These two facts justify the comparison of the mass-transfer coefficient values with an aim of identifying the controlling mechanisms for the mass-transfer phenomena in the different systems.

Comparison of eqs 4–6 reveals some interesting facts. The exponent over (P/V) is lower in the case of a reactor where energy has been introduced in the form of ultrasonic vibrations as compared to the reactor where energy is introduced by virtue of mechanical agitation. This can be attributed to the fact that a mechanically agitated contactor creates more convective currents as compared to the sonochemical reactors (where more turbulence is generated), which dominate the transport phenomena. Thus, the effective utilization of the ultrasonic power is much less as compared to the energy dissipated in the form of mechanical agitation. A detailed discussion about the relative extents of turbulence and convective currents has been presented in our earlier work.[28] Further, the exponent over V_g in the case of the ultrasonic horn is comparable to that obtained in the case of the mechanically agitated contactor whereas both are quite less when compared to the value obtained with the ultrasonic bath. A higher dependency of K_La on the V_g in the case of ultrasonic bath can be attributed to the placement of the sparger. Since the sparger is located above the transducers, not all the sparged gas comes under the influence of the transducers. With an increase in the V_g, this fraction of the sparged gas coming under the action of cavitational activity would increase (due to higher downward momentum) and hence contribute to the further enhancement obtained in the presence of ultrasound. In the case of the ultrasonic horn, the sparger is located below the transducer similar to a conventional mechanically agitated contactor, and hence, all the introduced gas comes under the influence of an energy dissipating device leading to a similar dependency of the K_La on V_g.

Figure 11 gives the relative values of the mass-transfer coefficient in different reactors as a function of gas superficial velocity at constant power density into the system. It can be seen from the figure that the highest value is obtained in the case of a mechanically agitated contactor at similar gas velocity and power density thereby confirming the importance of convective fluid motion as discussed earlier followed by the ultrasonic horn (confirming the important of sparger location leading to maximum gas being influenced by the ultrasonic action) and least in the case of the the ultrasonic bath.

Conclusions

Using ultrasonic irradiations results in the intensification of mass-transfer phenomena though the extent of intensification strongly depends on the operating

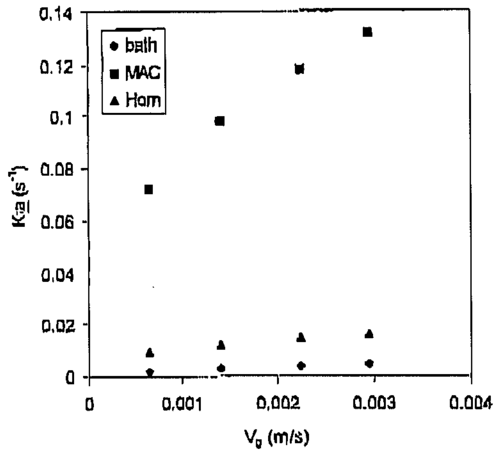

Figure 11. Comparison of mass-transfer coefficient in different reactors at constant power density of 11.71 kW/m³; MAC data estimated from equation reported by Linek et al.[15]

parameters including the type of reactors used for irradiation and the relative geometrical orientation of the sparger and the transducers. The following important conclusions/design information can be drawn based on the results reported in this work:

1. In the case of the ultrasonic horn, use of ultrasound results in about 50–110% enhancement in the mass-transfer coefficient over that obtained in its absence. The extent of intensification significantly depends on the gas flow rate (more intensification at lower gas flow rate) as well as on the power dissipation into the system (more intensification at higher power dissipation).

2. The position of the sparger also plays a crucial role in deciding the intensification obtained due to ultrasonic irradiation. The position should be such that all the introduced gas should come under the influence of the cavitational activity or in the path of acoustic streaming; i.e., it should be nearer to the transducers and also should assist the natural tendency of the gas movement.

3. The presence of sodium chloride gives enhanced rates of mass transfer due to the formation and maintenance of smaller bubbles. Further, the extent of enhancement due to the presence of NaCl is higher at higher ultrasonic power dissipation, possibly due to the synergistic mechanisms of intensification (i.e., by formation of smaller bubbles).

4. Degassing also plays a crucial role and intensification is only observed at lower frequency of operation due to lower degassing rates as compared to high-frequency reactors (absolutely no intensification in K_La is obtained). Thus, using low-frequency reactors appears to be more favorable as compared to high-frequency reactors (the disadvantages of high-frequency reactors are already well-discussed in the literature).

5. Design correlations have been presented for the estimation of the mass-transfer coefficient in the standard format. Comparison with the results of mechanically agitated contactors leads to a conclusion that liquid convective motion is more dominant in deciding the rates of gas–liquid mass transfer as compared to the liquid-phase turbulence.

Acknowledgment

The authors acknowledge the funding of the Indo-French Center for Promotion of Advanced Research (Centre Franco-Indien Pour La Promotion de La Recherche Avancee), New Delhi, India, for the collaborative research work.

Nomenclature

a = specific interfacial area (m^2/m^3)
$C^*_{O_2}$ = dissolved oxygen saturation concentration (mmol/m^3)
C_{O_2} = dissolved oxygen concentration at time t (mmol/m^3)
$d(C_{O_2})/dt$ = rate of change of dissolved oxygen concentration (mmol/$m^3 \cdot s$)
f = frequency of irradiation (kHz)
K_L = true liquid side mas-transfer coefficient (ms^{-1})
K_La = overall gas−liquid mass-transfer coefficient (s^{-1})
P = ultrasonic power dissipation into the system (W)
t = time of irradiation (s)
V = volume of the liquid (m^3)
V_g = gas superficial velocity ($m \cdot s^{-1}$)

Greek Characters

τ_p = time constant for the probe (s)

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Received for review September 5, 2003
Revised manuscript received January 14, 2004
Accepted January 23, 2004

IE0341146