Rate intensification of mass transfer process using ferrofluids

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The rate of inter-phase mass transfer process is of central importance in several processes in the chemical industry. This rate depends on the mass transfer coefficient, which in turn is determined by molecular processes taking place in a region close to the phase interface. The mass transfer coefficient, therefore, is not substantially influenced by the mixing processes taking place away from the interface. In this study the authors present a novel strategy for enhancement of mass transfer rates by employing ferrofluids in the 'interfacial region' and causing them to oscillate using a magnetic field external to the equipment. Taking a gas-liquid system as an example to illustrate the strategy, it is shown that 40-50% increase in mass transfer rates are easily achieved, and that the increase depends on the ferrofluid loading and the strength of the magnetic field employed. Some limitations of the methods employed in the present work are also discussed, and it is possible that much higher enhancements are potentially possible.

1 Introduction

Mass transfer operations are of central importance in chemical process industry. Not only do they form the major unit operations such as distillation, gas adsorption and liquid extraction, but also are they of importance in any reactive process where the reactants happen to be distributed in different phases. Absorption of carbon dioxide in hot carbonate-bicarbonate buffers (a process of importance in the fertilizer industry), and several liquid phase oxidations used in the manufacture of a variety of petrochemicals and polymer intermediates, may be cited as examples of the latter class of applications. In all these cases, the rate of the process (and hence the design of process equipment) is often limited by the rate of the inter-phase mass transfer process involved. In reactive processes of the type mentioned above, if the reaction happens to be a complex one in which the desired product(s) can get consumed by unwanted secondary reactions, limitations due to mass transfer rates can lower not only the rate but also the selectivity. There is thus a case for examining methods to improve mass transfer rates in a number of process situations.

Mass transfer rates depend on the product of the physical mass transfer coefficient ($k_1$) and interfacial area per unit volume ($\bar{a}$). Conventional methods for improving mass transfer rates seek to improve this product (known as the volumetric mass transfer coefficient) by increasing mixing and turbulence in the bulk of the phase or phases involved. Usually, and especially in bubble and drop systems, these techniques succeed more in increasing than in increasing $k_1$. Even here, there are limitations; the power input needed may become too high to be economical, or the required flow-rates may be impractical because of hydrodynamic limitations such as flooding. More importantly, in a number of situations, it is an improvement in $k_1$ that is of far greater consequence than that of $\bar{a}$. This would be the case, for example, in the applications of mass transfer with chemical reaction referred to in the previous paragraph, where the extent of mass transfer limitations is determined by a parameter (called the Hatta number) which depends on $k_1$ and is independent of $\bar{a}$.

The limitations of the conventional methods mentioned above in increasing $k_1$ may be understood in terms of the theories of mass transfer\textsuperscript{1,2}, according to which the mass transfer flux (rate per unit area, proportional to $k_1$) is determined by molecular diffusion in a region close to the interface. The film theory makes this diffusion out to be a steady state process in an essentially stagnant layer next to the interface, while penetration and surface renewal
theories explain this as an unsteady state process, in surface elements which are brought to the interface from the bulk by the mixing process, and are recycled to the bulk after a length of stay at the interface. In any case, what is relevant to us in the present context is the distance from the interface within which molecular processes operate, which can be understood as the thickness of the stagnant film in the film theory or as a ‘penetration depth’ in the penetration theory. Typical mass transfer rates observed in industrial contractors suggest this distance to be of the order of microns. Methods which agitate the bulk of the phase outside this region are therefore of limited value in influencing mass transfer fluxes. If it were possible to somehow ‘stir’ and induce mixing in this interfacial region, we may expect to get much greater improvements in the mass transfer coefficient.

What the authors describe in this paper is, a method to achieve just this, by employing ferrofluids. Ferrofluids are composed of 3-15 nm particles of solid single domain magnetic particles coated with a molecular layer of dispersant and suspended in a liquid carrier, which may be either water or oil. True ferrofluids are stable colloidal suspensions and are kept from phase separating by the action of brownian forces. If such a fluid is added to the continuous phase of, say a gas-liquid dispersion, because of the fine particles size, the magnetic particles can approach the interface quite closely, to distances well within the interfacial region. Since the particles try to follow the direction of an imposed magnetic field external magnetic field can be employed to move the particles around and thereby cause mixing in the interfacial region.

While ferrofluids have been talked about in the context of the analogous process of heat transfer, the phenomenon exploited there is quite different, and to the best of our knowledge, no published work is available which seeks to exploit the magnetic property of these fluids in the manner described in this work. The work is concerned with exploring the feasibility of the idea, and if the idea can be established as more than an academic curiosity, further studies may be directed towards the engineering aspects of reactor design and so on. The method is expected to be particularly effective in cases where mass transfer is difficult, such as in viscous fluids. The magnetic property of the ferrofluid can also be exploited in collecting the fluid and recycling it.

Fig. 1 — Schematic of the experimental set-up incorporating the wetted wall column. The electric coil arrangement to provide the magnetic field is also shown.

2 Methodology

In order to test the efficacy of the proposed technique in improving mass transfer rates, measurements of mass transfer rates in chosen gas-liquid systems have been made in controlled situations, both in the presence and absence of ferrofluids. As shown in Fig. 1, a coil, carrying alternating current at the mains frequency (50 Hz) surrounds the gas-liquid contactor and provides a periodically changing external magnetic field. The following control experiments have also been used in certain cases to establish the effect of the proposed strategy beyond doubt: mass transfer rates in the presence of ferrofluid but without the external field, and in the presence of the field but without the ferrofluid.

Two steps of contactor have been used in these studies. The first is the Wetted Wall Column (WWC) which has the liquid running down the
inside of a tube as a thin film, and gas rising through the centre of the tube. Often used in the study of mass transfer phenomena, this is a 'model contactor', in that the hydrodynamics and the molecular processes at the interface can be exactly described, and hence, the mass transfer coefficient can be theoretically calculated. The mass transfer area is also exactly known, being the inner surface of the liquid curtain. This device thus makes it possible to see effects on the mass transfer coefficients directly. However, the hydrodynamics are different from what would prevail in the near-interface region in a bubbling type industrial contactor, and the question of extrapolating the results to the industrial situation is therefore not easy to answer. The second contactor used is a bubble column (Fig. 2), and is more representative of the type of gas-liquid contact that occurs in a large class of industrial gas-liquid contactors. In this, the gas is sparged as bubbles into a volume of liquid held in the column.

An often-used method to characterize the mass transfer performance of gas-liquid contactors employs 'model reactions' with known kinetic features, and this has been done in the present work also. The interpretation of the data from such experiments is based on the theory of mass transfer with chemical reactions, salient features of which we shall briefly review. A 'gas-liquid' reaction such as:

\[ A(\text{gas}) + bB(\text{liq}) \rightarrow \text{Products (liq)} \]  

occurs in one of several 'regimes', depending on the relative rates of mass transfer and chemical reaction, which is indicated by the value of the dimensionless parameter, Hatta number. The Hatta number for a reaction which is of order \( m \) in \( A \) (gas phase reactant) and order \( n \) in \( B \) (liquid phase reactant), is given by:

\[ Ha = \sqrt{M} = \frac{1}{k_i} \left[ \frac{2D_{ij} \cdot c_{A0}^n \cdot (c_A^*)^{m-1}}{(m+1)} \right] \]  

Table 1 shows the important regimes that are possible, and their salient features. The regime classification is based on the locale of the reaction. If the liquid can be thought of as composed of an 'interfacial region' and a 'bulk region' that lies outside, slow reactions are those whose occurrence in the interfacial region can be neglected, the gaseous solute crossing through the interfacial region practically without being reduced in amount.

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**Fig. 2** — Schematic of the experimental set-up incorporating the bubble column. The arrangement of magnetic field is not show, and is identical to that in the wetted wall column set up
by reaction there, and reacting in the bulk. Under two extreme situations shown, such reactions can become either totally kinetically controlled or totally diffusion controlled. Fast reactions, by contrast, occur completely in the interfacial region, practically the entire solute flux being consumed within this region before it can reach the bulk. Such reactions, by virtue of the fact that they operate within the region of molecular diffusion processes, do influence mass transfer rates. This influence is quantified by the 'Enhancement factor' \( E \), which shows the extent to which the mass transfer coefficient is increased by the occurrence of the reaction in the interfacial region. The absorption rate per unit liquid volume \( N_A \) is in general given by:

\[
N_A \tilde{a} = E k \tilde{a} (c_A^* - c_A)
\]  

...(3)

particular modifications of this equation holding in different regimes as shown in Table 1. Thus, in general, we may say that if \( E \) is higher than one, the occurrence of the reaction within the mass-transfer film (the interfacial region of the previous paragraphs) is significant, and that, the higher the value of \( E \), the closer to the interface is the reaction completed. Two other dimensionless groups influence the regime in some cases as shown in Table 1. The first is:

\[
P = \frac{k_m c_B^n (c_A^*)^{n-1}}{k_i \tilde{a}}
\]  

...(4)

which is of importance in the slow reaction regime and determines whether kinetic control or diffusion control or something in between these extremes prevails. The second:

\[
E_m = \sqrt{\frac{D_A}{D_B} \left( 1 + \frac{D_B c_B}{b D_A c_A} \right)}
\]  

determines the maximum limit to the enhancement factor in a given system. This limit is realized in the case of the instantaneous reaction regime, which occurs when the reaction rate is so fast that the \( A \) and \( B \) cannot co-exist; they diffuse towards each other and annihilate each other at a plane located in the interfacial region. This is thus a case of total diffusion control.

Regimes that fall in between the ones listed are possible; thus, the value of Hatta number may be between 1 and 3, in which case the regime is in between 'slow' and 'fast'. These have been discussed in the literature and approximate expressions to calculate the properties of such 'transition' regimes are available. For example, for the transition region between slow and fast (\( H_a \approx 1 \)), Danckwerts' surface renewal theory provides the expression:

\[
E = \sqrt{1 + H_a^2}
\]  

...(6)

It is the fact that \( E \) [and hence the absorption rate of Eq. (3)] depends on different factors in different regimes (as shown in Table 1) that is exploited in the measurement of mass transfer parameters. For example, it may be verified that the absorption rate in the fast reaction regime in independent of \( k_i \) but is proportional to \( \tilde{a} \), while in
the instantaneous reaction regime, it is proportional to \( k_1 \). Again, it is easily verified that the expression given in Eq. (6) allows an independent calculation of \( k_1 \) and \( \dot{d} \) from absorption rate measurements in the slow-to-fast transition regime. By an appropriate choice of the model reaction and experimental conditions, the required regime may be engineered (and verified), and hence the relevant mass transfer parameter determined.

Two model reaction systems have been used in the present work, and the relevant features of these will now be described.

2.1 Absorption of \( \text{CO}_2 \) in carbonate-bicarbonate buffers

The reactions in this system are:

\[
\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- \\
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+ \tag{7}
\]

(the latter being followed by a very rapid reaction between \( \text{H}^+ \) and \( \text{OH}^- \)). Roberts & Danckwerts\(^4\) have studied this system in detail. Both the reactions are first order in the concentration of \( \text{CO}_2 \) and thus will display pseudo-first order overall kinetics in the buffer solutions, in which the concentration of \( \text{OH}^- \) remains constant. The second order rate constant \( k_{\text{OH}} \) of the first of these reactions at 25 °C is 10 m\(^3\)/mol s, while the pseudo-first order constant, \( k_{\text{H}_2\text{O}} \) of the second reaction is 0.0257 s\(^{-1}\). Thus in the buffer solutions used by the above authors, where the concentration of \( \text{OH}^- \) was not less than 10\(^{-1}\) gion/m\(^3\), the second reaction did not make any substantial contribution to the rate of absorption of \( \text{CO}_2 \).

The concentration of \( \text{OH}^- \) in the buffer solutions is given by the expression:

\[
C_{\text{OH}^-} = \frac{K_w c_{\text{CO}_3^-}}{K_2 c_{\text{HCO}_3^-}} \tag{9}
\]

where \( K_w = C_{\text{H}_2\text{O}} \times C_{\text{OH}^-} \), and

\[
K_2 = \frac{C_{\text{H}} + c_{\text{CO}_3^-}}{c_{\text{HCO}_3^-}} \tag{10}
\]

The values of the dissociation constants \( K_2 \) and \( K_w \) at any temperature depend on the ionic strength. The total pseudo-first order rate constant, \( k_1 \), may be written as:

\[
k_1 = k_{\text{H}_2\text{O}} + (k_{\text{OH}} - K_w c_{\text{CO}_3^-} / K_2 c_{\text{HCO}_3^-}) \tag{11}
\]

and thus a plot of \( k_1 \) against \( c_{\text{CO}_3^-} / c_{\text{HCO}_3^-} \) in solutions of constant ionic strength might be expected to yield a straight line. Roberts and Danckwerts\(^4\) provide plots which show that such a relationship is obeyed within the limits of error by the less alkaline solutions, but that there is a falling off in the reported values of \( k_1 \) in the more alkaline solutions. This is because significant depletion of buffer took place near the surface of absorbing liquid at higher exposure times in their solutions. Their results thus provide guidelines for using this reaction system as a model reaction. Considering the typical values of mass transfer coefficient in a WWC, this reaction would be expected to occur in the instantaneous reaction regime and volumetric mass transfer coefficient can be measured.

An advantage of this reaction system is that the reaction only changes the carbonate-to-bicarbonate ratio (and hence the rate constant) somewhat, maintaining the pH constant up to a point because of the buffer capacity. When an expensive component such a ferrofluid forms part of the liquid, this has the advantage that the liquid can be re-used several times before discarding, thereby economising on the consumption of the ferrofluid in the experiments. The system is also convenient from the experimental point of view, since the absorption rate can be measured directly using a dead-end apparatus fed by an atmospheric pressure reservoir.

2.2 Absorption of \( \text{CO}_2 \) in sodium hydroxide solutions

In a solution of NaOH, carbon dioxide is absorbed according to the reaction:

\[
\text{CO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \tag{12}
\]

The reaction is first order in \( \text{CO}_2 \) and first order in \( \text{OH}^- \). The rate constant is 10 m\(^3\)/mol s at 25 °C. Because of the high value of the reaction rate constant, this reaction could be easily carried out in the instantaneous regime over a large range of mass transfer coefficients. This system is also experimentally convenient since both liquid and gas side measurements can be carried out with facility.
3 Materials and Methods

The ferrofluid for the experiments was mainly obtained from the Department of Physics at Bhavnagar University, Gujarat. Some preliminary experiments in the wetted wall column were however carried out using a sample provided by Ferrofluidics Corp., USA. Both were water-based ferrofluids. The properties of both these fluids are given in Table 2. The other chemicals used were of analytical grade and were locally procured from firms of repute.

The experimental apparatus was designed in-house and was fabricated in glass (SCAM labs, Mumbai). The coil to provide the external magnetic field was fabricated by Lab Magnet Physik, Andheri, Mumbai. The following sections briefly described the apparatus and the operating procedures.

Analytical procedures for carbon dioxide absorption in solutions of NaOH involved volumetry using standard oxalic acid solutions to estimate remaining NaOH. Absorption rates with the carbon dioxide/carbonate-bicarbonate buffer systems (used only in the WWC) were directly measured as gas uptake rates as described in the section below on WWC.

In some cases, using ferrofluids, it was necessary to thoroughly measure the particle sizes after the experiment. This was done using the particle sizing attachment (BI-MAS) of a Zeta-Plus instrument (Brookhaven Instrument Corporation, USA) which measures particle sizes in the colloidal range, with an upper limit of 3 μ.

3.1 Wetted wall column (WWC)

The column was of standard design and was made from a tube of 2.54 cm o.d. and 2.4 cm i.d. At the top, this tube enters and projects into a somewhat larger tube, the feed chamber. This chamber has a liquid inlet from the bottom. The liquid enters the column through the feed chamber, which serves to calm the liquid and distribute it uniformly around the circumference of the WWC. The liquid then flows smoothly down as a film on the inner surface of the WWC and is removed through four grooves (each 2.5 mm wide and 2 mm deep) in a PVC collar (of 30 mm length) placed at the bottom. The position of the collar can be adjusted to get different working heights (and hence exposure times) in the column. The design and use of the collar have been suggested to minimize the effect of the stagnant film which otherwise would tend to form at the bottom of the column due to the presence of adventitious surface active impurities in the liquid feed. The liquid is taken out through a liquid seal which maintains a liquid level about 1 cm below the top of the collar. Fig. 5 shows the WWC experimental set-up.

The gas enters the column through a central tube which opens into the column just above the collar, and leaves from an outlet in the center of the feed chamber. The outlet can be closed for dead-end measurements.

Calculations showed that by using a wetted length in the range 10-25 cm and liquid flow-rates in the range 1.5-3.0 cm/s (Reynolds numbers less than 50), the effect of the entrance region could be rendered negligible and the possibility of ripples in the film eliminated. These conditions therefore provided for satisfactory operation. The surface fluid in the WWC is akin to a penetration element of the penetration theory of gas-liquid mass transfer. Its contact time \( \tau \) with the gas can be calculated from the height of the film and the surface velocity of the film. The penetration theory then gives the mass transfer coefficient as:

<table>
<thead>
<tr>
<th>Ferrofluids used and their specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
</tr>
<tr>
<td>Source</td>
</tr>
<tr>
<td>Carrier liquid</td>
</tr>
<tr>
<td>Particle diameter (mean)</td>
</tr>
<tr>
<td>Saturation magnetization</td>
</tr>
<tr>
<td>Viscosity</td>
</tr>
<tr>
<td>Viscosity</td>
</tr>
</tbody>
</table>
\[ k_i = \sqrt{\frac{4D_A}{\pi t}} \quad \ldots (13) \]

In the range of length and flow rates used, it is possible to get a \( k_i \) in the range of \( 5 \times 10^{-3} \) to \( 9 \times 10^{-3} \) cm/s. Regime calculations show that, for these conditions, an instantaneous reaction regime is easily caused to occur with the CO\(_2\)-NaOH system at concentrations of NaOH of 25 mol/m\(^3\), which was the concentration used in all the experiments. The rate constant in the case of the second system (CO\(_2\)-buffer) depends on the carbonate-bicarbonate ratio as shown by Eq. (11) (and this fact may be made use of to get a range of Hatta numbers), but the regime will be in the transition regime between slow and fast \((Ha=1)\). Eq. (6) can, therefore, be used to calculate both \( k_i \) and \( a \) from the measured absorption rates with this system.

Due to the small extent of absorption in a WWC, the change in concentration of the liquid phase reagent in the column is small and the regimes will remain the same at the top and bottom of the column.

The magnetic field, when needed, is provided by an electric coil which surrounds the column and is co-axial with it (Fig. 5). The coil (made by Lab Magnet Physik, Mumbai) is in two identical parts in series each of 80 mm length, one mounted above the other, with a 10 mm gap in between which serves as an observation window for the WWC. The coil is wound on cylinders with an i.d. of 32 mm, and can be mounted vertically on a stand. Levelling screws are provided to render the cylindrical channel absolutely vertical, so that the WWC can be mounted vertically inside. The coil is connected to the mains AC power supply. The strength of the magnetic field can be varied by varying the input voltage through a variac, and the current can be measured with the help of an ammeter in line. The current can be correlated with the field strength. Measurements showed that the maximum field strengths achievable were: 600 gauss at the centre (axially and radially) of the 80 mm portions containing the coils, and 550 gauss at the centre of the gap between the coils.

The gas inlet was connected to a gas balloon, previously filled with the gas (carbon dioxide) saturated with water vapour at the temperature of interest (25-27 °C), through a soap film meter. The liquid was stored in a 6l constant head tank from which it was admitted into the feed chamber of the WWC. The experiment was typically started with a high flow rate of liquid and the column alignment fine-tuned to get an even distribution of liquid to form a film. The liquid flow rate is then adjusted to the required value, depending on the \( k_i \) desired. For the gas, the outlet is opened and the whole system purged thoroughly before closing the outlet. The gas then enters the column at the rate at which it is absorbed by the liquid film, and this rate is measured by the soap-film meter. Liquid samples can also be taken from the liquid flowing out, for chemical analysis.

Experiments in the WWC included both physical and chemical absorption experiments. Physical absorption (of CO\(_2\) into water) experiments were used only in the initial proving runs for the purpose of validating apparatus design and operating procedures. Chemical absorption experiments involved both the systems discussed earlier, and these systems were employed in experiments both with and without the ferrofluids. In experiments with ferrofluids, the required percentage of the fluid was added directly to the feed reservoir. Ferrofluid A (Table 2) was used in these experiments. Three values of the volumetric hold-up of the fluid were used: 0.8%, 1.6% and 2.0%. A constant magnetic field strength (66.67%) of the maximum) was used in all the experiments where the effect of the field was studied. Since there were difficulties in obtaining more of ferrofluid A, further experiments (in the bubble column) were carried out using ferrofluid B, supplied by the Department of Physics, Bhavnagar University.

3.2 Bubble column (BC)

The bubble column used in the present experiments is made out of a glass tube the same diameter as the WWC (24 mm i.d.) so that it can be mounted inside the coil to provide the magnetic field in exactly the same manner as the WWC. The height of the column was 400 mm. The gas sparger is a porous plate, of the same diameter as the column i.d., attached to the bottom of the column. The column is operated continuously with respect to the gas flow and batch-wise with respect to the liquid. Fig. 5 shows a schematic of the bubble column experimental set-up. The liquid was charged into the column with a small gas flow-rate and then
the flow-rate quickly adjusted to the desired value. The gas (carbon dioxide) was drawn from a cylinder fitted with a two stage regulator, and was metered through a pre-calibrated capillary flow-meter before being sparged into the column. The gas flow-rate was kept constant for a given experiment. Typically, the liquid solution was charged into the column with the gas going through, and the gas flow-rate adjusted quickly to the required value after complete charging. Sufficiently high flow-rates were used so as to avoid near-total absorption in the column. The experiments were carried out for a fixed duration of time, after which the gas flow was stopped and the liquid in the column taken out for chemical analysis. Every experiment was repeated at least twice to check reproducibility of results. In experiments with ferrofluid, the required amount of ferrofluid was added to the NaOH solution before charging into the column.

The fractional gas hold-up can be determined from measurements of the level of the aerated liquid during operation, \( z_F \), and that of the clear liquid (before gassing), \( z_L \), using:

\[
\varepsilon_G = \frac{(z_F - z_L)}{z_F} \tag{14}
\]

Mass transfer coefficients in bubbling systems may be estimated from the correlations given elsewhere. These correlations may be used to obtain a first estimate of these quantities useful in the planning of experiments. In particular, \( k_i \) may be estimated to be of the order of \( 2.11 \times 10^{-5} \) m/s in this apparatus. The expressions in Table 1 may be used to check that an instantaneous reaction regime is quite easily arranged with the carbon dioxide/NaOH system in this apparatus. In our experiments, a NaOH concentration of 100 mol/m³ was used, for which it is readily verified that the regime will be instantaneous reaction; the time of the experiment was fixed so as to maintain this regime throughout the experiment, even after taking into account the decrease in NaOH concentration due to absorption.

The arrangement of the magnetic field for the bubble column is done in a manner identical to that described above for the WWC.

Experiments in the bubble column were carried out to examine the effect of increasing the volumetric hold-up of the ferrofluid (up to 2.66%) and the field strength on the extent of enhancement produced. The experiments with varying holdup of the ferrofluid were carried out at maximum field strength, while the experiments with varying field strength were carried out for a hold-up of 1.33%.

4 Results and Discussion

Initially, several experiments were carried out to validate the design of experimental apparatus and experimental procedures. Sample results are shown in Tables 3 and 4. Table 3 shows the results of physical absorption experiments. Determination of \( k_d V_i \) from these experiments involves dividing the measured absorption rates by the saturation concentration of CO₂ in water at 1 atm and experimental temperature (27 °C), which has been estimated as 1.336 g/l. Theoretical values have been calculated from Eq. (13) and the known (geometric) area of gas-liquid contact. The agreement between calculated and experimentally measured mass transfer rates is seen to be satisfactory. Similar results were also obtained with other column heights.

Table 4 shows similar results obtained with the chemical absorption system CO₂–NaOH. Here the absorption rates have to be divided by \( E \cdot \varepsilon^{*} \) (as Table 1 makes clear for the case of instantaneous reaction regime) in order to obtain \( k_d V_i \). While the agreement is not as good as with physical absorption, it is seen to be satisfactory. One has to

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<table>
<thead>
<tr>
<th>S.No.</th>
<th>Liq. Flow rate ( \times 10^2 ), m³/s</th>
<th>Gas uptake rate ( \times 10^3 ), g/s</th>
<th>Contact time s</th>
<th>( k_d V_i \times 10^3 ), m³/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.57</td>
<td>0.93</td>
<td>0.68</td>
<td>0.729</td>
</tr>
<tr>
<td>2</td>
<td>2.00</td>
<td>0.85</td>
<td>0.82</td>
<td>0.665</td>
</tr>
<tr>
<td>3</td>
<td>1.14</td>
<td>0.69</td>
<td>1.17</td>
<td>0.531</td>
</tr>
</tbody>
</table>
bear in mind the fact that data interpretation here uses additional data such as diffusivities, whose estimates could carry some error. Results at other column heights were similar.

Table 4 — Validation of experimental design and procedures in wetted wall column using the chemical absorption of carbon dioxide in caustic solutions. Column height = 15.5 cm

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Liq. Flow rate</th>
<th>Gas uptake rate</th>
<th>Contact time</th>
<th>$k_d\hat{A}_V \times 10^4$, m$^3$/s</th>
<th>Theor.</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.125 $	imes 10^6$, m$^3$/s</td>
<td>1.32, $\times 10^3$, g/s</td>
<td>0.654</td>
<td>0.626</td>
<td>0.653</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.850 $	imes 10^6$, m$^3$/s</td>
<td>1.15, $\times 10^3$, g/s</td>
<td>0.929</td>
<td>0.525</td>
<td>0.565</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.580 $	imes 10^6$, m$^3$/s</td>
<td>1.11, $\times 10^3$, g/s</td>
<td>1.03</td>
<td>0.498</td>
<td>0.561</td>
<td></td>
</tr>
</tbody>
</table>

Data interpretation for the case of absorption of carbon dioxide in carbonate-bicarbonate buffers involves the use of the so-called ‘Danckwerts plot’ (Fig. 3). For a (pseudo) first order reaction of this type, use of Eq. (6) for the slow-fast transition regime to calculate the absorption rate gives, after slight rearrangement:

$$\left( \frac{N_d\hat{A}_V}{c_A} \right) = k_D_A(\hat{A}_V)^2 + (k_d\hat{A}_V)^2 \quad \ldots (15)$$

The equation shows that, if absorption rates are obtained at different values of $k_1$ (which may be obtained in this system by varying the carbonate to bicarbonate ratio), a plot of the left side of the equation may be made against the value of $k_1$, and, the interfacial area $\hat{A}_V$ and the volumetric mass transfer coefficient $k_d\hat{A}_V$ may be obtained from the slope and intercept, respectively, of the resulting straight line. A series of nine experiments carried out with carbonate-bicarbonate ratio varying from 0.5 to 1.4 was used to construct such a plot. Values of the mass transfer coefficient within 1% of theoretical and interfacial area within 2% of the geometric contact area were obtained.

It may thus be concluded that the construction and operating procedures for the column are adequately satisfactory for investigating the strategy proposed for enhancing mass transfer rates using ferrofluids and an external magnetic field (Fig. 4).

![Fig. 3 — Typical Danckwerts plot of data for carbonate/bicarbonate buffer solution containing 0.8% ferrofluid A (with magnetic field turned on)](image)

Data interpretation for the case of absorption of carbon dioxide in carbonate-bicarbonate buffers involves the use of the so-called ‘Danckwerts plot’ (Fig. 3). For a (pseudo) first order reaction of this type, use of Eq. (6) for the slow-fast transition regime to calculate the absorption rate gives, after slight rearrangement:

$$\left( \frac{N_d\hat{A}_V}{c_A} \right) = k_D_A(\hat{A}_V)^2 + (k_d\hat{A}_V)^2 \quad \ldots (15)$$

The equation shows that, if absorption rates are obtained at different values of $k_1$ (which may be obtained in this system by varying the carbonate to bicarbonate ratio), a plot of the left side of the equation may be made against the value of $k_1$, and, the interfacial area $\hat{A}_V$ and the volumetric mass transfer coefficient $k_d\hat{A}_V$ may be obtained from the slope and intercept, respectively, of the resulting straight line. A series of nine experiments carried out with carbonate-bicarbonate ratio varying from 0.5 to 1.4 was used to construct such a plot. Values of the mass transfer coefficient within 1% of theoretical and interfacial area within 2% of the geometric contact area were obtained.

It may thus be concluded that the construction and operating procedures for the column are adequately satisfactory for investigating the strategy proposed for enhancing mass transfer rates using ferrofluids and an external magnetic field (Fig. 4).

![Fig. 4 — Effect of ferrofluid hold-up on the enhancement produced by the proposed strategy. Data are from bubble column experiments](image)

Some results of experiments with ferrofluid A are shown in Table 5. In view of the excellent results obtained in the initial proving experiments, the absorption of carbon dioxide in carbonate/bicarbonate buffers was employed in these experiments. The results shown are obtained from Danckwerts plots of the data, as described above. A typical plot is shown in Fig. 5.

The fourth and fifth columns of Table 5 compare the mass transfer performances in the following two cases (both with the ferrofluid
added); one with the field turned on and the second with the field turned off. Since the contact area is constant in this case, such a comparison gives directly the effect of the proposed strategy on the mass transfer coefficient. If the surfactants in the liquid provide an interfacial resistance and lower mass transfer rates, such an effect would be present in both the sets being compared and the effect seen would, therefore, be entirely due to the oscillation of the magnetic particles in the interfacial region due to the action of the external field. An enhancement in the mass transfer coefficient of up to 26% is observed from the Table. It is also noted that the effect increases as the ferrofluid hold-up increases. However, the enhancement shows a tendency to saturate as the hold-up is increased, the increase from 1.6% to 2% being only marginal.

Further experiments with ferrofluid B were conducted in the bubble column apparatus, to see how the strategy would fare in a bubbling type contactor. The system used in this case was the absorption of carbon dioxide into caustic solutions. Since a theoretical calculation of $k\bar{a}$ in this case would only be approximate, being based on empirical correlations, the reliability and reproducibility of the experimental procedures was checked using repeat experiments.

Table 5 — Mass transfer performance of the WWC with ferrofluid added to the liquid phase, with and without the magnetic field. Results are from Danckwerts plots of experimental data. A liquid flow-rate of 2.9±1 cm$^3$/s was used in all the experiments.

<table>
<thead>
<tr>
<th>Expt</th>
<th>$v_l/N_l$</th>
<th>Temp, °C</th>
<th>$D_{A}V_l \times 10^6$, m$^3$/s</th>
<th>Field</th>
<th>Field</th>
<th>Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td></td>
<td></td>
<td></td>
<td>off</td>
<td>on</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>0.8</td>
<td>27</td>
<td>0.621</td>
<td>0.698</td>
<td>12.86</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.6</td>
<td>26</td>
<td>0.466</td>
<td>0.565</td>
<td>24.06</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>27</td>
<td>0.384</td>
<td>0.485</td>
<td>26.21</td>
<td></td>
</tr>
</tbody>
</table>

Since, in these experiments, the liquid is not flowing continuously, the rate equation has to be integrated over the time of the experiment to get the variation in concentration of NaOH in terms of the parameters of interest. The equation is:

$$\frac{dc_{B0}}{dt} = 2k\bar{a}E_{\alpha}c_{B}$$

where the 2 on the right hand side arises because of the stoichiometry of the reaction, and $E_{\alpha}$ is given by Eq. (5). Substituting and integrating from the known initial concentration $c_{B0}$ to the concentration $c_B$ at time $t$, and rearranging, we get the following expression for $k\bar{a}$:

$$k\bar{a} = \frac{D_{A}}{D_{B}} \ln \left[ 1 + \frac{D_{B}c_{B0}}{2D_{A}c_{A}} \right] \left[ 1 + \frac{D_{B}c_{B0}}{2D_{A}c_{A}} \right]$$

which may be used to calculate the volumetric mass transfer coefficient from the experimentally measured concentration drop after $t$ seconds.

Table 6 shows some typical results of the experiments. The experiments have been grouped to facilitate comparisons. In every group, calculation of mass transfer enhancement has been calculated with respect to the first member of the group, which is an experiment without added ferrofluid and without magnetic field, other conditions being identical. The reproducibility of the experiments can be seen by a comparison between runs 1(a) and (b), and between runs 1M(a) and (b). It is seen that the technique allows determination of the volumetric...
mass transfer coefficient usually to within 2-3%, and that the reproducibility is not far different in the experiments with and without ferrofluid. Experiments 2 and 2M show that turning on the magnetic field without the ferrofluid in the liquid has hardly any effect on the mass transfer coefficient. Similarly, either of these runs when compared with run 3 shows that, in the absence of the field, fluid alone has negligible effect on the mass transfer rates. Similar conclusions may be arrived at by comparisons among the runs 4 and 4M, and 5 and 5M. These results show that, if the surfactants in the ferrofluid preparation are able to act at all influence the mass transfer performance through increasing the interfacial area, the effect is slight.

By contrast, significant enhancements are obtained when the fluid is added and the field is also activated. The maximum enhancements obtained are in the range of 40-50%. It is seen here also that the effect increases with ferrofluid hold-up only up to a point, beyond which there is little increase. However, one possibility for this saturation behaviour in the present case is that, since an instantaneous reaction is being considered, the reaction place is within the interfacial region, and, in order to be active, the magnetic particles have to act in the space between this plane and the interface. An observation of relevance here was that, in caustic solutions, the ferrofluid tended to lose stability over a period of time, with the particles getting agglomerated to sizes in the micron range. Although, the duration of the experiment was short, it is possible that the effective particle size is larger than in the original ferrofluid, and increases with time during the experiment. Hence, the maximum potential of the method may not have been realised in these experiments.

Results from these and similar other experiments, including duplicates, have been plotted in Fig. 5 to show the effect of ferrofluid volumetric hold-up on the enhancement possible. The trends discussed above are brought out in the figure.

The above experiments were performed with the maximum field strength. It is of interest to see what effect the strength of the field has on the mass transfer enhancement produced. Such data, from experiments similar to those discussed above, but at different field strengths obtained by varying the input voltage to the coil producing the magnetic field, are shown in Fig. 5. The enhancement is here shown as a function of the input voltage itself, and shows that, over the range of variation possible in the present set-up, the field strength has a nearly proportional effect on the enhancement produced. One would expect this effect to saturate at high field

<table>
<thead>
<tr>
<th>Expt No.</th>
<th>Field</th>
<th>Temp, °C</th>
<th>Gas rate in, cm³/s</th>
<th>NaOH conc, mol/l</th>
<th>k_d x10⁵, s⁻¹</th>
<th>Enhancement %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Start</td>
<td>End</td>
<td></td>
</tr>
<tr>
<td>1(a)</td>
<td>Off</td>
<td>0.33</td>
<td>27</td>
<td>0.10</td>
<td>0.036</td>
<td>11.73</td>
</tr>
<tr>
<td>1(b)</td>
<td>Off</td>
<td>0.33</td>
<td>27</td>
<td>0.10</td>
<td>0.0355</td>
<td>11.86</td>
</tr>
<tr>
<td>1M(a)</td>
<td>On</td>
<td>0.33</td>
<td>27</td>
<td>0.10</td>
<td>0.0305</td>
<td>13.22</td>
</tr>
<tr>
<td>1M(b)</td>
<td>On</td>
<td>0.33</td>
<td>27</td>
<td>0.10</td>
<td>0.0315</td>
<td>12.94</td>
</tr>
<tr>
<td>2</td>
<td>Off</td>
<td>0.00</td>
<td>26</td>
<td>0.11</td>
<td>0.04</td>
<td>12.2</td>
</tr>
<tr>
<td>2M</td>
<td>On</td>
<td>0.00</td>
<td>26</td>
<td>0.11</td>
<td>0.038</td>
<td>12.69</td>
</tr>
<tr>
<td>3</td>
<td>Off</td>
<td>0.67</td>
<td>26</td>
<td>0.11</td>
<td>0.0375</td>
<td>12.82</td>
</tr>
<tr>
<td>3M</td>
<td>On</td>
<td>0.67</td>
<td>26</td>
<td>0.11</td>
<td>0.0265</td>
<td>15.87</td>
</tr>
<tr>
<td>4</td>
<td>Off</td>
<td>0.00</td>
<td>25</td>
<td>0.10</td>
<td>0.036</td>
<td>11.73</td>
</tr>
<tr>
<td>4M</td>
<td>On</td>
<td>0.00</td>
<td>25</td>
<td>0.10</td>
<td>0.037</td>
<td>11.48</td>
</tr>
<tr>
<td>5</td>
<td>Off</td>
<td>1.33</td>
<td>25</td>
<td>0.10</td>
<td>0.031</td>
<td>12.80</td>
</tr>
<tr>
<td>5M</td>
<td>On</td>
<td>1.33</td>
<td>25</td>
<td>0.10</td>
<td>0.017</td>
<td>17.50</td>
</tr>
<tr>
<td>6</td>
<td>Off</td>
<td>2.00</td>
<td>26</td>
<td>0.11</td>
<td>0.018</td>
<td>18.43</td>
</tr>
<tr>
<td>6M</td>
<td>On</td>
<td>2.00</td>
<td>26</td>
<td>0.11</td>
<td>0.033</td>
<td>13.6</td>
</tr>
<tr>
<td>7</td>
<td>Off</td>
<td>2.67</td>
<td>26</td>
<td>0.11</td>
<td>0.017</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Table 6 — Effect of the strategy of using ferrofluid with an external, time-periodic magnetic field on the mass transfer rates in a bubble column. All experiments were carried out for 45 s.
strengths, but a tapering off is not seen over the range explored in the present experiments.

5 Conclusions

The data presented in the present paper demonstrates conclusively the possibility of influencing near-interface phenomena in two-phase systems, through the use of ferrofluids and an external, periodically varying, magnetic field. In particular, the authors have explored the enhancement of gas-liquid mass transfer rates through this method of producing agitation in the interfacial region. The experiments show that the enhancements produced are directly and in substantial part attributable to the combination of the fluid and the field, and could not have been produced by either factor acting alone. In mass transfer controlled situations, a 50% increase in the volumetric mass transfer coefficient translates directly to a 50% reduction in equipment volume. Further, since the increase is through an influence exerted on the near-interface phenomena, such enhancements could have far-reaching effects on selectivities in fast gas-liquid reactions. Potential also exists for process improvements in situations involving viscous liquids, such as some fermentation broths and polymeric liquids, although there are other application-specific issues to be examined.

Encouraging as the present results are, it is believed that the technique should be capable of producing far greater enhancements that has been demonstrated here. Some of the reasons for this belief have been discussed in the previous section. Others have to do with the fact that, not all the relevant variables have been examined—it is conceivable that the frequency of oscillation of the field will be an important variable, to give but one example. Again, commercially available ferrofluids have been used, not one’s tailor-made to suit the present chemical systems.

While the results presented certainly qualify the phenomenon as one of academic and research interest, it is believed that the method has potential for commercial exploitation. This may call for specific ferrofluids for specific needs, and novel reactor designs to best exploit their potential.

Acknowledgements

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References

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Nomenclature

\( \hat{a} \) Interfacial area per unit liquid volume, \( L^{-1} \).

\( \hat{b} \) Symbol used for gas phase reactant.

\( \hat{b} \) Stoichiometric factor in the prototype gas-liquid reaction.

\( \hat{B} \) Symbol used for liquid phase reactant.

\( c_a \) Concentration of A in the bulk liquid, \( \text{mol} \ L^{-3} \).

\( c_a^* \) Concentration of A in the liquid at saturation, \( \text{mol} \ L^{-3} \).

\( c_b \) Final concentration of B in bubble column expt., \( \text{mol} \ L^{-3} \).

\( c_{bo} \) Concentration of B in liquid bulk, \( \text{mol} \ L^{-3} \).

\( c_{bi} \) Initial concentration of B in bubble column expt., \( \text{mol} \ L^{-3} \).

\( D_a \) Diffusivity of A in the liquid phase, \( L^2 T^{-1} \).

\( D_b \) Diffusivity of B in the liquid phase, \( L^2 T^{-1} \).

\( E_1 \) Enhancement factor due to chemical reaction.

\( E_{\text{inst}} \) Enhancement factor for an instantaneous reaction.

\( Ha \) Hatta number, defined in Eq. (2).

\( k_1 \) Rate constant for a pseudo first order reaction, \( T^{-1} \).

\( k_{mn} \) Rate constant for a \((m,n)\)th order reaction.
$k_l$ Physical mass transfer coefficient, $LT^{-1}$.

$K_w$ Solubility product for water.

$K_2$ Equilibrium constant defined in Eq. (10).

$m$ Reaction order with respect to A.

$n$ Reaction order with respect to B.

$N_A$ Absorption flux (rate per unit area), mol $L^{-2}T^{-1}$.

$P$ Dimensionless parameter defined in Eq. (4).

$V$ Liquid volume, $L^3$.

$e_0$ Gas hold-up in the bubble column.

$\tau$ Contact time between surface liquid elements and gas, $T$. 