The application of fine TiO₂ particles for enhanced gas absorption

M.V. Dagaonkar a, H.J. Heeres a,*, A.A.C.M. Beenackers a,1, V.G. Pangarkar b

a Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
b Department of Chemical Engineering, University of Mumbai, Matunga, Mumbai 400 019, India

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Abstract

The physical absorption of pure CO₂ in various liquids (water, hexadecane, and sunflower oil) containing micron sized TiO₂ particles has been investigated. Absorption studies were carried out in a batch stirred cell reactor at 298 K and initial pressures of 0.08 MPa. Solid loading and stirring intensities were varied systematically between 0–15 kg/m³ and 3.3–12.5 s⁻¹, respectively. Gas absorption rates are enhanced significantly in the presence of TiO₂ particles. Enhancement factors are a function of the solids loading and stirring intensity. Maximum enhancement factors of about 2 were observed for all solvents at low stirring intensities. The rate of gas absorption was theoretically analyzed using a heterogeneous unsteady state mass transfer model based on the Danckwerts surface renewal theory and a Langmuir-type particle to interface adhesion isotherm. This model not only predicts the trends in the observed enhancement factors very well but also gives an accurate quantitative picture.

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Keywords: Enhanced gas absorption; TiO₂ particles; Stirred cell reactor; Surface renewal model; Particle to interface adhesion isotherm

1. Introduction

The rate of gas absorption in a G–L or G–L–S contactor may be enhanced considerably by the presence of particles in the liquid-phase. To be effective, the particles have to be considerably smaller than the gas-liquid film thickness and need to have a high affinity for the component to be transferred [1–8]. Enhancement of the gas absorption rates due to the presence of small particles is explained by the so-called grazing or shuttle mechanism. It is assumed that the particles travel between the stagnant liquid mass transfer layer and the bulk of the liquid. Near the interface, the adsorptive particles are loaded with solute and the solute concentration in the liquid mass transfer layer will be reduced. As a consequence, the concentration gradient of the solute in the mass transfer layer will be increased, leading to enhanced gas absorption. After spending a certain time in the liquid side mass transfer layer, the particles return to the bulk of the liquid where the gas-phase component is desorbed and the particle regenerated [1–8].

A large number of experimental studies have been performed on the (physical) absorption of various gases in aqueous activated carbon slurries. The absorption rates increase with the activated carbon concentration until a certain concentration and then level off to a constant value [1–10]. Several explanations have been put forward to explain these effects. It is now widely accepted that, due to the hydrophobic properties of active carbon, the concentration of particles in the mass transfer zone is much higher than in the bulk of the suspension, leading to higher local absorption rates and higher enhancement factors [5,7,11,12].

Here, we describe our studies on the application of micron sized TiO₂ particles to enhance the absorption rates of CO₂ in various liquids. TiO₂ particles are potentially interesting to apply for enhanced gas absorption. Studies indicate that TiO₂ particles have a high adsorption affinity for certain gases (e.g. H₂, CO, CO₂, NH₃, etc.) [13,14]. Although the affinity may change dramatically in the presence of a liquid-phase, it certainly warrants further investigations. In addition, TiO₂ particles are relatively cheap and various grades are available with a broad spread in particle dimensions and distributions.

Enhancements in the gas absorption rates are expected to be a function of the hydrophobicity/hydrophilicity of the particles and as such are expected to be solvent depending. To study these effects for TiO₂ particles, the absorption experiments were carried out in three different solvents with a large spread in physical properties: water, hexadecane and sunflower oil.

* Corresponding author. Tel.: +31-50-363-4174; fax: +31-50-363-4479.
E-mail address: h.j.heeres@chem.rug.nl (H.J. Heeres).
1 Deceased on 19 April 2001.
Nomenclature

- $a$: gas-liquid interfacial area ($\text{m}^2/\text{m}^3$)
- $C_b$: mass of gas absorbing particles per unit volume of bulk of the suspension ($\text{kg}/\text{m}^3$)
- $C_{g}$: concentration of CO$_2$ in the gas-phase ($\text{mol}/\text{m}^3$)
- $C_{L}$: concentration of CO$_2$ in the liquid-phase ($\text{mol}/\text{m}^3$)
- $C^*_A$: concentration of component A in the liquid-phase at the gas-liquid interface ($\text{mol}/\text{m}^3$)
- $d_p$: particle diameter ($\text{m}$)
- $D_A$: solute diffusivity in the liquid-phase ($\text{m}^2/\text{s}$)
- $E$: enhancement factor ($-)$
- $H$: Henry number defined as $(C^*_A/C_{g})_{\text{equilibrium}}$ ($-)$
- $H_e$: Henry’s constant ($\text{Pa} \cdot \text{m}^3/\text{mol}$)
- $J_A$: mass transfer rate for the component A ($\text{mol}/\text{m}^2 \text{s}$)
- $k$: constant as defined in Eq. (4) ($-)$
- $k_d$: particle adhesion coefficient ($\text{m}^3/\text{kg}$)
- $K_L$: liquid side mass transfer coefficient ($\text{m}/\text{s}$)
- $K_{LS}$: liquid side mass transfer coefficient of the covered part of the gas-liquid interface ($\text{m}/\text{s}$)
- $K_L^*$: dimensionless liquid side mass transfer coefficient ($-)$
- $k_{pa}$: liquid side mass transfer coefficient ($\text{m}^3/\text{s}$)
- $m$: partition coefficient of the solute between the solid and the gas-phase ($-)$
- $p_{g}$: partial pressure of the solute gas ($\text{Pa}$)
- $R$: gas constant ($\text{J}/\text{mol} \cdot \text{K}$)
- $t$: time ($\text{s}$)
- $T$: temperature ($\text{K}$)
- $V_G$: gas volume ($\text{m}^3$)
- $V_L$: liquid volume ($\text{m}^3$)

Greek symbols

- $\zeta$: fraction of the gas-liquid interface covered by the adhering solid particles ($-)$
- $\zeta_{\text{max}}$: constant, as defined in Eq. (12) ($-)$
- $\rho_{pg}$: density of the solid particle ($\text{kg}/\text{m}^3$)
- $\sigma$: amount of carbon dioxide absorbed per unit mass of dry particles ($\text{mol}/\text{kg}$)

Superscripts

- $\text{H}_2\text{O}$: water
- $0$: value at time $t = 0$
- $\infty$: value at time $t = \infty$

2. Experimental

2.1. Reactor

The experiments were carried out in a thermostatic reactor of glass and stainless steel shown in Fig. 1. A six-bladed Rushton turbine stirrer was located centrally in the liquid at a height above the reactor bottom equal to half the reactor diameter. Four symmetrically mounted glass baffles increased the effectiveness of stirring and prevented the formation of a vortex. The pressure and temperature transducers together with valves 1 and 2 were connected to an Olivetti M240 computer, enabling automatic data collection and programmed reactor operation. The reactor dimensions are given in Table 1.

2.2. Chemicals

The TiO$_2$ particles were obtained from Degussa, Germany. The average particle size was determined with a Coulter Counter Multisizer II and found to be 3 $\mu$m. Hexadecane was purchased from Acros Organics, The Netherlands. The sunflower oil was a refined grade obtained from Unilever, Vlaardingen, The Netherlands. CO$_2$ (purity $>99.5\%$) was purchased from AGA GAS B.V., The Netherlands.
2.3. Experiments

All the experiments were carried out batchwise, both with respect to gas-phase and the slurry solution. The slurry volume was $1 \times 10^{-3} \text{m}^3$ and the slurry concentration varied between 0 and 15 kg/m$^3$. The operating conditions are listed in Table 2.

In a typical experiment, the reactor was filled with the slurry (TiO$_2$ in distilled water, hexadecane or sunflower oil). The liquid was degassed by closing valve 1 and opening valve 2. Once the slurry was equilibrated under the vapor pressure of water, valve 2 was closed and CO$_2$ was fed to the reactor up to a fixed pressure (0.08 MPa). After closing valve 1, the stirrer was started and the decrease of pressure due to the physical absorption of CO$_2$ was recorded over time.

The solubility of gas A in a liquid defined by Henry’s law, is expressed by

$$He = \frac{p_A}{C_A} \text{ at equilibrium}$$

(1)

In the absence of chemical reaction, the Henry coefficient may be calculated from the experimental data using the following equation:

$$He = \frac{p^n - p^{n,0}}{p^n - p^{\infty}} \cdot \frac{RTV_L}{V_0}$$

(2)

The experimental value of the Henry coefficient for CO$_2$ in water was found to be close to the value provided in the literature (3330 Pa m$^3$/mol). The values for CO$_2$ in hexadecane and sunflower oil were determined experimentally and were 3800 and 6600 Pa m$^3$/mol, respectively. These values are the average of at least three independent experiments.

Volumetric mass transfer coefficients were obtained from the physical absorption rate with time using the following equation:

$$k = \frac{V_0 He}{V_1 RT}$$

(4)

Eq. (3) is obtained from a mass balance for carbon dioxide for the gas-phase:

$$\frac{d(n_A)}{dt} = - \frac{V_0}{R_T} = - J_A A = - k_L (p_A - C_L)$$

(5)

The concentration of A in the liquid-phase ($C_L$) is eliminated by setting up a total mole balance for component A leading to

$$C_L = \frac{V_0}{RTV_L} (p_{A,0} - p_A)$$

(6)

Combination of Eqs. (5) and (6) leads to Eq. (3).

The rate of CO$_2$ absorption in the slurry follows from

$$J_A = \frac{V_0}{V_1 RT} \left( - \frac{dp_A}{dt} \right)$$

(7)

The experimental enhancement factor was calculated from

$$E = \frac{\text{gas absorption flux in the suspension}}{\text{gas absorption flux in a particle free liquid}}$$

(8)

For various model calculations, e.g. the theoretical enhancement factors, the diffusion coefficients of CO$_2$ in the various liquids are required. The value for CO$_2$ in water is reported to be $1.95 \times 10^{-3} \text{m}^2/\text{s}$ and for hexadecane $2.8 \times 10^{-5} \text{m}^2/\text{s}$ [16]. The diffusion coefficient of CO$_2$ in the sunflower oil applied in our experimental studies was calculated using the Wilke–Chang equation and estimated to be $8 \times 10^{-11} \text{m}^2/\text{s}$.

The partitioning coefficient of CO$_2$ between the solid and liquid-phase (m) is an important property of the system and was determined experimentally using the following relation:

$$m = \frac{\text{amount of carbon dioxide per unit volume of particle}}{\text{amount of carbon dioxide per unit volume of liquid}} \frac{\sigma_{pg}}{C_G R}$$

(9)

where $\sigma$ is the amount of gas absorbed by the particle per unit mass of dry catalyst particle. This value is determined experimentally by taking the difference in the moles absorbed in a slurry and the moles absorbed in pure solvent devoid of adsorptive particles. The experimental values range between 310 for sunflower oil and 630 for water. For hexadecane, an intermediate value of 580 was obtained.

4. Theory

Various stationary and instationary models have been developed to describe the effects of particles on gas absorption rates [3,5,7,9,17–25]. The early stationary film theory models developed in the eighties of the previous century were later shown to be the special cases of a general, unsteady state theory developed by Mehra [26]. A recent overview dealing with these theoretical aspects has been provided by Beenackers and van Swaaij [8]. Wimmers and Fortuin [20,21] developed the first models, which take into account a non-uniform distribution of the
particles. Later, Vinke [7] presented an enhanced gas absorption model (EGAM) based on their work on absorption of H₂ in the aqueous suspensions containing different concentrations of small carbon-supported or alumina-supported catalyst particles. The model is based on the film theory of mass transfer combined with a particle to interface adhesion isotherm to take into account a non-uniform distribution of the particles in the liquid phase.

Recently, Demmink et al. [12] formulated an unsteady state version of the EGAM model based on the surface renewal theory combined with particle to interface adhesion (SRPIA, surface renewal particle to interface adhesion model). This model has been applied to interpret the results obtained for acetylene absorption into aqueous solutions of iron chelates containing fine sulfur particles. This unsteady state model overcomes one of the basic limitations of the steady state film theory based EGAM model, i.e. the inability to account for transient effects like solute accumulation in the particles. For initial enhancement (i.e. enhancement when the bulk solute concentration is zero), the following expression for the theoretical enhancement factor was derived:

\[ E_{th} = \frac{J_a}{J_L} = 1 + \frac{1}{K_L} \left[ \frac{1}{3} \right] \left[ \frac{1}{(mK_L) + 1} \right] \tanh\left[ K_L \right] \] (10)

where \( \zeta \) is the surface fraction covered by particle and \( K_L \) a dimensionless mass transfer coefficient defined as:

\[ K_L = \frac{k_a d_p}{D_A} \] (11)

where \( k_a \) is the mass transfer coefficient, \( D_A \) the diffusion coefficient of the solute in the liquid phase and \( d_p \) the (average) particle size. \( \zeta \) is the surface fraction covered by particles. The relationship between \( \zeta \) and the particle concentration \( C_L \) in the liquid bulk is represented by a Langmuir-type adhesion isotherm:

\[ \frac{\zeta}{\zeta_{max}} = \frac{k_a C_L}{1 + k_a C_L} \] (12)

where \( k_a \) is the particle-to-gas interface adhesion constant and \( \zeta_{max} \) the maximum fractional coverage of the G-L interface. \( \zeta_{max} \) is a measure for the surface capacity of the particles and \( k_a \) a measure for the exchange equilibrium from particles moving to and away from the interface. Both parameters are a function of the speed of agitation. The values of \( \zeta \), \( k_a \) and \( \zeta_{max} \) are determined from the individual absorption experiments using a procedure given by Vinke et al. [7]. The calculated values for \( k_a \) and \( \zeta_{max} \) for the various experiments are given in Table 4.

According to the SRPIA model, the enhancement factor is a function of \( m \) and \( \zeta \) and \( K_L \) (see Eq. (11)). When varying the value of \( K_L \) at constant values of \( m \) and \( \zeta \), the model predicts a maximum in the enhancement factor. The position and actual value of this maximum is a function of the values of \( m \) and \( \zeta \). This implies the occurrence of two different mass transfer regimes: one for which the enhancement increases with an increase in \( K_L \) (capacity controlled regime) and one for which the enhancement decreases with increasing \( K_L \) values (transport-controlled regime).

In the transport-controlled regime, the effect of particles on the gas absorption rate is determined solely by the rate at which the particles adsorb the solute. This situation occurs when the capacity of the particles is very high, i.e. the particle may be regarded as an infinite sink. When the gas absorption process occurs in the transport-controlled regime, higher stirring intensities will lead to lower enhancement factors. This is due to the fact that at higher intensities (i.e. high \( K_L \) values), the contact time of the particles at the G-L interface decreases and as a result, the particles leave the interface with less solute adsorbed, resulting in lower absorption rates.

The other extreme is called the solubility controlled or capacity controlled regime. Here, the absorption rate depends solely on the ultimate capacity of the particles and not on the rate of transport of solute to the particles. An increase in the stirring intensity and thus the frequency at which the particles are refreshed at the G-L interface will result in higher overall absorption rates and enhancement factors. The mass transfer rates of solute from the liquid phase to the particles are not important in this regime and the particles are always fully saturated with solute.

Criteria to determine the regime for the absorption process have been derived for the SRPIA model. The transport-controlled regime holds when \( K_L^2 m \gg 12 \). For the capacity controlled regime, \( \tanh(K_L/4K)^{(3mK)} \) should be \( \ll 1 \) and \( mK \gg 3 \).

5. Results and discussion

5.1. Absorption of \( \text{CO}_2 \) in aqueous TiO\(_2\) slurries

Experiments were performed at different solid concentrations in the range of 0–1 kg/m\(^3\) and at speeds of agitation ranging from 3.3 to 9.2 s\(^{-1}\). The observed experimental enhancement factors as a function of the solid loading are presented in Fig. 2. The results clearly indicate that the enhancement factors are depending on both the solids loading and the stirrer speed. The highest enhancement factor for this system was observed at the lowest stirring intensity (3.3 s\(^{-1}\)) and found to be 2.0 for a solid loading of 1 kg/m\(^3\).

The enhancement factors increase with an increase in the solid loading, however, appear to level off and ultimately reach a constant value at higher solids loading. The minimum solids concentration for maximum enhancement is about 0.5–0.7 kg/m\(^3\) for the experiments at a stirring intensity of 3.3 s\(^{-1}\). This value is at the low end for the reported minimum solids concentration for various gas absorption studies in aqueous slurries containing small particles (0.2–10 kg/m\(^3\), see Table 3). The enhancement-loading
Fig. 2. Experimental enhancement factors as a function of solid loading at different stirrer speeds for the system TiO$_2$/water (○: 3.3 s$^{-1}$; △: 9.2 s$^{-1}$).

The solid lines represent theoretical curves for enhancement factor calculated using Eq. (10) and the best-fit values of $k_a$ and $\zeta_{\text{max}}$ (Table 4).

Profiles, i.e. a leveling off of the enhancement factors at high loading are typical for hydrophobic particles with a high affinity for the G–L interface [1–7,9,10].

The enhancement factor was found to decrease with an increase in the speed of agitation. This is evident when comparing the two extremes at a solid loading of 1 kg/m$^3$ (Fig. 2). The enhancement factor at low stirring intensity (3.3 s$^{-1}$) is nearly twice as high as for the highest speed of agitation (9.2 s$^{-1}$).

All observations, i.e. a leveling off of the enhancement factors at high solids loading and the effects of stirring speed are in accordance with the SRPIA model predictions. The leveling off at a high solids loading towards a constant enhancement value is the result of the fact that the surface fraction covered by particles ($\zeta$) reaches a maximum value ($\zeta_{\text{max}}$). A further increase in the particle loading does not lead to higher concentration of particles near the G–L interface and beneficial effects on the absorption rates of CO$_2$.

Table 3
Reported values for the solid loading for maximum enhancement

<table>
<thead>
<tr>
<th>Serial number</th>
<th>System</th>
<th>$C_{\text{max}}$ (kg/m$^3$)</th>
<th>$d_p$ (μm)</th>
<th>Speed (s$^{-1}$)</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O$_2$/glucose/Pt + ac. carbon [1]</td>
<td>1</td>
<td>$\leq 5$</td>
<td>1.9</td>
<td>3.4</td>
</tr>
<tr>
<td>2</td>
<td>CO$_2$/ac. Carbon [1]</td>
<td>2–3</td>
<td>$\leq 5$</td>
<td>2.9–7.8</td>
<td>3.92–2.28</td>
</tr>
<tr>
<td>3</td>
<td>Propane/ac. Carbon [3]</td>
<td>34</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>CO$_2$/Na$_2$CO$_3$ + ac. carbon [11]</td>
<td>2–3</td>
<td>$\leq 5$</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>O$_2$/Na$_2$SO$_3$ + ac. carbon [17,27]</td>
<td>1</td>
<td>$\leq 5$</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>O$_2$/Na$_2$S + ac. carbon [1,4,10]</td>
<td>1.6–1.6</td>
<td>$\leq 5$</td>
<td>–</td>
<td>1.7</td>
</tr>
<tr>
<td>7</td>
<td>O$_2$/aq. Glucose/Pt + ac. carbon [9,11]</td>
<td>0.4</td>
<td>$\leq 5$</td>
<td>2</td>
<td>3.2</td>
</tr>
<tr>
<td>8</td>
<td>CO$_2$/aq. Na$_2$SO$_3$ buffer/Pt + ac. carbon [9,10,17,28]</td>
<td>2–3</td>
<td>$\leq 20$</td>
<td>1.5</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>CO$_2$/alkaline amine + ac. carbon [29]</td>
<td>6</td>
<td>40% $&lt; 1$</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>H$_2$/ac. carbon [25]</td>
<td>0.6</td>
<td>10</td>
<td>3</td>
<td>3.3</td>
</tr>
<tr>
<td>11</td>
<td>Ethene/ac. carbon [25]</td>
<td>1.2</td>
<td>10</td>
<td>3</td>
<td>3.6</td>
</tr>
<tr>
<td>12</td>
<td>Propane/ac. carbon [23]</td>
<td>1.2</td>
<td>10</td>
<td>1.4</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>CO$_2$/ac. carbon [30]</td>
<td>0.2</td>
<td>4–10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>14</td>
<td>H$_2$/H$_3$PO$_4$ + NH$_4$NO$_3$ + ac. carbon [31]</td>
<td>1.5</td>
<td>40</td>
<td>13–30</td>
<td>3.6</td>
</tr>
</tbody>
</table>

* $C_{\text{max}}$: minimum solids loading for maximum enhancement.

$^E$: Enhancement factor as defined in Eq. (8).
in the liquid-phase are not expected. The values of TiO$_2$/water−

**Table 4** Calculated values for the values of Langmuir adhesion constants $k_a$ and $\zeta_{max}$

<table>
<thead>
<tr>
<th>System</th>
<th>Stirrer speed (s$^{-1}$)</th>
<th>$\zeta_{max}$</th>
<th>$k_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/water</td>
<td>3.3</td>
<td>7.5</td>
<td>9.2</td>
</tr>
<tr>
<td>TiO$_2$/hexadecane</td>
<td>3.3</td>
<td>10.6 (2.4)</td>
<td>5.9 (2.4)</td>
</tr>
<tr>
<td>TiO$_2$/sunflower oil</td>
<td>3.3</td>
<td>1.3 (0.3)</td>
<td>1.3 (0.3)</td>
</tr>
</tbody>
</table>

$\zeta_{max}$ at a stirrer speed of 3.3 s$^{-1}$ is presented in Fig. 2. It is evident that the observed trends for the enhancement factors as a function of the loading (leveling off at higher loading) as well as stirrer speed (lower enhancement at higher stirring intensities) are described properly by the model.

5.2. Absorption of CO$_2$ in hexadecane

Experiments were performed at different TiO$_2$ concentrations in the range of 0.1–10 kg/m$^3$ and at speeds of agitation ranging from 3.3 to 12.5 s$^{-1}$. The experimental enhancement factors as a function of the solid loading are presented in Fig. 3 for the extremes of the stirrer speeds (3.3 and 12.5 s$^{-1}$, see also Table 6). The highest enhancement factor for this system was found to be 1.9 for a solid loading of 10 kg/m$^3$ at a stirrer speed of 3.3 s$^{-1}$.

Analogous to the TiO$_2$/water systems, the enhancement factors level off at higher solids loading. Beyond a solid loading of about 4−6 kg/m$^3$, there is no significant enhancement in the rate of gas absorption. This is the minimum solid loading for maximum enhancement and is an order of magnitude higher than that found for the TiO$_2$/water system (0.5−0.7 kg/m$^3$).

It is interesting to compare the experimental enhancement factors at similar solid loading for the TiO$_2$/water and TiO$_2$/hexadecane system. The enhancement factors for hexadecane are lower than for water, especially at the low stirring intensities. For instance, at 3.3 s$^{-1}$ and a loading of 1 kg/m$^3$, the enhancement factors are 1.57 for hexadecane and 2.0 for water. According to the SRPIA model, enhancement factors are a function of the surface coverage $\xi$, the dimensionless mass transfer coefficient $K_d$ and the solute partition coefficient m (see Eq. (10)).

The values for the partitioning coefficient m do not differ dramatically (630 for water and 580 for hexadecane).
Fig. 3. Experimental enhancement factors as a function of solid loading at different stirrer speeds for the system TiO$_2$/hexadecane (3.3 s$^{-1}$, △: 12.5 s$^{-1}$). The solid lines represent theoretical curves for enhancement factor calculated using Eq. (10) and the best-fit values of $k_a$ and $\zeta_{\text{max}}$ (Table 4).

Differences are found for both the value of the dimensionless mass transfer coefficient $K_L$ and the surface coverage $\zeta$. The $K_L$ values for water are slightly higher than for hexadecane, mainly due to the differences in the diffusivity of carbon dioxide in both media. The fractional coverage of the surface with particles under similar hydrodynamic conditions differs significantly for both solvents. This is clearly expressed by the value of the particle to gas interface adhesion constant $k_a$ (Table 4). The $k_a$ values in water are significantly higher than for hexadecane. This implies that the titanium dioxide particles in water have a higher affinity for the G–L interface than in an apolar solvent like hexadecane. It suggests that titanium dioxide particles may be considered as rather hydrophobic. Additional information to support this conclusion may be obtained from contact angle measurements. When a liquid is placed on a solid, the liquid in most cases remains as a drop on the surface with a definite angle of contact between the liquid and solid-phase [32]. This contact angle is a measure for wetting tendency of a liquid. Small contact angles are indicative for a good wetting ability and adhesion between the liquid and solid-phase.

Contact angle measurements for a number of solvents in combination with TiO$_2$ have been reported [33]. Contact angles for water are higher than for typical organic solvents, indicating that titanium dioxide is indeed hydrophobic in nature.

Application of the SRPIA model to determine the absorption regime suggest that the absorption of CO$_2$ in TiO$_2$/hexadecane takes place in an intermediate regime, i.e. is neither capacity controlled nor transport-controlled. The solid curves in Fig. 3 are the theoretical enhancement factors calculated using the SRPIA model and the best-fit values of $k_a$ and $\zeta_{\text{max}}$. Agreement between experimental data and model prediction is very satisfactory.
5.3. Absorption of CO$_2$ in sunflower oil

The results of the CO$_2$ absorption experiments in TiO$_2$ dispersed in sunflower oil are given in Table 7 and shown in Fig. 4 in the form of enhancement factors as a function of solid loading. The highest enhancement factor for this system was found to be 2.2 for $C_s = 15$ kg/m$^3$ at 3.3 s$^{-1}$. The qualitative trends are again similar as for the TiO$_2$/water and TiO$_2$/hexadecane systems, i.e. a leveling off of the enhancement factor at higher particle loading and a lowering of the enhancement at higher stirring intensities. The major difference is the value of the minimum solids loading for maximum enhancement, which is significantly higher (>5 kg/m$^3$) than for the other two systems. Hence, higher solids loading are required for maximum enhancement in gas absorption rates.

Furthermore, the enhancement factors at a particular solid loading and stirring intensity for the TiO$_2$–sunflower oil system are always lower than for the other two systems. This is the result of the large difference in viscosities of the liquids, resulting in a significant lower value of the diffusion coefficient of CO$_2$ in the relatively viscous sunflower oil. As a result, the values of the liquid side mass transfer coefficient ($k_L$) for CO$_2$–sunflower oil are on average a factor of 2 lower than found for water.

The high viscosity of sunflower oil also has an impact on the absorption regime. The value of the parameter $K_{2Lm}$ is the highest for all solvents studied (>100) and it is evident that CO$_2$ absorption takes place in the transport-controlled regime.

6. Conclusions

This research has demonstrated that micron sized TiO$_2$ particles are capable of enhancing the physical absorption rate of CO$_2$ in various liquids (water, hexadecane, and sunflower oil). The maximum enhancement factors were found to be about 2 for all solvents under study. Enhancement factors were a function of the solid loading and the stirring intensity. Upon increasing the solid loading, the enhancement factor increases and then levels off to a constant value. The minimum solid loading required for maximum enhancement
was depending on the nature of the liquid-phase and increased upon going from water (0.5–0.7 kg/m³) to hexadecane (4–6 kg/m³) and sunflower oil (>5 kg/m³).

The experimental data were modeled using an unsteady state model based on the Danckwerts surface renewal theory using a particle to surface adhesion isotherm. This SRPIA model not only describes the observed effects in a qualitative way but also the quantitative agreement was very satisfactory. This implies that the TiO₂ particles are non-uniformly distributed between the bulk liquid-phase and the liquid film-layer and have a high affinity to stick to the gas–liquid interface.

Based on this study, it may be concluded that micron-sized TiO₂ particles may be attractive alternatives for active carbon materials to enhance mass transfer of gaseous components to a liquid-phase. Typical experimental problems encountered when using a natural product like active carbon materials to enhance mass transfer of gaseous components to a liquid-phase may be overcome by using well-defined TiO₂ particles. Further experimental work in typical industrial contactors (e.g. bubble column reactors) will be required to fully assess the potential of these interesting micron-sized TiO₂ particles for enhanced mass transfer rates.

References


