Effect of rheological properties on chemical absorption of carbon dioxide with MEA

Sang-Wook Park*, Tae-Young Kim, Byoung-Sik Choi and Jae-Wook Lee
Division of Chemical Engineering, Pusan National University, Pusan 609-735, Korea
1Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea
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Abstract
Rates of chemical absorption of CO₂ in water-in-oil (w/o) emulsion were measured in a flat-stirred vessel at 25°C. The w/o emulsion was composed of aqueous monoethanolamine (MEA) droplets as a dispersed phase and non-Newtonian viscoelastic benzene solutions of polybutene (PB) and polyisobutylene (PIB) as a continuous phase. The liquid-side-mass transfer coefficient (k_L) was obtained from the dimensionless empirical equation containing Deborah number expressed as the properties of pseudoplasticity of the non-Newtonian liquid. k_L was used to estimate the enhancement factor due to chemical reaction between CO₂ and MEA in the aqueous phase. PIB with elastic property of non-Newtonian liquid made the rate of chemical absorption of CO₂ accelerate compared with Newtonian liquid.

Keywords: chemical absorption, carbon dioxide, emulsion, MEA, non-Newtonian liquid

1. Introduction
Gas-liquid mass transfer in non-Newtonian liquid is an important example of gas absorption in pseudoplastic flow of industrial processes such as fermentation broth, slurry, and fluidized bed, et al. Variation of the volumetric liquid-phase mass transfer coefficient (k_Lα) in gas-dispersed systems consists of the liquid-side mass transfer coefficient (k_L) and the specific gas-liquid interfacial area (α). The former could be correlated with Reynolds and Schmidt numbers including liquid viscosity. It is likely that the latter varies not only with Newtonian liquid properties such as surface tension but also with some non-Newtonian and/or viscoelastic fluid properties.

Only use of the apparent viscosity of non-Newtonian fluids was not sufficient to obtain a unified correlation for k_Lα values. Due to the complexities of gas absorption in non-Newtonian media, the correlations obtained by these studies were limited to just a few kinds of non-Newtonian fluids such as Carbopol, carboxymethylcellulose (CMC), polyacrylate (PA), polyethylene oxide (PEO), polyacrylamide (PAA), and polyisobutylene (PIB) solutions. If considerable reduction of k_Lα is due to the viscoelasticity of the aqueous solution, then the extent to which data for the viscoelastic solution such as PAA deviate from those for the inelastic solution such as CMC should correlate with some measure of the solutions elasticity. The dimensionless numbers, which relate the elastic properties with the process parameters, are either Deborah number (De) defined as the ratio of the characteristic material time to the characteristic process time, or Weissenberg number (Wi) defined as the ratio of the first normal stress difference to the shear rate. Unified correlations has been proposed for k_Lα in Newtonian as well as non-Newtonian solutions by introducing the dimensionless term such as (1 + n₁Deⁿ₂)ⁿ, which is listed in Table 1. As shown in Table 1, values of the dimensionless group are different.

If the water-in-oil (w/o) emulsion system consists of the dispersed phase of the aqueous-solution containing reactant, and the continuous phase of the organic solvent having larger gas solubility than water, then the specific rate of absorption may be enhanced due to larger solubility and chemical reaction. A qualitative explanation of this phenomenon has been given by various authors (Linek and Benes, 1976; Bruining et al., 1986; Mehra et al., 1988; Park et al., 2002); after small droplets of a liquid immiscible with the continuous liquid phase absorb the gas in the hydrodynamic mass-transfer film, desorption of the gas takes place in the gas-poor bulk of the liquid.

There is little information about the effect of elastic properties on gas absorption into w/o emulsion composed of aqueous droplets as dispersed phase and non-Newtonian liquid as continuous phase. Park et al. presented the dimensionless term such as (1 + n₁Deⁿ₂)ⁿ, as shown in Table 1, to fit the experimental k_Lα of CO₂ absorption into non-Newtonian liquid (Park et al., 2003a) such as benzene solution of polybutene (PB) and polyisobutylene (PIB), and w/o emulsion (Park et al., 2003b) composed of water as dispersed phase and benzene solution of PB and PIB as con...
It is worthwhile to investigate the effect of non-Newtonian rheological behavior on the rate of chemical absorption in w/o emulsion, where a reaction between CO$_2$ and reactant occurs in the dispersed phase.

In this study, the chemical absorption mechanism of CO$_2$ into w/o emulsion composed of aqueous alkaline solution and benzene solution of PB and PIB is presented, and the measured absorption rates of CO$_2$ are compared with those obtained from the model based on the penetration theory with chemical reaction. The volumetric mass transfer coefficient obtained from the previous work (Park et al., 2003b) is used to estimate the enhancement factor due to chemical reaction.

2. Theory

In case of absorption of CO$_2$(A) into w/o emulsion with benzene solution of PB and PIB-aqueous MEA(B) solution as shown in Fig. 1, the mathematical model is developed to describe the absorption of CO$_2$ into the continuous benzene phase through the gas-liquid interface under unsteady-state and transfer into the dispersed aqueous droplets through the liquid-liquid interface under steady-state, where the chemical reaction of CO$_2$ occurs.

The following assumptions are made to set up the conservation equations:

1) Henry's law holds, 2) the reaction of CO$_2$ with reactant occurs in the aqueous droplets and is first-order with respect to both CO$_2$ and MEA, 3) isothermal condition prevails, 4) size and shape of the dispersed aqueous droplets are uniform and sphere, and 5) although the solubility (Budavori, 1989) of MEA in benzene at 25°C is 1.4%, this solubility is assumed to be zero.

Under these assumptions, the conservation equations of CO$_2$ transferred into the dispersed aqueous phase are given as

\[ D_{el} \left( \frac{dc_A}{dr} + \frac{2dc_A}{r \, dr} \right) = k \, c_A \, c_B \]  
\[ D_{el} \left( \frac{dc_B}{dr} + \frac{2dc_B}{r \, dr} \right) = \nu \, k \, c_A \, c_B \]  

Boundary conditions to be imposed are

r = R;  \quad c_A = c_A^* = H_c \, c_A, \quad \frac{dc_A}{dr} = 0 \]  
\[ r = 0; \quad \frac{dc_B}{dr} = 0 \]  

The stoichiometric coefficients, \( \nu \), in Eq. (2) for MEA was obtained from the reference, and its value was 2 (Hikita et al., 1979).

Eqs. (1), (2) and the boundary conditions are put into dimensionless forms as follows:

\[ \frac{d^2 \alpha_A}{dy^2} + \frac{2d\alpha_A}{dy} = m_A \, \alpha_A \, \alpha_B \]  
\[ \frac{d^2 \alpha_B}{dy^2} + \frac{2d\alpha_B}{dy} = m_B \, \frac{\alpha_A \, \alpha_B}{r_B \, q_B} \]  

where \( \alpha_A = c_A/c_A^*, \quad \alpha_B = c_B/c_B^*, \quad r = r/R, \quad m_A = R_k \frac{k \, c_{B0}/D_{el}}{v \, \alpha_A \, \alpha_B}, \quad r_B = D_{el}/D_{el}, \quad q_B = c_B^0/\nu \, \alpha_C^0 \).

The effectiveness factor here can be defined as

\[ E_f = \frac{4 \pi R^2 \, n_{A0}}{v \, \alpha_A \, \alpha_B} = \frac{3 \, m_A \, \frac{d\alpha_A}{dy}}{m_A \, \frac{d\alpha_A}{dy}} \bigg|_{y=1} \]  

where \( n_{A0} \) is the flux of CO$_2$ defined as \( D_{el} \frac{dc_A}{dr} \bigg|_{y=0} \).

The concentration of A in the droplets, \( \alpha_A \), is obtained from the numerical solution of Eqs. (5) and (6) with the boundary conditions, Eqs. (7) and (8), and then the value of

<table>
<thead>
<tr>
<th>Investigator</th>
<th>( n_1 )</th>
<th>( n_2 )</th>
<th>( n_3 )</th>
<th>polymer</th>
<th>contactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yagi and Yoshida, 1975</td>
<td>2</td>
<td>0.5</td>
<td>-0.67</td>
<td>CMC, PA</td>
<td>agitated vessel</td>
</tr>
<tr>
<td>Ranade and Ulbrecht, 1978</td>
<td>100</td>
<td>1</td>
<td>-0.67</td>
<td>CMC, PAA</td>
<td>stirred tank</td>
</tr>
<tr>
<td>Nakanoh and Yoshida, 1980</td>
<td>0.13</td>
<td>0.55</td>
<td>-1</td>
<td>CMC, PA</td>
<td>bubble column</td>
</tr>
<tr>
<td>Park et al., 2003a</td>
<td>100</td>
<td>1</td>
<td>-0.42</td>
<td>PB, PIB</td>
<td>agitated vessel</td>
</tr>
<tr>
<td>Park et al., 2003b</td>
<td>2461.3</td>
<td>1</td>
<td>-0.274</td>
<td>PB, PIB</td>
<td>agitated vessel</td>
</tr>
</tbody>
</table>
$E_f$ is obtained from Eq. (9). If the concentration of $B$ in the droplets, $c_{B_0}$ is constant, the value of $E_f$ can be obtained from the exact solution of Eq. (5).

If $c_{B_0}$ is equal to the interfacial constant concentration ($c_{B_i}$) between the continuous and dispersed phase, the reaction of $A$ with $B$ becomes to be a pseudo-1st-order reaction and the differential equation of Eq. (5) and the boundary conditions of Eqs. (7) and (8) are reduced to

$$\begin{align*}
\frac{d^2 \alpha_n}{dy^2} + \frac{2d \alpha_n}{dy} &= (m_n \eta) \alpha_n \\
y &= 1; \; \alpha_n = 1 \\
y &= 0; \; \frac{d \alpha_n}{dy} = 0
\end{align*}$$

(5a)

where, $\eta = \sqrt{c_{B_0}}$, $\alpha_n = c_B/c_{B_0}$.

The concentration profile of $A$ is derived from the exact solution of Eq. (5a) is given as follows:

$$\alpha_n = \frac{\sinh(m_n \eta y)}{\sinh(m_n \eta)}$$

(10)

Using Eqs. (9) and (10), $E_f$ is derived as

$$E_f = \frac{3}{m_n \eta \left[ \frac{1}{\tanh(m_n \eta)} - \frac{1}{m_n \eta} \right]}$$

(11)

To derive $\alpha_B$, the mass balance between the component $A$ and $B$ in the droplets is written as follows:

$$\frac{4}{3} \pi R^2 (c_{B_0} - c_B) = \nu \int_0^R 4 \pi r^2 (c_A^* - c_A) dr$$

(12)

Eq. (12) is put into dimensionless forms as follows:

$$1 - \alpha_B = 3 \frac{\int_0^1 y^{1/(1-\alpha_n)} dy}{q_B}$$

(13)

$\alpha_B$ is derived from Eq. (13) with Eqs. (9) and (10) as follows:

$$\alpha_B = 1 - \frac{1 - E_f}{q_B}$$

(14)

To derive the enhancement factor ($\phi$) due to a reaction between $CO_2$ and MEA in the dispersed phase, the conservation equation for the dissolved gas in the continuous phase with its volume fraction of $\varepsilon$ at unsteady-state is written as

$$\frac{\partial^2 c_A}{\partial z^2} = \frac{\partial C_A}{\partial t} + (1-\varepsilon) k_2 c_A c_B_0 E_f$$

(15)

Boundary and initial conditions are given as

$$\begin{align*}
z &= 0, \; t > 0; \; C_A = C_{A_i} \\
z > 0, \; t = 0; \; C_A = 0 \\
z &= \infty, \; t > 0; \; C_A = 0
\end{align*}$$

(16)

(17)

(18)

Eqs. (15) - (18) are put into the dimensionless form as follows:

$$\frac{\partial^2 \tilde{Y}_A}{\partial x^2} = \frac{\partial Y_A}{\partial t} + M E_f Y_A$$

(19)

where, $M = (1 - \varepsilon)$, $k_2 c_{B_0} H_i D_A / k_i^2$, $H_i = c_A^*/C_A$

The molar flux of $CO_2$ with chemical reaction at any contact time ($t$) is defined as

$$N_A = -D_A \frac{\partial \tilde{Y}_A}{\partial x} \bigg|_{x=0}$$

(23)

The mean molar flux of $CO_2$ during contact time ($t$) is written as

$$\overline{N}_A = \frac{1}{t} \int_0^t N_A dt$$

(24)

From comparison of the penetration model with the film model, the relation between $t$ and $k_2$ is derived as follows (Danckwerts, 1970b):

$$k_2 = \frac{2 \overline{N}_A}{C_{A_i} D_A / \pi t}$$

(26)

The enhancement factor ($\phi$) here defined as the ratio of molar flux with chemical reaction to that without chemical reaction, $\overline{N}_A/\overline{N}_A$ is described by using Eqs. (24) and (25) as follows:

$$\phi = \frac{\int t \frac{\partial \tilde{Y}_A}{\partial x} dt}{\int t \frac{\partial \tilde{Y}_A}{\partial x} dt}$$

(27)

Because the mass transfer coefficient of $CO_2$ in the dispersed phase ($k_{L2}$) can not be measured, it is calculated from the mass balance of $CO_2$ without chemical reaction in the aqueous drop transferred from the continuous phase.

The conservation equation of $CO_2$ transferred into the dispersed phase without chemical reaction from Eq. (1) at steady state is given as

$$\frac{d}{dr} \left( r^2 D_A \frac{dc_A}{dr} \right) = 0$$

(1.1)

Boundary conditions are given as

$$r = R; \; c_A = c_A^*$$

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In Eq. (9), the molar flux of CO\(_2\) without chemical reaction is defined as

\[
\frac{dc_A}{dr} = 0
\]

Integration of Eq. (1.1) gives

\[
c_A = -\frac{c_1}{D_{eA}} r + c_2
\]

(29)

From the boundary conditions and definition of \(n_A\) in Eq. (28), the constant \(c_1\) and \(c_2\) are \(-Rc_A^*\) and 0, respectively. Therefore, \(n_A\) is arranged as follows:

\[
n_A = \frac{D_{eA} c_A^*}{R}
\]

(30)

From comparison of Eq. (30) with the film theory, \(k_{1A}\) is presented as follows:

\[
k_{1A} = \frac{D_{eA}}{R}
\]

(31)

3. Experimental

3.1. Chemicals

All chemicals in this study were reagent grade, and used without further purification. Purity of both CO\(_2\) and N\(_2\) was more than 99.9%. The polymers used in this study were PB with the mean molecular weight of 680 (Daelim Industry Co., Ltd., Korea) and PIB with the mean molecular weight of 1000000 (Aldrich, U.S.A.). The benzene solutions of various concentrations of PB and PIB were used as Newtonian and non-Newtonian liquids, respectively. For the absorption experiments, the concentration of PB in the benzene solution was 20 and 30 wt%, and that of PIB was more than 99.9%. The polymers used in this study were PB and PIB were measured by a pycnometer (Fisher Scientific Co., U.S.A.). The benzene solutions of benzene solution in order to get the solubility of CO\(_2\) can be measured by the titration method with a dilute HCl solution (Totiwachwuthikul and Meisen, 1991), but the amount of CO\(_2\) dissolved in the benzene solution in this study can not be measured by this method, because CO\(_2\) does not dissociate in the benzene solution. The solubility of CO\(_2\) was obtained from the pressure measuring method, which measured the pressure difference of the CO\(_2\) between before and after equilibrium between gas and liquid phase along the procedure similar to those reported elsewhere (Kennard and Meisen, 1984). A digital pressure gauge made by Meriam Instrument (Meriam Mergauge, U.S.A.) was used to measure the pressure inside the saturator within ± 0.01 kPa. From the mass of CO\(_2\) dissolved in the emulsion and the known volume of emulsion in the saturator, the solubility of CO\(_2\) was calculated. The experimental procedure to get the solubility of CO\(_2\) was represented in the reported paper (Park et al., 2003a) in detail.

3.2. W/O emulsion

The w/o type emulsion was made from benzene solution of PB and PIB and water by the same procedure as those reported elsewhere (Park et al., 2002) by adding Tween 80 (Aldrich Chem. Co.) and Arlacel 83 (Aldrich Chem. Co.) as surfactant, and by using a homogenizer (Fisher Scientific Co.) in the range of agitation speed of 1500-10,000 rev/min. The mean size of aqueous droplets was measured by Image Analyzer (Leitz TAS Plus Co.), and its value was 4 \(\times\) 10\(^{-3}\) m.

3.3. Rheological properties of emulsion

The rheological properties of w/o emulsion were measured by the parallel disk type rheometer (Ares, Rheometrics, U.S.A.) of the diameter of 0.05 m and the gap of 0.001 m.

3.4. Rate of absorption

Absorption experiments were carried out in an agitated vessel. The absorption vessel was constructed of glass of 0.102 m inside diameter and of 0.151 m in height. Four equally spaced vertical baffles, each one-tenth of the vessel diameter in width, were attached to the internal wall of the vessel. The liquid phase was agitated with an agitator driven by a 1/4 Hp variable speed motor without agitation in gas phase because of pure CO\(_2\) gas. A straight impeller with 0.05 in length and 0.02 m in width was used as the liquid phase agitator, and located at the middle position of the liquid phase. The gas and emulsion in the vessel were agitated with the agitation speed of 200 rev/min. The absorption rates of CO\(_2\) were measured along the procedure similar to those reported elsewhere (Park et al., 2003a) at 25°C and an atmospheric pressure. The absorption rate of CO\(_2\) was measured using the observed values of the cumulative volume of CO\(_2\) for the change of absorption time. The experimental procedure was represented in the reported paper (Park et al., 2003a) in detail.

3.5. Solubility of CO\(_2\) in emulsion

In general, the concentration of CO\(_2\) dissolved in the aqueous solution in order to get the solubility of CO\(_2\) can be measured by the titration method with a dilute HCl solution (Totiwachwuthikul and Meisen, 1991), but the amount of CO\(_2\) dissolved in the benzene solution in this study can not be measured by this method, because CO\(_2\) does not dissociate in the benzene solution. The solubility of CO\(_2\) was obtained from the pressure measuring method, which measured the pressure difference of the CO\(_2\) between before and after equilibrium between gas and liquid phase along the procedure similar to those reported elsewhere (Kennard and Meisen, 1984). A digital pressure gauge made by Meriam Instrument (Meriam Mergauge, U.S.A.) was used to measure the pressure inside the saturator within ± 0.01 kPa. From the mass of CO\(_2\) dissolved in the emulsion and the known volume of emulsion in the saturator, the solubility of CO\(_2\) was calculated. The experimental procedure to get the solubility of CO\(_2\) was represented in the reported paper (Park et al., 2003a) in detail.

3.6. Density and interfacial tension

The densities of the emulsion with benzene solution of PB and PIB were measured by a pycnometer (Fisher Scientific Co., U.S.A.). The surface tension of benzene and the interfacial tension between water and benzene solution of various concentration of PIB and PB were measured by the double capillary technique with the glass capillary of inside radius of...
7.65 \times 10^{-4} \text{ and } 1.55 \times 10^{-3} \text{ cm along the procedure similar to those reported elsewhere (Kay and McClure, 1970).}

4. Rheological and physicochemical properties of emulsion and CO$_2$

In order to get the values of $E_f$ in Eq. (9) and $\phi$ in Eq. (27), it is necessary to know the physicochemical properties such as $k_1$, $k_2$, $\rho$, $\mu$, $D_e$, $\sigma$, solubilities of CO$_2$ in dispersed and continuous phase, and diffusivities of CO$_2$ and MEA. These values are obtained as mentioned below.

4.1. Rheological properties

We assume that a power-law model, which has been widely used for shear-dependent viscosity, can be represented the non-Newtonian flow behavior of emulsions.

\[
\tau = K \dot{\gamma}^n \quad (32)
\]
\[
\mu = K \dot{\gamma}^{n-1} \quad (33)
\]
\[
N_1 = A \dot{\gamma}^b \quad (34)
\]

where $n$, $K$, $b$, and $A$ are material parameters depending on temperature.

These parameters were obtained from the dependence of $\tau$ and $N_1$ on $\dot{\gamma}$.

In order to observe the dependence of $\tau$ and $N_1$ on $\dot{\gamma}$ and $N_1$ of the w/o emulsion were measured according to the change of $\dot{\gamma}$ by the rheometer.

Fig. 2 shows typically the logarithmic plot of shear stress versus shear rate for the emulsion with benzene solutions of PB of 30 wt% containing PIB of 1 wt%, respectively. The best straight-line fit was determined by the least-squares method with the plots in Fig. 2. From the intercept and slope of the line, the values of $K$ and $n$ were evaluated. Also, Fig. 3 shows the logarithmic plot of primary normal stress difference versus shear rate for the same solution in Fig. 2. As shown in Fig. 3, the plots are linear, but the values of the primary normal stress difference of emulsion with benzene and benzene solution of 30 wt% PB are zero. From the intercept and slope of the straight line in benzene solution of 30 wt% PB and 1 wt% PIB, the values of $A$ and $b$ were evaluated. The parameters, $K$, $n$, $A$ and $b$ for the emulsion with benzene solution of various concentration of PB and PIB are give in Table 2.

One of parameters used frequently to represent the characteristics of viscoelasticity is known as the characteristic time of the liquid defined as

\[
\lambda = \frac{N_1}{\mu \dot{\gamma}} \quad (35)
\]

In terms of the parameters $K$, $A$, $n$, and $b$ defined by Eqs. (32) and (34), the characteristic time, $\lambda$, can be expressed as

\[
\lambda = \frac{A}{K} \dot{\gamma}^{b-n-1} \quad (36)
\]

The dimensionless numbers, which relate the elastic properties with the process parameters are either Deborah number, or Weissenberg number. In Deborah number (De), the characteristic liquid time is measured against a characteristic process time, which is considered to be related in same way to the reciprocal of the impeller speed for stirred tanks, and it is derived with Eq. (36) as follows.

\[
De = \lambda N = \left( \frac{A}{K} \dot{\gamma}^{b-n-1} \right) N \quad (37)
\]
The shear rate, $\gamma$ in Eq. (37) is obtained from the equation,

$$\gamma = \frac{4N}{n}$$

(Park et al., 2003b).

To observe the effect of the concentration of PIB and the speed of impeller on De calculated from Eq. (37), De is plotted against the concentration of PIB with speed of impeller as parameter in Fig. 4 with the shear rate for the typical concentration of PB of 20 wt%. As shown in Fig. 4, De increases with increase of the concentration of PIB and the speed of impeller. Dependence of De on the concentration of PIB is reasonable because of the elasticity of PIB, and the impeller speed makes De increase in the agitated vessel with the viscoelasticity liquid.

### 4.2. Reaction rate constant

In the reaction of CO$_2$ with MEA (Hikita et al., 1979), the reaction rate constants were estimated as follows.

$$\log k_2 = 10.99 - \frac{2152}{T}$$

### 4.3. Solubility of CO$_2$

The solubility of CO$_2$ in water was taken as 0.0328 kmol/m$^3$ (Hikita et al., 1976) at 25°C and 0.101 MPa. The solubility of CO$_2$ in MEA (Hikita et al., 1979) solution was estimated as follows:

$$\log \left( \frac{c_A^*}{c_{Aw}^*} \right) = 0.3c_{aw}/(1 + 0.963c_{bo})$$

The solubilities of CO$_2$ in benzene solution of PB and PIB and in the w/o emulsion at 25°C and 0.101 MPa were measured using the pressure measuring method, and the measured value in benzene was 0.1107 kmol/m$^3$.

### 4.4. Diffusivities of CO$_2$ and MEA

The diffusivity of CO$_2$ in benzene estimated from the Wilke-Chang equation (Danckwerts, 1970a), $D_A$, was $3.853 \times 10^{-9}$ m$^2$/s at 25°C.

The diffusivity of CO$_2$ in MEA (Danckwerts and Shama, 1966) solution, $D_{eb}$ was estimated as follows:

$$D_{eb} = (1.9686 - 0.1843c_{bo} - 0.0429b_0) \times 10^{-9}$$

The diffusivity of MEA in aqueous MEA solution, $D_{eb}$, was obtained from assumption that the ratio of $D_{eb}$ to $D_{eb}$ was equal to the ratio in water (Nijssing et al., 1959). The diffusivity of CO$_2$ and MEA in water at 25°C were taken as $1.97 \times 10^{-9}$ m$^3$/s (Hikita et al., 1976) and $1.1 \times 10^{-10}$ m$^3$/s (Danckwerts and Shama, 1966), respectively.

The diffusivity of a solute of a small size such as CO$_2$, O$_2$ or CH$_4$ in a polymer solution depends on the viscosity of the solution and the molecular weight of the polymer. The diffusivity of CO$_2$, $D_c$, in the benzene solution of PB and PIB was obtained from the following equation suggested by Lohse et al. (1981), which was modified from the Stokes-Einstein equation, and correlated with the molecular weight of the mixed polymer in the solution.

$$D_c = \left( \frac{\eta}{\eta_0} \right)^{3/2} \frac{M_c}{M_p}$$

The molecular weight of the mixed polymer in the ben-
zene solution of PB and PIB was calculated by the addition rule as follow:

\[ M_F = x_{PB} \times M_{PB} + x_{PIB} \times M_{PIB} \]  

(39)

where, \( x_{PB} \) and \( x_{PIB} \) are mole fraction of PB and PIB, respectively.

In case that a solute is absorbed into w/o emulsion, the presence of the microphase (dispersed phase) has an effect on the diffusivity of the solute in the continuous phase, and the effective diffusivity (Wubs et al., 1991), \( D_{eff} \), was obtained by the empirical equation as follows,

\[ \frac{D_{eff}}{D_c} = 1 + \frac{1.209(\alpha - 1)(1 - \epsilon)}{(1 - \alpha)(1 - \epsilon)}^{1/3} + 0.806 \alpha \]  

(40)

where \( \alpha = \frac{2\zeta}{1 - \zeta} \left( \frac{\zeta}{1 - \zeta} \right) \ln(\zeta - 1) \) and \( \zeta = \frac{H_A D_{ela}}{D_c} \).

The parameter, \( \zeta \) is the ratio of the diffusivity through the microphase and the diffusivity through the continuous phase with a correction for differences in solubilities in the microphase and continuous phase expressed by the distribution coefficient, \( H_A \), which is obtained from the ratio of the solubility of CO\(_2\) in benzene to that in aqueous solution.

4.5. Liquid-side mass transfer coefficient of CO\(_2\)

The mass transfer coefficient, \( k_L \), of CO\(_2\) in CO\(_2\)/emulsion system without MEA in the aqueous droplets was estimated by using the empirical equation (Park et al., 2003b) correlating the relationship between \( k_L \) and the experimental variables in the w/o emulsion of non-Newtonian liquid as follows.

\[ k_L = \frac{6.348 \times 10^{-9} (d \hat{N} / \mu)^{2.536} (\mu / \mu_o)^{2.397}}{(1 + 2461.3 \Delta e)^{0.121} (\sigma / \sigma_o)^{0.039}} \]  

(41)

The values of solubility of CO\(_2\), density of emulsion, diffusivity of CO\(_2\) and interfacial tension are given in Table 2.

5. Results and discussion

To observe the effect of rheological properties of w/o emulsion on the rate of chemical absorption, the absorption rate of CO\(_2\) into w/o emulsion with the dispersed phase of aqueous MEA solution was measured by change of MEA concentration in the aqueous phase. The typical experimental conditions are follows as; agitation speed of 200 rev/min, aqueous droplet size of 40 \( \mu \)m in emulsion prepared at agitation speed of 5000 rev/min using a homogenizer, volume fraction of continuous phase of 0.6, and the concentrations of PB of 20 and 30 wt%, and these of PIB of 0~1.0 wt%.

To observe the effect of viscoelasticity on the mass transfer coefficient of CO\(_2\), \( k_L \), in w/o emulsion of H\(_2\)O/(PB/PIB/ Bz) system, the effect of viscosity on \( k_L \) was observed. The viscosity of the w/o emulsion and \( k_L \) were estimated using Eqs. (33) and (41), respectively. Fig. 5 and 6 show typically plots of viscosity of w/o emulsion against PIB concentration and \( k_L \) against \( \mu \) at PB of 30 wt%, respectively. As shown in Fig. 5 and 6, the viscosity increase with increasing PIB concentration, and \( k_L \) decreases with increasing the viscosity. Note that mass transfer coefficient of a solute in the liquid phase is in inverse proportional to the viscosity of the liquid phase, because the diffusivity of the solute is in inverse proportional to the viscosity.

The mass transfer coefficient of CO\(_2\) in the Newtonian liquid under assumption that the non-Newtonian liquid of the continuous phase with PIB excludes the elastic property, i.e., \( D_e = 0 \), was obtained from the following equation representing the Newtonian behavior in Eq. (41),
The calculated value of $k_L$ from Eq. (42) for change of PIB concentration of 0.1~1 wt% was plotted as a circle symbol in Fig. 6. As shown in Fig. 6, $k_L$ of Newtonian liquid decreases with increasing the viscosity, and is smaller than that of non-Newtonian liquid. This means that the elasticity of PIB accelerates the mass transfer coefficient.

The rate of physical absorption of CO$_2$ in the w/o emulsion was estimated from correlation of Eqs. (25) and (26) as follows:

$$R_{Ao} = k_L a C_{Ai}$$

where $a$ is the contact interfacial area between gas and liquid.

$R_{Ao}$ were calculated from Eq. (43) using $k_L$ of Newtonian and non-Newtonian liquid in Fig. 6 and plotted against the PIB concentration, respectively, in Fig. 7. As shown in Fig. 7, $R_{Ao}$ containing the elasticity of non-Newtonian behavior is larger than $R_{Ao}$ without elastic property. From the results of Fig. 4 and 7, this means that the elasticity of PIB increases the rate of physical absorption.

To ascertain the reaction of CO$_2$ with MEA to be a pseudo-1st-order reaction, it is necessary to observe the effect of chemical reaction on the rate of mass transfer of CO$_2$ in the heterogeneous reaction system. Depending on the relative rates of diffusion and reaction, the system may be classified into four regimes such as very slow reactions, slow reactions, fast reactions, and instantaneous reactions (Daraiswany and Sharma, 1984).

In this system, the diffusion rate of CO$_2$ into the dispersed aqueous phase from the continuous phase and the reaction rate of CO$_2$ with MEA in the dispersed phase are considered to determine the reaction regime.

Table 3. Classification of Reaction Regime

<table>
<thead>
<tr>
<th>$c_{Bo}$ (kmol/m$^3$)</th>
<th>$\frac{D_{eA}k^2c_{Bo}}{k_{LL}}$</th>
<th>$\frac{c_{Bo}D_{eA}D_{eB}}{\nu}$</th>
<th>$c_{Ai}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>22.03</td>
<td>1.14</td>
<td>0.1</td>
</tr>
<tr>
<td>0.5</td>
<td>50.08</td>
<td>5.7</td>
<td>0.5</td>
</tr>
<tr>
<td>1.0</td>
<td>71.98</td>
<td>11.39</td>
<td>1.0</td>
</tr>
<tr>
<td>1.5</td>
<td>89.1</td>
<td>17.09</td>
<td>1.5</td>
</tr>
<tr>
<td>2.0</td>
<td>103.37</td>
<td>22.78</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The values of $\frac{D_{eA}k^2c_{Bo}}{k_{LL}}$ and $c_{Bo}\frac{D_{eA}D_{eB}}{\nu c_{Ai}}$ were calculated using the physicochemical properties such as $D_{eA}$, $D_{eB}$, $k_2$, $c_A*$ in the range of the MEA concentration of 0.1~2.0 kmol/m$^3$, and were listed in the Table 3. As shown in Table 3, $\frac{D_{eA}k^2c_{Bo}}{k_{LL}}$ is larger than 1, and the value of is larger than that of $c_{Bo}\frac{D_{eA}D_{eB}}{\nu c_{Ai}}$. Therefore, the reaction of CO$_2$ with MEA is the instantaneous reaction regime, and the concentration of B reagent in the dispersed aqueous phase may be considered as a constant value such as $c_{Bi}$ during reaction with CO$_2$. Therefore, Eq. (11) can be used to get the value of $E_f$, which is needed to calculate the enhancement factor.

To observe the effect of elasticity of PIB on the chemical reaction of CO$_2$ with MEA, the rate of chemical absorption of CO$_2$ into w/o emulsion with dispersed phase of MEA aqueous solution was measured at PB of 20 and 30 wt% and PIB of 0.1~1 wt% for MEA concentration of 0.1~2.0 kmol/m$^3$. Fig. 8 shows typical plot of the mean molar rate of chemical absorption, $R_A$, against the concentration of PIB at MEA concentration of 1 kmol/m$^3$. The solid line curves represent the calculated mean molar flux using Eq. (24) multiplied by contract interfacial area ($a$) at the contact time ($4D_{eA}/\pi k_L^2$) which is obtained from Eq. (26).

As shown in Fig. 8, $R_A$ has a constant value at PIB of 0.1 kmol/m$^3$. **Fig. 7.** Effect of PIB on physical absorption rate in w/o emulsion with PB of 30 wt%.

**Fig. 8.** Effect of PIB on the rate of chemical absorption at $c_{Bo}=1$ kmol/m$^3$.  

$k_Ld\bar{f}/D_{eB} = 6.348 \times 10^{-9}(d\bar{N}p/\mu)^{2.536}$ (42)
Effect of rheological properties on chemical absorption of carbon dioxide with MEA

The rate of chemical absorption, \( R_A \), is expressed from the definition of the enhancement factor, \( \phi \), as follows.

\[
R_A = \phi R_{Ao}
\]  

(44)

The value of \( \phi \) is calculated using Eq. (27), and Fig. 9 shows a typical plot of \( \phi \) against the concentration of PIB at MEA concentration of 1 kmol/m\(^3\) and PB of 20 and 30 wt%.

As shown in Fig. 9, the enhancement factor increases with increasing of PIB concentration, and its value at PB concentration of 30 wt% is larger than that of 20 wt%.

Decrease of \( k_L \) with increase of PIB concentration as shown in Fig. 6 makes the dimensionless parameter (M) increase. M is a major parameter increasing the enhancement factor (Park, et al., 2002). Meanwhile, decrease of \( k_L \) makes \( R_{Ao} \) decrease as shown in Fig. 7. From these results and Eq. (28), \( R_A \) may be almost constant as shown in Fig. 8.

To observe the effect of concentration of MEA on the rate of chemical absorption, the rate of chemical absorption was measured for the change of MEA concentration. Fig. 10 shows typically a plot of \( R_A \) against MEA concentration at PB of 30 wt% and PIB of 1 wt%.

As shown in Fig. 10, \( R_A \) increases with increasing MEA concentration. The rates of chemical absorption into w/o emulsion with the non-Newtonian and Newtonian liquid as the continuous phase are shown as a solid and dotted line in Fig. 10, respectively, which are calculated from Eq. (44). The value of \( k_L \) in the former comes from Eq. (41) and that in the latter from Eq. (42). As shown in Fig. 10, the value of the dotted line is smaller than that of the solid line. This means that the elastic due to PIB also accelerates the rate of chemical absorption.

6. Conclusions

Carbon dioxide was absorbed into water-in-oil (w/o) emulsion composed of aqueous monoethanolamine (MEA) droplets as a dispersed phase and benzene solutions of polybutene (PB) and polyisobutene (PIB) as a continuous phase in a flat-stirred vessel at 25°C.

A mathematical model was developed as a combination of physical absorption into the continuous phase through the gas-liquid interface on the basis of the penetration model and chemical absorption into the dispersed phase through the liquid-liquid interface on the basis of film model. The mass transfer coefficient and rate of physical absorption were increased due to non-Newtonian elasticity compared with that of Newtonian viscosity. The volumetric mass transfer coefficient containing the elastic properties such as Deborah number was used to estimate the enhancement factor for the chemical absorption. The measured rate of chemical absorption increased with increasing reactant concentration and was independent of PIB concentration.

Acknowledgements

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Nomenclature

\( A \) : rheological properties defined in Eq. (34),
Sang-Wook Park, Tae-Young Kim, Byoung-Sik Choi and Jae-Wook Lee

\[ a \text{ : contact area at interface of gas-liquid per liquid volume, [1/m]} \]
\[ b \text{ : rheological properties defined in Eq. (34)} \]
\[ C_A \text{ : concentration of CO}_2\text{ in continuous phase, [kmol/m}^3\text{]} \]
\[ c_A \text{ : concentration of CO}_2\text{ in dispersed phase, [kmol/m}^3\text{]} \]
\[ c_A^* \text{ : solubility of CO}_2\text{ in dispersed phase, [kmol/m}^3\text{]} \]
\[ C_{Al} \text{ : solubility of CO}_2\text{ in a continuous phase, [kmol/m}^3\text{]} \]
\[ c_{Aw} \text{ : solubility of CO}_2\text{ in water, [kmol/m}^3\text{]} \]
\[ c_B \text{ : concentration of MEA in dispersed phase, [kmol/m}^3\text{]} \]
\[ c_{Bo} \text{ : feed concentration of MEA in dispersed phase, [kmol/m}^3\text{]} \]
\[ c_{Bi} \text{ : concentration of MEA at } r=0 \text{ in dispersed phase, [kmol/m}^3\text{]} \]
\[ d \text{ : diameter of impella, [m]} \]
\[ D_A \text{ : diffusivity of CO}_2\text{ in benzene, [m}^2\text{/s]} \]
\[ D_e \text{ : Deborah number defined in Eq. (37)} \]
\[ D_A \text{ : diffusivity of CO}_2\text{ in dispersed phase, [m/s]} \]
\[ D_{Aw} \text{ : diffusivity of CO}_2\text{ in dispersed phase in benzene solution of PIB and PB, [m/s]} \]
\[ D_{Bw} \text{ : diffusivity of MEA in dispersed phase in benzene solution of PIB and PB, [m/s]} \]
\[ D_{Aw} \text{ : diffusivity of MEA in dispersed phase, [m/s]} \]
\[ D_{Bw} \text{ : diffusivity of MEA in water, [m/s]} \]
\[ D_s \text{ : diffusivity of CO}_2\text{ in dispersed phase, [m/s]} \]
\[ D_{eg} \text{ : effective diffusivity of CO}_2\text{ in emulsion, [m}^2\text{/s]} \]
\[ H_A \text{ : dimensionless solubility defined as } \frac{c_A}{C_{Al}} \]
\[ K \text{ : rheological properties defined in Eq. (32), [Ns/m}^2\text{]} \]
\[ k_L \text{ : mass transfer coefficient of CO}_2\text{ in continuous phase, [m/s]} \]
\[ k_{LL} \text{ : mass transfer coefficient of CO}_2\text{ in dispersed phase, [m/s]} \]
\[ k_{OA} \text{ : volumetric mass transfer coefficient, [1/s]} \]
\[ k_2 \text{ : 2nd-order-reaction constant, [m}^3\text{/kmol s]} \]
\[ M \text{ : dimensionless modulus defined as } (1-\varepsilon)k^2_{BO}H_3D_2/k_2^2 \]
\[ M_o \text{ : molecular weight of benzene, [kg/kmol]} \]
\[ M_p \text{ : molecular weight of polymer, [kg/kmol]} \]
\[ M_{PB} \text{ : molecular weight of PB, [kg/kmol]} \]
\[ m_A \text{ : dimensionless modulus defined as } \frac{R_o}{k_c^2f_D/Q_0} \]
\[ n \text{ : rheological properties defined in Eq. (32)} \]
\[ N \text{ : impeller speed, [1/s]} \]
\[ N_1 \text{ : primary normal stress difference defined in Eq. (34), [N/m}^2\text{]} \]
\[ N_A \text{ : molar flux of CO}_2\text{ at gas-liquid interface with chemical reaction in benzene at any contact time [kmol/m}^2\text{]} \]
\[ \bar{N}_a \text{ : mean molar flux of CO}_2\text{ at gas-liquid interface with chemical reaction in benzene during any contact time [kmol/m}^2\text{]} \]
\[ \alpha \text{ : dimensionless parameter defined in Eq. (40)} \]
\[ \alpha_A \text{ : dimensionless concentration of CO}_2\text{ in aqueous phase defined as } c_A/c_{Aw} \]
\[ \alpha_{Bi} \text{ : dimensionless concentration of B in dispersed phase defined as } c_B/c_{Bo} \]
\[ \alpha_B \text{ : dimensionless concentration of B in aqueous phase defined as } c_B/c_{Bi} \]
\[ \gamma \text{ : shear rate, [1/s]} \]
\[ \sigma \text{ : interfacial surface tension between water and benzene solution of PIB and PB, [N/m]} \]
\[ \sigma_e \text{ : interfacial surface tension between water and benzene solution of PB, [N/m]} \]
\[ \epsilon \text{ : volume fraction of benzene phase in the emulsion} \]
\[ \zeta \text{ : dimensionless parameter defined in Eq. (40)} \]
\[ \theta \text{ : dimensionless time define as } k_2^2t/D_2 \]
\[ \lambda \text{ : characteristic liquid time, [s]} \]
\[ \mu \text{ : viscosity of liquid, [Ns/m}^2\text{]} \]
\[ \mu_o \text{ : viscosity of benzene, [Ns/m}^2\text{]} \]
\[ \nu \text{ : stoichiometric coefficient in chemical reaction of CO}_2\text{ with amine} \]
\[ \rho \text{ : density of non-Newtonian liquid, [kg/m}^3\text{]} \]
\[ \tau \text{ : shear stress, [N/m}^2\text{]} \]
\[ \phi \text{ : enhancement factor} \]

**Greek letters**

\[ \alpha \text{ : dimensionless parameter defined in Eq. (40)} \]
\[ \alpha_A \text{ : dimensionless concentration of CO}_2\text{ in aqueous phase defined as } c_A/c_{Al} \]
\[ \alpha_{Bi} \text{ : dimensionless concentration of B in dispersed phase defined as } c_B/c_{Bi} \]
\[ \alpha_B \text{ : dimensionless concentration of B in aqueous phase defined as } c_B/c_{Bo} \]
\[ \gamma \text{ : shear rate, [1/s]} \]
\[ \sigma \text{ : interfacial surface tension between water and benzene solution of PIB and PB, [N/m]} \]
\[ \sigma_e \text{ : interfacial surface tension between water and benzene solution of PB, [N/m]} \]
\[ \epsilon \text{ : volume fraction of benzene phase in the emulsion} \]
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\[ \rho \text{ : density of non-Newtonian liquid, [kg/m}^3\text{]} \]
\[ \tau \text{ : shear stress, [N/m}^2\text{]} \]
\[ \phi \text{ : enhancement factor} \]

**Subscripts**

\[ A \text{ : CO}_2 \]
\[ B \text{ : reactant [amine]} \]
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\[ E \text{ : Aqueous} \]
\[ i \text{ : gas-liquid interface} \]
\[ o \text{ : bulk body} \]
\[ w \text{ : pure water phase} \]
\[ * \text{ : liquid-liquid interface} \]

References


