# W/O 에멀션액막에서 이산화탄소와 AMP의 화학반응

박 상 욱† · 최 병 식 · 김 성 수* · 이 재 욱**

부산대학교 응용화학공학부, *부산카톨릭대학교 환경과학부, **서강대학교 화학공학과
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# Chemical Reaction of Carbon Dioxide with AMP in w/o Emulsion Membrane

Sang-Wook Park†, Byoung-Sik Choi, Seong-Soo Kim*, and Jae-Wook Lee**

Department of Chemical Engineering, Pusan National University, Pusan 609-735, Korea
*School of Environmental Science, Catholic University of Pusan, Pusan 609-757, Korea
**Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea

요　약: 본 연구에서는 준 회분식 교반조를 사용하여 polybutene (PB)와 polyisobutylene (PIB)고분자를 용해한 벤젠 용액을 연속상, 물을 불연속상으로 구성한 w/o 에멀션액막에 $CO_2$을 흡수시켜 흡수속도를 측정하였다. 점탄성을 나타내는 Deborah 수를 사용하여 점탄성 비뉴튼액체에서 구한 부피물질전달계수 $(k_L a)$를 고찰하고, 수용액에 첨가한 2-amino-2-methyl-1-propanol(AMP)와 $CO_2$의 반응 메카니즘을을 해석하였다.

Abstract: Carbon dioxide was absorbed into water-in-oil (w/o) emulsion composed of aqueous 2-amino-2-methyl-1-propanol (AMP) droplets as a dispersed phase and benzene solutions of polybutene and polyisobutylene as a continuous phase in a flat-stirred vessel to investigate the effect of non-Newtonian rheological behavior on the rate of chemical absorption of $CO_2$, where the reaction between $CO_2$ and AMP in the aqueous phase was assumed to be a pseudo-first-order reaction. It was expressed that PIB with elastic property made the rate of chemical absorption of $CO_2$ accelerated by comparison of mass transfer coefficient of $CO_2$ in the non-Newtonian liquid with that in the Newtonian liquid.

## 1. Introduction

Gas-liquid mass transfer in non-Newtonian liquid is an important example of gas absorption in pseudo-plastic flow of industrial processes such as a fermentation broth, slurry, and fluidized bed, et al. Variation of the volumetric liquid-phase mass transfer coefficient $(k_L a)$ in gas-dispersed systems consists of the liquid-side mass transfer coefficient $(k_L)$ and the specific gas-liquid interfacial area(a). 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 $k_L a$ 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 $k_L a$ is due to the viscoelasticity of the aqueous solution, then the extent to which data for the viscoelastic solution such

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**Table 1.** Coefficients of Dimensionless Group Gas-liquid Mass Transfer

| Investigator | $n_1$ | $n_2$ | $n_3$ | polymer | contactor |
|---|---|---|---|---|---|
| Yagi and Yoshida [1] | 2 | 0.5 | -0.67 | CMC, PA | agitated vessel |
| Ranade and Ulbrecht [2] | 100 | 1 | -0.67 | CMC, PAA | stirred tank |
| Nakanoh and Yoshida [3] | 0.13 | 0.55 | -1 | CMC, PA | bubble column |
| Park et al. [4] | 100 | 1 | -0.42 | PB, PIB | agitated vessel |
| Park et al. [5] | 2461.3 | 1 | -0.274 | PB, PIB | agitated vessel |

as PAA deviate from those for the inelastic solution such as CMC should correlate with some measure of the solution's 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 $k_La$ in Newtonian as well as non-Newtonian solutions by introducing the dimensionless term such as $(1+n_1De^{n_2})^{n_3}$, 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[6-9]: 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 $(1+n_1De^{n_2})^{n_3}$, as shown in Table 1, to fit the experimental $k_La$ of $CO_2$ absorption into non-Newtonian liquid[4] such as benzene solution of polybutene (PB) and polyisobutylene (PIB), and w/o emulsion[5] composed of water

as dispersed phase and benzene solution of PB and PIB as continuous phase in an agitation vessel.

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 AMP 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. AMP was used ax a reagent of $CO_2$. The volumetric mass transfer coefficient obtained from the previous work[5] 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 AMP(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 AMP, 3) isothermal condition prevails, 4) size and shape of the dispersed
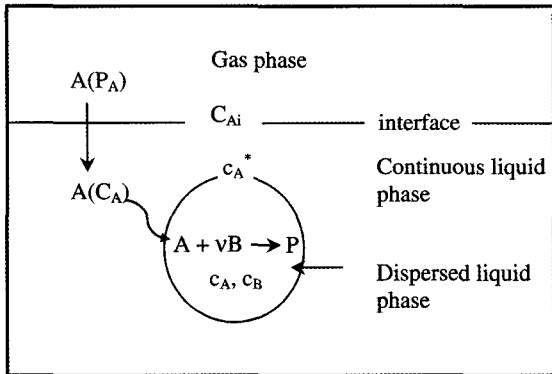
Fig. 1. Chemical absorption path of gas(A) into w/o emulsion.

aqueous droplets are uniform and sphere, and 5) although the solubility[10] of AMP in benzene at 25°C is 2.7%, 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

$$D_{eA}\left(\frac{d^2c_A}{dr^2} + \frac{2}{r}\frac{dc_A}{dr}\right) = k_2 c_A c_B \qquad (1)$$

$$D_{eB}\left(\frac{d^2c_B}{dr^2} + \frac{2}{r}\frac{dc_B}{dr}\right) = v k_2 c_A c_B \qquad (2)$$

Boundary conditions to be imposed are

$$r = R; \quad c_A = c_A^* = H_A C_A, \quad \frac{dc_B}{dr} = 0 \qquad (3)$$

$$r = 0; \quad \frac{dc_A}{dr} = \frac{dc_B}{dr} = 0 \qquad (4)$$

R is a radius of aqueous droplet in the benzene solution. The stoichiometric coefficients(n) in Eq. (2) for AMP was obtained from the reference, and its value was 1[11].

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

$$\frac{d^2\alpha_A}{dy^2} + \frac{2}{y}\frac{d\alpha_A}{dy} = m_A^2 \alpha_A \alpha_B \qquad (5)$$

$$\frac{d^2\alpha_B}{dy^2} + \frac{2}{y}\frac{d\alpha_B}{dy} = \frac{m_A^2}{r_B q_B}\alpha_A\alpha_B \qquad (6)$$

$$y = 1; \quad \alpha_A = 1, \quad \frac{d\alpha_B}{dy} = 0 \qquad (7)$$

$$y = 0; \quad \frac{d\alpha_A}{dy} = \frac{d\alpha_B}{dy} = 0 \qquad (8)$$

where $\alpha_A = c_A/c_A^*$, $\alpha_B = c_B/c_{Bo}$, $y = r/R$, $m_A = R\sqrt{k_2 c_{Bo}/D_{eA}}$, $r_B = D_{eB}/D_{eA}$, $q_B = c_{Bo}/vc_A^*$.

The effectiveness factor here can be defined as

$$E_f = \frac{4\pi R^2 n_A}{(4/3)\pi R^3 k_2 c_A^* c_{Bo}} = \frac{3}{m_A^2}\frac{d\alpha_A}{dy}\Big|_{y=1} \qquad (9)$$

where $n_A$ is the flux of $CO_2$ defined as $D_{eA}dc_A/dr \mid_{r=R}$.

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 $E_f$ is obtained from Eq. (9). If the concentration of B in the droplets, $c_B$ is constant, the value of $E_f$ can be obtained from the exact solution of Eq. (5).

If $c_B$ is equal to the interfacial constant concentration ($c_{Bi}$) 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

$$\frac{d^2\alpha_A}{dy^2} + \frac{2}{y}\frac{d\alpha_A}{dy} = (m_A\eta)^2\alpha_A \qquad (5a)$$

$$y = 1; \quad \alpha_A = 1 \qquad (7a)$$

$$y = 0; \quad \frac{d\alpha_A}{dy} = 0 \qquad (8a)$$

where, $\eta = \sqrt{\alpha_{Bi}}$, $\alpha_{Bi} = c_{Bi}/c_{Bo}$

The concentration profile of A is derived from the

exact solution of Eq. (5a) is given as follows:

$$\alpha_A = \frac{\sinh(m_A\eta y)}{y \sinh(m_A\eta)}$$ (10)

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

$$E_f = \frac{3}{m_A\eta}\left[\frac{1}{\tanh(m_A\eta)} - \frac{1}{m_A\eta}\right]$$ (11)

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

$$\frac{4}{3}\pi R^3(c_{Bo} - c_{Bi}) = v\int_0^R 4\pi r^2(c_A^* - c_A)dr$$ (12)

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

$$1 - \alpha_{Bi} = \frac{3}{q_B}\int_0^1 y^2(1 - \alpha_A)dy$$ (13)

$\alpha_{Bi}$ is derived from Eq. (13) with Eqs. (9) and (10) as follows:

$$\alpha_{Bi} = 1 - \frac{1 - E_f}{q_B}$$ (14)

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

$$D_A\frac{\partial^2 C_A}{\partial z^2} = \frac{\partial C_A}{\partial t} + (1-\varepsilon)k_2 c_A^* c_{Bo}E_f$$ (15)

Boundary and initial conditions are given as

$$z = 0, \quad t > 0; \quad C_A = C_{Ai}$$ (16)

$$z > 0, \quad t = 0; \quad C_A = 0$$ (17)

$$z = \infty, \quad t > 0; \quad C_A = 0$$ (18)

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

$$\frac{\partial^2 Y_A}{\partial x^2} = \frac{\partial Y_A}{\partial \theta} + ME_f Y_A$$ (19)

$$x = 0, \quad \theta > 0; \quad Y_A = 1$$ (20)

$$x > 0, \quad \theta = 0; \quad Y_A = 0$$ (21)

$$x = \infty, \quad \theta > 0; \quad Y_A = 0$$ (22)

where, $Y_A = C_A/C_{Ai}$, $\theta = k_L^2\, t/D_A$, $x = k_L z/D_A$, $M = (1-\varepsilon)k_2 c_{Bo}H_A D_A/k_L^2$, $H_A = c_A^*/C_A$

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

$$N_A = -D_A\frac{\partial C_A}{\partial z}\Big|_{z=0}$$ (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)

The mean molar flux without chemical reaction based on the penetration model during contact time has been derived as follows[12]:

$$\overline{N_A^o} = 2C_{Ai}\sqrt{\frac{D_A}{\pi t}}$$ (25)

From comparison of the penetration model with the film model, the relation between t and $k_L$ is derived as follows[13]:

$$k_L = 2\sqrt{\frac{D_A}{\pi t}}$$ (26)

The enhancement factor ($\phi$) here defined as the ratio of molar flux with chemical reaction to that without

chemical reaction, $\overline{N_A}/\overline{N_A^o}$, is described by using Eqs. (24) and (25) as follows:

$$\phi = -\frac{\sqrt{M}}{t}\int_0^t \frac{\partial Y_A}{\partial x}\Big|_{x=0} dt \qquad (27)$$

Because the mass transfer coefficient of $CO_2$ in the dispersed phase($k_{LL}$) 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

$$\frac{d}{dr}\left(r^2 D_{eA}\frac{dc_A}{dr}\right) = 0 \qquad (1.1)$$

Boundary conditions are given as

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

$$r = 0; \quad \frac{dc_A}{dr} = 0$$

In Eq. (9), the molar flux of $CO_2$ without chemical reaction is defined as

$$n_A = -D_{eA}\frac{dc_A}{dr}\Big|_{r=R} \qquad (28)$$

Integration of Eq. (1.1) gives

$$c_A = -\frac{c_1}{D_{eA}r} + c_2 \qquad (29)$$

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:

$$n_A = \frac{D_{eA}c_A^*}{R} \qquad (30)$$

From comparison of Eq. (30) with the film theory,

$k_{LL}$ is presented as follows:

$$k_{LL} = \frac{D_{eA}}{R} \qquad (31)$$

## 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 0.1, 0.2, 0.5, 1.0 wt%, and that of AMP in the aqueous solution was in the range of $0 \sim 2.0$ kmol/m$^3$. Volume fraction of benzene in emulsion was fixed as a value of 0.6.

### 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[9] 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 $4 \times 10^{-5}$ 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[4] 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[4] 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[14], 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 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[15]. A digital pressure gauge made by Meriam Instrument (Meriam Merigauge, 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[4] 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 $7.65 \times 10^{-4}$ and $1.55 \times 10^{-3}$ cm along the procedure similar to those reported elsewhere[16].

## 4. Rheological and Physicochemical Poperties 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 $k_L$, $k_2$, $\rho$, $\mu$, $D_e$, $\sigma$, solubilities of $CO_2$ in dispersed and continuous phase, and diffusivities of $CO_2$ and AMP. 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.

$$\tau = K\gamma^n \tag{32}$$

$$\mu = K\gamma^{n-1} \tag{33}$$

$$N_1 = A\gamma^b \tag{34}$$

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 $\gamma$.

In order to observe the dependence of $\tau$ and $N_1$ on $\gamma$, $\tau$ and $N_1$ of the w/o emulsion were measured according to the change of $\gamma$ 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
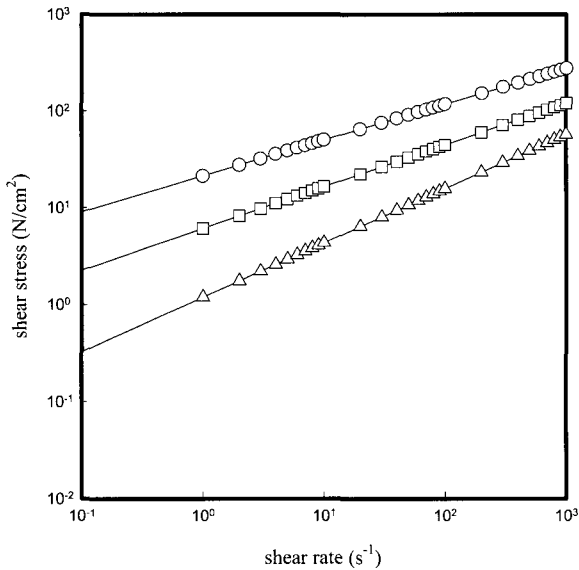
Fig. 2. Shear stress of $H_2O$/(PIB/PB/Bz) emulsion as a function of shear rate. ($\triangle$:Bz, $\square$: PB(30)/Bz, $\bigcirc$: PIB(1)/PB(30)/Bz)
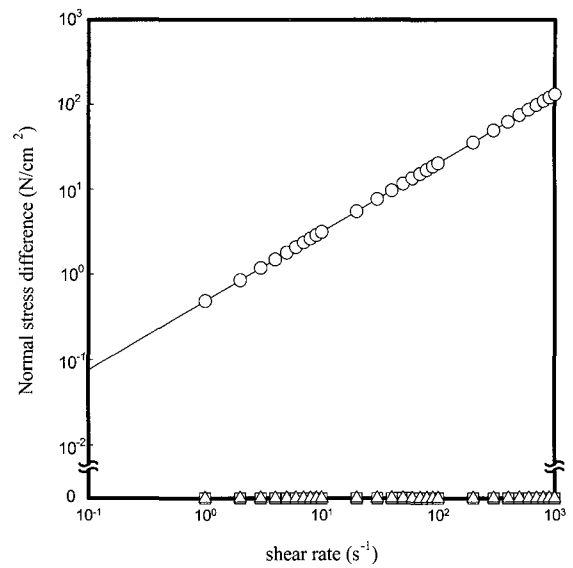


Fig. 3. Normal stress difference of $H_2O$/(PIB/PB/Bz) emulsion as a function of shear rate. ($\triangle$:Bz, $\square$: PB(30)/Bz, $\bigcirc$: PIB(1)/PB(30)/Bz)

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

$$\lambda = \frac{N_1}{\mu \gamma^2} \tag{35}$$

Table 2. The Physicochemical and Rheological Properties of $CO_2$ and w/o Emulsion with Void Fraction of Continuous Phase of 0.6

| PB (wt%) | PIB (wt%) | Interfacial tension (N/m) | Diffusivity $(m^2/s) \times 10^9$ | Solubility $(kmol/m^3)$ | Density $(kg/m^3)$ | Rheological properties | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | n | K | b | A |
| 0 | 0 | 34.7 | 1.98 | 0.095 | 949.6 | 0.560 | 1.196 | 0 | 0 |
| | 0 | 25.7 | 1.38 | 0.079 | 953.0 | 0.458 | 5.035 | 0 | 0 |
| | 0.1 | 24.7 | 1.70 | 0.077 | 939.4 | 0.436 | 6.974 | 0.704 | 0.078 |
| 20 | 0.2 | 24.6 | 1.74 | 0.074 | 942.4 | 0.415 | 8.559 | 0.735 | 0.085 |
| | 0.5 | 23.4 | 1.76 | 0.073 | 948.3 | 0.401 | 9.835 | 0.798 | 0.124 |
| | 1.0 | 21.8 | 1.68 | 0.073 | 963.9 | 0.396 | 17.453 | 0.897 | 0.274 |
| | 0 | 24.5 | 1.03 | 0.076 | 950.7 | 0.431 | 6.114 | 0 | 0 |
| | 0.1 | 24.1 | 1.43 | 0.073 | 939.6 | 0.417 | 7.385 | 0.704 | 0.086 |
| 10 | 0.2 | 23.8 | 1.53 | 0.071 | 941.1 | 0.408 | 10.641 | 0.732 | 0.193 |
| | 0.5 | 22.9 | 1.57 | 0.069 | 945.1 | 0.443 | 11.239 | 0.751 | 0.293 |
| | 1.0 | 20.8 | 1.61 | 0.067 | 948.8 | 0.396 | 17.350 | 0.810 | 0.786 |
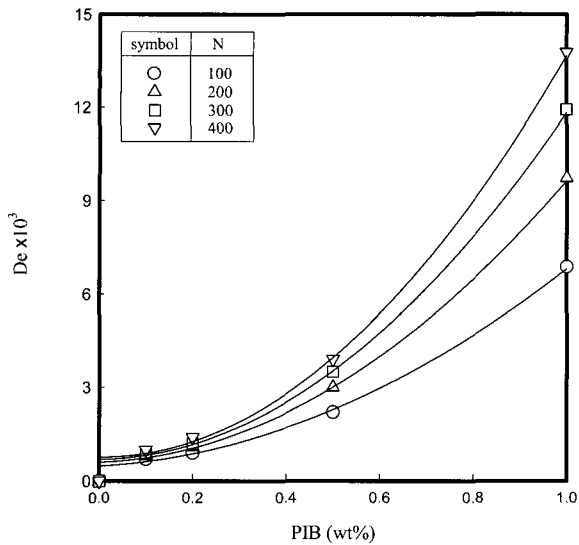
**Fig. 4.** Effect of concentration of PIB on Deborah number at PB of 20 wt%.

In terms of the parameters K, A, n, and b defined by Eqs. (28) and (30), the characteristic time, $\lambda$, can be expressed as

$$\lambda = \frac{A}{K} \gamma^{b-n-1} \tag{36}$$

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:

$$De = \lambda N = \frac{A}{K} \gamma^{b-n-1} N \tag{37}$$

The shear rate, $\lambda$ in Eq. (37) is obtained from the equation, $\lambda = 4\pi N/n$ [5].

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 AMP[11], the reaction rate constants were estimated as follows:

$$\log k_2 = 10.986 - \frac{2551.2}{T}$$

## 4.3. Solubility of $CO_2$

The solubility of $CO_2$ in water was taken as 0.0328 $kmol/m^3$[17] at 25°C and 0.1013 MPa. The solubility of $CO_2$ in AMP[18] solution was estimated as follows:

$$c_A^* = 3.328 \times 10^{-2} - 3.76 \times 10^{-3} c_{Bo} + 4 \times 10^{-4} c_{Bo}^2$$

The solubilities of $CO_2$ in benzene solution of PB and PIB and in the w/o emulsion at 25°C and 0.1013 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 AMP

The diffusivity of $CO_2$ ($D_A$) in benzene estimated from the Wilke-Chang equation[19] was $3.853 \times 10^{-9}$ $m^2/s$ at 25°C.

The diffusivity of $CO_2$ ($D_{eA}$)[18] in AMP solution was estimated as follows:

$$D_{eA} = 2.1625 \times 10^{-9} - 6.85 \times 10^{-10} c_{Bo} + 7 \times 10^{-11} c_{Bo}^2$$

The diffusivity of AMP ($D_{eB}$) in aqueous AMP solution was obtained from assumption that the ratio of $D_{eB}$ to $D_{eA}$ was equal to the ratio in water[20]. The diffusivities of $CO_2$ and AMP in water at 25°C were taken as $1.97 \times 10^{-9}$ $m^2/s$ [17] and $7.24 \times 10^{-10}$ $m^2/s$[19], 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.[21], which was modified from the Stoke-Einstein equation, and correlated with the molecular weight of the polymer in the solution.

$$D_c/D_A = (\mu_o/\mu)^{3.7\sqrt{M_o/M_p}} \tag{38}$$

The molecular weight of the mixed polymer in the benzene solution of PB and PIB, $M_P$, was calculated by the addition rule as follow:

$$M_P = x_{PB} \times M_{PB} + x_{PIB} \times M_{PIB} \tag{39}$$

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 ($D_{eff}$) was obtained by the empirical equation as follows[22],

$$\frac{D_{eff}}{D_c} = 1 + \frac{1.209(\alpha-1)(1-\varepsilon)}{(1-a)(1-\varepsilon)^{1/3}+0.806\alpha} \tag{40}$$

where $\alpha = \frac{2\zeta}{\zeta-1}(\frac{\zeta}{\zeta-1}\ln\zeta-1)$ and $\zeta = \frac{H_A D_{eA}}{D_c}$

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 AMP in the aqueous droplets was estimated by using the empirical equation[5] correlating the relationship between $k_L a$ and the experimental variables in the w/o emulsion of non-Newtonian liquid as follows.

$$k_L a d^2 / D_{eff} = 6.348 \times 10^{-9}(d^2 N\rho/\mu)^{2.536}(\mu/\mu_o)^{2.397}$$
$$(1+2461.3De)^{-0.274}(\sigma/\sigma_o)^{-0.039} \tag{41}$$

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 AMP solution was measured according to change of reactant concentration in the aqueous phase under the typical experimental conditions such 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 $H_2O/(PB/PIB/Bz)$ system, the effect of viscosity on $k_L$ was observed. The viscosity of the w/o emulsion and $k_L$ were estimated using Eqs. (29) and (41), respectively, and Fig. 5 and 6 show typically plots of viscosity of w/o emulsion against the 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.
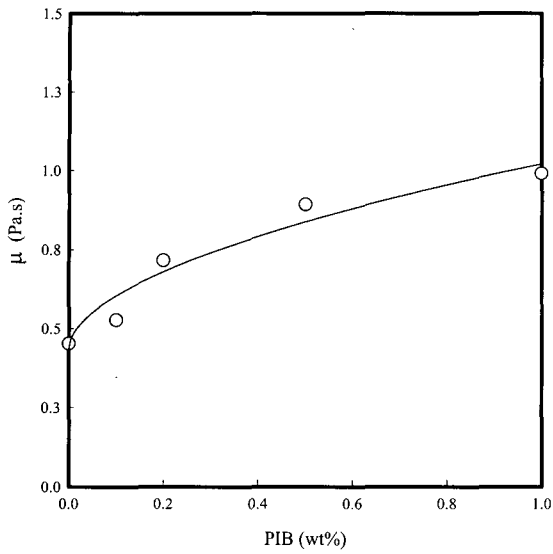
**Fig. 5.** Effect of PIB concentration on viscosity of w/o emulsion with PB of 30 wt%.
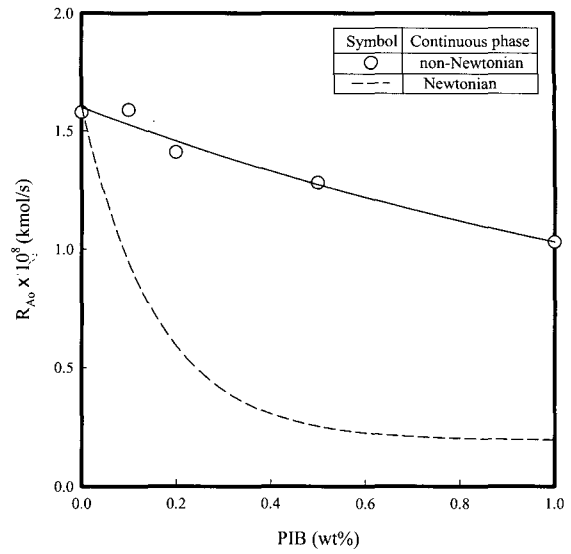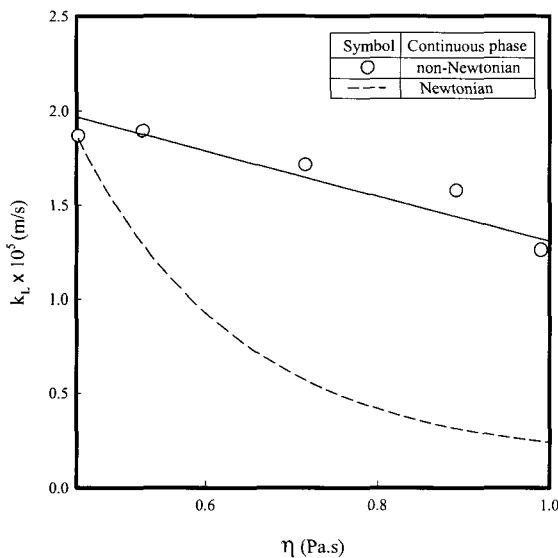


**Fig. 6.** Effect of viscosity on the mass transfer coefficient for w/o emulsion with PB of 30 wt% and PIB of 0.1~1 wt%.

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),



**Fig. 7.** Effect of PIB on physical absorption rate in w/o emulsion with PB of 30 wt%.

$$k_L a d^2 / D_{eff} = 6.348 \times 10^{-9} (d^2 N \rho / \mu)^{2.536} \quad (42)$$

The calculated value of $k_L$ from Eq. (32) according to the change of PIB concentration of 0.1~1 wt% was plotted as a triangle 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 $CO_2$ ($R_{Ao}$) in the w/o emulsion was estimated using a equation correlating Eqs. (25) and (26) as follows:

$$R_{Ao} = k_L a C_{Ai} \quad (43)$$

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.

**Table 3.** Classification of reaction regime

| $c_{BO}$(kmol/m$^3$) | $\sqrt{D_{eA}k_2 d_{BO}/k_{LL}}$ | $c_{BO}\sqrt{D_{eB}/D_{eA}}/(vc_A^*)$ |
|---|---|---|
| 0.1 | 4.53 | 0.92 |
| 0.5 | 10.82 | 4.62 |
| 1.0 | 16.67 | 9.24 |
| 1.5 | 22.34 | 13.86 |
| 2.0 | 28.31 | 18.48 |

To ascertain the reaction of $CO_2$ with AMP 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, for convenience the system may be classified into four regimes such as very slow reactions, slow reactions, fast reactions, and instantaneous reactions[23].

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 AMP in the dispersed phase are considered to determine the reaction regime. Because the mass transfer coefficient of $CO_2$ ($k_{LL}$) in the dispersed phase 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 are considered to determine the reaction regime.

The values of $\sqrt{D_{eA}k_2 c_{BO}}/K_{LL}$ and $c_{BO}\sqrt{D_{eB}/D_{eA}}/(vc_A^*)$ were calculated using the physicochemical properties such as $D_{eA}$, $D_{eB}$, $k_2$, $c_A^*$ in the range of the AMP concentration of 0.1~2.0 kmol/m$^3$, and were listed in the Table 3. As shown in Table 3, $\sqrt{D_{eA}k_2 c_{BO}}/k_{LL}$ is larger than 1, and the value of $\sqrt{D_{eA}k_2 c_{BO}}/k_{LL}$ is larger than that of $c_{BO}\sqrt{D_{eB}/D_{eA}}/(vc_A^*)$. Therefore, the system of chemical reaction of $CO_2$ with AMP 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, equation (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 AMP, the rate of chem-
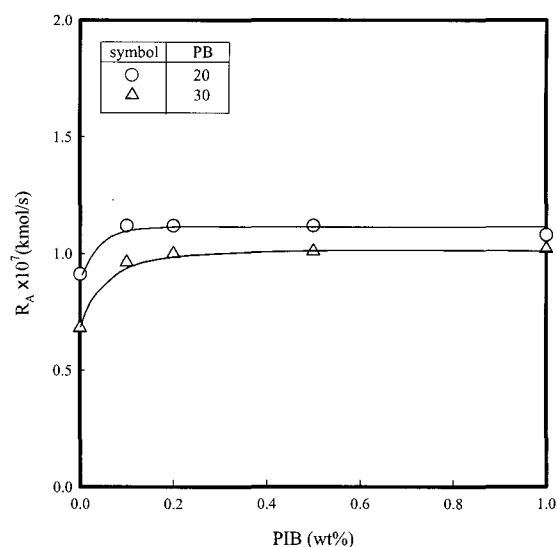


**Fig. 8.** Effect of PIB on the rate of chemical absorption at $c_{Bo}$=1 kmol/m$^3$.

ical absorption of $CO_2$ into w/o emulsion with dispersed phase of AMP aqueous solution was measured at PB of 20 and 30 wt% and PIB of 0.1~1 wt% according to AMP 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 AMP 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 $(4D_A/\pi k_L^2)$ which is obtained from Eq. (26).

As shown in Fig. 8, $R_A$ has a constant value at PIB of 0.1~1 wt% except PIB of 0. But, $R_A$ should be decrease with increasing the PIB concentration because of a tendency to decrease of $R_{Ao}$ as shown in Fig. 7. The reason why $R_A$ does not decrease with increasing PIB concentration may be explained using the enhancement factor, $\phi$, as below.

$R_A$ is expressed from the definition of as follows.

$$R_A = \phi R_{Ao} \qquad (44)$$

The value of $\phi$ is calculated using Eq. (27), and Fig. 9 shows a typical plot of $\phi$ against the concentration of PIB at AMP concentration of 1 kmol/m$^3$ and
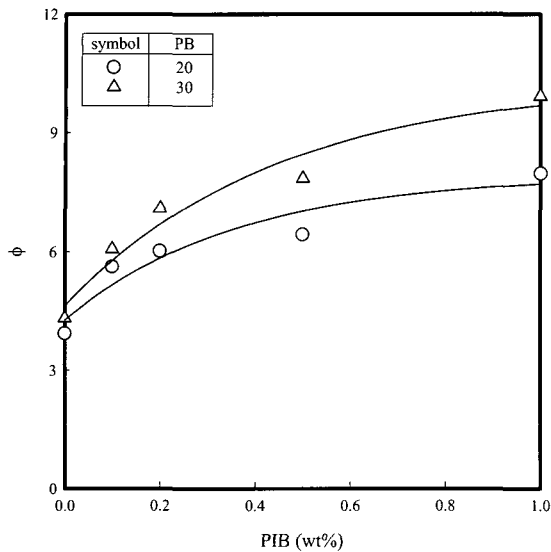
Fig. 9. Effect of PIB on the enhancement factor at $c_{Bo}=1$ kmol/m$^3$.



Fig. 10. Effect of AMP concentration on the rate of chemical absorption into the w/o emulsion with PB of 30 wt% and PIB of 1 wt%.

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, increased, which is a major parameter increasing the enhancement factor[9]. Meanwhile, decrease of $k_L$ makes $R_{Ao}$ decreased 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 AMP on the rate of chemical absorption, the rate of chemical absorption was measured according to the change of AMP concentration. Fig. 10 shows typically a plot of $R_A$ against AMP concentration at PB of 30 wt% and PIB of 1 wt%.

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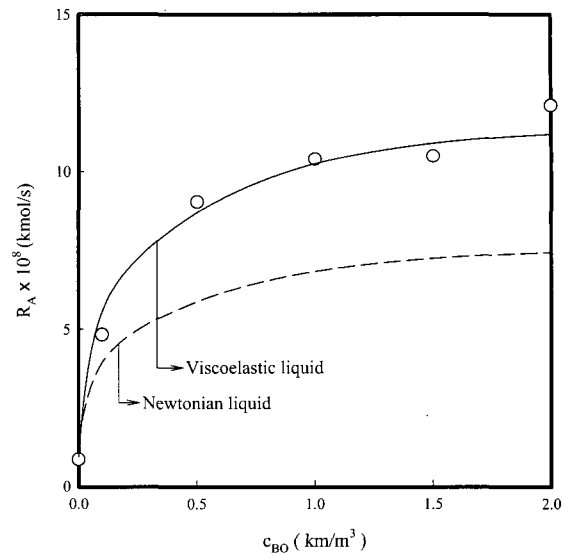
Eq. (42). As shown in Fig. 10, the value of the dotted line smaller than that of the solid line. This means that the elastic due to PIB also accelerates the rate of chemical absorption.

## 6. Conclusions

Rates of chemical absorption of $CO_2$ in w/o emulsion were measured in a flat-stirred vessel at 25°C. The w/o emulsion was composed of aqueous AMP droplets as a dispersed phase and non-Newtonian viscoelastic benzene solutions of PB and PIB as a continuous phase.

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.

## Acknowledgement

## Nomenclature

$C_A$    concentration of $CO_2$ in continuous phase, [kmol/m$^3$]

$c_A$    concentration of $CO_2$ in dispersed phase, [kmol/m$^3$]

$c_B$    concentration of AMP in dispersed phase, [kmol/m$^3$]

$d$    diameter of impeller, [m]

$k_2$    $2^{nd}$-order-reaction constant, [m$^3$/kmol s]

$M_o$    molecular weight of benzene, [kg/kmol]

$M_{PB}$    molecular weight of PB, [kg/kmol]

$M_{PIB}$    molecular weight of PIB, [kg/kmol]

$N$    impeller speed, [1/s]

$r$    radial distance in aqueous phase,[m]

$t$    time, [s]

$T$    temperature, [K]

$z$    coordinate in film thickness direction in benzene phase, [m]

### Greek letters

$\gamma$    shear rate, [1/s]

$\sigma$    interfacial surface tension between water and benzene solution of PIB and PB, [N/m]

$\sigma_o$    interfacial surface tension between water and benzene solution of PB, [N/m]

$\mu$    viscosity of liquid, [Ns/m$^2$]

$\mu_o$    viscosity of benzene, [Ns/m$^2$]

$\nu$    stoichiometric coefficient in chemical reaction of $CO_2$ with amine

$\rho$    density of non-Newtonian liquid, [kg/m$^3$]

$\tau$    shear stress, [N/m$^2$]

$\phi$    enhancement factor

### Subscripts

A    $CO_2$

B    AMP

e    aqueous

i    gas-liquid interface

o    bulk body

w    water phase

*    liquid-liquid interface

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