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Absorption of Carbon Dioxide into Non-Newtonian Liquid. III. Effect of Chemical Reaction

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ABSTRACT

Carbon dioxide was absorbed into water-in-oil (w/o) emulsion composed of aqueous diethanolamine (DEA) droplets as a dispersed phase and benzene solutions of polybutene (PB) and polyisobutylene (PIB) 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 CO₂, where the reaction between CO₂ and DEA in the aqueous phase was assumed to be a pseudo-first-order reaction. The liquid-side-mass-transfer coefficient, k_L , which was obtained from the dimensionless empirical equation containing the properties of pseudoplasticity of the non-Newtonian liquid, was used to estimate the enhancement factor due to chemical reaction. It was expressed that PIB with elastic property

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accelerated the rate of chemical absorption of CO₂ by the comparison of k_L in the non-Newtonian liquid with that in the Newtonian liquid.

Key Words: Chemical absorption; Carbon dioxide; Emulsion; DEA; Non-Newtonian liquid.

INTRODUCTION

Gas–liquid mass transfer in non-Newtonian liquid is an important example of gas absorption in pseudoplastic flow relevant to industrial process such as fermentation broth, slurry, fluidized bed, etc. Variation of the volumetric liquid-phase mass-transfer coefficient, $k_L a$, in gas-dispersed systems consists of the variation of the mass-transfer coefficient, k_L , and that of the specific gas–liquid interfacial area, a . The former could be correlated with the Reynolds and Schmidt numbers, which include 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.

Mere 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, polyethylene oxide, polyacrylamide (PAA), and polyisobutylene (PIB) solutions. If some substance is to be given to the suggestion that the 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 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 the Deborah number, De , defined as the product of the material's characteristic relaxation time and the characteristic flow time, or the Weissenberg number, Wi , defined as the ratio of the first normal stress difference to the shear rate. Unified correlations has been proposed for $k_L a$ in Newtonian as well as non-Newtonian solutions by introducing the dimensionless term such as $(1 + n_1 De^{n_2})^{n_3}$, which is listed in Table 1. As shown in Table 1, figures in the dimensionless term are different from one another.

If the system is the water-in-oil (w/o) emulsion such that the dispersed phase is the aqueous solution containing reactant and the continuous phase is the organic solvent having larger solubility of gas than water, then the specific rate of absorption may be enhanced because of larger solubility and chemical reaction. A qualitative explanation of this phenomenon has been given by

Table 1. Coefficients of dimensionless group gas–liquid mass transfer.

Investigator	n_1	n_2	n_3	Polymer	Contactors
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]	2,461.3	1	−0.274	PB, PIB	Agitated Vessel

various authors:^[6–9] small droplets of a liquid immiscible with the continuous liquid phase absorb the gas in the hydrodynamic mass-transfer film, after which 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 the w/o emulsion composed of aqueous droplets as a dispersed phase and the non-Newtonian liquid as a continuous phase. Park et al. presented the dimensionless term such as $(1 + n_1 De^{n_2})^{n_3}$, as shown in Table 1, to fit the experimental $k_L a$ of CO₂ absorption into non-Newtonian liquid^[4] such as benzene solution of polybutene (PB) and PIB, and w/o emulsion^[5] composed of water as a dispersed phase and a benzene solution of PB and PIB as a continuous phase in an agitation vessel.

It is considered worthwhile to investigate the effect of non-Newtonian rheological behavior on the rate of chemical absorption in w/o emulsion, where a reaction between CO₂ and the reactant occurs in the dispersed phase.

In this study, the chemical absorption mechanism of CO₂ into w/o emulsion composed of aqueous alkaline solution, and benzene solution of PB and PIB is presented, and the measured absorption rates of CO₂ are compared with those obtained from the model based on the penetration theory with chemical reaction. Diethanolamine (DEA) was used as a reagent of CO₂. The volumetric mass-transfer coefficient obtained from the previous work^[5] is used to estimate the enhancement factor due to a chemical reaction.

THEORY

In the case of absorption of CO₂ (A) into a w/o emulsion with a benzene solution of PB and PIB–aqueous DEA (B) solution as shown in Fig. 1, the

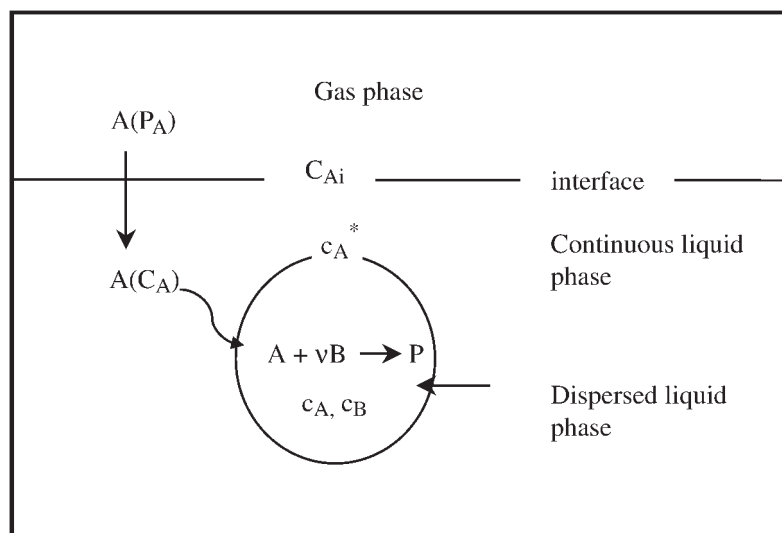


Figure 1. Chemical absorption path of gas (A) into w/o emulsion.

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 DEA; (3) isothermal condition prevails; (4) size and shape of the dispersed aqueous droplets are uniform and spherical, respectively; and (5) although the solubility^[10] of DEA in benzene at 25°C are 4.2%, this solubility in benzene solution is assumed to be zero.

Under these assumptions, the conservation equations of CO_2 transferred into the dispersed aqueous phase are given as:

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

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

Boundary conditions to be imposed are:

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

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

The stoichiometric coefficients, ν , in Eq. (2) for DEA was obtained from the reference and its value was 2.^[11]

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

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

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

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

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

where $\alpha_A = c_A/c_A^*$, $\alpha_B = c_B/c_{B0}$, $y = r/R$, $m_A = R\sqrt{k_2 c_{B0}/D_{eA}}$, $r_B = D_{eB}/D_{eA}$, $q_B = c_{B0}/\nu c_A^*$.

The effectiveness factor here can be defined as:

$$E_f = \frac{4\pi R^2 n_A}{(4/3)\pi R^3 k_2 c_A^* c_{B0}} = \frac{3}{m_A^2} \left. \frac{d\alpha_A}{dy} \right|_{y=1} \quad (9)$$

where n_A is the flux of CO₂ defined as $D_{eA} dc_A/dr|_{r=R}$.

The concentration of A in the droplets, α_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 a pseudo-first-order reaction, and the differential equation of Eq. (5) and the

boundary conditions of Eqs. (7) and (8) are reduced to

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

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

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

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

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

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

In addition, by using Eqs. (9) and (10), E_f is derived as

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

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

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

Equation (12) is put into dimensionless forms as follows:

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

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

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

To derive the enhancement factor, ϕ , due to a reaction between CO_2 and DEA in the dispersed phase, the conservation equation for the dissolved gas in the continuous phase with its volume fraction of ε at unsteady state is written as

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

Boundary and initial conditions are given as

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

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

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

Equations 15–18 are put into the dimensionless form as follows:

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

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

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

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

where $Y_A = C_A/C_{Ai}$, $\theta = k_L^2 t/D_A$, $x = k_L z/D_A$, $H_A = c_A^*/C_A$.

The molar flux of CO₂ with chemical reaction at any contact time t is defined as

$$N_A = -D_A \left. \frac{\partial C_A}{\partial z} \right|_{z=0} \quad (23)$$

The mean molar flux of CO₂ during contact time, t , is written as

$$\bar{N}_A = \frac{1}{t} \int_0^t N_A dt \quad (24)$$

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

$$\bar{N}_A^o = 2C_{Ai} \sqrt{\frac{D_A}{\pi t}} \quad (25)$$

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

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

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

$$\phi = -\frac{\sqrt{M}}{t} \int_0^t \left. \frac{\partial Y_A}{\partial x} \right|_{x=0} dt \quad (27)$$

The value of $\partial Y_A / \partial x$ in Eq. (27) was obtained from the numerical solution of Eq. (19) by the finite difference method with centered difference formula for variable x and forward difference formula for variable θ , and the contact time in Eq. (27) was calculated from $4D_A / (\pi k_L^2)$, with k_L obtained from Eq. (26).

EXPERIMENTAL

Chemicals

All chemicals in this study were of reagent grade and were 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 supplied by Daelim Industry Co. Ltd., Korea, and PIB with the mean molecular weight of 1,000,000 supplied by Aldrich, USA. 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, and 1.0 wt%, and that of DEA in the aqueous solution was in the range of 0–2.0 kmol/m³. Volume fraction of benzene in emulsion was fixed as a value of 0.6.

W/O Emulsion

The w/o type emulsion made from benzene solution of PB and PIB and water was made by the same procedure as those reported elsewhere^[9] by adding Tween 80 (Aldrich Chem. Co., USA) and Arlacel 83 (Aldrich Chem. Co., USA) as surfactant, by using a homogenizer (Fisher Scientific Co., USA) in the range of agitation speed of 1500–10,000 rev/min, and the mean size of aqueous droplets was measured by Image Analyzer (Leitz TAS Plus Co., Germany) and its value was 4×10^{-5} m.

Rheological Properties of Emulsion

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

Rate of Absorption

Absorption experiments were carried out in an agitated vessel. The absorption vessel was constructed by 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 CO₂ gas. A straight impeller with 0.05 m length and 0.02 m in width was used as the liquid-phase agitator and was 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 CO₂ were measured along the procedure similar to those reported elsewhere^[5] at 25°C and an atmospheric pressure. The absorption rate of CO₂ was measured by using the observed values of the cumulative volume of CO₂ for the change of absorption time. The experimental procedure was duplicated, as reported in detail in published papers.^[5]

Solubility of CO₂ in Emulsion

In general, the concentration of CO₂ dissolved in the aqueous solution to get the solubility of CO₂ can be measured by the titration method with a dilute HCl solution,^[14] but the amount of CO₂ dissolved in the benzene solution in this study cannot be measured by this method because CO₂ does not dissociate in the benzene solution. The pressure-measuring method was used in this study to measure the pressure difference of CO₂ before and after equilibrium between a gas and a liquid phase and is similar to the procedure reported elsewhere^[15] to get the solubility of CO₂ in the emulsion at 25°C. A digital pressure gauge made by Meriam instrument (Meriam Merigauge, USA) was used to measure the pressure inside the saturator within ± 0.01 kPa. From the mass of CO₂ dissolved in the emulsion and the known volume of emulsion in the saturator, the solubility of CO₂, C_{Ai} , was calculated. The experimental procedure to get the solubility of CO₂ was duplicated that as reported in published research^[9] in detail.

Density of Emulsion

The densities of the emulsion with benzene solution of PB and PIB were measured at 25°C within 0.1 kg/m³ by weighing with a pycnometer (Fisher Scientific Co., USA) and were found to be identical within experimental accuracy to the density of water.

Interfacial Tension Between Water and Benzene Solution

The surface tension of benzene and the interfacial tension between a water and a benzene solution of various concentration of PIB and PB were measured by the double capillary technique with a glass capillary with an inside radius of 7.65×10^{-4} and 1.55×10^{-3} cm, with a procedure similar to those reported elsewhere.^[16]

RHEOLOGICAL AND PHYSICOCHEMICAL PROPERTIES OF EMULSION AND CO₂

To get the values of E_f in Eq. (9) and ϕ in Eq. (27), it is necessary to know the physicochemical properties such as k_L , k_2 , ρ , μ , D_e , σ , solubilities of CO₂ in dispersed and continuous phase, and diffusivities of CO₂ and DEA. These values are obtained as mentioned below.

Rheological Properties

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

$$\tau = K\gamma^n \quad (28)$$

$$\mu = K\gamma^{n-1} \quad (29)$$

$$N_1 = A\gamma^b \quad (30)$$

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

These parameters were obtained from the dependence of τ and N_1 on γ .

To observe the dependence of τ and N_1 on γ , τ and N_1 of the w/o emulsion were measured according to the change of γ by the rheometer.

Figure 2 shows the typical logarithmic plot of shear stress vs. shear rate for the emulsion with benzene solutions, PB of 30 wt%, and PB of 30 wt% containing PIB of 1 wt%. 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. In addition, Fig. 3 shows the logarithmic plot of primary normal stress difference vs. 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 a 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,

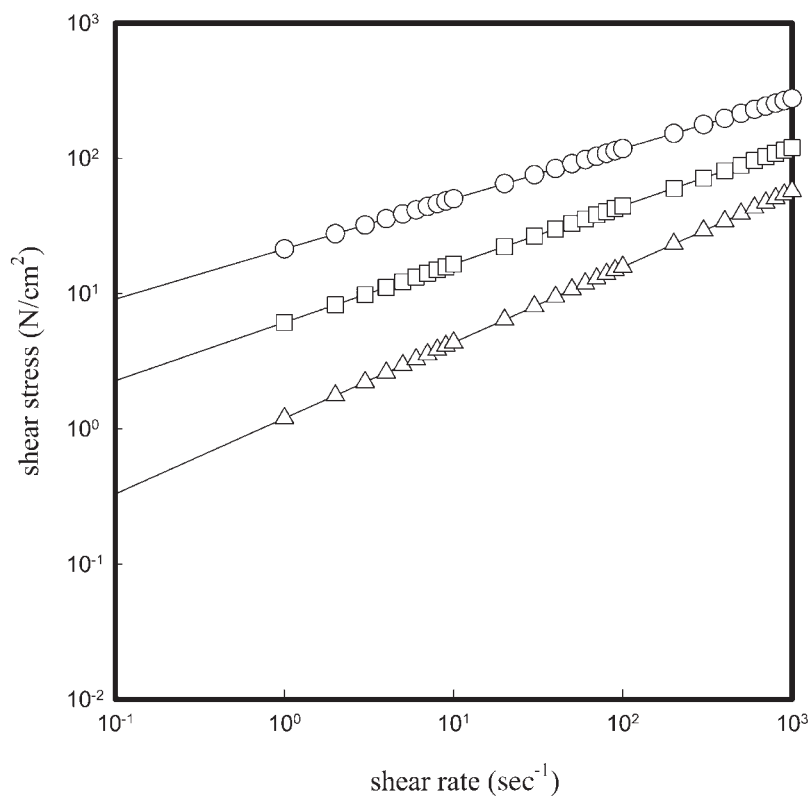


Figure 2. Shear stress of H₂O/(PIB/PB/Bz) emulsion as a function of shear rate.
key: Δ , Bz; \square , PB (30)/Bz; \circ , PIB (1)/PB (30)/Bz.

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 given in Table 2.

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

$$\lambda = \frac{N_1}{\mu \gamma^2} \quad (31)$$

By using Eqs. (29) and (30), λ is rearranged as

$$\lambda = \frac{A}{K} \gamma^{b-n-1} \quad (32)$$

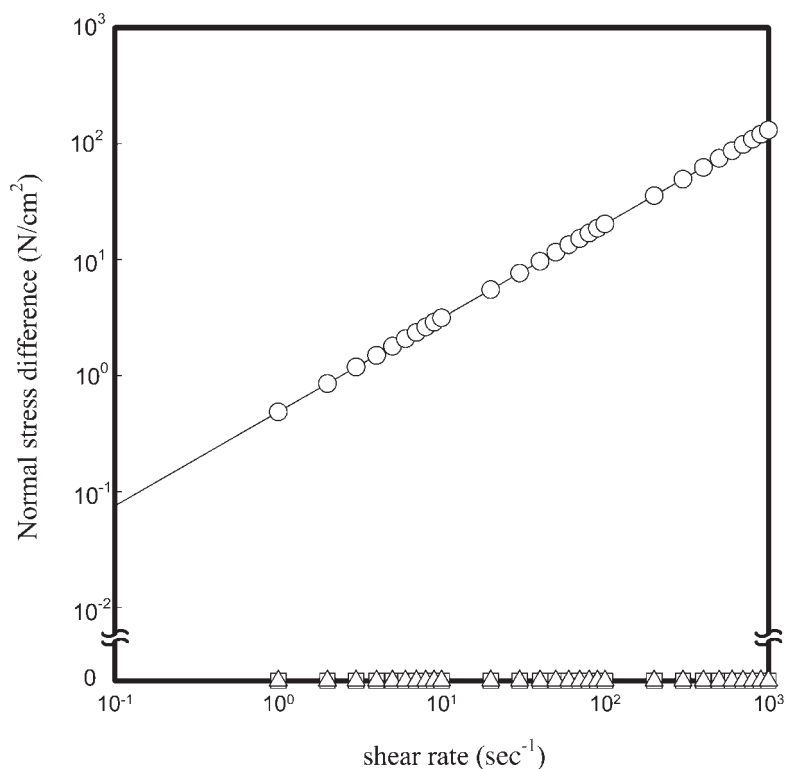


Figure 3. Normal stress difference of H₂O/(PIB/PB/Bz) emulsion as a function of shear rate. key: △, Bz; □, PB (30)/Bz; ○, PIB (1)/PB (30)/Bz.

The dimensionless numbers, which relate the elastic properties with the process parameters are either the Deborah number or the Weissenberg number. In the Deborah number, De , the characteristic liquid time is measured against a characteristic process time, which is considered to be related in the same way to the reciprocal of the impeller speed for stirred tanks, and it is derived with Eq. (32) as follows.

$$De = \lambda N = \frac{A}{K} \gamma^{b-n-1} N \quad (33)$$

The shear rate, γ , in Eq. (33) is obtained from the equation $\gamma = 4\pi N/n$.^[5]

To observe the effect of the concentration of PIB and the speed of impeller on Deborah number De , calculated from Eq. (33), De is plotted against the concentration of PIB with the speed of the impeller as a parameter in Fig. 4,

Table 2. The physicochemical and rheological properties of CO₂ and w/o emulsion with void fraction of continuous phase of 0.6.

PB (wt%)	PIB (wt%)	Interfacial tension (N/m)	Diffusivity (m ² /sec) × 10 ⁹	Solubility (kmol/m ³)	Density (kg/m ³)	Rheological properties			
						<i>n</i>	<i>K</i>	<i>b</i>	<i>A</i>
0	0	34.7	1.98	0.095	949.6	0.560	1.196	0	0
20	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
	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
30	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
	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

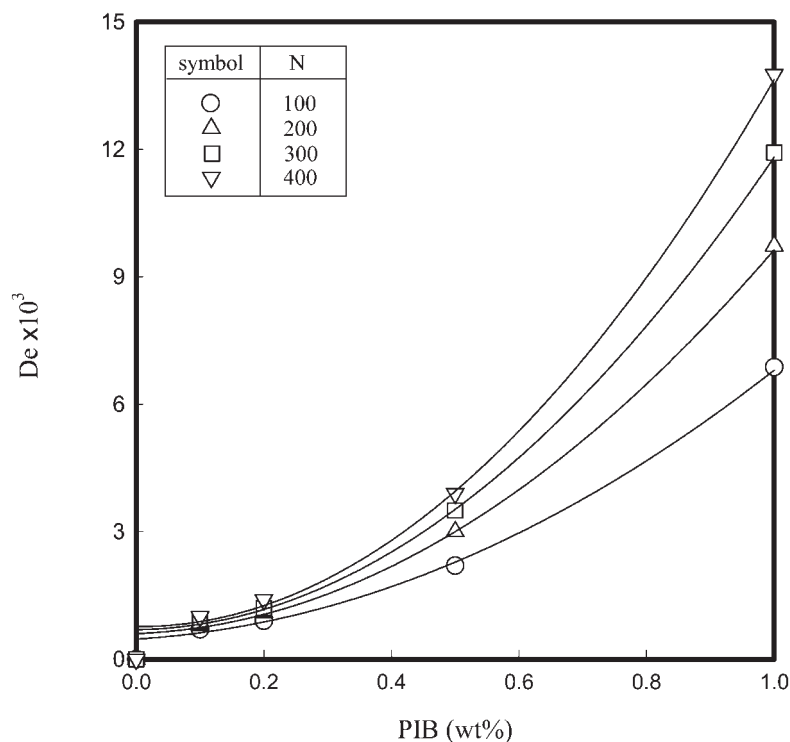


Figure 4. Effect of concentration of PIB on Deborah number at PB of 20 wt%.

with the shear rate for the typical concentration of PB of 20 wt%. As shown in Fig. 4, De increases with an increase in the concentration of PIB and the speed of the impeller. Dependence of De on the concentration of PIB is reasonable because of the elasticity of PIB, and the impeller speed makes the Deborah number increase in the agitated vessel with the viscoelasticity liquid.

Reaction Rate Constant

In the reaction of CO_2 with DEA,^[11] the reaction rate constants were estimated as follows:

$$\log k_2 = 10.4493 - \frac{2274.5}{T}$$

Solubility of CO₂

The solubility of CO₂ in water was taken as 0.0328 kmol/m³ [17] at 25°C and 0.101 Mpa. The solubility of CO₂ in DEA [11] solution was estimated as follows:

$$\log\left(\frac{c_A^*}{c_{Aw}^*}\right) = -(1.0406 \times 10^{-4} + 6.8433 \times 10^{-6} c_{Bo} + 1.33633 \times 10^{-8} c_{Bo}^2 - 1.1549 \times 10^{-12} c_{Bo}^3)$$

The solubilities of CO₂ in benzene solution of PB and PIB and in the w/o emulsion at 25°C and 0.101 Mpa were measured by using the pressure-measuring method, and the measured value in benzene was 0.1107 kmol/m³.

Diffusivities of CO₂ and DEA

The diffusivity of CO₂ in benzene estimated from the Wilke–Chang equation, [18] D_A , was 3.853×10^{-9} m²/sec at 25°C

The diffusivity of CO₂ in DEA [19] solution, D_{eA} , was estimated as follows:

$$D_{eA} = (1.9886 - 0.8103 c_{Bo} - 0.1771 c_{Bo}^2) \times 10^{-9}$$

The diffusivity of DEA in aqueous DEA solution, D_{eB} , was obtained from the assumption that the ratio of D_{eB} to D_{eA} was equal to the ratio in water. [20] The diffusivity of CO₂ and DEA in water at 25°C were taken as 1.97×10^{-9} [17] and 6.67×10^{-10} m²/sec, [19] respectively.

The diffusivity of a solute of a small size such as CO₂, O₂, or CH₄ in a polymer solution depends on the viscosity of the solution and the molecular weight of the polymer. The diffusivity of CO₂, 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 mixed polymer in the solution.

$$\frac{D_c}{D_A} = \left(\frac{\eta_o}{\eta}\right)^{3.7\sqrt{M_o/M_p}} \quad (34)$$

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

$$M_p = x_{PB} \times M_{PB} + x_{PIB} \times M_{PIB} \quad (35)$$

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

In the case where 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,^[22] D_{eff} , was obtained by the empirical equation as follows,

$$\frac{D_{\text{eff}}}{D_c} = 1 + \frac{1.209(\alpha - 1)(1 - \varepsilon)}{(1 - \alpha)(1 - \varepsilon)^{1/3} + 0.806\alpha} \quad (36)$$

where

$$\alpha = \frac{2\zeta}{\zeta - 1} \left(\frac{\zeta}{\zeta - 1} \ln \zeta - 1 \right), \quad \zeta = \frac{H_A D_{eA}}{D_c}$$

The parameter ζ 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.

Liquid-Side Mass-Transfer Coefficient of CO_2

The mass-transfer coefficient, k_L , of CO_2 in CO_2 /emulsion system without DEA 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:

$$\begin{aligned} \frac{k_L a d^2}{D_{\text{eff}}} &= 6.348 \times 10^{-9} \left(\frac{d^2 N \rho}{\mu} \right)^{2.536} \left(\frac{\mu}{\mu_o} \right)^{2.397} \\ &\times (1 + 2461.3 De)^{-0.274} \left(\frac{\sigma}{\sigma_o} \right)^{-0.039} \end{aligned} \quad (37)$$

The values of solubility of CO_2 , density of emulsion, diffusivity of CO_2 , and interfacial tension are given in Table 2.

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 DEA solution was measured according to the change in DEA concentration in the aqueous phase under the typical experimental conditions, such as agitation speed of 200 rev/min, aqueous droplet size of 40 μm in emulsion prepared at agitation speed of 5000 rev/min by

using a homogenizer, volume fraction of continuous phase of 0.6, and the concentrations of PB of 20 and 30 wt%, and those of PIB of 0–1.0 wt%.

To observe the effect of viscoelasticity on the mass-transfer coefficient of CO₂, k_L , in w/o emulsion of H₂O/(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 by using Eqs. (29) and (37), respectively, and Figs. 5 and 6 typically show plots of viscosity of w/o emulsion against the PIB concentration and k_L against μ at PB of 30 wt%, respectively. The value of the specific interfacial area, a , which was necessary to get k_L from Eq. (37), was 9.66 m²/m³.

As shown in Figs. 5 and 6, the viscosity increases 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 proportion to the viscosity of the liquid phase, because the diffusivity of the solute is in inverse proportion to the viscosity.

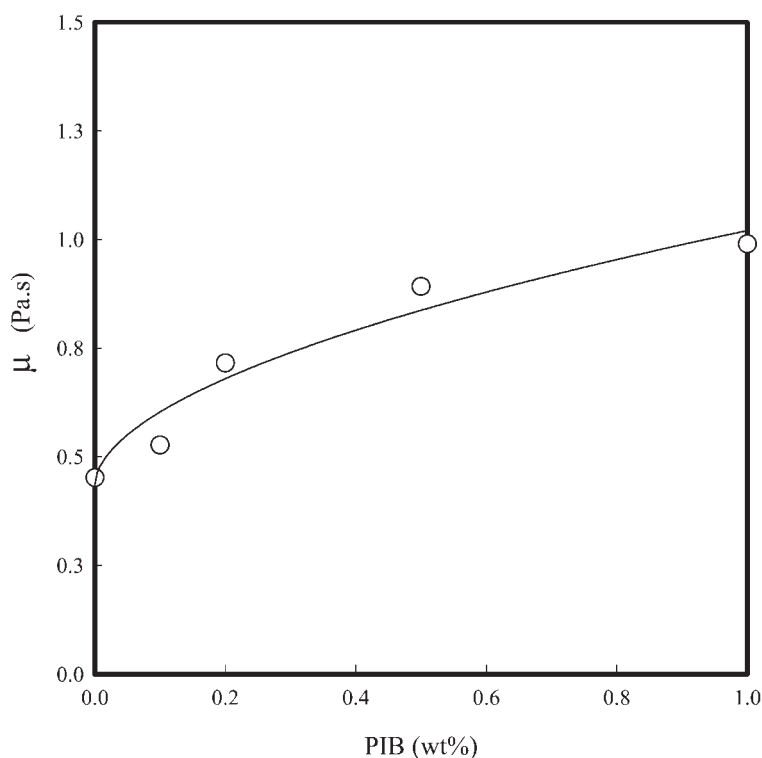


Figure 5. Effect of PIB concentration on viscosity of w/o emulsion with PB of 30 wt%.

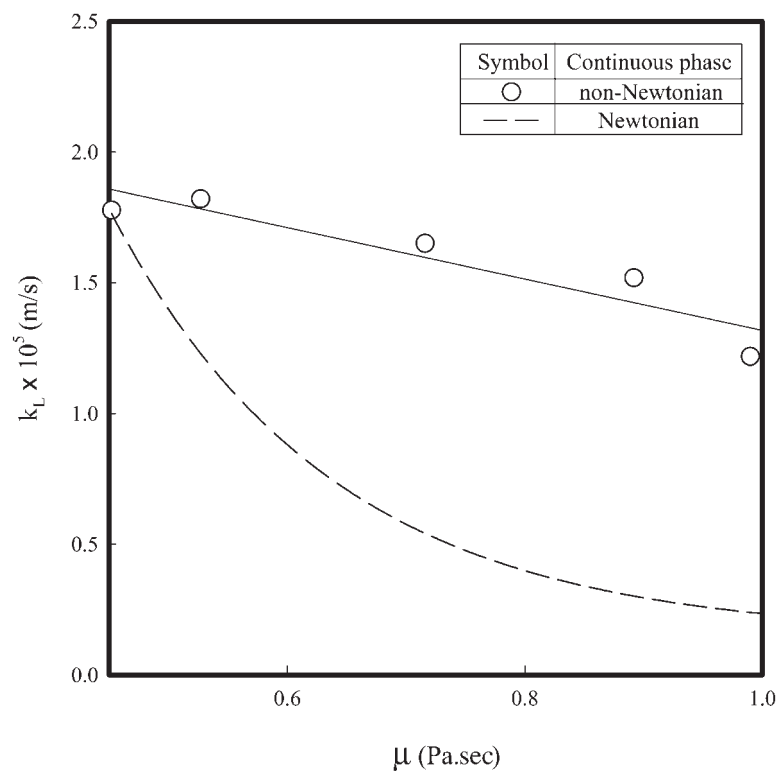


Figure 6. Effect of viscosity on the mass-transfer coefficient for w/o emulsion with PB of 30 wt% and PIB of 0.1–1 wt%.

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. (37),

$$\frac{k_L a d^2}{D_{\text{eff}}} = 6.348 \times 10^{-9} \left(\frac{d^2 N \rho}{\mu} \right)^{2.536} \quad (38)$$

The calculated value of k_L from Eq. (38) according to the change of PIB concentration of 0.1–1 wt% was plotted as a dotted line 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 CO₂ in the w/o emulsion was estimated by using a equation correlating Eqs. (25) and (26) as follows:

$$R_{Ao} = k_L a C_{Ai} \quad (39)$$

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

R_{Ao} were calculated from Eq. (39) by 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. Therefore, the elasticity of PIB may makes the rate of physical absorption increased.

To ascertain the reaction of CO₂ with DEA to be a pseudo-first-order reaction, it is necessary to observe the effect of the chemical reaction on the rate of mass transfer of CO₂ in the heterogeneous reaction system. By

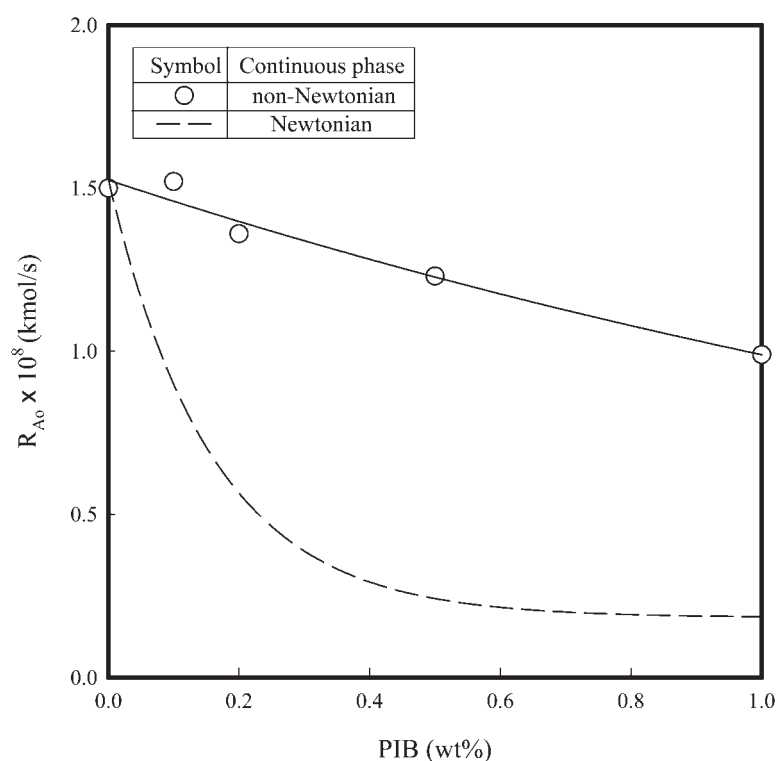


Figure 7. Effect of PIB on physical absorption rate in w/o emulsion with PB of 30 wt%.

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 CO₂ into the dispersed aqueous phase from the continuous phase, and the reaction rate of CO₂ with DEA in the dispersed phase are considered to determine the reaction regime. Because the mass-transfer coefficient of CO₂ in the dispersed phase, k_{LL} , cannot be measured, it is calculated from the mass balance of CO₂ without a chemical reaction in the aqueous drop transferred from the continuous phase.

The conservation equation of CO₂ transferred into the dispersed phase without a chemical reaction from Eq. (1) at steady state is given as:

$$\frac{d}{dr} \left(r^2 D_{eA} \frac{dc_A}{dr} \right) = 0 \quad (1a)$$

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 CO₂ without chemical reaction is defined as:

$$n_A = -D_{eA} \frac{dc_A}{dr} \Big|_{r=R} \quad (40)$$

Integration of Eq. (1a) gives:

$$c_A = -\frac{c_1}{D_{eA}r} + c_2 \quad (41)$$

From the boundary conditions and definition of n_A in Eq. (40), the constant c_1 and c_2 are $-Rc_A^*$ and 0, respectively. Therefore, n_A is arranged as follows:

$$n_A = \frac{D_{eA}c_A^*}{R} \quad (42)$$

From comparison of Eq. (42) with the film theory, k_{LL} is presented as follows:

$$k_{LL} = \frac{D_{eA}}{R} \quad (43)$$

By using the values of D_{eA} and R in this study, k_{LL} is 2.691×10^{-5} m/sec.

The values of $\sqrt{D_{eA}k_2c_{B0}}/k_{LL}$ and $c_{B0}\sqrt{D_{eB}/D_{eA}}/(vC_A^*)$ were calculated by using the physicochemical properties, such as D_{eA} , D_{eB} , k_2 , C_A^* , in the range of the DEA concentration of 0.1–2.0 kmol/m³ and are listed in Table 3. As shown in Table 3, $\sqrt{D_{eA}k_2c_{B0}}/k_{LL}$ is larger than 1 and the value of $\sqrt{D_{eA}k_2c_{B0}}/k_{LL}$ is larger than that of $c_{B0}\sqrt{D_{eB}/D_{eA}}/(vC_A^*)$. Therefore, the system of a chemical reaction of CO₂ with DEA 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 CO₂. Therefore, Eq. (11) can be used to get E_f , which is needed to calculate the enhancement factor.

To observe the effect of elasticity of PIB on the chemical reaction of CO₂ with DEA, the rate of chemical absorption of CO₂ into the w/o emulsion with a dispersed phase of the DEA aqueous solution was measured at PB of 20 and 30 wt% and PIB of 0.1–1 wt%, according to a DEA concentration of 0.1–2.0 kmol/m³. Figure 8 shows a typical plot of the mean molar rate of chemical absorption, R_A , against the concentration of PIB at a DEA concentration of 1 kmol/m³. The solid line curves represent the calculated mean molar flux where using Eq. (24) multiplied by contract interfacial area, a , at the contact time, $4D_A^2/\pi k_L^2$, 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. However, R_A should decrease with increase of the PIB concentration, because of a tendency to decrease R_{A0} , as shown in Fig. 7. The reason why R_A does not decrease with increasing PIB concentration may be explained by using the enhancement factor, ϕ , as below.

The rate of chemical absorption, R_A , is expressed from the definition of ϕ as follows:

$$R_A = \phi R_{A0} \quad (44)$$

The value of ϕ is calculated by using Eq. (27), and Fig. 9 shows a typical plot of ϕ against the concentration of PIB at DEA concentration of 1 kmol/m³ and of PB of 20 and 30 wt%.

Table 3. Classification of reaction regime.

c_{B0} (kmol/m ³)	$\sqrt{D_{eA}k_2c_{B0}}/k_{LL}$	$c_{B0}\sqrt{D_{eB}/D_{eA}}/(vC_A^*)$
0.1	7.45	0.89
0.5	18.03	4.44
1.0	27.95	8.87
1.5	36.81	13.31
2.0	44.35	17.74

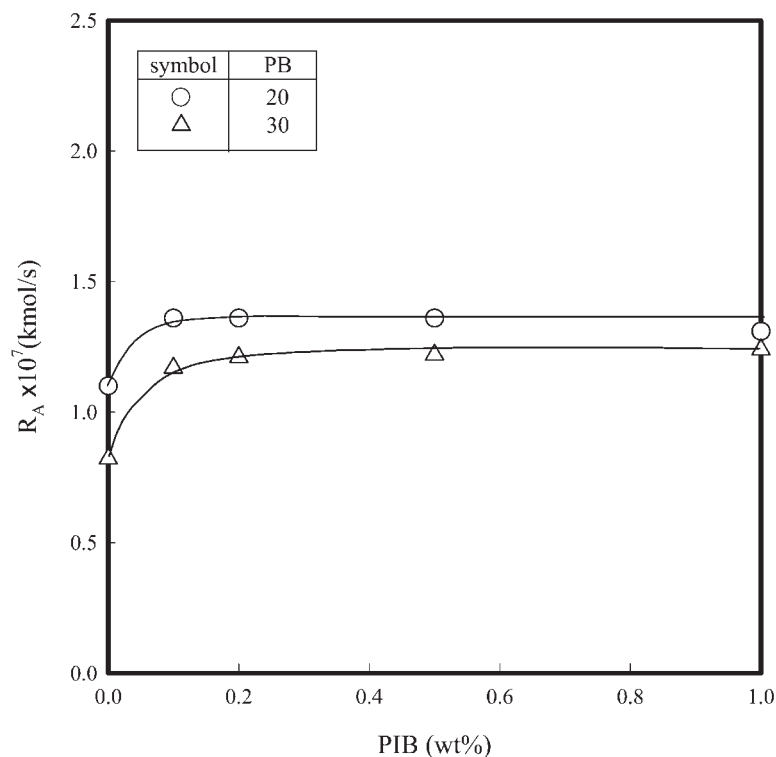


Figure 8. Effect of PIB on the rate of chemical absorption at $c_{B0} = 1 \text{ kmol/m}^3$.

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

A decrease of k_L with an increase of PIB concentration, as shown in Fig. 6, increasing the dimensionless parameter, M , which is a major parameter, increasing the enhancement factor.^[9] Meanwhile, a decrease of k_L makes R_{A0} decrease, as shown in Fig. 7. From these results and Eq. (40), R_A may be almost constant, as shown in Fig. 8.

To observe the effect of the concentration of DEA on the rate of chemical absorption, the rate of chemical absorption was measured according to the change of DEA concentration. Figure 10 typically shows a plot of R_A against DEA concentration at PB of 30 wt% and PIB of 1 wt%.

As shown in Fig. 10, R_A increases with an increasing DEA concentration. The rates of chemical absorption into w/o emulsion with the non-Newtonian and Newtonian liquids as the continuous phase are shown as a solidline and a

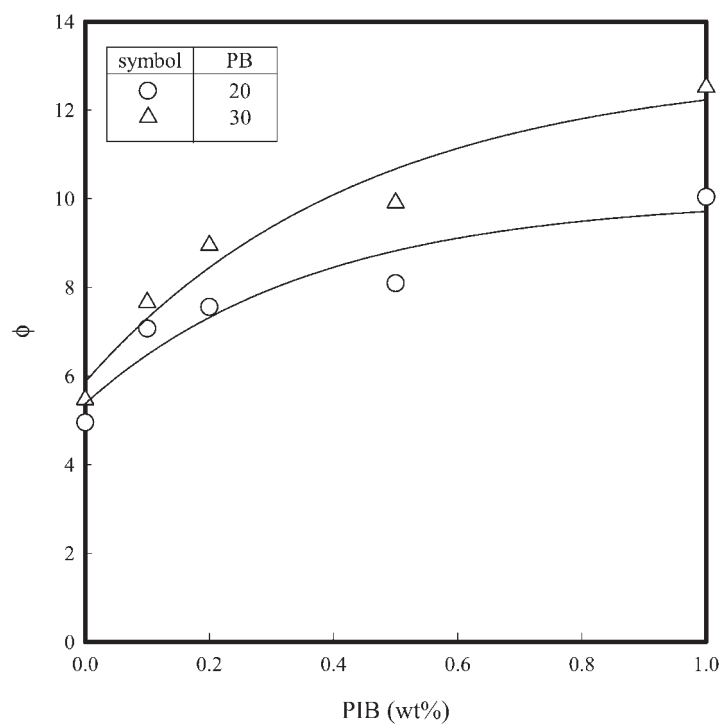


Figure 9. Effect of PIB on the enhancement factor at $c_{B0} = 1 \text{ kmol/m}^3$.

dotted line in Fig. 10, respectively, which are calculated by using Eq. (44). The value of k_L in the former comes from Eq. (37) and that in the latter from Eq. (38). As shown in Fig. 10, the value of the dotted line is smaller than that of the solid line. This means that the elasticity due to PIB also accelerates the rate of chemical absorption.

CONCLUSIONS

Rates of chemical absorption of CO₂ in w/o emulsion were measured in a flat-stirred vessel at 25°C. The w/o emulsion was composed of aqueous DEA 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

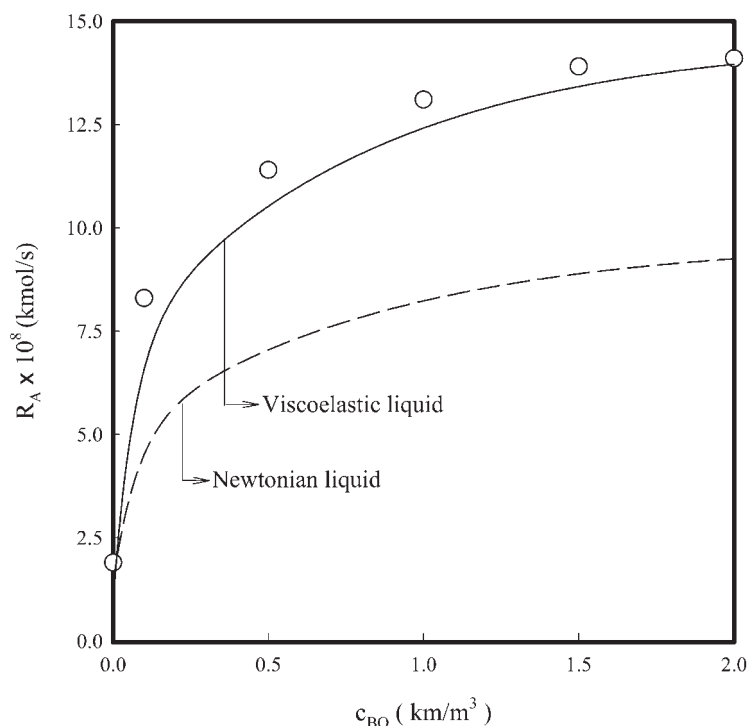


Figure 10. Effect of DEA concentration on the rate of chemical absorption into the w/o emulsion with PB of 30 wt% and PIB of 1 wt%.

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.

NOMENCLATURE

A	rheological properties defined in Eq. (30) (Ns ^b /m ²)
a	contact area at interface of gas–liquid per liquid volume (1/m)
b	rheological properties defined in Eq. (30)

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_A^*	solubility of CO ₂ in dispersed phase (kmol/m ³)
C_{Ai}	solubility of CO ₂ in a continuous phase (kmol/m ³)
c_{Aw}^*	solubility of CO ₂ in water (kmol/m ³)
c_B	concentration of DEA in dispersed phase (kmol/m ³)
c_{Bo}	feed concentration of DEA in dispersed phase (kmol/m ³)
c_{Bi}	concentration of DEA at $r = R$ in dispersed phase (kmol/m ³)
d	diameter of impella (m)
D_A	diffusivity of CO ₂ in the benzene (m ² /sec)
D_c	diffusivity of CO ₂ in continuous phase (m ² /sec)
De	Deborah number defined in Eq. (33)
D_{eA}	diffusivity of CO ₂ in dispersed phase (m/sec)
D_{eAw}	diffusivity of CO ₂ in water (m/sec)
D_{eB}	diffusivity of DEA in dispersed phase (m/sec)
D_{eBw}	diffusivity of DEA in water (m/sec)
D_{eff}	effective diffusivity of CO ₂ in emulsion (m ² /sec)
H_A	dimensionless solubility defined as c_A^*/C_{Ai}
K	rheological properties defined in Eq. (28) (Ns ⁿ /m ²)
k_L	mass-transfer coefficient of CO ₂ in continuous phase (m/sec)
k_{LL}	mass-transfer coefficient of CO ₂ in dispersed phase (m/sec)
$k_L a$	volumetric mass-transfer coefficient (L/sec)
k_2	second-order-reaction constant (m ³ /kmol sec)
M	dimensionless modulus defined as $(1 - \varepsilon)k_2 c_{Bo} H_A D_A/k_L^2$
M_o	molecular weight of benzene (kg/kmol)
M_p	molecular weight of polymer (kg/kmol)
M_{PB}	molecular weight of PB (kg/kmol)
M_{PIB}	molecular weight of PIB (kg/kmol)
m_A	dimensionless modulus defined as $R\sqrt{k_2 c_{Bo}/D_{eA}}$
n	rheological properties defined in Eq. (28)
N	impeller speed (L/sec)
N_1	primary normal stress difference defined in Eq. (30) (N/m ²)
N_A	molar flux of CO ₂ at gas–liquid interface with chemical reaction in benzene at any contact time (kmol/m ² sec)
\bar{N}_A	mean molar flux of CO ₂ at gas–liquid interface with chemical reaction in benzene during any contact time (kmol/m ² sec)
\bar{N}_A^o	mean molar flux of CO ₂ at gas–liquid interface without chemical reaction in benzene during contact time (kmol/m ² sec)
n_A	mass-transfer rate of CO ₂ from benzene phase into aqueous phase (kmol/m ² sec)

r	radial distance in aqueous phase (m)
R	radius of aqueous droplet in benzene phase
R_A	instantaneous molar absorption rate of CO_2 (kmol/sec)
r_B	diffusivity ratio defined as D_{eB}/D_{eA}
q_B	dimensionless concentration defined as c_{B0}/c_A^*
q_B^0	dimensionless concentration defined as $c_{B0}/\nu H_A C_{Ai}$
t	time (sec)
T	temperature (K)
x	dimensionless coordinate in film thickness direction in benzene phase defined as $k_L z/D_A$
x_{PB}	mole fraction of PB
x_{PIB}	mole fraction of PIB
Y_A	dimensionless concentration in benzene phase
y	dimensionless radial coordinate defined as r/R
z	coordinate in film thickness direction in benzene phase (m)

Greek Letters

α	dimensionless parameter defined in Eq. (36)
α_A	dimensionless concentration of CO_2 in aqueous phase defined as c_A/c_{Ao}
α_{Bi}	dimensionless concentration of B_{oi} in dispersed phase defined as c_B/c_{Bi}
α_B	dimensionless concentration of B in aqueous phase defined as c_B/c_{Bo}
γ	shear rate (1/sec)
σ	interfacial surface tension between water and benzene solution of PIB and PB (N/m)
σ_o	interfacial surface tension between water and benzene solution of PB (N/m)
ε	volume fraction of benzene phase in the emulsion
ζ	dimensionless parameter defined in Eq. (36)
θ	dimensionless time defined as $k_L^2 t/D_A$
λ	characteristic liquid time (sec)
μ	viscosity of liquid, (Ns/m ²)
μ_o	viscosity of benzene (Ns/m ²)
ν	stoichiometric coefficient in chemical reaction of CO_2 with amine
ρ	density of non-Newtonian liquid (kg/m ³)
τ	shear stress (N/m ²)
ϕ	enhancement factor

Subscripts

A	CO ₂
B	reactant [amine]
e	aqueous
i	gas–liquid interface
o	bulk body
w	pure water phase

Superscript

*	liquid–liquid interface
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