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Abstract: Carbon dioxide was absorbed into aqueous polyethylene oxide (PEO) solution containing diethanolamine (DEA) in a flat-stirred vessel to investigate the effect of non-Newtonian rheological behavior of PEO on the chemical absorption rate of CO_2, where the reaction between CO_2 and DEA was assumed to be a first-order reaction with respect to the concentration of CO_2 and DEA, respectively. A unified correlation equation containing Deborah number, which reflects the viscoelastic properties of the non-Newtonian liquid, was used to obtain the volumetric liquid-side mass transfer coefficient of carbon dioxide in aqueous PEO solution. The elastic properties of PEO accelerated the absorption rate of CO_2 compared with that of a Newtonian liquid based on the same values of viscosity.

Keywords: Absorption, carbon dioxide, polyethylene oxide, diethanolamine, viscoelastic liquid

INTRODUCTION

The dependence of shear stress on shear rate of a fluid in hydrodynamic system is different according to the type of the fluid, i.e., Newtonian or non-Newtonian fluid, and the mass transfer coefficient of a solute in one

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phase is in inverse proportion to the viscosity of its phase due to the inverse proportion of viscosity to diffusivity. The apparent viscosity of Ònon-Newtonian fluids is not sufficient to obtain a unified correlation for the liquid-side mass transfer coefficient (k_L) of gas in the case of gas absorption into non-Newtonian fluids. Because of the complexities of gas absorption in non-Newtonian media, the correlations obtained by these studies have been 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 a considerable reduction of k_La is due to the viscoelasticity of the aqueous solution, then the extent to which data for a 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. A dimensionless number, such as Deborah number (De), which relates the elastic properties to the process parameters, is used to correlate the volumetric liquid-side mass transfer coefficient (k_La) with properties of non-Newtonian liquids. Unified correlations have been proposed for k_La in Newtonian as well as non-Newtonian solutions by introducing the dimensionless term, such as $(1 + n_1DE^{n_2})^{n_3}$; they are listed in Table 1. As shown in Table 1, values in the dimensionless group are different each other, and the polymers in Table 1 act as a reduction or increment agent in the absorption rate of gas (1–8).

There is little information about the effect that elastic properties have on the absorption of gas accompanied by a chemical reaction in non-Newtonian liquid. Park et al. presented the effect of elasticity of polyisobutylene (PIB) (4) in the benzene solution of polybutene (PB) and PIB on the absorption rate of CO_2, and that (5) in w/o emulsion composed of aqueous solution as dispersed phase and benzene solution of PB and PIB as continuous phase in an agitation vessel. They showed that PIB accelerated the absorption rate of CO_2. Also, the effect of PAA (6) and PEO (7) in an aqueous solution on the absorption rate of

Table 1. Coefficients of dimensionless group in the 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
Park et al. (6)	54.7	1	−0.45	PAA	Agitated vessel
Park et al. (7)	8.33	1.31	1	PEO	Agitated vessel

CO_2 was investigated. The polymers used in their papers act as accelerators of the absorption rate of CO_2 in the non-Newtonian viscoelastic liquid based on the same viscosity of the solution.

To investigate the effect that the behavior of non-Newtonian liquid has on the gas absorption continuously, an aqueous PEO solution was used as a viscoelastic material in this study. The absorption rates of CO_2 were measured in aqueous PEO solutions containing diethanolamine (DEA) and they were compared with those estimated by the mass transfer with chemical reaction, based on the film theory. Deborah number, which was obtained from a power-law model of the relationship between the measured shear stress and primary normal stress difference against the shear rate of the aqueous PEO solution, was used to obtain a unified correlation between the values of k_La in water and that in aqueous PEO solutions.

THEORY

The problem to be considered is that a gaseous species A (CO_2) dissolves into the liquid phase, and then, reacts irreversibly with species B (DEA) according to

$$CO_2 + \nu R_2NH \rightarrow R_2NCO_2^- + R_2NH_2^+ \tag{1}$$

where R represents the functional groups on the secondary amine and ν in Eq. (5) for DEA was 2 (8).

Species B is a nonvolatile solute, which has been dissolved into the liquid phase prior to its introduction into the gas absorber. It is assumed that gas phase resistance to absorption is negligible by using pure species A, and thus the concentration of species A at the gas-liquid corresponds to equilibrium with the partial pressure of species A in the bulk gas phase.

The chemical reaction of Eq. (1) is assumed to be second-order (8) as follows:

$$r_A = k_2 C_A C_B \tag{2}$$

Under the assumptions mentioned above, the conservation equations of species A and B, based on the film theory with chemical reaction and boundary conditions are put into the dimensionless form as follows:

$$\frac{d^2a}{dx^2} = M\,ab \tag{3}$$

$$\frac{d^2b}{dx^2} = \nu rqMab \tag{4}$$

$$x = 0; \quad a = 1, \quad \frac{db}{dx} = 0 \tag{5}$$

$$x = 1; \quad a = 0, \quad b = 1 \tag{6}$$

where $M = D_A k_2 C_{B_o}/k_L^2$, $a = C_A/C_{Ai}$, $b = C_B/C_{Bo}$, $x = z/z_L$, $q = \nu C_{Ai}/C_{Bo}$, $r = D_A/D_B$ and subscript, i and o mean gas-liquid interface and feed, respectively.

The enhancement factor (β) here is defined as the ratio of molar flux with a chemical reaction to that without chemical reaction:

$$\beta = -\left.\frac{da}{dx}\right|_{x=0} \tag{7}$$

The value of β is used to estimate the absorption rate (R_A) of CO_2 with chemical reaction as follows:

$$R_A = \beta R_{Ao} = \beta k_L a\, C_{Ai} V_L \tag{8}$$

where R_{Ao} is the absorption rate of CO_2 in water and V_L, volume of the liquid phase.

To ensure the fast reaction in the diffusion film with the depletion of the liquid phase reactant as shown in Eq. (2), the following equation is used (9):

$$1 < \beta < \beta_i \tag{9}$$

β_i is an enhancement factor for an instantaneous reaction and defined as follows:

$$\beta_i = 1 + 1/(rq) \tag{10}$$

EXPERIMENTAL

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 polymer used in this study was polyethylene oxide (PEO) with the mean molecular weight of 200,000 (by Aldrich Chemical Company, U.S.A.) and DEA (Aldrich, U.S.A.) was used as reagent grade without purification.

The gas-liquid contactor used to absorb CO_2 was a stirred tank made of glass (0.075 m inside diameter, 0.13 m in height), which attached equally four spaced vertical baffles; it was operated continuously with respect to the gas and batch-wise with respect to the liquid phase. A straight impeller with 0.034, 0.04, and 0.05 m in length and 0.017 m in width was used as the liquid phase agitator, and located at the middle position of the liquid phase. The absorption rate of CO_2 was obtained from the difference between the inlet and outlet flow rates of CO_2 in the concentrations of PEO of 10–30 g/L and DEA of 0–3 $kmol/m^3$ under the typical conditions of the agitation speed of 50 rev/min with the impeller size of 0.034 m at 101.3 N/m^2 and 25 following the procedure reported elsewhere (7).

PHYSICOCHEMICAL AND RHEOLOGICAL PROPERTIES

The solubility (C_{APi}) of CO_2 in the aqueous PEO solutions was obtained by the pressure measuring method, which measured the pressure difference of CO_2 between before and after equilibrium in gas and liquid phase similar to the procedure reported elsewhere (10). The experimental procedure was identical to that described earlier (7). The solubility (C_{Ai}) of CO_2 in aqueous DEA solution was estimated as follows (8):

$$\mathrm{Log}\,(C_{Ai}/C_{APi}) = -(1.0406\times 10^{-4} + 6.8433\times 10^{-6}C_{Bo} + 1.33633\times 10^{-8}C_{Bo}^2 - 1.1549\times 10^{-12}C_{Bo}^3) \qquad (11)$$

The density (ρ) of the aqueous solution of PEO was measured within 0.1 kg/m^3 by weighing with a pycnometer (Fisher Scientific Co., USA) and was found to be identical within experimental accuracy to the density of water.

The apparent viscosity (μ_L) of aqueous solution of PEO and that of water (μ_w) was measured with Brookfield viscometer (Brookfield Eng. Lab. Inc, USA).

The reaction rate constant (k_2) of the reaction of CO_2 with DEA was estimated as follows (11).

$$\log k_2 = 10.4493 - \frac{2274.5}{T} \qquad (12)$$

The diffusivity (D_{AB}) of CO_2 in aqueous DEA solution was estimated as follows (11):

$$D_{AB} = (1.9886 - 0.8103\,C_{Bo} - 0.1771\,C_{Bo}^2)\times 10^{-9} \qquad (13)$$

Diffusivity (D_B) of DEA in aqueous DEA solution was obtained from assumption that the ratio of D_B to D_{AB} was equal to the ratio in water (12). The diffusivity of CO_2 and DEA in water at 25 were taken as $1.97\times 10^{-9}\ m^2/s$ (13) and $6.67\times 10^{-10}\ m^2/s$ (11), respectively.

The power of viscosity in the Wilke − Chang equation, which is used to estimate the diffusivity in the dilute solution, changes −1 to −2/3 in the concentrated solution such as a polymer solution (14). Therefore, the diffusivity (D_A) of CO_2 in the aqueous PEO solution was corrected by the viscosity of the aqueous PEO solution as follows:

$$D_A = D_{AB}(\mu_w/\mu)^{2/3} \qquad (14)$$

Material parameters of K, n, A and b in a power-law model such as $\tau = K\gamma^n$ and $N_t = A\gamma^b$ were obtained from the measurement of shear stress (τ) and primary normal stress difference (N_1) for the change of the shear rate (γ) 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.

The physical properties, such as solubility, diffusivity of CO_2, density, and apparent viscosity, and the rheological properties, such as K, n, A and b of aqueous PEO solution are given in Table 2.

The k_La was obtained by the following equation, which presents the relationship between k_La and rheological behavior of the aqueous PEO solution (7) under the conditions of the agitation speed of 50–400 rev/min with the impeller size of 0.034, 0.04, and 0.05 m.

$$k_L a d^2/D_A = 12.56\ (d^2 N\rho/\mu)^{0.48}\ (1 + 8.33\mathrm{De}^{1.31}) \tag{15}$$

where De is defined as the ratio of the characteristic material time (λ) to the characteristic process time (t) as follows:

$$\mathrm{De} = \lambda/t = \frac{A}{K}\gamma^{b-n-1}N \tag{16}$$

where N is the speed of impeller and the shear rate is obtained in case of agitation of liquid in a cylindrical vessel as follows (15):

$$\gamma = 4\pi N/n \tag{17}$$

RESULTS AND DISCUSSION

To observe the effect that the elasticity of PEO and reactivity of DEA have on R_A in the non-Newtonian liquid containing a reactant (DEA), the absorption rate of CO_2 was measured in the range of PEO concentration of 10–30 g/L for various DEA concentration of 0–3 kmol/m^3 under the typical conditions of the agitation speed of 50 rev/min with the impeller size of 0.034 m. The measured values of the absorption rate (R_A, exp), the enhancement factors (β_{exp}), and β_i, which was calculated from Eq. (10), are given in Table 3. As shown in Table 3, Eq. (9) was satisfied, and then, the reaction of CO_2 with DEA under the experimental condition as mentioned above is a fast reaction regime.

Figure 1 shows the measured value of R_A against DEA concentration as circles in the aqueous PEO solution at a fixed concentration of PEO (30 g/L) and as triangles in water, respectively. As shown in Fig. 1, the R_A increases upon increasing DEA concentration due to increase of β as mentioned below and it approaches to the calculated one very well.

The lines in Fig. 1 are the values of R_A calculated using Eq. (8) using k_La, β, C_{Ai} and V_L, where V_L was as 3×10^{-4} m^3, a, 14.29 m^2/m^3, C_{Ai} from Eq. (11) at a given DEA concentration, and β estimated by Eq. (7) and a solution of Eq. (3) and (4) using a numerical analysis of the finite element method using the physicochemical properties listed in Table 2. The k_La in the dashed line was obtained from Eq. (15) with $\mu = \mu_w$ and De = 0, and the k_La in the solid line with $\mu = \mu_L$ and De > 0, and the k_La in the dotted line with

Table 2. The physicochemical and rheological properties of CO_2 and aqueous PEO solution

C (kg/m^3)	Viscosity ($N \cdot sm^2$)10^3	Diffusivity (m^2/s) $\times 10^9$	Solubility ($kmol/m^3$)	Density (kg/m^3)	Rheological propertie			
					n (−)	K ($Ns^n \cdot m^2$)	b (−)	A ($Ns^n \cdot m^2$)
0	1	1.950	0.039	1000	1	0.001	—	—
10	3.05	1.875	0.034	1001.4	0.529	0.019	0.103	0.134
20	8.17	1.811	0.029	1003.2	0.485	0.416	0.099	1.255
30	14.9	1.774	0.028	1004.8	0.453	0.895	0.084	2.766

Table 3. Experimental data for the reaction of CO2 with DEA

PEO (kg/m^3)	C_{Bo}	$R_{A,exp} \times 10^8$	β_{exp}	β_i
10	0.5	0.83	1.268	2.52
	1.0	1.06	1.633	5.03
	1.5	1.68	2.572	7.55
	2.0	2.36	3.630	10.06
	2.5	3.15	4.830	12.58
	3.0	3.72	5.706	15.09
20	0.5	0.71	1.305	2.95
	1.0	1.02	1.869	5.90
	1.5	1.58	2.893	8.85
	2.0	2.04	3.751	11.80
	2.5	2.87	5.278	14.75
	3.0	3.72	6.824	17.70
30	0.5	0.56	1.295	3.10
	1.0	0.83	1.909	6.20
	1.5	1.25	2.880	9.30
	2.0	1.72	3.977	12.40
	2.5	2.49	5.756	15.50
	3.0	2.98	6.883	18.60

$\mu = \mu_L$ and De $= 0$. We assumed that the aqueous PEO solution with $\mu = \mu_L$ and De$=0$ would be an imaginary solution to act as a Newtonian liquid. If the aqueous PEO solution in this study would have only viscous behavior with De of 0, the R_A should be value of the dotted line. But, the R_A is larger than that of the imaginary solution. This means that the effect of the elasticity of the aqueous PEO solution on R_A is stronger than the effect of viscosity, in other words, the elasticity of the aqueous PEO solution accelerates R_A based on the same viscosity of the solution.

Figure 2 shows the measured and calculated values of β against PEO concentration of 0–30 g/L using a parameter of DEA concentration as various symbols and solid line, respectively. As shown in Fig. 2, the values of β increase with increasing concentrations of PEO and DEA, and the measured values approach to the calculated values very well. This means that β is dependent on the reactant reactivity and the rheological behavior of the non-Newtonian liquid.

Figure 3 shows the measured and calculated values of k_La against PEO concentration of 0–30 g/L as open circle and solid line, respectively. The calculated k_La was obtained from Eq. (15) with $\mu = \mu_L$ and De > 0. As shown in Fig. 3, k_La decreases with increasing the PEO concentration and the measured values approach to the calculated values very well.

Figure 4 shows the plots of the absorption rate of CO_2 against the PEO concentration for various DEA concentrations. As shown in Fig. 4, R_A decreases with increasing PEO concentration at a fixed concentration of

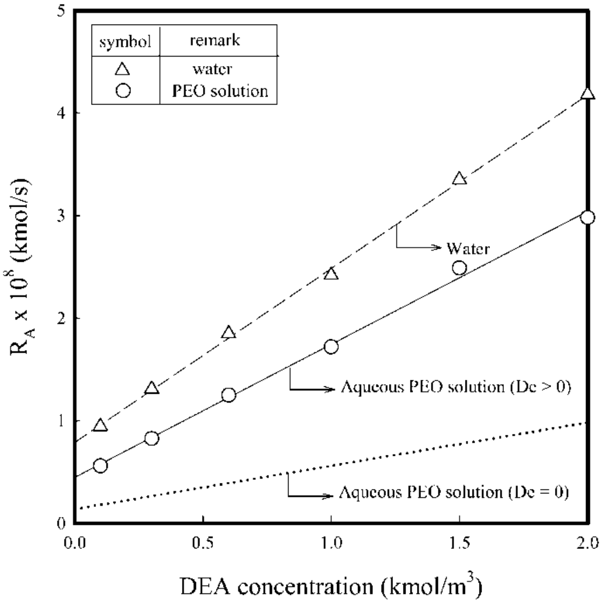

Figure 1. Comparison of elasticity with viscosity of PEO in DEA solution. (PEO = 30 kg/m^3, d = 30 mm, N = 50 rpm).

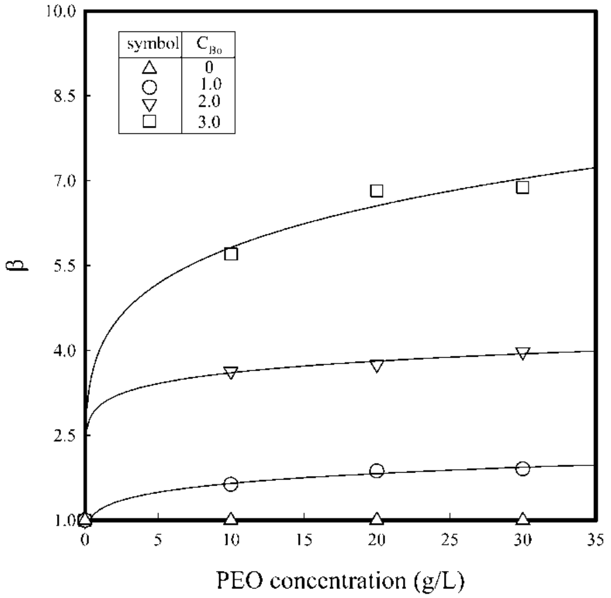

Figure 2. Effect of PEO concentration on enhancement factor for various DEA concentrations.

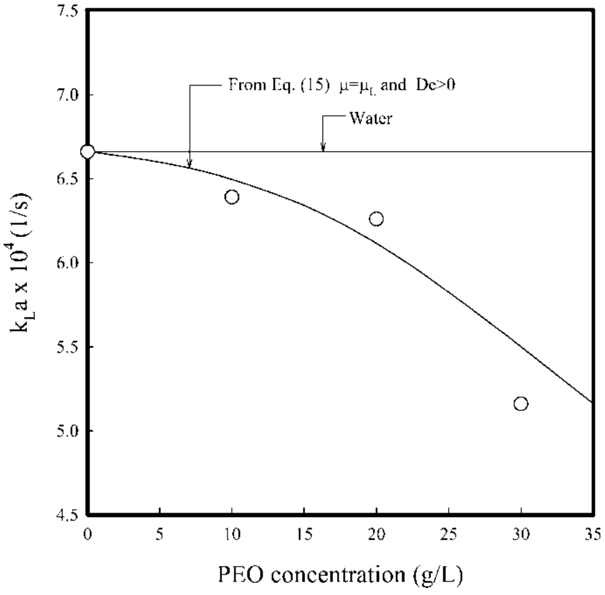

Figure 3. Effect of PEO concentration on k_La at d = 0.034 m and N = 50 rpm.

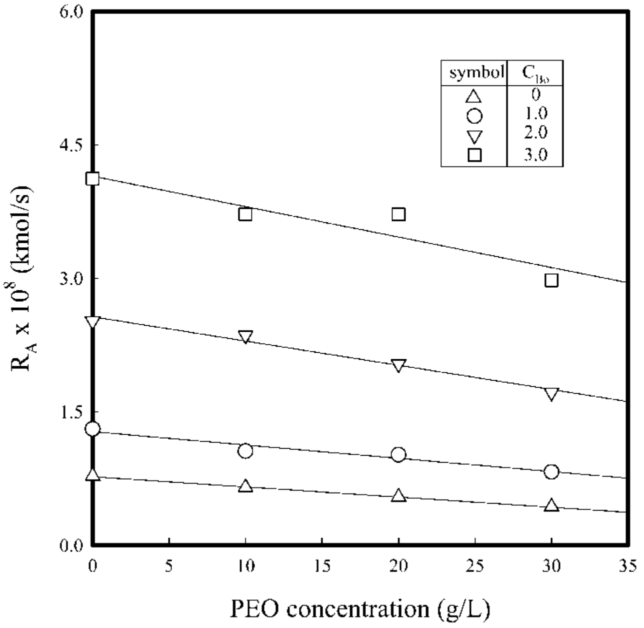

Figure 4. Effect of PEO concentration on absorption rate for various DEA concentrations.

DEA. The solid lines present the values of R_A obtained using Eq. (8). It might be said that the dependence of R_A on PEO concentration was caused mainly by k_La rather than β and C_{Ai} as known in the results of Figs. 2, 3 and a little decrease of C_{Ai} with increasing PEO concentration as shown in Table 2.

CONCLUSIONS

The measured rate of the chemical absorption of carbon dioxide into the aqueous PEO solution of 0–30 g/L with DEA of 0–3 $kmol/m^3$ in a flat-stirred vessel with the impeller size of 0.034 m and its agitation speed of 50 rev/min at 25 and 0.101 MPa was compared with that estimated from the model based on the film theory accompanied by chemical reaction using k_La, which was obtained from a unified correlation equation containing Deborah number. The reaction between DEA and CO_2 was considered under the condition of a fast reaction regime. The R_A is dependent of the reactivity of DEA and the elasticity of the aqueous PEO solution. The elasticity accelerated the absorption rate of CO_2 compared with that of a Newtonian liquid based on the same values of viscosity.

Greek Letters

β	enhancement factor
β_{exp}	measured enhancement factor
β_i	instantaneous enhancement factor
γ	shear rate (1/s)
λ	the materials' characteristic relaxation time (sec)
μ	viscosity of liquid ($N \cdot s/m^2$)
μ_w	viscosity of water ($N \cdot s/m^2$)
ν	stoichiometric coefficient
ρ	density of liquid (kg/m^3)
τ	shear stress (N/m^2)

Subscripts

A	CO_2
B	DEA
i	gas-liquid interface

NOMENCLATURE

a	specific gas-liquid area (m^2/m^3)
C_i	concentration of species, i ($kmol/m^3$)

d	diameter of impeller (m)
De	Deborah number defined as λ/t
D_i	diffusivity of species, i (m^2/s)
k_2	reaction rate constant in reaction (1) ($m^3/kmol \cdot s$)
k_L	liquid-side mass transfer coefficient of CO_2 in absorbent (m/s)
N_1	primary normal stress difference ($kg/m \cdot s^2$)
V_L	volume of the liquid phase(m^3)
k_L	liquid-side mass transfer coefficient of CO_2 in absorbent (m/s)
r_A	reaction rate in Eq. (2) ($kmol/m^3 \cdot s$)
R_A	chemical absorption rate of CO_2 (kmol/s)
$R_{A,\ exp}$	measured absorption rate of CO_2 (kmol/s)
R_{Ao}	physical absorption rate of CO_2 (kmol/s)
t	the characteristic process time (sec)
T	temperature(K)
z	diffusion coordinate of CO_2 (m)
z_L	film thickness (m)

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