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Influence of polyethylene oxide on absorption of carbon dioxide into aqueous *N*-methyldiethanolamine solution

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Abstract−Carbon dioxide was absorbed into aqueous polyethylene oxide (PEO) solution containing *N*-methyldiethanolamine (MDEA) 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 MDEA was assumed to be a first-order reaction with respect to the concentration of CO_2 and MDEA, respectively. A unified correlation equation containing the Deborah number, which reflects the viscoelastic properties of a 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.

Key words: Absorption, Carbon Dioxide, Polyethylene Oxide, *N*-Methyldiethanolamine, 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 phase is in inverse proportion to the viscosity of its phase due to the inverse proportion of viscosity to diffusivity. The apparent viscosity of non-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 a 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 from one another, and the polymers in Table 1 act as a reduction or increment agent in the absorption rate of gas.

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

To investigate the effect that the behavior of a non-Newtonian liquid has on the gas absorption in series, 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 *N*-methyldiethanolamine (MDEA) and they were compared with those estimated by the mass transfer with chemical reaction, based on film theory. The 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 (MDEA) according to

$$A+\nu B\rightarrow P \qquad (1)$$

where the stoichiometric coefficients (ν) in Eq. (1) for MDEA was 1 [8].

Species B can be assumed as a nonvolatile solute that 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.

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Table 1. Coefficients of dimensionless Deborah number, $(1+n_1De^{n_2})^{n_3}$ for gas-liquid mass transfer correlation

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

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:

$$\frac{d^2a}{dx^2}=\mathrm{Mab} \tag{3}$$

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

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

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

where $M=D_Ak_2C_{Bo}/k_L^2$, $a=C_A/C_{Ai}$, $b=C_B/C_{Bo}$, $x=z/z_L$, $q=\nu C_{Ai}/C_{Bo}$, $r=D_A/D_B$ 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:

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

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

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 a mean molecular weight of 200,000 (by Aldrich chemical company, U.S.A.) and MDEA (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) with four equally spaced vertical baffles attached; 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 MDEA of 0-2 kmol/m^3 under the typical conditions of an agitation speed of 50 rev/min with an impeller size of 0.034 m. at 101.3 N/m^2 and 25 °C 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 [9]. 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]:

$$C_{Ai}=1/[2824900\mathrm{Exp}(-2119/T)/101.3] \tag{9}$$

The density (ρ) of the aqueous solution of PEO was measured to 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 a Brookfield viscometer (Brookfield Eng. Lab. Inc, USA).

The reaction rate constant (k_2) in the reaction of CO_2 with MDEA was estimated as follows [8]:

$$k_2=4.01\times10^8\mathrm{Exp}(-5400/T) \tag{10}$$

The diffusivity (D_{AB}) of CO_2 in aqueous MDEA solution was estimated as follows [8]:

$$D_{AB}=2.35\times10^{-6}\ \mathrm{Exp}(-2119/T) \tag{11}$$

Diffusivity (D_B) of MDEA in aqueous DEA solution was obtained from assumption that the ratio of D_B to D_{AB} is equal to the ratio in water [10]. The diffusivity of CO_2 and MDEA in water at 25 °C was taken as 1.97×10^{-9} m^2/s [11] and 8.1×10^{-10} m^2/s [8], respectively. Diffusivity (D_A) of CO_2 in the aqueous PEO solution was corrected with viscosity of the aqueous PEO solution as follows [12]:

$$D_A=D_{AB}\,(\mu_w/\mu_L)^{2/3} \tag{12}$$

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

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

C (kg/m^3)	Viscosity (Ns/m^2)×10^3	Diffusivity (m^2/s)×10^9	Solubility (kmol/m^3)	Density (kg/m^3)	Rheological property			
					n (−)	K (Ns^n·m^2)	b (−)	A (Ns^n·m^2)
0	1	1.950	0.039	1,000	1.0	0.001	-	-
10	3.05	1.875	0.034	1,001.4	0.529	0.019	0.103	0.134
20	8.17	1.811	0.029	1,003.2	0.485	0.416	0.099	1.255
30	14.9	1.774	0.028	1,004.8	0.453	0.895	0.084	2.766

of 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 $k_L a$ was obtained, which presents the relationship between $k_L a$ 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, as follows:

$$k_L a d^2/D_A = 12.56(d^2 N\rho/\mu)^{0.48}(1+8.33De^{1.31}) \tag{13}$$

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

$$De = \lambda/t = \frac{A}{K}\gamma^{b-n-1}N \tag{14}$$

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 [13]:

$$\gamma = 4\pi N/n \tag{15}$$

RESULTS AND DISCUSSION

To observe the effect that the elasticity of PEO and reactivity of MDEA have on R_A in a non-Newtonian liquid containing a reactant (MDEA), the absorption rate of CO_2 was measured in the range of PEO concentration of 10-30 g/L for various MDEA concentration of 0-2 kmol/m^3 under the typical conditions of the agitation speed of 50 rev/min with the impeller size of 0.034 m.

Fig. 1 shows the measured value of R_A against MDEA 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 MDEA concentration due to increase of β as mentioned below and it approaches the calculated one very well.

The lines in Fig. 1 are the values of R_A calculated by using Eq. (8) with $k_L a$, β, C_{Ai} and V_L, where V_L was 3×10^{-4} m^3, a, 14.29 m^2/m^3, C_{Ai} from Eq. (10) at a given MDEA concentration, and β estimated by Eq. (7) and a solution of Eq. (3) and (4) using a numerical analysis of the finite element method from the physicochemical properties listed in Table 2. The $k_L a$ in the dashed line was obtained from Eq. (13) with $\mu=\mu_w$ and De=0, and the $k_L a$ in the solid line with $\mu=\mu_L$ and De>0, and the $k_L a$ in the dotted line with $\mu=\mu_L$ and De=0. We assumed that an 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 the value of the dotted line.

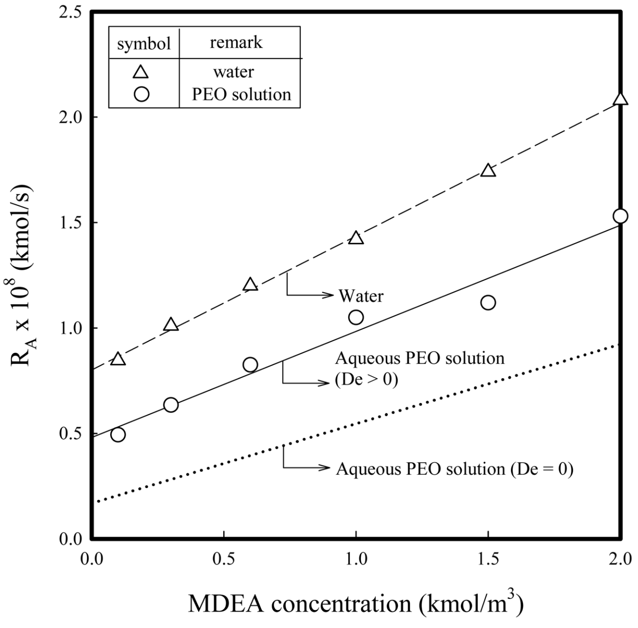

Fig. 1. Comparison of elasticity with viscosity of PEO in MDEA solution (PEO=30 kg/m^3, d=30 mm, N=50 rpm).

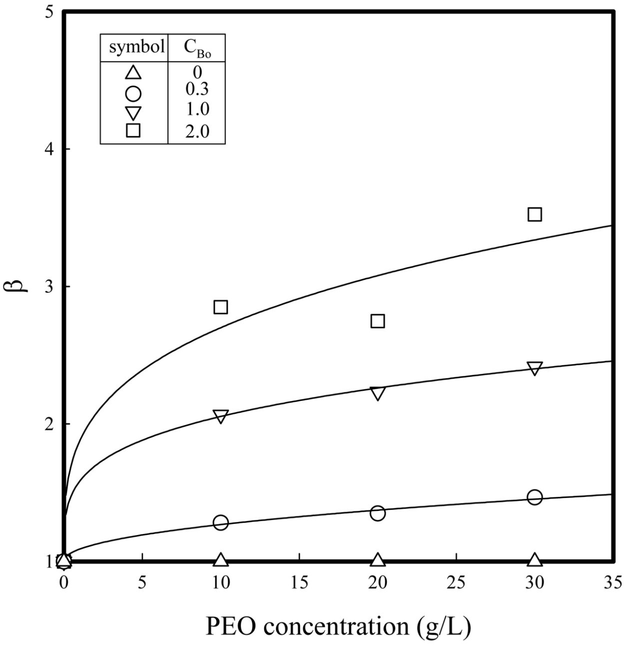

Fig. 2. Effect of PEO concentration on enhancement factor for various MDEA concentrations.

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.

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

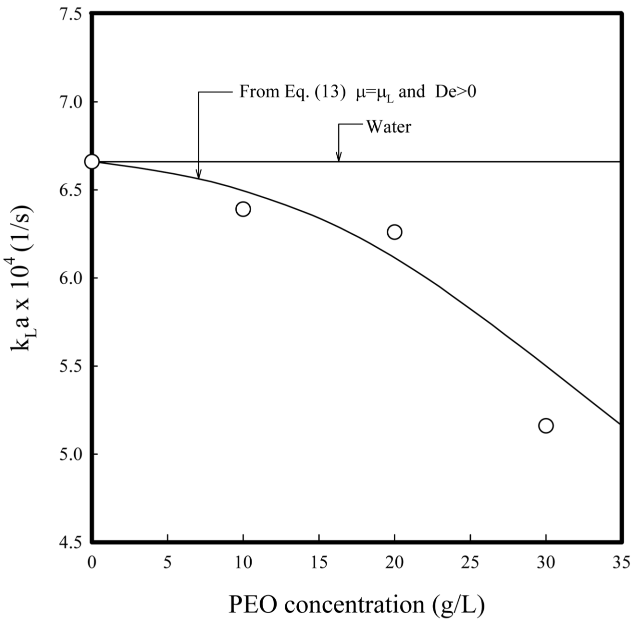

Fig. 3. Effect of PEO concentration on k_La at d=0.034 m and N= 50 rpm.

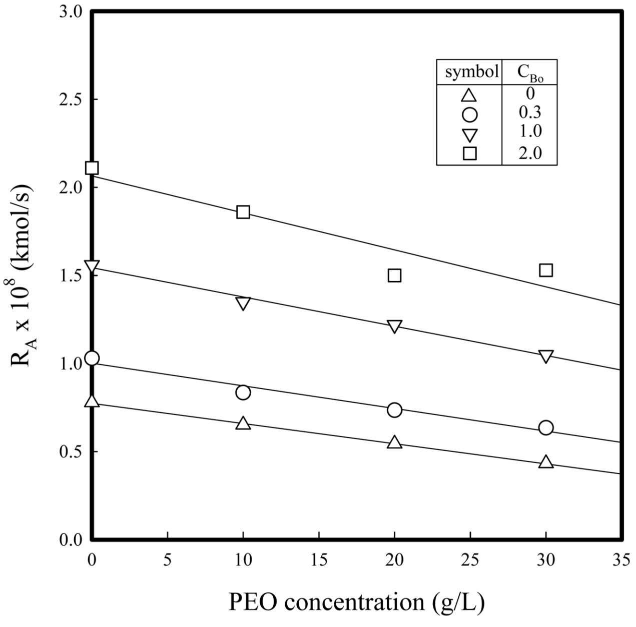

Fig. 4. Effect of PEO concentration on absorption rate for various DEA concentrations.

Fig. 3 shows the measured and calculated values of k_La against PEO concentration of 0-30 g/L as open circles and solid line, respectively. The calculated k_La was obtained from Eq. (13) 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 the calculated values very well.

Fig. 4 shows the plots of the absorption rate of CO_2 against the PEO concentration for various MDEA concentrations. As shown there, R_A decreases with increasing PEO concentration at a fixed concentration of MDEA. The solid lines represent the values of R_A obtained by 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 shown in the results of Fig. 2, 3 and a little decrease of C_{Ai} with increasing PEO concentration as shown in Table 2.

CONCLUSIONS

The measured rate of chemical absorption of carbon dioxide into the aqueous PEO solution of 0-30 g/L with MDEA of 0-2 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 °C 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 the Deborah number. The R_A is dependent on the reactivity of MDEA at a fixed PEO concentration and the elasticity of the aqueous PEO solution at a fixed MDEA concentration. The elasticity accelerated the absorption rate of CO_2 compared with that of a Newtonian liquid based on the same values of viscosity.

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NOMENCLATURE

a : specific gas-liquid contact area [m^2/m^3]
C_i : concentration of species, i [kmol/m^3]
d : diameter of impeller [m]
D_i : diffusivity of species, i [m^2/s]
r_A : reaction rate in Eq. (2) [kmol/m^3·s]
T : temperature [°K]
z : diffusion coordinate of CO_2 [m]
z_L : film thickness [m]

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