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Absorption of Carbon Dioxide into Non-Newtonian Liquid. I. Effect of Viscoelasticity

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ABSTRACT

Carbon dioxide was absorbed into benzene solutions of PB (polybutene) and PIB (polyisobutylene) in an agitated vessel to get the liquid-side volumetric mass transfer coefficient (k_La). The effect of liquid-phase viscosity, pseudoplasticity, and viscoelasticity of the benzene solutions of PB and PIB, and speed and size of impeller on the gas-liquid mass transfer have been investigated. The elastic properties, considered in the form of the Deborah number, were found to decrease the volumetric mass transfer coefficient. On the basis of experimental data of k_La, a dimensionless equation for k_La was proposed by using the Deborah number.

Key Words: Carbon dioxide; Gas absorption; Non-Newtonian liquid; Viscoelasticity; Mass transfer coefficient.

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INTRODUCTION

In a number of industrial processes, water-soluble polymers known as thickeners are added to the processed liquid to control its viscosity or its consistency, as the case may be. Examples are found in emulsion and suspension polymerization, in food processing, in hydrometallurgy, and in biological reactors.

Gas-liquid mass transfer in non-Newtonian liquid is an important example of gas absorption in pseudoplastic flow relevant to industrial process. Variation of the volumetric liquid-phase mass transfer coefficient, $k_{\mathrm{L}}a$, 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 $k_{\mathrm{L}}a$ values in Newtonian and non-Newtonian fluids. 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), and polyacrylamide (PAA) solutions. If some substance is to be given to the suggestion that the considerable reduction of $k_{\mathrm{L}}a$ 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 characteristic material time and the agitation speed, or the Weissenberg number, Wi, defined as the ratio of the first normal stress difference to the shear rate.

Unified correlations have been proposed for $k_{\mathrm{L}}a$ in Newtonian as well as non-Newtonian solutions by introducing the dimensionless term such as $(1 + n_1\mathrm{De}^{n_2})^{n_3}$, which is listed in Table 1. As shown in Table 1, figures in the dimensionless term are different from one another.

Suh et al.[4] also proposed the dimensionless term such as $(1 + 0.18\mathrm{Wi}^{0.93})^{-1}$ to fit the experimental $k_{\mathrm{L}}a$ of O_2 absorption in a bubble column using CMC, PAA, and Xanthan as non-Newtonian liquids. Vlaev et al.[5] used the apparent viscosity of the non-Newtonian liquid, and proposed the dimensionless equation such as $\mathrm{Sh} = 9.71 \times 10^{-7}\mathrm{Re}^{2.47}(\mu/\mu_{\mathrm{w}})^{2.1}$ for

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

the oxygen transfer in colloidal dispersions of corn starch in water using a stirred vessel.

Kawase et al.[6] presented a theoretical model for k_La in bubble columns using non-Newtonian fluids based on Higbie's penetration theory and Kolmogoroff's theory of isotropic turbulence. They used the flow behavior index, n, in the power law liquid of Ostwald de Waele to correlate k_La with the modified Schmidt and Reynolds number.

There is little information about the effect of elastic properties on gas absorption in the organic solvent soluble non-Newtonian fluids.

The present work was intended to obtain a unified correlation for k_La in the organic solvent soluble Newtonian and non-Newtonian fluids in a flat agitated vessel and to observe the effect of elasticity of non-Newtonian liquid on k_La. The particular system chosen for this study was carbon dioxide absorption in benzene solutions of polybutene (PB) and polyisobutylene (PIB) with varying the rheological properties.

EXPERIMENTAL

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 polymer additives 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 1000000 supplied by Aldrich (U.S.A.). The benzene solutions of PB and of PIB of various concentrations 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%.

Rheological Properties of Benzene Solution

The rheological properties of these benzene solutions were measured by the parallel disk type rheometer of the diameter of 0.05 m and the gap of 0.001 m (Ares, Rheometrics, U.S.A.)

Volumetric Mass Transfer Coefficient

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 0.02, 0.034, 0.05, and 0.07 m 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 benzene solution in the vessel were agitated with the agitation speed of 0–400 rev/min. The absorption rates of CO_2 were measured along the procedure similar to those reported elsewhere[7] at 25°C and an atmospheric pressure. A sketch of the experimental set up is presented in Fig. 1. A typical experimental run was carried out as follows:

The vent valve A is initially closed and the purge value B is open. CO_2 is flowed continuously through the absorber C, to make sure that the latter is filled with CO_2 at the start of the experiment. During this initial period,

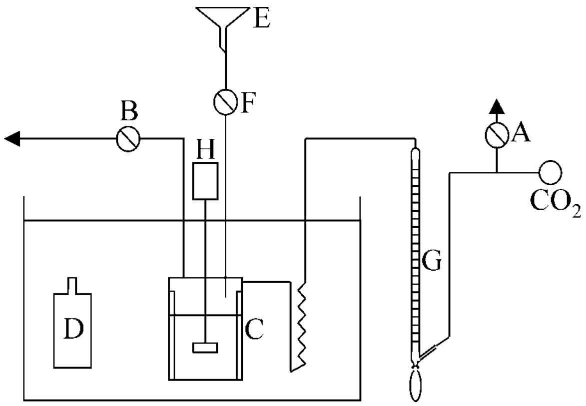

Figure 1. Schematic diagram of agitated vessel.

the water bath temperature is brought up to the desired value, and the liquid batch is kept in bottle D inside the water bath. At the start of the experiment, the liquid batch is poured into funnel E and the agitator H in C is started. The liquid feed valve F is opened, the purge value B is closed, and the vent valve A is opened, as simultaneously as possible. Measurements are started at the soap film meter G by taking care that there are always two soap films in the meter so that a continuous reading of the cumulative volume of CO_2, which has flowed through the soap film meter, $V(t)$, can be recorded as a function of time. The volumetric mass transfer coefficient k_La, was calculated by the following equation with the initial volumetric absorption rates of CO_2, $V(t_1)/t_1$, obtained from the cumulative volume of CO_2 which has flowed through the soap film meter.

$$k_La = \frac{P_T - P_B^o}{V_L C_{Ai} RT} \frac{V(t_1)}{t_1} \tag{1}$$

where P_T is the atmospheric pressure, P_B^o, the vapor pressure of benzene, V_L, the volume of liquid phase, C_{Ai}, the solubility of CO_2 in benzene solution, $V(t_1)$, the cumulative volume of CO_2 during the absorption time, t_1.

Solubility of CO_2 in Benzene Solution

In general, the concentration of CO_2 dissolved in the aqueous solution to get the solubility of CO_2 can be measured by the titration method with a dilute HCl solution,[8] but the amount of CO_2 dissolved in the benzene solution in this study cannot be measured by this method, because CO_2 does not dissociate in the benzene solution. The pressure-measuring method was used in this study by measuring 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[9] to get the solubility of CO_2 in the benzene solution at 25°C. The experimental method may be summarized as follows:

The CO_2 feeder, which was made of a cylindrical stainless steel of $3.73 \times 10^{-4} m^3$, was filled with pure CO_2 to the desired pressure. The pressure in feeder was then measured to within ± 0.01 kPa by digital pressure gauge (Meriam Merigauge, Meriam Instrument, U.S.A.). The CO_2 saturator, which consisted of a 5.45×10^{-4} m^3 glass of 0.07 m inside diameter with a magnetic stirrer set at about 200 rev/min, was charged with $5 \times 10^{-5} m^3$ of the desired benzene solution of PB and PIB and was filled with pure CO_2 to the atmospheric pressure. The feeder and saturator were placed in the water bath to maintain the temperature at 25°C. The feeder was connected to the saturator, and CO_2 was admitted into the saturator until the pressure was not changed. After equilibrium was established, which was indicated by the attainment of a constant pressure and which usually took less than 30 min. The total pressure in feeder and saturator was measured and the quantity of CO_2 in benzene solution was calculated from the pressure change. The amount of CO_2 in the benzene solution was determined from the pressure of pure CO_2 fed into the feeder and the partial pressure of CO_2 in the feeder and saturator. To calculate the latter, the vapor pressure of the benzene solution was assumed to be the same as for pure benzene and was taken from Perry and Chilton.[10]

From knowledge of the pressure of pure CO_2 in feeder, the total pressure in the feeder and saturator, and the vapor pressure of the CO_2-free benzene solution, the solubility of CO_2 in the liquid phase was calculated by the following method.

First, the amount of CO_2 in the vapor phase was determined by assuming that the phase obeyed Dalton's law, i.e., the total pressure exerted by the vapor phase equals the sum of the partial pressures of the individual components. The partial pressure of CO_2 in the vapor phase, P_A, was, therefore, simply taken as the difference between the total measured pressure, P_T, and the vapor pressure of the CO_2-free benzene solution, P_B^o, i. e.,

$$P_A = P_T - P_B^o \tag{2}$$

By knowing the partial pressure of CO_2, the volume of the vapor phase (determined from the internal volume of the saturator and the volume of benzene solution introduced), and the temperature, we could find the number of moles of CO_2 in the vapor phase by using an equation of state. The vapor in the saturator assumed to be an ideal gas because the total pressure was about 1 atm.

Once the number of moles of CO_2 in the vapor phase, m_v, had been found, the mass of CO_2 in the benzene solution, m_L was obtained by subtracting the mass of CO_2 in the vapor phase from the total mass of CO_2 fed to the feeder, m_f, i.e.,

$$m_L = m_f - m_v \tag{3}$$

From the mass of CO_2 dissolved in the benzene solution and the known volume of benzene solution in the saturator, the solubility of CO_2, C_{Ai}, could be easily calculated. The value of C_{Ai} was used to get $k_L a$ in Eq. (1).

Density of Benzene Solution

The densities of the benzene solutions of PB and PIB were measured at 25°C to within $\pm 0.1\,\mathrm{kg/m^3}$ by weighing with a pycnometer (Fisher Scientific Co., U.S.A.) and were found to be identical within experimental accuracy to the density of water.

Apparent Viscosity of Benzene Solution

The apparent viscosities of the benzene solution of PB and PIB were measured by using Cannon-Fenske viscometer at 25°C.

RESULTS AND DISCUSSION

Rheological and Physicochemical Properties of the Liquid and CO_2

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

$$\tau = K\gamma^n \tag{4}$$

$$\eta = K\gamma^{n-1} \tag{5}$$

$$N_1 = A\gamma^b \tag{6}$$

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 benzene solution were measured according to the change of γ by the rheometer.

Figure 2 shows typically the logarithmic plot of shear stress vs. shear rate for the benzene solutions of PB of 30 wt% and of 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. Also, 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

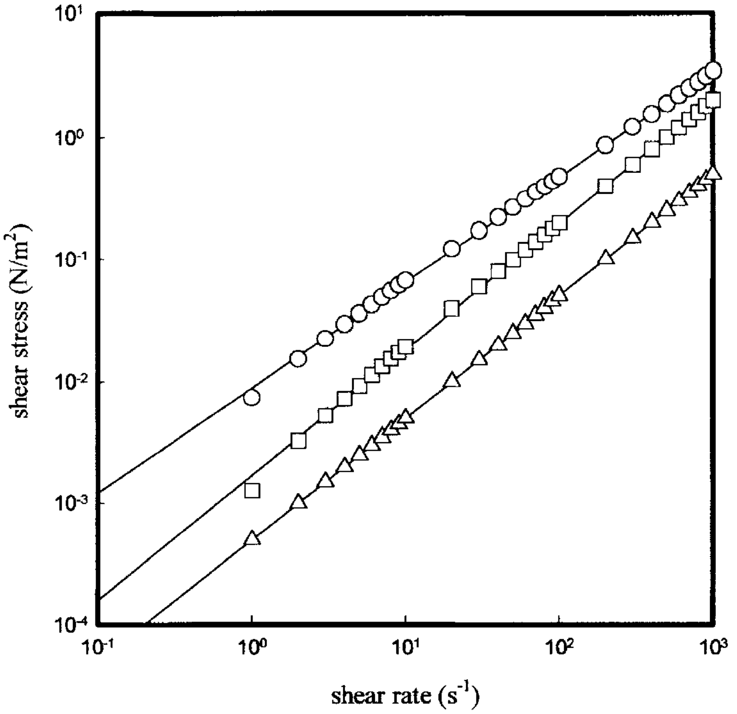

Figure 2. Shear stress of benzene solution as a function of shear rate. (△: Bz, □: Bz(30)/Bz, ○: PIB(1)/PB(30)/Bz).

difference of benzene and benzene solution of 30 wt% PB are zero. From the intercept and slope of the straight line in the 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 benzene solution of various concentration of PB and PIB are give in Table 2.

As shown in Table 2, note that only the benzene solutions of PIB show any measurable primary stress difference, and therefore they are considered viscoelastic.

A frequently used measure of viscoelasticity is known as the characteristic time of the liquid defined as

$$\lambda = \frac{N_1}{\eta\gamma^2} \tag{7}$$

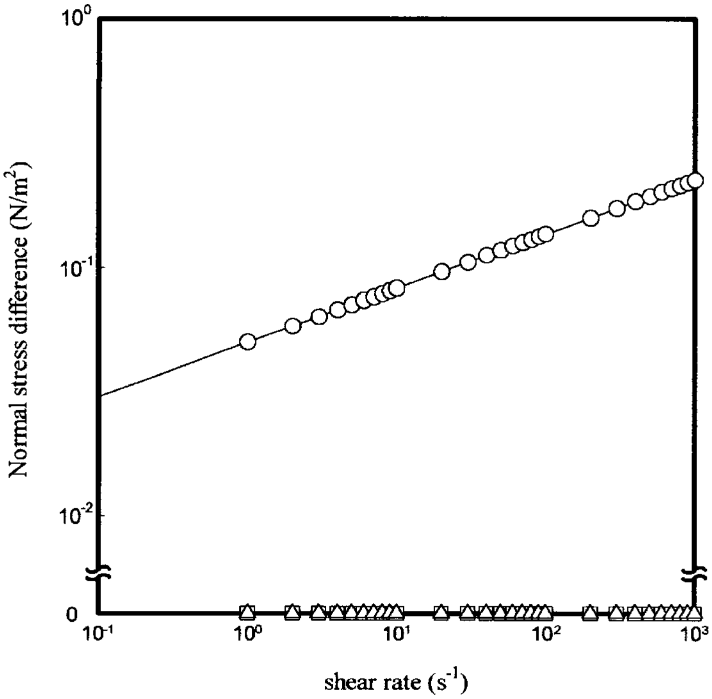

Figure 3. Normal stress difference of benzene solution as a function of shear rate (△: Bz, □: Bz(30)/Bz, ○: PIB(1)/PB(30)/Bz).

In terms of the parameters K, A, n, and b defined by Eqs. (5) and (6), the characteristic time, λ, can be expressed as

$$\lambda = \frac{A}{K}\gamma^{b-n-1} \tag{8}$$

The characteristic time is plotted against γ in Fig. 4 by using Eq. (8) for the four concentrations of PIB in the benzene solution of PB 20 wt% with the rheological properties in Table 2. As shown in Fig. 4, λ decreases as the shear rate and the concentration of PIB decrease. This means that the more the concentration of PIB increases, the stronger the benzene solution depends on the elasticity.

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

Table 2. The physicochemical and rheological properties of CO_2 and benzene solution.

Benzene solution					Rheological properties			
PB (wt%)	PIB (wt%)	Diffusivity (m^2/s) $\times 10^9$	Solubility ($kmol/m^3$)	Density (kg/m^3)	n	$K \times 10^3$	b	$A \times 10^3$
0	0	3.85	0.114	880.0	1	0.63	0	0
20	0	2.87	0.108	925.3	1	1.1	0	0
	0.1	3.01	0.107	925.3	0.980	1.2	0.001	4
	0.2	3.08	0.105	925.4	0.975	1.4	0.017	7
	0.5	3.13	0.104	925.6	0.960	2.0	0.062	13
	1.0	2.91	0.104	926.2	0.880	6.5	0.222	35
30	0	2.16	0.105	925.4	1	1.7	0	0
	0.1	2.29	0.104	925.4	0.974	1.9	0.001	5
	0.2	2.53	0.102	925.5	0.960	2.2	0.020	10
	0.5	2.60	0.101	925.9	0.953	3.6	0.059	20
	1.0	2.68	0.101	926.4	0.841	8.8	0.219	50

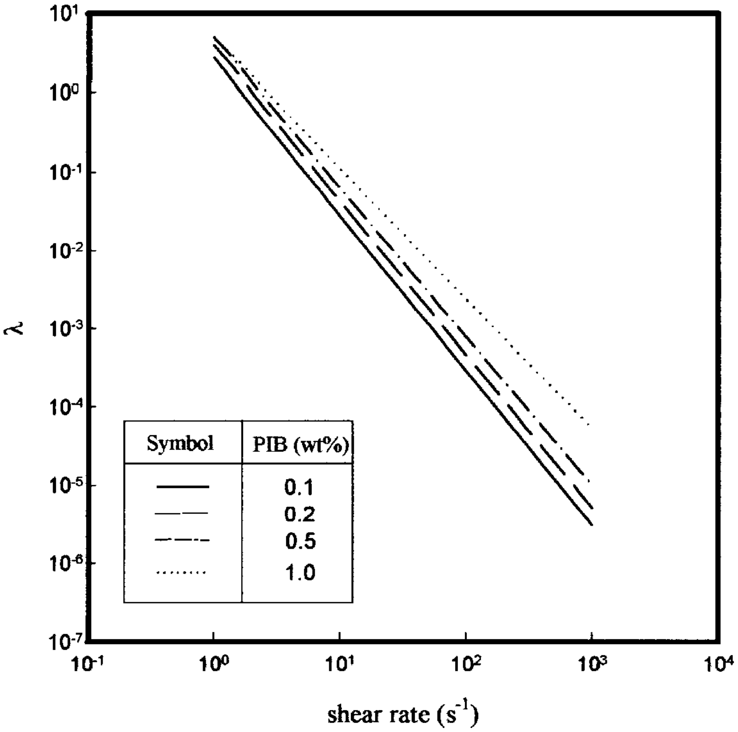

Figure 4. Characteristic times of solution as a function of shear rate γ at 20 wt% PB.

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. (8) as follows.

$$\mathrm{De} = \lambda N = \frac{A}{K}\gamma^{b-n-1}N \tag{9}$$

It is obvious from Eq. (5) that the viscosity, η, depends on the shear rate, and thus η is not a material parameter. It is particularly difficult to determine the value of η in the stirred tank where the shear rate is linked to the impeller speed. The shear rate of a non-Newtonian fluid is of importance in fixing the rheological or viscometric behavior of such a material, and it depends on the hydrodynamic characteristics of the fluid.

An apparent viscosity based on an average shear rate in the agitated vessel as proposed by Nishikawa et al.[11] is defined as

$$\eta = \tau/\gamma_{\mathrm{avg}} \tag{10}$$

Metzner and Otto[12] found that in applying Eq. (10) to correlate rates of viscous dissipation in agitated vessels, the average shear rate γ_{avg} could be simply related to the impeller speed by

$$\gamma_{\mathrm{avg}} = \mathrm{A_s}N \tag{11}$$

where $\mathrm{A_s}$ is a proportionality constant. They gave a general equation from use in viscometric equipment approximating a long cylinder rotating in an infinite fluid as follow:

$$\gamma_{\mathrm{avg}} = \frac{4\pi}{n}N \tag{12}$$

The viscosity of the power-law liquid is a function of shear rate as shown in Eq. (5), and the average shear rate depends on the impeller speed in the baffled tank as shown in Eq. (12). Therefore, the apparent viscosity can be estimated from the following equation, which is derived from Eqs. (5) and (12).

$$\eta = Kn^{1-n}(4\pi N)^{n-1} \tag{13}$$

Nishikawa et al.[11] correlated the average shear rate with the superficial gas velocity of air, U_{G}, in CMC solution of the bubble column by the equation, $\gamma_{\mathrm{avg}} = 50\,U_{\mathrm{G}}$. Yagi and Yoshida[1] related the average shear rate to the impeller speed, N, in the sparged agitated vessel by $\gamma_{\mathrm{avg}} = 11.5N$. Suh et al.[4] presented the effective shear rate correlated with $U_{\mathrm{G}}^{1/(n+1)}$ in the bubble column.

Calderbank and Moo-Young[13] extended the Metzner-Otto approach to allow the proportionality constant, As, in Eq. (11) to be a function of the flow behavior index n

$$\gamma_{\mathrm{avg}} = BN\left(\frac{4n}{3n+1}\right)^{\left(\frac{n}{1-n}\right)} \tag{14}$$

For pseudoplastic fluids, they determined the value of the constant B by matching power numbers for non-Newtonian agitation to the corresponding correlation for Newtonian agitation. The reported value for B for turbines and propellers was 11 (± 10%).

Perez and Sandall[14] derived the apparent viscosity for the liquid and impeller used in their work from Eqs. (5) and (14).

$$\eta = K(11N)^{n-1}\left(\frac{3n+1}{4n}\right)^{n} \tag{15}$$

The apparent viscosity given by Eq. (13) or (15) depends on not only the rheological properties but also the agitation speed of impeller.

To observe the features of the measured and calculated apparent viscosity, the measured apparent viscosity is plotted against the concentration of PIB and PB in Fig. 5. In this figure, the solid and dotted line are the values from Eqs. (13) and (15) with impeller speed of 100 rev/min as a typical case, respectively. As shown in Fig. 5, the measured viscosity increase with increase of the concentration of PIB and PB and calculated values do not approach these measured, although the calculated values from Eqs. (13) and (15) are

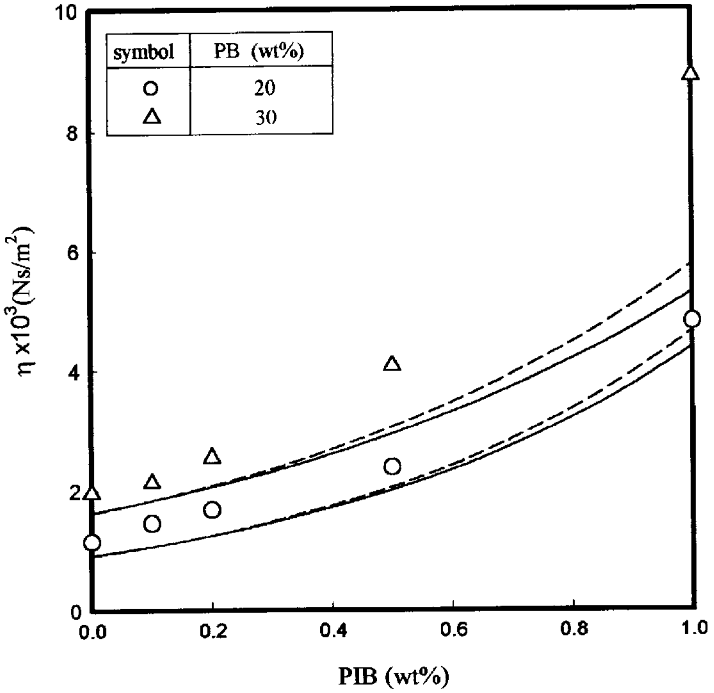

Figure 5. Effect of concentration of PIB in PIB/PB/Bz solution on apparent viscosity. [solid line: calculated from Eq. (13), dotted line: calculated from Eq. (15)].

almost equal each other. This may be the cause that the flow pattern of falling liquid in the capillary of Cannon–Fenske viscometer does not have a concern in the agitation of the liquid in the baffled vesser.

To observe the effect of the concentration of PIB and the speed of impeller on Deborah number, De, calculated from Eq. (9) is plotted against the concentration of PIB in Fig. 6 by using the shear rate obtained from Eq. (12) for the typical concentration of PB of 20 wt%. As shown in Fig. 6, De increases with increase of the concentration of PIB and decrease of 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 the Deborah number decrease in the agitated vessel with the viscoelasticity liquid.

The diffusion coefficient of 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 diffusion coefficient of CO_2 in the benzene solution was obtained from the following equation suggested by Lohse et al.,[15] which was modified from the Stoke-Einstein equation,

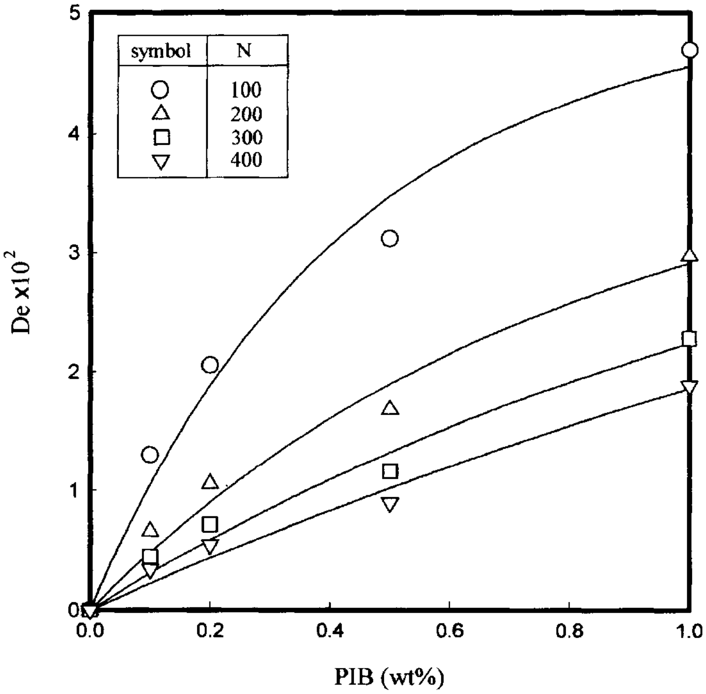

Figure 6. Effect of concentration of PIB on Deborah number at PB of 20 wt%.

and correlated with the molecular weight of the polymer in the solution.

$$D_L/D_o = (\eta_o/\eta)^{3.7\sqrt{M_o/M_p}} \tag{16}$$

The molecular weight of the polymer in the benzene solution of PB and PIB was calculated by the addition rule as follow;

$$M_P = x_{PB} \times M_{PB} + x_{PIB} \times M_{PIB} \tag{17}$$

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

The diffusion coefficient of CO_2 in benzene at 25°C, D_o, was obtained from the Wilke-Chang Equation[16], and its value was $3.85 \times 10^{-9}\ m^2/s$.

The calculated diffusivity of CO_2 from Eq. (16), the measured solubility of CO_2, apparent viscosity, and density of the benzene solution of various concentrations of PB and PIB are given in Table 2.

Empirical Correlation

There have been several studies of gas absorption by agitated Newtonian liquids across a gas-liquid interface. Sandall and Patel[17] have summarized this work and have obtained data of their own. A dimensional analysis indicates that the mass transfer coefficient may be corrected by an equation of form

$$k_L d/D_L = C(d^2 N\rho/\eta)^b(\eta/\rho D_L)^c \tag{18}$$

Sideman et al.[18] provide a review of mass transfer in mechanically agitated gas-liquid dispersions. For these cases, the gas flow rate and the physical properties of the gas will affect the mass transfer rate. These authors point out the form that the mass transfer correlations take for the bubbling case.

$$k_L a d^2/D_L = C(d^2 N\rho/\eta)^b(\eta/\rho D_L)^c(d v_s/\sigma)^e(\eta_g/\eta)^f \tag{19}$$

The term on the left side of Eq. (19) is a modified Sherwood number, which includes the effective interfacial area; the terms on the right side are the impeller Reynolds number, the Schmidt number, a dimensionless gas flow group, and the ratio of dispersed phase and continuous phase viscosities.

Eqs. (18) and (19) cannot be used directly to correlate mass transfer data with non-Newtonian liquids because the liquid viscosity, which appears in these equations, is not defined for non-Newtonian liquids. However, in this work[18] it is proposed to use an apparent viscosity as used by Sandall and

Patel[17] and Skelland and Dimmick[19] in correlating heat transfer rates to non-Newtonian liquids in agitated vessels.

To observe the effect of the impeller speed and size on the volumetric mass transfer coefficient, the measured values of k_La in the benzene solution of PB of 20 and 30 wt% with the typical concentration of PIB of 0.1 wt% were plotted against the speed of the impeller in Fig. 7. As shown in Fig. 7, k_La increases with increase of the speed and size of the impeller, and k_La increases rapidly in the range of the impeller speed above 200 rev/min.

To observe the effect of the concentration of PB and PIB on the volumetric mass transfer coefficient, the measured values of k_La were plotted typically against the change of concentration of PIB with a parameter of the concentration of PB at the impeller speed of 300 rev/min and the impeller size of 0.07 m in Fig. 8. As shown in Fig. 8, k_La decreases with increase of PIB concentration, and k_La in the benzene solution of 20 wt% PB is larger than that

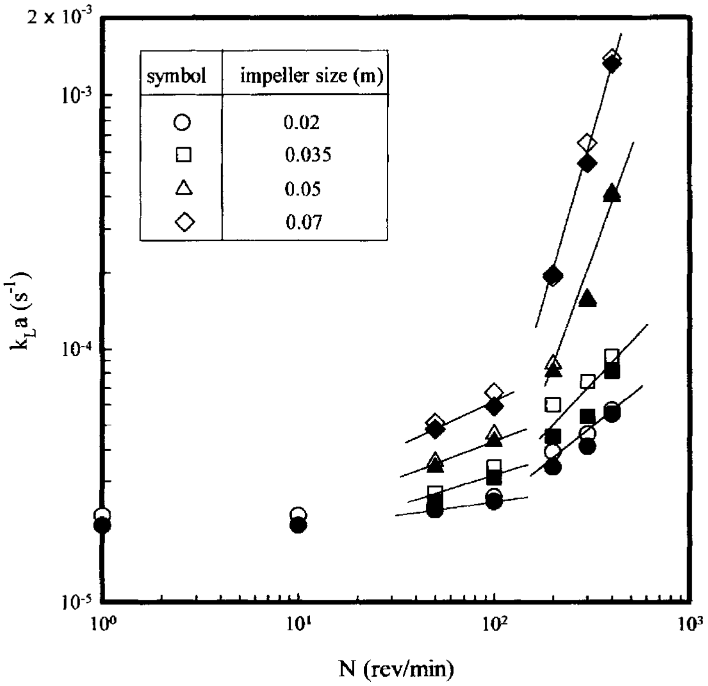

Figure 7. Effect of agitation speed and impeller size on volumetric mass transfer coefficient in PIB(0.1 wt%)/PB/Bz solution. (empty symbol: 20 wt% PB, black symbol: 30 wt% PB).

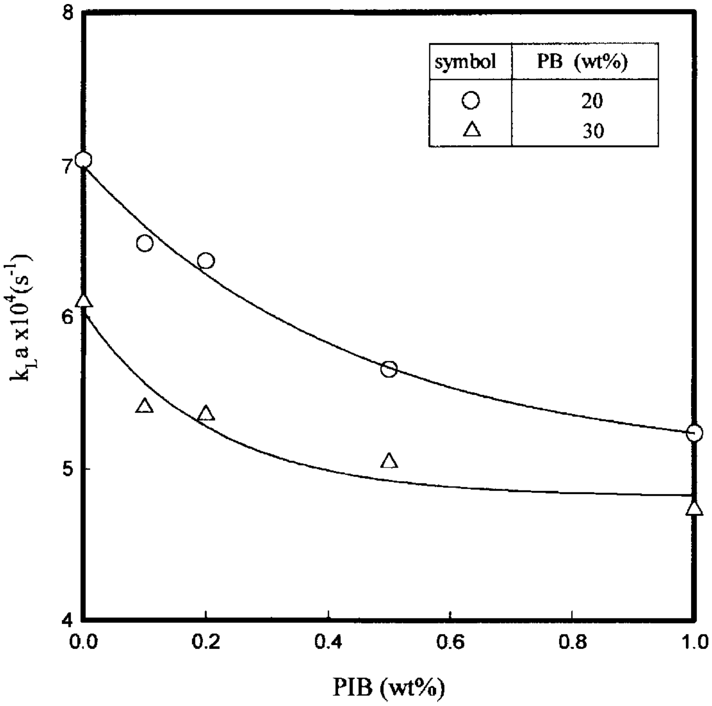

Figure 8. Effect of concentration of PIB on volumetric mass transfer coefficient. ($N = 300$ rev/min, $d = 0.07$ m).

of 30 wt% PB. It is obvious that the pseudoplastic (PB) and viscoelastic (PIB) liquid lead to reduction of the volumetric mass transfer coefficient.

In analyzing the relationship between the volumetric mass transfer coefficient and the experimental variables such as the concentration of PB and PIB, and the speed and size of the impeller, the following influences may be considered: diffusivity, viscosity, and rheological properties of the liquid phase.

It is customary to express the influence of viscosity on the mass transfer coefficient in terms of Schmidt number defined as $\eta/\rho D_L$, in which the viscosity is related to the diffusion coefficient. As shown in Table 2, the diffusion coefficient of CO_2 in polymer solutions of PIB does not vary significantly from that for PB solution; thus, the use of a dimensionless Schmidt number is not warranted. Instead, the dimensionless ratio of viscosity (η/η_o) was used to correlate the effect of viscosity because the viscosity of the benzene solution of PIB and PB in the agitated vessel depends on the speed of impeller and the rheological properties as shown in Eqs. (13) or (15).

To correlate the volumetric mass transfer coefficient with the experimental variables such as the concentrations of PIB and PB, the speed and size of the impeller, and the rheological properties of the benzene solutions, Sherwood number, Sh, and Reynolds number, Re, are defined as follows;

$$\mathrm{Sh} = k_{\mathrm{L}} a d^2 / D_{\mathrm{L}} \tag{20}$$

$$\mathrm{Re} = d^2 N \rho / \eta \tag{21}$$

To correlate the volumetric mass transfer coefficient with the operational variables by the dimensionless group, Sherwood number is plotted against Reynolds number with the experimental variables such as the measured values

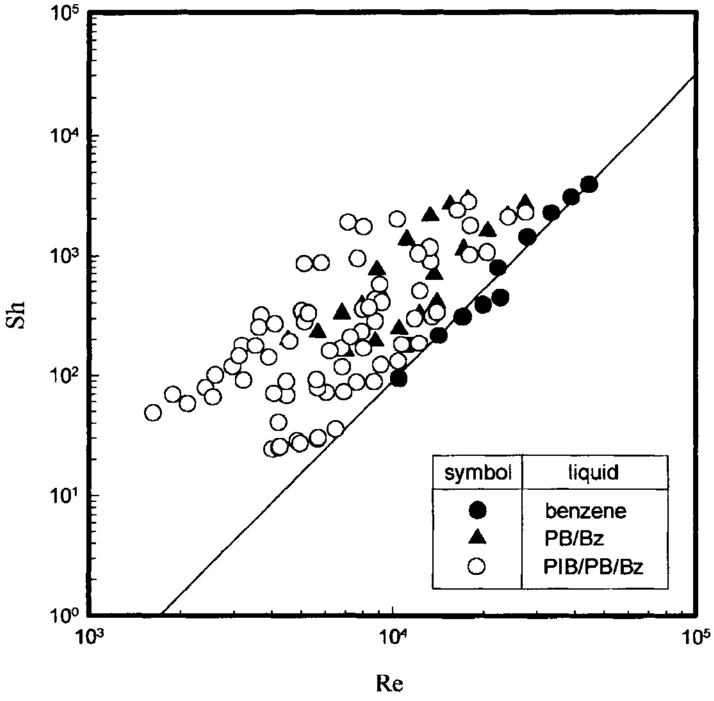

Figure 9. Dimensionless correlation of the volumetric mass transfer coefficient of CO_2 in Bz, PB/Bz, and PIB/PB/Bz solution.

of k_La of CO_2 in the benzene solution of PIB of 0–1 wt%, and PB of 20 and 30 wt% at the impeller speed of 200–400 rev/min with the impeller size of 0.02–0.07 m, the viscosity of the benzene solution of PIB and PB using Eq. (13), and physical properties such as D_L and ρ in Table 2.

Figure 9 shows logarithmic plots of Sh against Re, in which the black circles, the black triangles, and the empty circles represent the plots in benzene, benzene solution of PB (PB/Bz), and benzene solution of PIB and PB (PIB/PB/Bz), respectively. As shown in Fig. 9, the plots in benzene are linear, but other plots are nonlinear. The slope and intercept from the straight line of plots in benzene by the least-square method are obtained, and their values are 2.54 and 6.39×10^{-9}, respectively.

To lessen the deviation of the plots in PB/Bz from those in benzene as shown in Fig. 9, a simple multiple regression exercise was used with the plots of Sh combined with the dimensionless ratio of viscosity, η/η_o, against Re in case of PB/Bz solution, and the best value of the exponent of the viscosity ratio

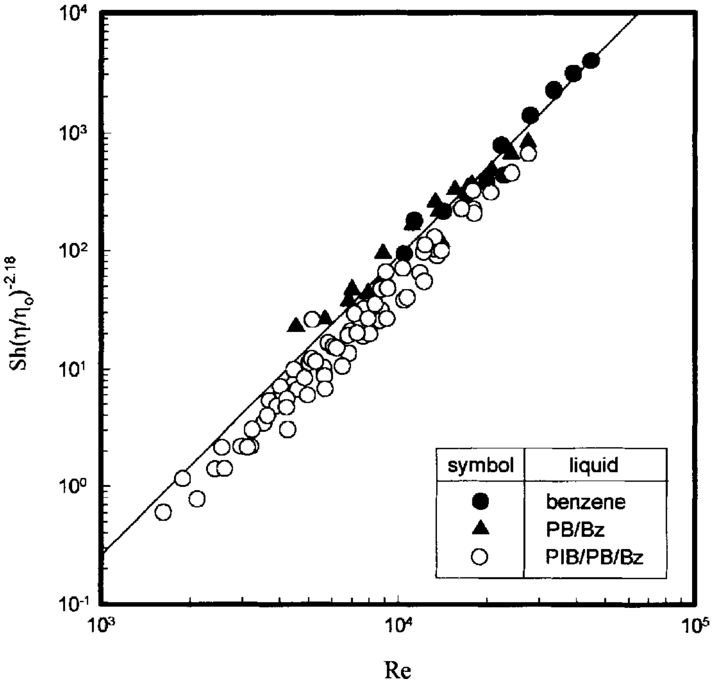

Figure 10. Dimensionless correlation of the volumetric mass transfer coefficient of CO_2 in Bz, PB/Bz, and PIB/PB/Bz solution with corrected specific viscosity.

is 2.18 with its standard deviation of 5.69%, and the correlation is plotted in Fig. 10.

It can be seen that all the data for the viscoelastic PIB solutions deviated considerably from the inelastic PB solutions. A new term of $\mathrm{Sh}(\eta/\eta_o)^{-2.18}$ combined with the elasticity such as $(1 + \mathrm{m_1 De})^{\mathrm{m_2}}$ against Re was used to apply the behavior of non-Newtonian viscoelastic liquid to the empirical term of $\mathrm{Sh}(\eta/\eta_o)^{-2.18}$ in PB/Bz solution. A simple multiple regression exercise gave the values of m_1 and m_2, and their values are 100 and 0.42 with the standard deviation of 10.38%, respectively, as shown in Fig. 11.

Figure 11 shows that this deviation can be eliminated by including the Deborah number in the correlation. Using a total of 104 data points for 11 different solutions, the multiple regression analysis comes up with

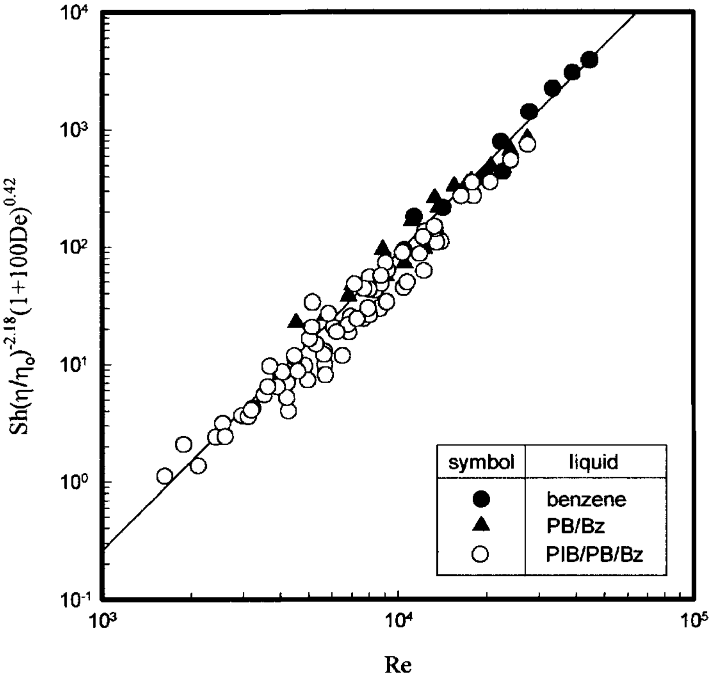

Figure 11. Dimensionless correlation of the volumetric mass transfer coefficient of CO_2 in Bz, PB/Bz, and PIB/PB/Bz solution incorporating Deborah number.

a correlation as follows;

$$\frac{k_L a d^2}{D_L} = 6.39 \times 10^{-9} \left(\frac{d^2 N \rho}{\eta} \right)^{2.54} \left(\frac{\eta}{\eta_o} \right)^{2.18} (1 + 100\mathrm{De})^{-0.42} \tag{22}$$

The coefficient 100 in the last term on the right-hand side is an arbitrary one chosen to match the order of magnitude of 100 De with unity. For inelastic liquid, the last term becomes equal to 1.

When we analyze Eq. (22) for the overall effect of viscosity on the mass transfer coefficient, it comes out as $k_L a \propto \eta^{-0.36}$, which compares well with the finding of Perez and Sandall,[14] Yagi and Yoshida,[1] and Ranade and Ulbrecht.[2]

CONCLUSIONS

Absorption rates of carbon dioxide into Newtonian, pseudoplastic, and viscoelastic liquids were measured in an agitated vessel of 0.1-m diameter with four sizes of impeller of 0.02, 0.034, 0.05, and 0.07 m. The benzene solutions of PB and PIB were used as pseudoplastic and viscoelastic liquid, respectively, and the concentration range of PIB were 0.1–1.0 wt%, and concentrations of PB were 20 and 30 wt%. The rheological properties of the benzene solutions such as n, K, b, and A, were used to correlate the characteristic time presenting the elastic properties with the volumetric mass transfer coefficient. The elastic properties, considered in the form of the Deborah number, were found to decrease the value of the volumetric mass transfer coefficient.

An empirical correlation of the volumetric mass transfer coefficient incorporating Deborah number was obtained as follows,

$$\frac{k_L a d^2}{D_L} = 6.39 \times 10^{-9} \left(\frac{d^2 N \rho}{\eta} \right)^{2.54} \left(\frac{\eta}{\eta_o} \right)^{2.18} (1 + 100\mathrm{De})^{-0.42}$$

NOMENCLATURE

A	rheological properties defined in Eq. (6), (Ns^b/m^2)
a	contact area at interface of gas-liquid per liquid volume, (1/m)
b	rheological properties defined in Eq. (6)
C_{Ai}	solubilities of CO_2 in absorbent ($kmol/m^3$)

d	diameter of impella (m)
De	Deborah number defined in Eq. (9)
D_L	diffusivity of CO_2 in solution (m^2/s)
D_o	diffusivity of CO_2 in benzene (m^2/s)
K	rheological properties defined in Eq. (4) (Ns^n/m^2)
k_L	liquid side mass transfer coefficient of CO_2 (m/s)
$k_L a$	volumetric mass transfer coefficient (1/s)
M_o	molecular weight of benzene (kg/kmol)
M	molecular weight of polymer (kg/kmol)
M_{PB}	molecular weight of PB (kg/kmol)
M_{PIB}	molecular weight of PIB (kg/kmol)
m_f	number of mole of CO_2 in the vapor (kmol)
m_L	number of mole of CO_2 in the benzene solution (kmol)
m_V	number of mole of fed CO_2 to feeder (kmol)
n	rheological properties defined in Eq. (4)
N	impeller speed (1/s)
N_1	primary normal stress difference defined in Eq. (4) (N/m^2)
P_A	partial pressure of CO_2 (kPa)
P_B^o	vapor pressure of benzene (kPa)
P_T	total pressure (kPa)
R	universal gas law constant (atm m^3/mol °K)
Re	modified Reynold number defined as $d^2 N\rho/\eta$
Sh	modified Sherwood number defined as $k_L a d^2/D$ L
T	temprature (°K)
t_1	absorption time (s)
V_L	volume of absorbent (m^3)
$V(t_1)$	cumulative volume of CO_2 during the absorption time t_1 (m^3)
v_s	superficiaql gas velocity (m/s)
x_{PB}	mole fraction of PB
x_{PIB}	mole fraction of PIB

Greek letters

γ	shear rate (1/s)
λ	characteristic liquid time (s)
η	viscosity of non Newtonian liquid (Ns/m^2)
η_g	viscosity of gas (Ns/m^2)
η_o	viscosity of benzene (Ns/m^2)
ρ	density (kg/m^3)
σ	interfacial surface tension (kg/s^2)
τ	shear stress (N/m^2)

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