Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Absorption of Carbon Dioxide into Non-Newtonian Liquid. II. Effect of w/o Emulsion

Sang-Wook Park[a]; In-Joe Sohn[a]; Se-Gon Sohn[a]; Hidehiro Kumazawa[b]
[a] Division of Chemical Engineering, Pusan National University, Pusan, Korea [b] Department of Chemistry and Biochemical Engineering, Toyama University, Toyama, Japan

To cite this Article Park, Sang-Wook , Sohn, In-Joe , Sohn, Se-Gon and Kumazawa, Hidehiro(2003) 'Absorption of Carbon Dioxide into Non-Newtonian Liquid. II. Effect of w/o Emulsion', Separation Science and Technology, 38: 16, 3983 — 4007
To link to this Article: DOI: 10.1081/SS-120024715
URL: http://dx.doi.org/10.1081/SS-120024715

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 16, pp. 3983–4007, 2003

Absorption of Carbon Dioxide into Non-Newtonian Liquid. II. Effect of w/o Emulsion

**Sang-Wook Park,[1,*] In-Joe Sohn,[1] Se-Gon Sohn,[1]
and Hidehiro Kumazawa[2]**

[1]Division of Chemical Engineering, Pusan National University,
Pusan, Korea
[2]Department of Chemistry and Biochemical Engineering,
Toyama University, Toyama, Japan

ABSTRACT

Carbon dioxide was absorbed into water-in-oil (w/o emulsion) composed of aqueous droplets as dispersed phase and benzene solutions of polybutene (PB) and polyisobutylene (PIB) as continuous phase in an agitated vessel to get the liquid-side volumetric mass transfer coefficient (k_La). The effect of viscosity, pseudoplasticity, viscoelasticity, and interfacial tension of the emulsion, and speed and size of impeller on the gas–liquid mass transfer were 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

---

[*]Correspondence: Sang-Wook Park, Division of Chemical Engineering, Pusan National University, Pusan 609-735, Korea; E-mail: swpark@pusan.ac.kr.

DOI: 10.1081/SS-120024715 0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

data of k_La, a dimensionless empirical equation for k_La was proposed using the Deborah number and interfacial tension as follows:

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

Key Words: Carbon dioxide; Gas absorption; Non-Newtonian liquid; Viscoelasticiy; Mass transfer coefficient; Emulsion; Interfacial tension.

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 a fermentation broth, slurry, and fluidized bed. Variation of the volumetric liquid–phase mass-transfer coefficient, k_La, 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_La values. Due to the complexities of gas absorption in non-Newtonian media, the correlations obtained by these studies were limited to just a few kinds of non-Newtonian fluids, such as Carbopol, carboxymethylcellulose (CMC), polyacrylate (PA), polyethylene-oxide (PEO), and polyacrylamide (PAA) solutions. If some substance is to be given to the suggestion that the considerable reduction of k_La 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 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_La 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 one another.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

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

Investigator	n_1	n_2	n_3	Polymer	Contactor
Yagi and Yoshida[1]	2	0.5	− 0.67	CMC, PA	Agitated vessel
Ranade and Ulbrecht[2]	100	1	− 0.67	CMC, PAA	Stirred tank
Nakanoh and Yoshida[3]	0.13	0.55	− 1	CMC, PA	Bubble column
Park et al.[11]	100	1	− 0.42	PB, PIB	Agitated vessel

Suh et al.[4] have also proposed the dimensionless term such as $(1 + 0.18\mathrm{Wi}^{0.93})^{-1}$ to fit the experimental k_La 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 $\mathrm{Sh} = 9.71 \times 10^{-7}\mathrm{Re}^{2.47}(\mu/\mu_w)^{2.1}$ for the oxygen transfer in colloidal dispersions of cornstarch 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.

If the system is w/o type 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 various authors:[7–10] 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 water-in-oil emulsion composed of aqueous droplets as dispersed phase and non-Newtonian liquid as continuous phase. Park et al.[11] presented the dimensionless term, such as $(1 + n_1\mathrm{De}^{n_2})^{n_3}$, as shown in Table 1, to fit the experimental k_La of CO_2 absorption into non-Newtonian liquid, such as benzene solution of polybutene and polyisobutylene, in an agitated vessel.

The present work as a series of studies[11] about the absorption of CO_2 into non-Newtonian liquids was intended to obtain a unified correlation for k_La in the w/o emulsion composed of water as a dispersed phase and non-Newtonian fluids as a continuous phase in a flat agitated vessel, and to observe the effect of elasticity of non-Newtonian liquid in emulsion on k_La. The particular system chosen for this study was carbon dioxide absorption into emulsion with continuous phase of 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 a mean molecular weight of 680 supplied by Daelim Industry Co. Ltd., Korea, and PIB with a 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, 1.0 wt%, and volume fraction of water in emulsion was fixed as a value of 0.4.

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[10] by adding Tween 80 (Aldrich Chemical Co.) and Arlacel 83 (Aldrich Chemical Co.) as surfactant, by using a homogenizer (Fisher Scientific Co.) in the range of agitation speed of 1500 to 10,000 rev/min. The mean size of aqueous droplets was measured by an 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 0.05 m in diameter with a gap of 0.001 m (Ares, Rheometrics, USA).

Volumetric Mass Transfer Coefficient

Absorption experiments were carried out in an agitated vessel. The absorption vessel was constructed of glass with a 0.102 m inside diameter and 0.151 m in height. Four equally spaced vertical baffles, each one-tenth of the vessel diameter in width, were attached to the internal wall of the vessel. The liquid phase was agitated with an agitator driven by a 1/4 Hp variable speed motor without agitation in gas phase because of pure CO_2 gas. A straight impeller with 0.05 and 0.07 m length and 0.02 m width was used as the liquid-phase agitator, and located at the middle position of the liquid phase. The gas and emulsion in the vessel were agitated with agitation speeds of 200, 300, and 400 rev/min. The absorption rates of CO_2 were measured along a procedure similar to those reported elsewhere[10,11] at 25°C and at atmospheric pressure. The volumetric mass-transfer coefficient, k_La, was obtained using the observed values of the cumulative volume of CO_2 for the change of absorption time if the gas–liquid interface was kept constant or not. The experimental procedure was duplicated that as reported in published research[10,11] in detail.

Solubility of CO_2 in Emulsion

In general, the concentration of CO_2 dissolved in aqueous solution to get the solubility of CO_2 can be measured by the titration method with a dilute HCl solution,[12] 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 similar to the procedure reported elsewhere[13] to get the solubility of CO_2 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 CO_2 dissolved in the emulsion and the known volume of emulsion in the saturator, the solubility of CO_2, C_{Ai}, was calculated. The experimental procedure to get the solubility of CO_2 was duplicated that as reported in published research[11] 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/m^3 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 water and benzene solution of various concentrations of PIB and PB were

Table 2. Physicochemical and rheological properties of CO_2 and w/o emulsion with void fraction of water of 0.4.

PB (wt%)	PIB (wt%)	Interfacial tension (N/m × 10^3)	Diffusivity (m^2/s) × 10^9	Solubility (kmol/m^3)	Density (kg/m^3)	Rheological properties			
						n	K	b	A
0	0	34.7	1.98	0.095	949.6	0.560	1.196	0	0
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	6.975	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	11.453	0.897	0.342
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	0.684	0.086
	0.2	23.8	1.53	0.071	941.1	0.408	10.041	0.702	0.099
	0.5	22.9	1.57	0.069	945.1	0.443	11.239	0.751	0.213
	1.0	20.8	1.61	0.067	948.8	0.371	21.350	0.810	0.486

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.[14]

Solubility of CO_2, density of emulsion, and interfacial tension are given in Table 2.

RESULTS AND DISCUSSION

Rheological and Physicochemical Properties of the Emulsion and CO_2

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

$$\tau = K\gamma^{n} \tag{1}$$

$$\eta = K\gamma^{n-1} \tag{2}$$

$$N_1 = A\gamma^{b} \tag{3}$$

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 1 shows the typical logarithmic plot of shear stress vs shear rate for the emulsion with benzene solutions of PB of 30 wt% and of PB of 30 wt% containing PIB of 1 wt%, respectively. The best straight-line fit was determined by the least-squares method with the plots in Figure 1. From the intercept and slope of the line, the values of K and n were evaluated. Also, Figure 2 shows the logarithmic plot of primary normal stress difference vs shear rate for the same solution in Figure 1. As shown in Figure 2, the plots are linear, but the values of the primary normal stress difference of emulsion with benzene and benzene solution of 30 wt% PB are zero. From the intercept and slope of the straight line in benzene solution of 30 wt% PB and 1 wt% PIB, the values of A and b were evaluated. The parameters, K, n, A, and b for the emulsion with benzene solution of various concentration of PB and PIB are give in Table 2.

As shown in Table 2, the w/o emulsion with benzene and benzene solution of PB show non-Newtonian liquid, and only the emulsion with benzene solutions of PIB show any measurable primary stress difference. Therefore, they are considered to be viscoelastic.

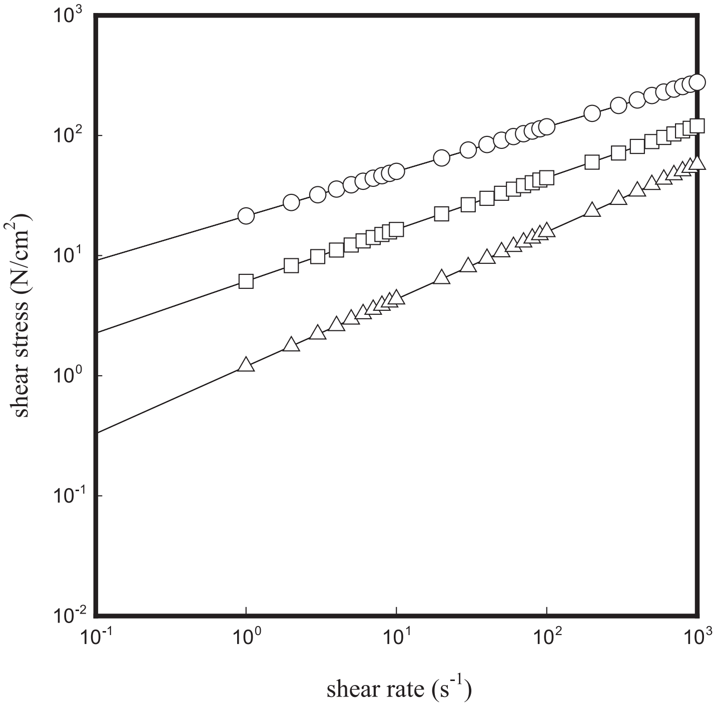

Figure 1. Shear stress of H_2O/(PIB/PB/Bz) emulsion as a function of shear rate. (△: Bz, □: Bz(30)/Bz, ○: PIB(1)/PB(30)/Bz).

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

$$\lambda = \frac{N_1}{\eta\gamma^2} \tag{4}$$

In terms of the parameters K, A, n, and b defined by Eqs. 1 and 3, the characteristic time, λ, can be expressed as

$$\lambda = \frac{A}{K}\gamma^{b-n-1} \tag{5}$$

From Eq. 5, the characteristic time is plotted against shear rate in Figure 3 with concentrations of PIB as a parameter in the benzene solution of PB 20 wt% using the rheological properties in Table 2. As shown in Figure 3, λ decreases as the shear rate increases, and the concentration of PIB

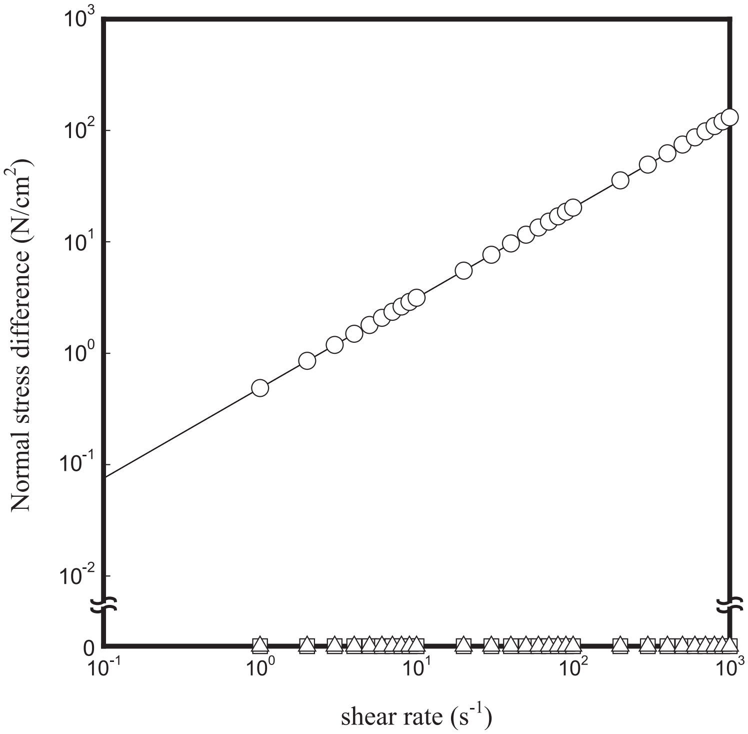

Figure 2. Normal stress difference of H_2O/(PIB/PB/Bz) emulsion as a function of shear rate. (△: Bz, □: Bz(30)/Bz, ○: PIB(1)/PB(30)/Bz).

decreases. This means that the more the concentration of PIB increases, the more the emulsion 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 against a characteristic process time, which is considered to be related in same way to the reciprocal of the impeller speed for stirred tanks, and it is derived with Eq. 5 as follows.

$$\mathrm{De} = \lambda \mathrm{N} = \frac{\mathrm{A}}{\mathrm{K}} \gamma^{\mathrm{b-n-1}} \mathrm{N} \tag{6}$$

It is obvious from Eq. 2 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

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

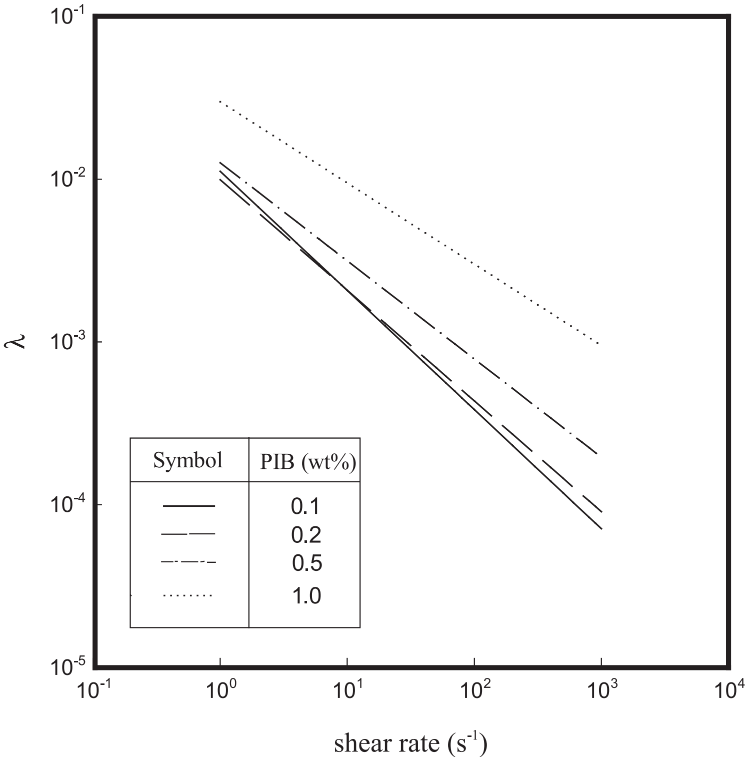

Figure 3. Characteristic times of emulsion as a function of shear rate at PB of 20 wt%.

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.[15] is defined as

$$\eta = \tau/\gamma_{\mathrm{avg}} \tag{7}$$

Metzner and Otto[16] found that in applying Eq. 7 to correlate rates of viscous dissipation in agitated vessels, the average shear rate γ_{avg} could be simply related to the impeller speed by

$$\gamma_{\mathrm{avg}} = A_sN \tag{8}$$

where 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 follows:

$$\gamma_{avg} = \frac{4\pi}{n} N \tag{9}$$

The viscosity of the power-law liquid is a function of shear rate, as shown in Eq. 2, and the average shear rate depends on the impeller speed in the baffled tank, as shown in Eq. 9. Therefore, the apparent viscosity can be estimated from the following equation, which is derived Eqs. 2 and 9.

$$\eta = K n^{1-n} (4\pi N)^{n-1} \tag{10}$$

Nishikawa et al.[15] correlated the average shear rate with the superficial gas velocity of air, U_G, in CMC solution of the bubble column by the equation, $\gamma_{avg} = 50\ U_G$. Yagi and Yoshida[1] related the average shear rate to the impeller speed, N, in the sparged agitated vessel by $\gamma_{avg} = 11.5$ N. Suh et al.[4] presented the effective shear rate correlatd with $U_G^{1/(n+1)}$ in the bubble column.

Calderbank and Moo-Young[17] extended the Metzner–Otto approach to allow the proportionality constant, As, in Eq. 8 to be a function of the flow behavior index, n

$$\gamma_{avg} = BN \left(\frac{4n}{3n+1} \right)^{\left(\frac{n}{1-n}\right)} \tag{11}$$

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[18] derived the apparent viscosity for the liquid and impeller used in their work from Eqs. 2 and 11.

$$\eta = K(11N)^{n-1} \left(\frac{3n+1}{4n} \right)^n \tag{12}$$

The apparent viscosity given by Eq. 10 or Eq. 12 depends upon not only the rheological properties, but also the agitation speed of impeller.

To observe the effect of the concentration of PIB and the speed of impeller on Deborah number, De, calculated from Eq. 6, is plotted against the concentration of PIB with the speed of the impeller as a parameter

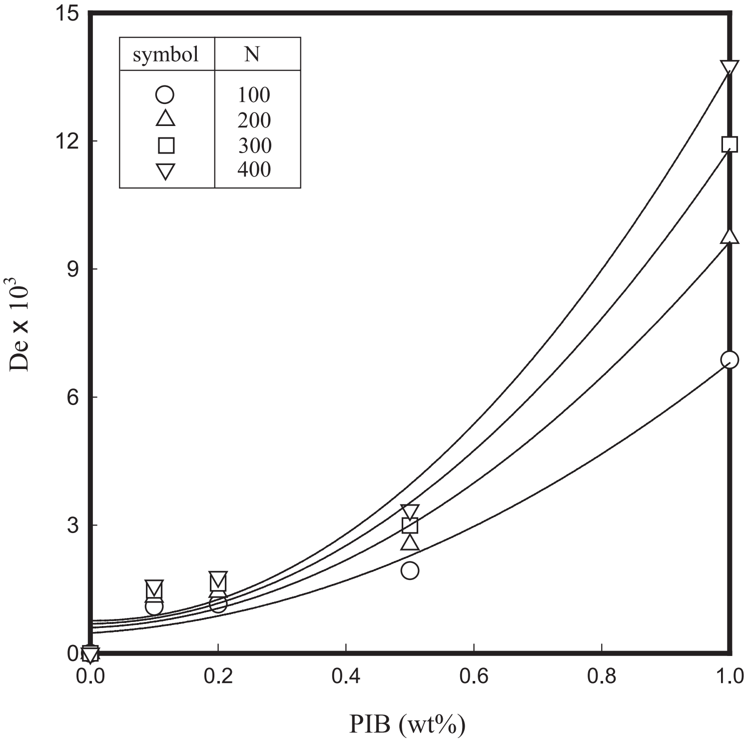

Figure 4. Effect of concentration of PIB on Deborah number at PB of 20 wt%.

in Figure 4, with the shear rate obtained from Eq. 9 for the typical concentration of PB of 20 wt%. As shown in Figure 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.

The diffusion coefficient of a solute of a small size, such as CO_2, O_2, or CH_4, in a polymer solution depends on the viscosity of the solution and the molecular weight of the polymer. The diffusion coefficient of CO_2 in the benzene solution was obtained from the following equation, suggested by Lohse et al.[19] which was modified from the Stoke–Einstein equation and correlated with the molecular weight of the polymer in the solution.

$$D_c/D_o = (\eta_o/\eta)^{3.7\sqrt{M_o/M_p}} \tag{13}$$

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

$$M_P = x_{PB} \times M_{PB} + x_{PIB} \times M_{PIB} \tag{14}$$

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,[20] and its value was 3.85×10^{-9} m^2/s.

In case a solute is absorbed into w/o emulsion, the presence of the microphase (dispersed phase) has an effect on the diffusivity of the solute in the continuous phase, and the effective diffusivity, D_{eff}, was obtained by the empirical equation[21] as follows:

$$\frac{D_{eff}}{D_c} = 1 + \frac{1.209(\alpha - 1)\varepsilon}{(1-\alpha)\varepsilon^{1/3} + 0.806\alpha} \tag{15}$$

where

$$\alpha = \frac{2\zeta}{\zeta - 1}\left(\frac{\zeta}{\zeta - 1}\ln\zeta - 1\right), \quad \zeta = \frac{m_A D_d}{D_c}$$

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, m_A.

The effective diffusivity of CO_2 in the w/o emulsion with the benzene solution of various concentrations of PB and PIB was calculated from Eq. 15 with D_c from Eq. 13, and are given in Table 2. As shown in Table 2, the effective diffusivity decreased as the concentration of PB decreased and as the concentration of PIB increased because of the elastic behavior of PIB.

Empirical Correlation

There have been several studies of gas absorption by agitated Newtonian liquids across a gas–liquid interface. Sandall and Patel[22] summarized this work and obtained data of their own. A dimensional analysis indicates that the mass-transfer coefficient may be corrected by an equation of form

$$k_L d/D_L = C(d^2 N\rho/\eta)^b(\eta/\rho D_L)^c \tag{16}$$

Sideman et al.[23] 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.

$$k_L a d^2/D_L = C(d^2 N\rho/\eta)^b(\eta/\rho D_L)^c(d v_s/\sigma)^e(\eta_g/\eta)^f \tag{17}$$

The term on the left side of Eq. 17 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. 16 and 17 cannot be used directly to correlate mass-transfer data with non-Newtonian liquids since the liquid viscosity that appears in these equations is not defined for non-Newtonian liquids. However in their work,[23] it is proposed to use an apparent viscosity as used by Sandall and Patel,[22] and Skelland and Dimmick[24] in correlating heat-transfer rates to non-Newtonian liquids in agitated vessels.

To observe the effect of the concentration of PIB with the impeller speed and size as parameters on the volumetric mass-transfer coefficient, the measured values of k_La in the emulsion with a concentration of PB of 20 wt% and 30 wt% were plotted against PIB concentrations in Figures 5 and 6. As shown in Figures 5 and 6, k_La increased with an increase in the speed, size of the impeller, and concentration of PIB. Also, k_La with PB of 20 wt% was larger than those of 30 wt%. PIB increased k_La in the range of PIB concentration below 0.2 wt% at an impeller size of 0.05 m and agitation speed of 200 rev/min.

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 a Schmidt number, defined as $\eta/\rho\ D_L$, in which the viscosity is related to the diffusion coefficient. As shown in Table 2, the effective diffusivity of CO_2 in the emulsion does not vary significantly from that for PB solution, and 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 emulsion in the agitated vessel depends on the speed of impeller and the rheological properties, as shown in Eq. 10 or Eq. 12.

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

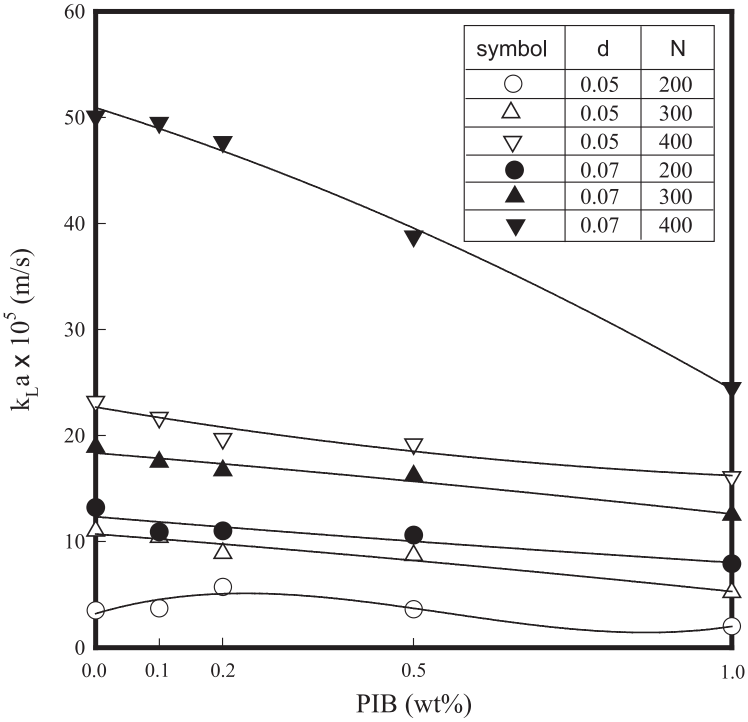

Figure 5. Effect of PIB concentration on the volumetric mass-transfer coefficient with impeller speed and size as parameters at PB of 20 wt%.

emulsion, Sherwood number, Sh, and Reynolds number, Re, are defined as follows:

$$\mathrm{Sh} = k_L a d^2 / D_{\mathrm{eff}} \tag{18}$$

$$\mathrm{Re} = d^2 N \rho / \eta \tag{19}$$

To correlate the volumetric mass-transfer coefficient with the operational variables by the dimensionless group, the Sherwood number is plotted against the Reynolds number with the experimental variables, such as the measured values of k_La of CO_2 in the emulsion with the benzene solution of PIB of $0 \sim 1$ wt%, and PB of 20 and 30 wt% at an impeller speed of 200 to 400 rev/min, with an impeller size of 0.05 and 0.07 m, the viscosity of the emulsion using Eq. 10, and physical properties, such as D_{eff} and ρ, in Table 2.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

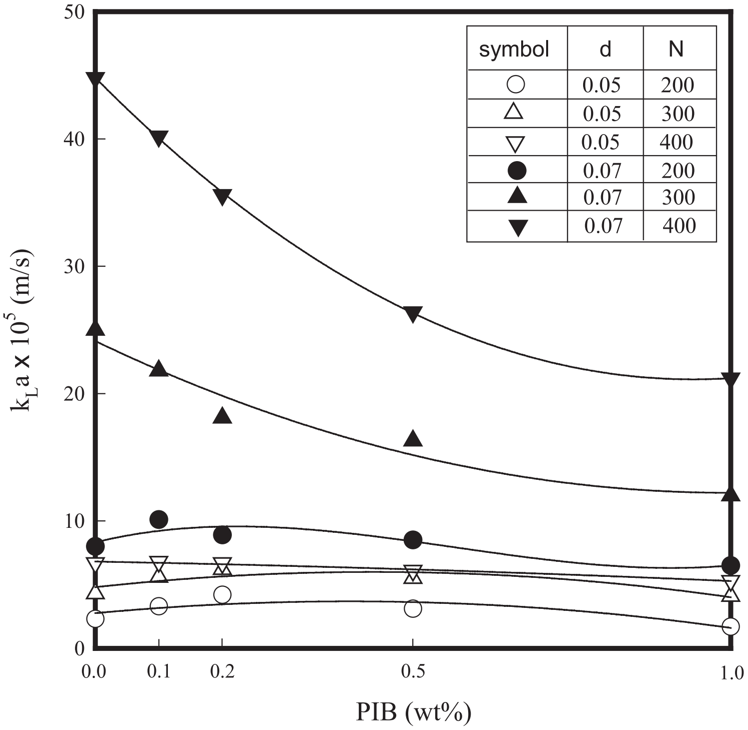

Figure 6. Effect of PIB concentration on the volumetric mass-transfer coefficient with impeller speed and size as parameters at PB of 30 wt%.

Figure 7 shows logarithmic plots of Sh against Re with several kinds of absorbents, in which the black circles, the black squares, and the empty circles represent the plots for benzene, emulsion with benzene and benzene solution of PB as continuous phase, and emulsion with benzene solution of PIB and PB as continuous phase, respectively. As shown in Figure 7, the plots in benzene are linear, but other plots are nonlinear and scattered far from the plots in benzene. The slope and intercept from the straight line of the plots in benzene by the least-squares method were obtained. Their values are 2.536 and 6.348×10^{-9}, with a standard deviation of 5.4%, respectively.

To lessen the deviation of the plots for emulsion of H_2O/Bz, H_2O/PB/Bz, and H_2O/PIB/PB/Bz from those in benzene as shown in Figure 7, a simple multiple regression exercise was used for the plots of Sh combined with the dimensionless ratio of viscosity, η/η_0, against Re in the case of

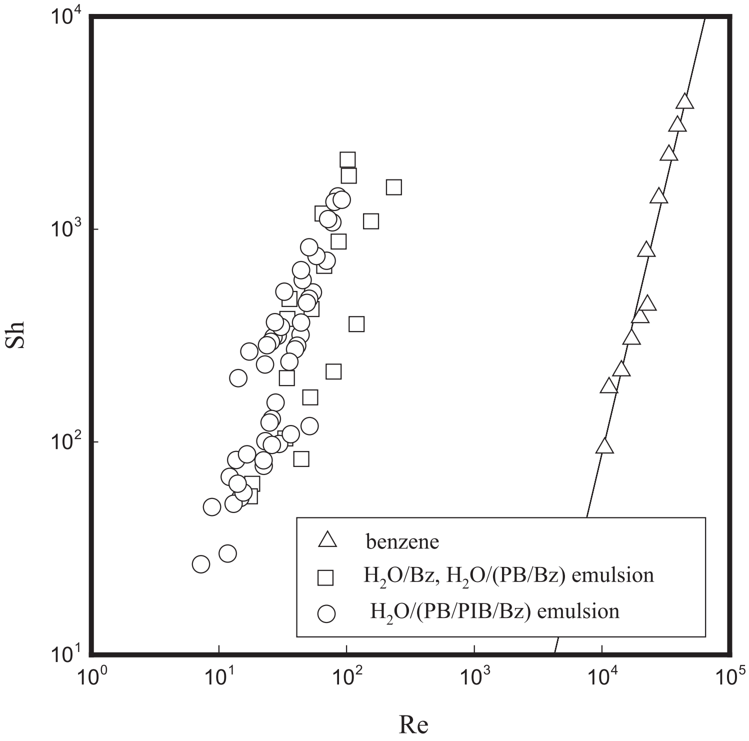

Figure 7. Dimensionless correlation of volumetric mass-transfer coefficient of CO_2 in Bz, H_2O/Bz, H_2O/PB-Bz, and H_2O/(PIB/PB/Bz) emulsion.

emulsion of H_2O/Bz, H_2O/PB/Bz, H_2O/PIB/PB/Bz. The best value of the exponent of the viscosity ratio is 2.397, with a standard deviation of 14.6%, for the emulsion with H_2O/Bz, H_2O/PB/Bz, and a standard deviation of 18.4%, for the emulsion with H_2O/PIB/PB/Bz, and the correlation is plotted in Figure 8. As shown in Figure 8, the plots for the emulsion of H_2O/Bz, H_2O/PB/Bz lie on a straight line, which presents the non-Newtonian behavior of pseudoplastic behavior.

It can be seen that all the data for the viscoelastic PIB solutions deviated considerably from the inelastic PB solutions. A new term of $Sh(\eta/\eta_0)^{-2.397}$ combined with the elasticity, such as $(1 + m_1De)^{m2}$ against Re, was used to apply the behavior of non-Newtonian viscoelastic liquid to the empirical term of $Sh(\eta/\eta_0)^{-2.397}$ in case of the emulsion with PB/Bz solution. A simple multiple regression exercise gave the values of m_1 and m_2, and their values are 2461.3 and 0.274, with a standard

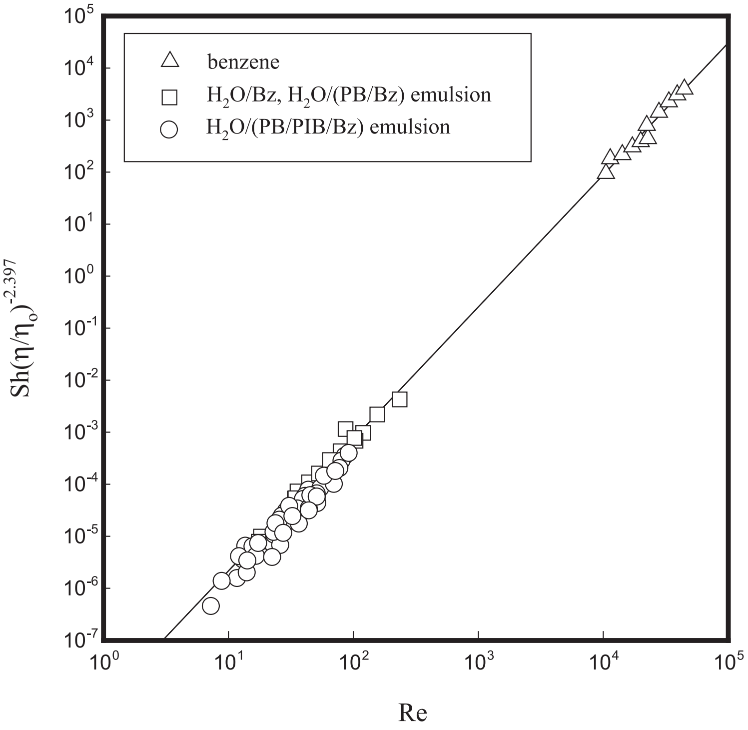

Figure 8. Dimensionless correlation of volumetric mass-transfer coefficient of CO_2 in Bz, H_2O/Bz, H_2O/(PB/Bz), and H_2O/(PIB/PB/Bz) emulsion with corrected specific viscosity.

deviation of 13.9%, respectively, as shown in Figure 9. Figure 9 shows that this deviation can be eliminated by including the Deborah number in the correlation.

It was reported that the effect of surface tension as one of the properties of liquids on the volumetric mass-transfer coefficient was found to be significant in a bubble or sparged column for the gas absorption into Newtonian and non-Newtonian fluids.[3–6,18] They showed an empirical dimensionless equation containing Sh correlated with a Bond number, B_0, defined as $gd^2\rho/\sigma$. Because the contact type and the absorbent in this study are different from those used in the previously cited research, the dimensionless group is used as the ratio of interfacial tension between water and the benzene solution of PIB and PB to that between water and

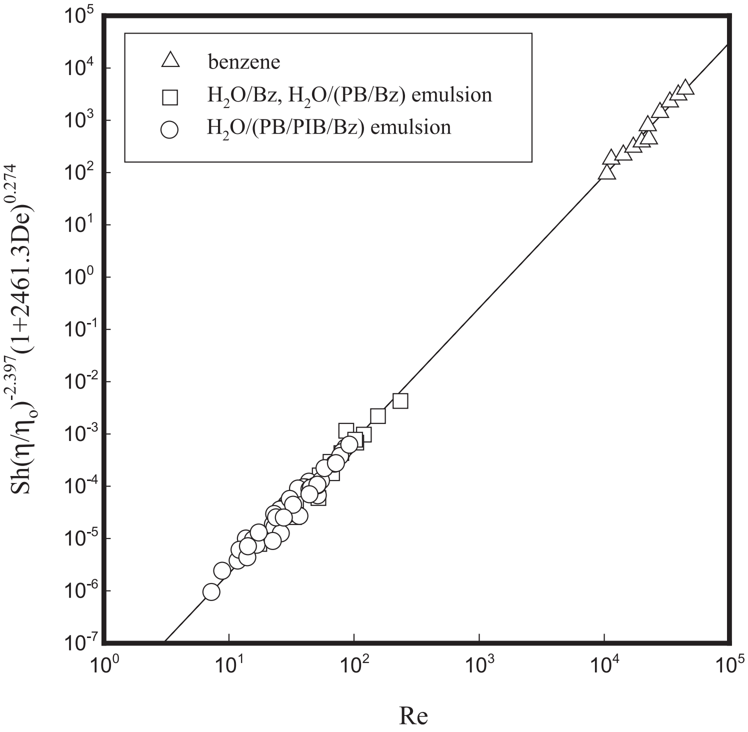

Figure 9. Dimensionless correlation of volumetric mass-transfer coefficient of CO_2 in Bz, H_2O/Bz, H_2O/(PB/Bz), H_2O/(PIB/PB/Bz) emulsion incorporating Deborah number.

the benzene solution of PB, σ/σ_0, rather than to use B_0 to effect the interfacial tension on k_La.

A new term of $Sh(\eta/\eta_0)^{-2.397}$ $(1+2461.3De)^{0.274}$ combined the ratio of the interfacial tension, $(\sigma/\sigma_0)^{m3}$ against Re was used to apply the behavior of non-Newtonian liquid to the empirical term of $Sh(\eta/\eta_0)^{-2.397}$ $(1+2461.3De)^{0.274}$ in case of the emulsion with PIB/PB/Bz solution. A simple multiple regression exercise gave the value of m_3, and its value is 0.039 with a standard deviation of 13.8%, as shown in Figure 10.

Comparing, Figure 9 to Figure 10, the standard deviations of the data; the former of 13.9%, the latter of 13.8%, are the same as each other, because the change of the interfacial tension according to the change of PIB concentration are small in the range of PIB concentrations used in this

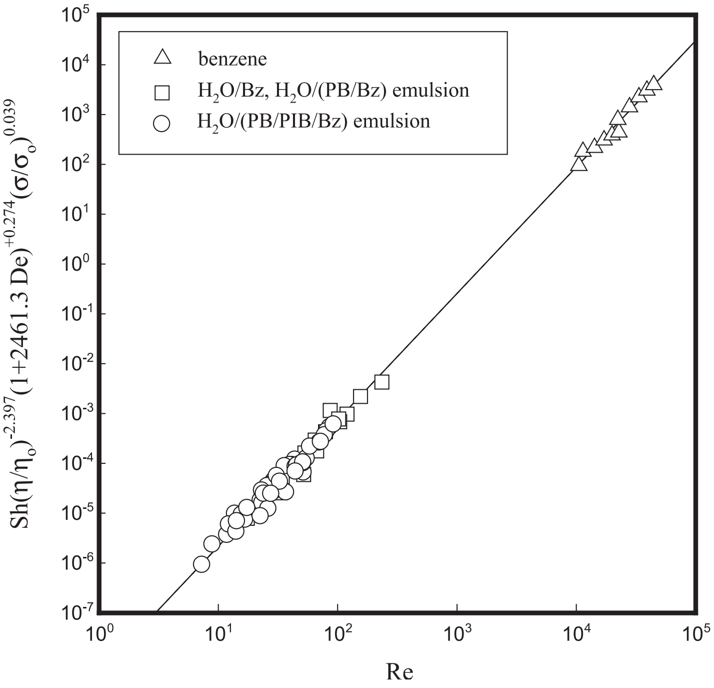

Figure 10. Dimensionless correlation of volumetric mass-transfer coefficient of CO_2 in Bz, H_2O/Bz, H_2O/(PB/Bz), H_2O/(PIB/PB/Bz) emulsion with corrected interfacial tension.

study. But the term explaining the corrected interfacial tension could be used to correlate the volumetric mass-transfer coefficient with the dimensionless groups.

Using a total of 77 data points for twelve different solutions, multiple regression analysis came up with a correlation as follows:

$$k_La d^2/D_{eff} = 6.348\times10^{-9}(d^2N\rho/\eta)^{2.536}(\eta/\eta_o)^{2.397} \times(1+2461.3De)^{-0.274}(\sigma/\sigma_o)^{-0.039} \quad (20)$$

When we analyze Eq. 20 for the overall effect of viscosity on the mass-transfer coefficient, it comes out as $k_La \propto \eta^{-0.139}$, which compares with the findings of Yagi and Yoshida,[1] Ranade and Ulbrecht,[2] and Perez and Sandall,[18] where their values were -0.36.

Figure 11 shows that all of the k_La data with Newtonian (benzene) and non-Newtonian liquids of the emulsion with H_2O/Bz, H_2O/PB/Bz, and H_2O/

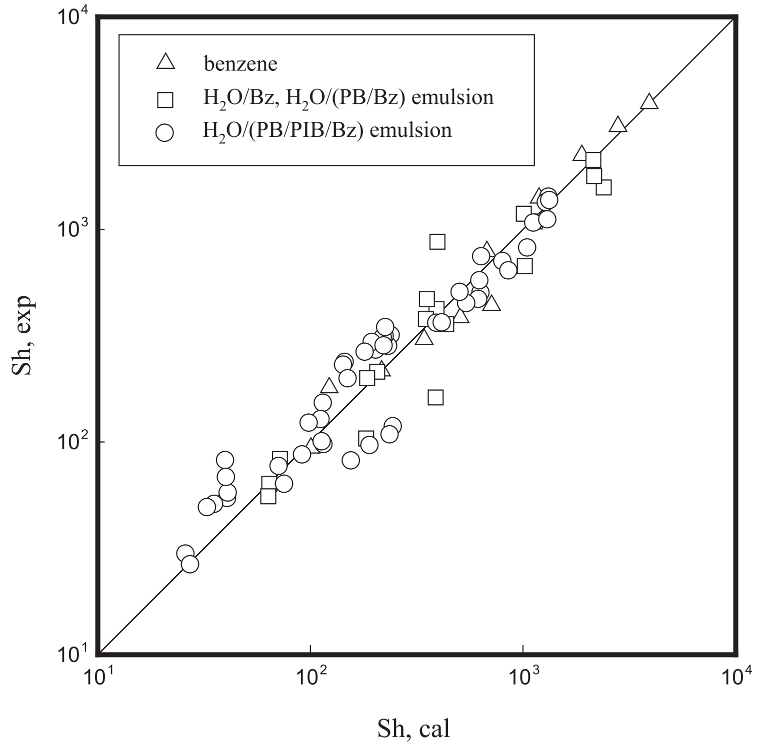

Figure 11. Comparison of volumetric mass-transfer coefficient data for non-Newtonian liquids with proposed correlation.

PIB/PB/Bz of various concentrations of PB and PIB at impeller sizes of 0.05 and 0.07 m and agitation speeds of 200, 300, and 400 rev/min agree with a standard deviation of 13.8% and a mean deviation of 29.4%, with the prediction by Eq. 20.

CONCLUSION

Absorption rates of carbon dioxide into the emulsion consisted of a benzene solution of PB and PIB as continuous phase, and water as dispersed phase, were measured in an agitated vessel of 0.1-m diameter with two sizes of impellers, 0.05 and 0.07 m, at an agitation speed of 200, 300, and 400 rev/min, where the concentration range of PIB were 0.1 to 1.0 wt%, and those of PB, 20 and 30 wt%. The emulsion of H_2O/Bz and H_2O/

PB/Bz looks like a pseudoplasic fluid, and that of H_2O/PIB/PB/Bz does like viscoelastic fluid. The measured rheological properties of the emulsion, such as n, K, b, and A, were used to correlate the characteristic time presenting the elastic properties with the volumetric mass-transfer coefficient based on Newtonian liquid of benzene. The elastic properties, considered in the form of a Deborah number, were found to decrease the value of the volumetric mass transfer coefficient.

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

$$\begin{aligned} k_L a d^2/D_{eff} &= 6.348 \times 10^{-9}(d^2 N\rho/\eta)^{2.536}(\eta/\eta_o)^{2.397} \\ &\quad \times (1 + 2461.3De)^{-0.274}(\sigma/\sigma_o)^{-0.039} \end{aligned}$$

ACKNOWLEDGMENT

This work was supported by grant No. (R01-2000-00326) from the Basic Research Program of the Korea Science & Engineering Foundation.

NOMENCLATURE

A	rheological properties defined as in Eq. 3, (Ns^b/m^2)
a	contact area at interface of gas–liquid per liquid volume, (1/m)
b	rheological properties defined as in Eq. 3
B_o	Bond number defined as gd^2/σ
C_{Ai}	solubilities of CO_2 in absorbent, ($kmol/m^3$)
d	diameter of impeller, (m)
D_c	diffusivity of CO_2 in benzene solution, (m^2/s)
De	Deborah number defined as in Eq. 6
D_{eff}	effective diffusivity of CO_2 in emulsion, (m^2/s)
D_o	diffusivity of CO_2 in benzene, (m^2/s)
K	rheological properties defined as in Eq. 1, (Ns^n/m^2)
k_L	liquid side mass-transfer coefficient of CO_2, (m/s)
k_La	volumetric mass-transfer coefficient, (1/s)
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	ratio of the solubility of CO_2 in water to that in benzene solution
n	rheological properties defined as in Eq. 1

N	impeller speed, (1/s)
N_1	primary normal stress difference defined as in Eq. 3, (N/m^2)
Re	modified Reynold number defined as $d^2N\rho/\eta$
Sh	modified Sherwood number defined as k_Lad^2/D_{eff}
v_s	superficial gas velocity, (m/s)
x_{PB}	mole fraction of PB
x_{PIB}	mole fraction of PIB

Greek Letters

γ	shear rate, (1/s)
γ_{avg}	average 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 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)
τ	shear stress, (N/m^2)

REFERENCES

1. Yagi, H.; Yoshida, F. Gas absorption by Newtonian and non-Newtonian fluids in sparged agitated vessel. Ind. Eng. Chem. Process Des. Dev. **1975**, *14* (4), 488–493.
2. Ranade, V.R.; Ulbrecht, J.J. Influence of polymer additives on the gas–liquid mass transfer in stirred tanks. AIChE. J. **1978**, *24* (5), 796–803.
3. Nakanoh, M.; Yoshida, F. Gas absorption by Newtonian and non-Newtonian liquids in a bubble column. Ind. Eng. Chem. Process Des. Dev. **1980**, *19* (1), 190–195.
4. Suh, I.-S.; Schumpe, A.; Deckwer, W.-D. Gas–liquid mass transfer in the bubble column with viscoelastic liquid can. J. Chem. Eng. **1991**, *69*, 506–512.
5. Vlaev, S.D.; Valeva, M.; Popov, R. Gas–liquid mass transfer in stirred non-Newtonian corn-starch dispersions. J. Chem. Eng. Jpn. **1994**, *27* (6), 723–726.
6. Kawase, Y.; Halard, B.; Moo-Young, M. Theoretical prediction of

volumetric mass transfer coefficients in bubble columns for Newtonian and non-Newtonian fluids. Chem. Eng. Sci. **1987**, *42* (7), 1609–1617.

7. Linek, V.; Benes, P.A. Study of the mechanism of gas absorption into oil–water emulsions. Chem. Eng. Sci. **1976**, *31*, 1037–1046.
8. Bruining, W.J.; Joosten, G.E.H.; Beenackers, A.A.C.M.; Hofman, H. Enhancement of gas–liquid mass transfer by a dispersed second liqiud phase. Chem. Eng. Sci. **1986**, *41* (7), 1873–1877.
9. Mehra, A.; Pandit, A.; Sharma, M.M. Inensification of multiphase reactions through the use of a microphase—II. Exp. Chem. Eng. Sci. **1988**, *43* (4), 913–927.
10. Park, S.W.; Cho, H.B.; Sohn, I.J.; Kumazawa, H. Gas absorption into w/o emulsion with aqueous amine liquid droplets. Sep. Sci. Technol. **2002**, *37* (3), 639–661.
11. Park, S.W.; Sohn, I.J.; Park, D.W.; Oh, K.J. Absorption of carbon dioxide into non-Newtonian liquid. I. Effect of viscoelasticity. Sep. Sci. Technol. **2002**, *38* (6), 1361–1384.
12. Totiwachwuthikul, P.; Meisen, A.; Lim, C.J. Solubility of CO_2 in 2-amino-2-methyl-1-propanol solutions. J. Chem. Eng. Data **1991**, *36*, 130–133.
13. Kennard, M.L.; Meisen, A. Solubility of carbon dioxide in aqueous diethanolamine solutions at elevated temperature and pressures. J. Chem. Eng. Data **1984**, *29*, 309–312.
14. Kay, M.; McClure, D.W. A simple, surface and interfacial tension experiment. J. Chem. Educ. **1970**, *47* (7), 540–541.
15. Nishkawa, M.; Kato, H.; Hashimoto, H. Heat transfer in aerated tower filled with non-Newtonian liquid. Ind. Eng. Chem. Process Des. Dev. **1977**, *16*, 133–137.
16. Metzner, A.B.; Otto, R.E. Agitation of non-Newtonian fluids. AIChE. J. **1957**, *3* (1), 3–10.
17. Calderbank, P.H.; Moo-Young, M.B. The power characteristics of agitators for the mixing of Newtonian and non-Newtonian fluids. Trans. Inst. Chem. Eng. **1959**, *37*, 173–185.
18. Perez, J.F.; Sandall, O.C. Gas absorption by non-Newtonian fluid in agitated vessel. AIChE. **1974**, *20* (4), 770–775.
19. Lohse, M.; Quicker, G.; Deckwer, D.-W. Diffusivity and solubility of carbon dioxide in diluted polymer solutions. AIChE. J. **1981**, *27* (4), 626–631.
20. Danckwerts, P.V. *Gas–Liquid Reactions*; McGraw-Hill Book Company: New York, 1970; 15.
21. Wubs, H.J.; Beenackers, A.A.C.M.; Krishna, R. Absorption of hydrogen sulfide in aqueous solutions of iodine—a critical review. Chem. Eng. Sci. **1991**, *46* (2), 703–706.

22. Sandall, O.C.; Patel, K.G. Heat transfer to non-Newtonian pseudoplastic fluids in agitated vessels. Ind. Eng. Chem. Process Des. Dev. **1970**, *9* (1), 139–144.
23. Sideman, S.; Hortacsu, O.; Fulton, J.W. Mass transfer in gas–liquid contacting systems. Ind. Eng. Chem. **1966**, *58* (7), 32–47.
24. Skelland, A.H.P.; Dimmick, G.R. Heat transfer between coils and non-Newtonian fluids with propeller agitation. Ind. Eng. Chem. Process Des. Dev. **1969**, *8*, 267–274.

Received December 2002
Revised March 2003