Desorption of Carbon Dioxide from Aqueous Electrolyte Solutions Supersaturated with Carbon Dioxide in an Agitated Vessel

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In a previous paper (Hikita and Konishi, 1984), the mechanism of the bubbling desorption of carbon dioxide from supersaturated water in a baffled agitated vessel has been reported, and the empirical correlations of the volumetric liquid phase mass transfer coefficient for the bubbles in the agitated liquid and of the enhancement factor for the volumetric mass transfer coefficient for the free liquid surface due to bubbling have been presented. However, for the analysis of the experimental data on the chemical absorption accompanied by the bubbling desorption of volatile reaction products, it is desirable to know the effect of the presence of electrolyte on the mass transfer characteristics. In this work, the experiments were carried out on the desorption of carbon dioxide from aqueous electrolyte solutions supersaturated with carbon dioxide using the same agitated vessel as used in the previous work (Hikita and Konishi, 1984), and the effect of the presence of electrolyte in water on the volumetric mass transfer coefficient for the bubbles and the enhancement factor of the volumetric mass transfer coefficient for the free liquid surface was studied.

EXPERIMENTAL

The experimental apparatus and the procedure were almost the same as those in the previous work (Hikita and Konishi, 1984). The baffled agitated vessel of 12.3 cm I.D., in which the liquid level was kept equal to the vessel diameter, was used as the carbon dioxide desorber. All the desorption experiments were carried out in a continuous manner with respect to both the gas and liquid, and the liquid temperature was kept at 25°C.

The desorbing liquids used were aqueous electrolyte solutions supersaturated with carbon dioxide. Sodium chloride, sodium sulfate, barium chloride, and sodium bicarbonate were used as the electrolytes. The carbon dioxide was desorbed from the aqueous electrolyte solutions into pure carbon dioxide stream saturated with water vapor. The partial pressure of carbon dioxide in the gas phase was constant at 98.2 kPa. For the case of aqueous barium chloride solutions, the experiments were also performed on the desorption of carbon dioxide into pure nitrogen stream saturated with water vapor. In this case, the carbon dioxide partial pressure was varied from 0.146 to 2.39 kPa. The gas stirrer was driven at a constant speed of 9.17 s^{-1}, and the stirring speeds of the liquid stirrer were 1.00, 1.67, 3.33, and 5.00 s^{-1}. The experimental conditions are listed in Table 1.

The physical properties of the electrolyte solutions used are also given in Table 1. The saturated concentrations C_s of carbon dioxide in aqueous electrolyte solutions were predicted from the partial pressure of carbon dioxide in gas phase and the Henry's law constant for carbon dioxide in water at 25°C, 2,990 Pa·m^3/mol (Linke and Seidell, 1958), by correcting for the salting-out effect according to the method of van Krevelen and Hoftijzer (1948). The diffusivities D_L of carbon dioxide in aqueous electrolyte solutions were estimated from the value of 1.97×10^{-9} m^2/s for carbon dioxide in water at 25°C (Peaceman, 1951) by using the method of Ratcliff and Holdcroft (1963). The volumetric liquid phase mass transfer coefficient $k_{Lf}a_f$ for the free liquid surface in the agitated vessel under nonbubbling conditions was calculated from the value of the liquid phase mass transfer coefficient k_{Lf}, which was predicted from the empirical equation in the previous work (Hikita et al., 1975), and the value of the effective interfacial area A_f, which was assumed to be the same as the geometric interfacial area. The densities and viscosities of the solutions were measured by conventional methods.

RESULTS AND DISCUSSION

For the aqueous barium chloride solutions, both the carbon dioxide desorption rates into carbon dioxide stream and into nitrogen stream were measured under conditions where the barium chloride concentration, the liquid phase Reynolds number *Re* and the relative supersaturation σ of the solution were kept the same. In this case, therefore, the volumetric liquid phase mass transfer coefficient $k_{Lb}a_b$ for the bubbles generated in the agitated liquid

TABLE 1. EXPERIMENTAL CONDITIONS AND PHYSICAL PROPERTIES OF SOLUTIONS USED

Electrolyte	Conc. of Electrolyte, mol/m^3	Saturated Conc. of CO_2, C_s, mol/m^3	Relative supersaturation, σ	*Re*	$D_L \times 10^9$, m^2/s	$k_{Lf}a_f \times 10^4$, s^{-1}
NaCl	500	29.3	0.118–0.603	4,530, 13,600	1.90	1.15, 2.48
	1,000	26.2	0.109–0.589	4,410, 13,200	1.82	1.11, 2.39
	2,000	20.9	0.123–0.564	4,180, 12,500	1.67	1.03, 2.21
Na_2SO_4	125	30.1	0.121–0.600	4,490, 13,500	1.92	1.15, 2.49
	250	27.7	0.112–0.798	4,340, 13,000	1.86	1.12, 2.41
$BaCl_2$	500	26.3	0.102–0.564	4,500, 13,500	1.82	1.12, 2.41
	700	24.1	0.0738–0.661	2,650 8,820	1.76	1.08, 2.34
$NaHCO_3$	125	31.0	0.110–0.386	4,460, 13,400	1.94	1.16, 2.50
	250	29.3	0.130–0.539	4,380, 13,100	1.90	1.14, 2.45
	500	26.2	0.126–0.498	4,240, 12,700	1.83	1.10, 2.37

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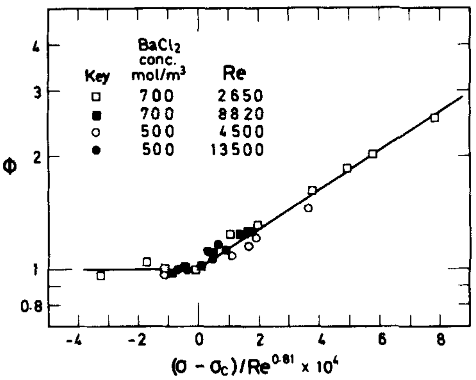

Figure 1. Enhancement factor ϕ for the bubbling desorption of carbon dioxide from aqueous barium chloride solutions at 25°C.

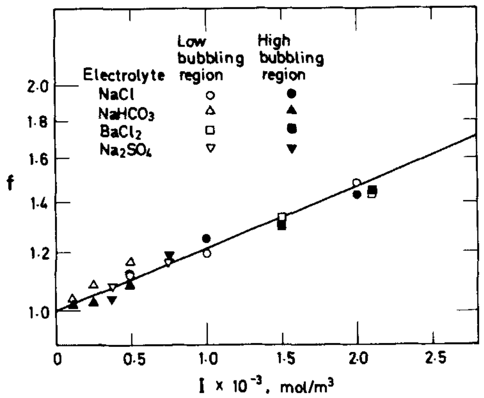

Figure 3. Effect of the presence of electrolyte on $k_{Lb}a_b$ as a function of ionic strength of the solution.

and the enhancement factor ϕ of the volumetric mass transfer coefficient $k_{Lf}a_f$ for the free liquid surface due to the bubbling in the liquid could be simultaneously determined from the measured desorption rates using the same equation as presented previously (Hikita and Konishi, 1984).

In Figure 1, the observed values of ϕ for the bubbling desorption of carbon dioxide from 500 and 700 mol/m^3 aqueous barium chloride solutions obtained at various Re values are plotted on semilogarithmic coordinates against the value of $(\sigma - \sigma_c)Re^{-0.81}$. Two solid straight lines in this figure represent the following equations, which were obtained for the ϕ value for pure water in the previous work (Hikita and Konishi, 1984).

For the low bubbling region ($\sigma < \sigma_c$)

$$\phi = 1 \tag{1}$$

and for the high bubbling region ($\sigma > \sigma_c$)

$$\log\phi = 522(\sigma - \sigma_c)Re^{-0.81} \tag{2}$$

where σ_c is the value of σ at the intersection of Eqs. 1 and 2 and is given by

$$\sigma_c = 1.81\, Re^{-0.25} \tag{3}$$

As can be seen in Figure 1, the observed ϕ values are in good agreement with the solid lines with an average deviation of 3.2%. This indicates that the presence of electrolyte in water does not appreciably affect the ϕ value. Therefore, it was assumed that for the desorption of carbon dioxide from aqueous solutions of electrolytes other than barium chloride the enhancement factor ϕ was independent of the presence of electrolyte.

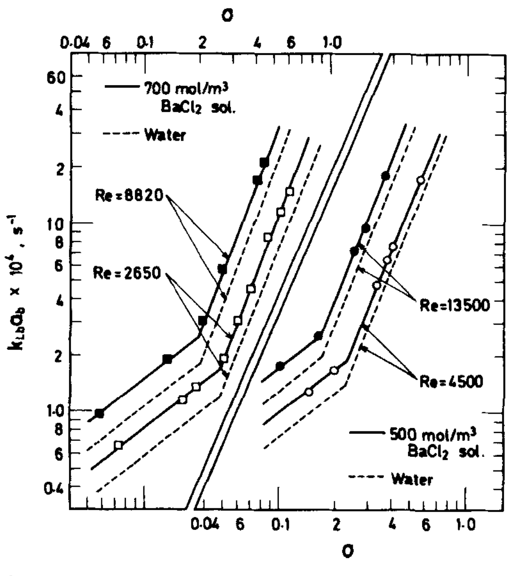

Figure 2. Volumetric liquid phase mass transfer coefficient for bubbles $k_{Lb}a_b$ for the bubbling desorption of carbon dioxide from aqueous barium chloride solutions at 25°C.

In Figure 2, the observed values of $k_{Lb}a_b$ for the bubbling desorption of carbon dioxide from 500 and 700 mol/m^3 aqueous barium chloride solutions are plotted on logarithmic coordinates against the σ value of the solution with the Re value as parameter. The dashed lines in this figure represent the $k_{Lb}a_b$ values for the bubbling desorption of carbon dioxide from supersaturated water and were calculated from the following empirical equations presented in the previous paper (Hikita and Konishi, 1984).

For the low bubbling region ($\sigma < \sigma_c$)

$$k_{Lb}a_b = 6.77 \times 10^{-6}Re^{0.50}\sigma^{0.78} \tag{4}$$

and for the high bubbling region ($\sigma > \sigma_c$)

$$k_{Lb}a_b = 2.45 \times 10^{-6}Re^{0.93}\sigma^{2.5} \tag{5}$$

As can be seen in this figure, the $k_{Lb}a_b$ value in the low bubbling region is proportional to the 0.78 power of σ, while the $k_{Lb}a_b$ value in the high bubbling region varies as the 2.5 power of σ, in the same manner as for the $k_{Lb}a_b$ value for the bubbling desorption of carbon dioxide from supersaturated pure water. The cross-plot of $k_{Lb}a_b$ vs. Re at a constant value of σ shows that the $k_{Lb}a_b$ value varies as $Re^{0.50}$ in the low bubbling region and as $Re^{0.93}$ in the high bubbling region, as well as for the $k_{Lb}a_b$ value obtained for the supersaturated water. Further, it can be seen that the $k_{Lb}a_b$ values for aqueous barium chloride solutions are somewhat larger than those for water.

For the carbon dioxide desorption from the aqueous solutions of electrolytes other than barium chloride, the $k_{Lb}a_b$ values were obtained from the measured desorption rates into carbon dioxide stream by using the following equation:

$$k_{Lb}a_b = \frac{N - \phi k_{Lf}a_f V(C - C_s)}{V(C - C_s)} \tag{6}$$

where N is the carbon dioxide desorption rate, V is the volume of the agitated liquid, C is the bulk concentration of carbon dioxide, C_s is the saturated concentration of carbon dioxide, and $k_{Lf}a_f$ is the volumetric liquid phase mass transfer coefficient for the free liquid surface. The ϕ value for each electrolyte solution was calculated from Eqs. 1 and 2.

The effects of σ and Re on the $k_{Lb}a_b$ value for all the aqueous electrolyte solutions used in the present work were found to be the same as those for pure water. Thus, the $k_{Lb}a_b$ values for the electrolyte solutions can be correlated by the following equations.

For the low bubbling region ($\sigma < \sigma_c$)

$$k_{Lb}a_b = cRe^{0.50}\sigma^{0.78} \tag{7}$$

and for the high bubbling region ($\sigma > \sigma_c$)

$$k_{Lb}a_b = c'Re^{0.93}\sigma^{2.5} \tag{8}$$

where the coefficients c and c' depend on the nature and concentration of the electrolyte.

In Figure 3, the ratios of the coefficients c and c' calculated for each electrolyte solution to the coefficients in Eqs. 4 and 5, respectively—i.e, $c/6.77 \times 10^{-6}$ and $c'/2.45 \times 10^{-6}$—are plotted on semilogarithmic coordinates against the ionic strength I of the electrolyte solution. The ratio $c/6.77 \times 10^{-6}$ or $c'/2.45 \times 10^{-6}$, which will hereafter be designated as f, is the correction factor, i.e., the factor by which the $k_{Lb}a_b$ value is increased by the presence of electrolyte in water. It can be seen that the ratio f increases with an increase in the value of I. The larger $k_{Lb}a_b$ values for the electrolyte solutions may be explained by the increase in the interfacial area a_b caused by the occurrence of small bubbles owing to the coalescence hindering property of the electrolyte solutions (Zieminski and Whittemore, 1971; Burckhart and Deckwer, 1975). The solid straight line through the data points is represented by the following equation.

For $0 < I < 2{,}100$ mol/m^3

$$f = c/6.77 \times 10^{-6} = c'/2.45 \times 10^{-6} = 10^{8.36\times10^{-5}I} \qquad (9)$$

All the values of f obtained in both the low and high bubbling regions agree well with the above equation with an average deviation of 3.5%. Thus, the $k_{Lb}a_b$ value for the desorption of carbon dioxide from the electrolyte solutions can be calculated from Eqs. 7 to 9.

NOTATION

C = bulk concentration of dissolved carbon dioxide in solution, mol/m^3
C_s = saturated concentration of dissolved carbon dioxide in solution, mol/m^3
c,c' = coefficients in Eqs. 7 and 8, s^{-1}
D_L = liquid-phase diffusivity of dissolved carbon dioxide, m^2/s
f = correction factor for effect of presence of electrolyte in water
I = ionic strength of electrolyte solution, mol/m^3
$k_{Lb}a_b$ = volumetric liquid-phase mass transfer coefficient for bubbles, s^{-1}
$k_{Lf}a_f$ = volumetric liquid-phase mass transfer coefficient for free liquid surface, s^{-1}
N = measured desorption rate of carbon dioxide into pure carbon dioxide stream, mol/s
Re = liquid-phase Reynolds number
V = volume of liquid in vessel, m^3

Greek Letters

σ = relative supersaturation of solution, $(C - C_s)/C_s$
σ_c = relative supersaturation at intersection of Eqs. 1 and 2 or Eqs. 4 and 5
ϕ = enhancement factor of $k_{Lf}a_f$ due to bubbling

LITERATURE CITED

Burckhart, R., and W. D. Deckwer, "Bubble Size Distribution and Interfacial Areas of Electrolyte Solutions in Bubble Columns," *Chem. Eng. Sci.*, **30**, 351 (1975).

Hikita, H., S. Asai, H. Ishikawa, and Y. Saito, "Kinetics of Absorption of Chlorine in Aqueous Acidic Solutions of Ferrous Chloride," *Chem. Eng. Sci.*, **30**, 607 (1975).

Hikita, H., and Y. Konishi, "Desorption of Carbon Dioxide from Supersaturated Water in an Agitated Vessel," *AIChE J.*, **30**, 945 (1984).

Linke, W. F., and A. Seidell, *Solubilities of Iorganic and Metal-Organic Compounds*, 4th Ed., I, 459, van Nostrand, New York (1958).

Peaceman, D. W., "Liquid-Side Resistance in Gas Absorption with and without Chemical Reaction," Sc.D. Thesis, Massachusetts Institute of Technology (1951).

Ratcliff, G. A., and J. G. Holdcroft, "Diffusivities of Gases in Aqueous Electrolyte Solutions," *Trans. Inst. Chem. Engrs.*, **41**, 315 (1963).

van Krevelen, D. W., and P. J. Hoftijzer, "On the Solubility of a Gas in Aqueous Solutions," *21st Int. Congr. Ind. Chem., Brussels*, 168 (1948).

Zieminski, S. A., and R. C. Whittemore, "Behavior of Gas Bubbles in Aqueous Electrolyte Solutions," *Chem. Eng. Sci.*, **26**, 509 (1971).

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