The application of our previously reported idea to the three-phase distillation column is quite successful, thus presenting a powerful procedure. The present procedure has the simplicity of the boiling point type method as well as great stability in finding out rigorous solutions satisfying all the basic equations derived.

Nomenclature

F	= flow rate of feed stream	[g-mol/h]
H	= molar enthalpy of vapor	[J/g-mol]
H^*	= molar enthalpy of vapor of pure component	[J/g-mol]
H_F	= molar enthalpy of feed	[J/g-mol]
h	= molar enthalpy of liquid	[J/g-mol]
h^*	= molar enthalpy of liquid of pure component	[J/g-mol]
K	= vapor-liquid equilibrium ratio	[—]
K^+	= liquid-liquid equilibrium ratio	[—]
L	= flow rate of liquid stream	[g-mol/h]
$\bar{L}$	= overall flow rate of liquid stream defined by Eq. (4)	[g-mol/h]
m	= total number of components	[—]
N	= number of total theoretical stages	[—]
R	= reflux ratio	[—]

T	= temperature	[K]
U	= flow rate of liquid sidestream	[g-mol/h]
V	= flow rate of vapor stream	[g-mol/h]
W	= flow rate of vapor sidestream	[g-mol/h]
x	= liquid mole fraction	[—]
$\bar{x}$	= overall liquid mole fraction defined by Eq. (1)	[—]
y	= vapor mole fraction	[—]
z_F	= feed mole fraction	[—]

η = phase-splitting parameter defined by Eq. (4) [—]

<Subscripts>

i	= component index
j	= stage index

<Superscript>

'	= second liquid phase
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Literature Cited

- 1) Block, U. and B. Hegner: *AIChE J.*, **22**, 582 (1976).
- 2) Ferraris, G. B. and M. Morbidelli: *AIChE J.*, **27**, 881 (1981).
- 3) Kinoshita, M., I. Hashimoto and T. Takamatsu: *J. Chem. Eng. Japan*, **16**, 370 (1983).
- 4) Nelder, J. A. and R. Mead: *Comput. J.*, **7**, 308 (1965).
- 5) Renon, H. and J. M. Prausnitz: *AIChE J.*, **14**, 135 (1968).

EFFECT OF CHLORINE HYDROLYSIS REACTION ON ABSORPTION OF CHLORINE INTO AQUEOUS SODIUM BICARBONATE SOLUTIONS

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In a previous paper⁵⁾ the authors reported on the kinetics of the absorption of Cl_2 into aqueous NaHCO_3 solutions accompanied by the desorption of CO_2 in a baffled agitated vessel operated batchwise. The measured absorption rates of Cl_2 and the desorption rates of CO_2 were in good agreement with the theoretical predictions from the chemical absorption theory based on the Lévêque model, which assumes no effect of the Cl_2 hydrolysis reaction. For absorption into dilute NaHCO_3 solutions, however, the Cl_2 hydrolysis reaction may be considered to make an appreciable contribution to the absorption rate of Cl_2 . In the present work, absorption experiments were carried out in the same agitated vessel as in the previous work⁵⁾ using a very dilute NaHCO_3 solution of $B_f = 33.0 \text{ mol/m}^3$. The present experimen-

tal results and the previous data⁵⁾ obtained with NaHCO_3 solutions of concentrations below 254 mol/m^3 were analyzed by the chemical absorption theory which takes into account the effect of the Cl_2 hydrolysis reaction.

1. Chemical Absorption Mechanism

When Cl_2 is absorbed into aqueous NaHCO_3 solutions, the following reactions may take place in the liquid phase:

Reactions (1) and (3) are instantaneous irreversible

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reactions and reactions (2) and (4) are reversible reactions of finite reaction rates, as discussed in the previous paper.⁵⁾ Therefore, the absorption of Cl_2 into aqueous NaHCO_3 solutions can be regarded as a process of absorption accompanied by two instantaneous irreversible reactions represented by reactions (1) and (3) and two reversible reactions of finite reaction rates represented by reactions (2) and (4).

According to the reaction scheme described above, the concentration profile of each species in the liquid phase will be similar to that shown in Fig. 1. In this case, reaction (4) may occur with a finite reaction rate in region 1 and reactions (1) and (3) and the following two reactions may take place irreversibly and instantaneously at the reaction plane.

(The equilibrium constants of reactions (5) and (6) are $2.25 \times 10^3 \text{ m}^3/\text{mol}^3$ and $3.44 \times 10^4 \text{ m}^3/\text{mol}^6$ at 25°C and infinite dilution; reaction (5) is very fast with a rate constant of $58.5 \text{ m}^3/\text{mol} \cdot \text{s}^7$ at 25°C and infinite dilution, and reaction (6) is a proton transfer reaction and may be regarded as instantaneous.) Further, in region 2, reaction (2) will proceed reversibly at a finite reaction rate.

When Cl_2 is absorbed into a concentrated NaHCO_3 solution, the Cl_2 hydrolysis reaction may be suppressed and will make a negligible contribution to the absorption rate of Cl_2 , since HOCl and Cl^- ions of high concentrations are formed in region 1. The concentration profile of each species in this case will be as shown in the previous paper.⁵⁾

The experimental results obtained in the present work were analyzed by using the chemical absorption theory based on the Lvque model as in the previous papers.^{4,5)} For the present problem, an approximate analytical solution of the differential equations describing the diffusion of all species in the liquid phase was obtained by replacing the diffusivity ratios in the analytical solution based on the film model by the two-thirds roots. The absorption rate of Cl_2 , N_A , and the desorption rate of CO_2 , N_C , are given by

$$N_A = \beta_A k_{LA} A_i \quad (7)$$

and

$$N_C = \beta_C k_{LC} (C_r - C_i) \quad (8)$$

with

$$\beta_A = \frac{\gamma \left(1 - \frac{E_i F_i J_i}{K_4 A_i} \right)}{\tanh(\gamma/\beta_C)} + \frac{\gamma}{K_4} \frac{E_i F_i J_i}{A_i} \quad (9)$$

$$\beta_C = \beta_A \left/ \left[\beta_A - \left(\frac{D_B}{D_A} \right)^{2/3} \frac{B_0}{A_i} - \left(\frac{D_G}{D_A} \right)^{2/3} \frac{G_0}{A_i} \right] \right. \quad (10)$$

Fig. 1. Concentration profiles for absorption of Cl_2 into aqueous NaHCO_3 solution.

$$\gamma = \sqrt{k_4 D_A} / k_{LA} \quad (11)$$

where β_A and β_C are the reaction factors for the absorption of Cl_2 and the desorption of CO_2 , respectively. The concentration of CO_2 at the reaction plane, C_r , is given by

$$C_r = C_i + \frac{1}{\beta_C} \left[C_0 - C_i + \left(\frac{D_B}{D_C} \right)^{2/3} B_0 \right] \quad (12)$$

Further, the concentrations of HOCl , Cl^- ions and H^+ ions, E_i , F_i and J_i respectively, are given by

$$E_i = E_0 + \left(\frac{D_B}{D_E} \right)^{2/3} B_0 + 2 \left(\frac{D_G}{D_E} \right)^{2/3} G_0 + \left(\frac{D_J}{D_E} \right)^{2/3} J_i \quad (13)$$

$$F_i = F_0 + \left(\frac{D_B}{D_{F2}} \right)^{2/3} B_0 + \left(\frac{D_G}{D_{F2}} \right)^{2/3} G_0 + \left(\frac{D_J}{D_{F1}} \right)^{2/3} J_i \quad (14)$$

$$J_i = (\beta_A - 1) \left(\frac{D_A}{D_J} \right)^{2/3} A_i - \left(\frac{D_B}{D_J} \right)^{2/3} B_0 - \left(\frac{D_G}{D_J} \right)^{2/3} G_0 \quad (15)$$

Substituting Eq. (12) into Eq. (8) gives the following expression for N_C :

$$N_C = k_{LC} \left[C_0 - C_i + \left(\frac{D_B}{D_C} \right)^{2/3} B_0 \right] \quad (16)$$

This equation indicates that the desorption rate N_C of CO_2 is independent of the Cl_2 hydrolysis reaction represented by reaction (4).

If the Cl_2 hydrolysis reaction can be neglected, that is, when both K_4 and k_4 equal zero, Eqs. (9) and (10) lead to

$$\beta_A = \beta_C = 1 + \left(\frac{D_B}{D_A} \right)^{2/3} \frac{B_0}{A_i} + \left(\frac{D_G}{D_A} \right)^{2/3} \frac{G_0}{A_i} \quad (17)$$

and Eq. (15) reduces to

$$J_i = 0 \quad (18)$$

Equation (17) is identical to Eq. (19) given in the previous paper.⁵⁾

2. Experimental

The agitated vessel was of 12.3 cm i.d. and was the same as that used in the previous work.⁵⁾ The experimental procedure was also similar to that employed in the previous work.⁵⁾ The vessel was operated batchwise with respect to the liquid. Experiments were carried out at atmospheric pressure and at 25°C. The absorbing liquid used was an aqueous NaHCO₃ solution of an initial concentration of 33.0 mol/m³. The gas phase was pure Cl₂ saturated with water vapor, and its feed rate was maintained at approximately 1.6×10^{-5} m³/s. The liquid and gas stirrers were driven at constant speeds of 1.67 and 9.17 s⁻¹, respectively. The duration of the experimental run was 43 min. The absorption rate of Cl₂ and the desorption rate of CO₂ were determined by the same methods as used in the previous work.⁵⁾

3. Results and Discussion

3.1 Prediction of physical properties

When the dissolved Cl₂ reacts with NaHCO₃ in solution, an aqueous solution containing HOCl, NaCl and HCl exists near the gas-liquid interface. The interfacial concentrations of HOCl, NaCl and HCl, E_i , F_i and J_i respectively, are given by Eqs. (13) to (15). Therefore, as the liquid-phase diffusivity and the physical solubility for each of the two gases and the equilibrium constant and the reaction rate constant of reaction (4), the values for this mixed solution should be used for the analysis of the experimental results. The effects of the presence of HCl on the liquid-phase diffusivity, physical solubility and equilibrium constant of reaction (4) were assumed to be negligible, since the interfacial concentration J_i of HCl was very low (less than 8.4 mol/m³).

The forward rate constant k_4 of reaction (4) at 25°C was taken to be equal to 15.4 s^{-1} ,¹⁾ and the equilibrium constant K_4 of reaction (4) at 25°C was taken as $3.94 \times 10^2 \text{ mol}^2/\text{m}^6$.²⁾ The effects of the ionic strength of the solution on these values were assumed to be negligible. The other physical properties of the present system were estimated by the same methods as used in the previous work.⁵⁾

3.2 Comparison of experimental results with theory

The measured desorption rate N_C of CO₂ from an aqueous NaHCO₃ solution of $B_f = 33.0 \text{ mol/m}^3$ was found to vary from 3.7×10^{-4} to $3.5 \times 10^{-4} \text{ mol/m}^2 \cdot \text{s}$ as the bulk concentration B_0 of NaHCO₃ in the solution decreased from 23.0 to 6.8 mol/m³. These experimental data were in good agreement with the theoretical predictions from Eq. (16), the average deviation being 1.2%. (The graph of N_C vs. B_0 was omitted in this paper for brevity.) It should be noted that the CO₂ desorption rate is independent of the Cl₂ hydrolysis reaction, as mentioned above.

Fig. 2. Absorption rate of Cl₂ into aqueous NaHCO₃ solutions at 25°C: —, theoretical absorption rate which takes into account the effect of Cl₂ hydrolysis reaction; ----, theoretical absorption rate which assumes a negligible effect of Cl₂ hydrolysis reaction.

Figure 2 shows the experimental results for the adsorption of Cl₂ into an aqueous NaHCO₃ solution of $B_f = 33.0 \text{ mol/m}^3$ as a log-log plot of the Cl₂ absorption rate N_A vs. the NaHCO₃ bulk concentration B_0 . In this figure, the experimental data for NaHCO₃ solutions of $B_f = 64.1$, 127 and 254 mol/m³ which were obtained in the previous work⁵⁾ are also shown. The solid lines represent the theoretical absorption rates which take into account the effect of the Cl₂ hydrolysis reaction, and were calculated from Eqs. (7), (9) to (11), and (13) to (15). The dashed lines show the theoretical absorption rates which assume that the effect of the Cl₂ hydrolysis reaction is negligible, and were calculated from Eqs. (7) and (17). Thus, the distance between the solid and dashed lines for each solution is a measure of the effect of the Cl₂ hydrolysis reaction on the absorption rate. It can be seen in the figure that the solid lines for solutions of $B_f = 33.0$, 64.1 and 127 mol/m³ lie about 34, 15 and 3.0% above the dashed lines for the same solutions, and that for a solution of $B_f = 254 \text{ mol/m}^3$ both the theoretical lines agree well within about 0.4%. The measured absorption rates of Cl₂ shown in Fig. 2 are in good agreement with the solid lines rather than the dashed lines, with an average deviation of 2.9%, indicating that for NaHCO₃ solutions of low concentrations the effect of the Cl₂ hydrolysis reaction on the absorption rate cannot be neglected.

Nomenclature

A	= concentration of Cl ₂ in solution	[mol/m ³]
B	= concentration of HCO ₃ ⁻ ions in solution	[mol/m ³]
C	= concentration of CO ₂ in solution	[mol/m ³]
D	= liquid-phase diffusivity	[m ² /s]
E	= concentration of HOCl in solution	[mol/m ³]
F	= concentration of Cl ⁻ ions in solution	[mol/m ³]
G	= concentration of OCl ⁻ ions in solution	[mol/m ³]
J	= concentration of H ⁺ ions in solution	[mol/m ³]
K_4	= equilibrium constant of reaction (4)	[mol ² /m ⁶]
k_4	= forward rate constant of reaction (4)	[s ⁻¹]

N_A	= absorption rate of Cl_2	$[\text{mol}/\text{m}^2 \cdot \text{s}]$
N_C	= desorption rate of CO_2	$[\text{mol}/\text{m}^2 \cdot \text{s}]$
β_A	= reaction factor for the desorption of Cl_2	$[-]$
β_C	= reaction factor for the absorption of CO_2	$[-]$
γ	= parameter defined by Eq. (11)	$[-]$

<Subscripts>

A	= Cl_2
B	= HCO_3^- ions
C	= CO_2
E	= HOCl
F	= Cl^- ions
f	= initial concentration
G	= OCl^- ions
i	= gas-liquid interface
J	= H^+ ions
r	= reaction plane
0	= bulk of liquid
1	= region 1

2 = region 2

Literature Cited

- 1) Brian, P. L. T., J. E. Vivian and C. Piazza: *Chem. Eng. Sci.*, **21**, 551 (1966).
- 2) Connick, A. E. and Y. T. Chia: *J. Am. Chem. Soc.*, **81**, 1280 (1959).
- 3) Harned, H. S. and B. B. Owen: "The Physical Chemistry of Electrolytic Solutions," 3rd ed., p. 691, Reinhold, New York (1958).
- 4) Hikita, H., S. Asai, H. Ishikawa and Y. Saito: *Chem. Eng. Sci.*, **30**, 607 (1975).
- 5) Hikita, H., S. Asai and Y. Konishi: *J. Chem. Eng. Japan*, **16**, 42 (1983).
- 6) Morris, J. C.: *J. Phys. Chem.*, **70**, 3798 (1966).
- 7) Pinsent, B. R. W., L. Pearson and F. J. W. Roughton: *Trans. Faraday Soc.*, **52**, 1512 (1956).

EXTRACTION RATE OF PROPIONIC ACID WITH LONG-CHAIN ALKYLAMINE IN HORIZONTAL RECTANGULAR CHANNEL

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In this paper, the extraction rate of propionic acid with *n*-hexane solutions of Amberlite LA-2 (hereafter called LA-2) and of tri-*n*-octylamine (hereafter called TOA) in a horizontal rectangular channel are measured, and the results are interpreted by the interfacial reaction model proposed in the previous paper.⁵⁾

1. Experimental Procedure

Experimental apparatus and procedures are the same as those described previously.⁵⁾ Flow rates of an aqueous and organic phases were equalized and varied from $0.3 \times 10^{-6} \text{ m}^3/\text{s}$ to $0.8 \times 10^{-6} \text{ m}^3/\text{s}$, in which range no ripples were observed at the interface.

2. Results and Discussion

Experimental results are shown in Figs. 1 and 2 where $\bar{Sh}$ ($= (\Delta C_A \bar{u}_A h^2 / C_{A0} D_A x_L)$) is plotted against $\alpha\sqrt{\beta}$ ($= (C_{A0}/C_{B0})\sqrt{D_A/D_B}$) at constant Graetz number, Gz ($= (\bar{u}_A h^2 / D_A x_L)$) = 346. Diffusion coefficients, D_A and D_B , were estimated from an equation of Wilke *et al.*,⁷⁾ that is, $D_A = 0.9 \times 10^{-9} \text{ m}^2/\text{s}$ and $D_B = 1.4 \times 10^{-9} \text{ m}^2/\text{s}$ for LA-2 and $1.5 \times 10^{-9} \text{ m}^2/\text{s}$ for TOA.

It has been known that propionic acid (A) reacts with the amines (B) to form A_nB ($n=1, 2, 3$ and 4)

type species. In the range of $\alpha\sqrt{\beta} < 10$, the concentration of A_4B species can be assumed to be negligibly small compared with others.^{4,6)} The reaction scheme can be assumed to be the same as that given in the extraction of acetic acid with the amines⁵⁾ as shown in Fig. 3,* where k_{a01}° , k_{sn1}° and k_{dn1}° ($n=1, 2$ and 3) are the rate constants, and K_{a01} , K_{sn1} and K_{dn1} ($n=1, 2$ and 3) are the equilibrium constants.

When the reaction proceeds only at the interface, the fundamental equations and the boundary conditions can be derived as given in the previous paper.^{3,5)} The relations between $\bar{Sh}$ and $\alpha\sqrt{\beta}$ are obtained by solving these equations.

Dotted lines in Figs. 1 and 2 are the calculated results³⁾ assuming that A_3B type species are formed irreversibly and instantaneously at the interface. The broken lines in Figs. 1 and 2 are the calculated results assuming that all steps in Fig. 3 equilibrate instantaneously at the interface. The fact that most experimental $\bar{Sh}$ values fall under the broken lines indicates that the extraction rate is affected by the

* Assuming that the amines (B) reacts with the acid (A) dissolved in the organic phase, the relation between $\bar{Sh}$ and $\alpha\sqrt{\beta}$ can be calculated analytically,¹⁾ and the value of $\bar{Sh}$ should be independent of $\alpha\sqrt{\beta}$. It is assumed therefore that B reacts with A at the interface.