Removal of Atomospheric Pollutants

(2) Treatment of Deodorant Liquor*

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大気汚染物質除去に関する研究

(2) 悪臭除去薬液の処理

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Absorption rates of carbon dioxide into aqueous solutions of sodium phenoxide were measured using a laminar liquid-jet, a wetted wall column and a stirred tank absorber with a plain gas-liquid interface. The rate constant of the second-order reaction between carbon dioxide and sodium phenoxide solution was derived as 20.2 l/mol sec from the absorption data with the wetted wall column under the fast-reaction regime.   The experimental data with three types of absorbers could be predicted by the theory of absorption accompanied by the second-order reaction, using measured physico-chemical properties and derived reaction rate constant.

INTRODUCTION

The extraction of phenols from their alkaline solutions by passing a gas rich in carbon dioxide is an essential process of the production of tar acids. In addition, this extraction process may be applied to the recovery of phenols from the alkaline liquor that is used for removing phenols as an obnoxious air-pollutant. In spite of such an applicability, little has been published on this system. Briggs and Thompson[1] studied carbon dioxide absorption in commercial carbolates with a laminar liquid-jet apparatus. Measured enhancement factor was qualitatively correlated with a reaction-diffusion modulus. Recently Ross and Mustafa[2] carried out the absorption into an aqueous solution of sodium phenoxide using a stirred tank absorber with a plain gas-liquid interface. Particularly the influence of the liberation of a phenol as a second immiscible liquid phase was discussed on the rate of absorption and the presence of phenol in the reaction mixture was found to increase the rate of

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absorption.

However it is surprising that the reaction kinetics is not established yet. Thus, it is the purpose of this work to fundamentally investigate the reaction kinetics and the mass transfer characteristics of this system on the basis of chemical absorption theory. To this end, the absorption of pure carbon dioxide into aqueous solutions of sodium phenoxide was performed using a liquid-jet, a wetted wall column and a stirred tank absorber with a plain gas-liquid interface.

EXPERIMENTAL

Chemical absorption

The experiment for chemical absorption has been carried out over a wide range of contact time. For this purpose three different types of absorbers, namely, a laminar liquid-jet, a wetted wall column and a batch stirred tank absorber with a plain gas-liquid interface were used. The contact times for the laminar liquid-jet and wetted wall column absorbers range from 0.0025 to 0.025 sec and from 0.15 to 0.80 sec, respectively. Some detailed description on the absorbers is given elsewhere[3~4]. The gas phase was pure carbon dioxide saturated with water vapor at atmospheric pressure and the absorbent was aqueous sodium phenoxide solution. However, in experiments with the stirred tank absorber, the absorbent for each batch was a reaction mixture corresponding to a specified conversion of the reaction between carbon dioxide and sodium phenoxide solution. For every absorption run with stirred vessel there were several minutes during which the absorption rate was essentially a constant. The initial rate of absorption into each batch of absorbent was volumetrically determined using a soap-bubble meter and was taken to be the absorption rate under a pseudo-steady state. Through each run absorbent content was maintained 500 cc and agitator impeller speed was 105 rpm. Absorption rates with the liquid-jet and the wetted wall column were measured using a soap-bubble meter, as well.

All the experimental runs were performed at a constant temperature of 25 C in an air thermostat bath for the liquid-jet and the wetted wall column and in a water bath for the stirred tank absorber, respectively.

Solubility and diffusivity measurement

The calculation of the reaction rate constant and the enhancement factor requires a knowledge of physical solubility and diffusivity of carbon dioxide in the aqueous solutions of sodium phenoxide under consideration. However, these cannot be measured directly because of the occurrence of chemical reaction.

The physical solubility of carbon dioxide in aqueous solutions of sodium phenoxide can be estimated from the correlation by van Krevelen and Hoftyzer[5]. But there is no information available on the contribution of anion $(C_6H_5O^-)$, x_a, to the salting-out parameter. Thus in order to obtain the value of x_a, the solubility of nitrous oxide in aqueous sodium phenoxide solutions was measured in the same apparatus as in the previous paper[6~7]. As shown in that work, the reliability of the apparatus and procedure has been confirmed.

For diffusivity, the similarity in mass and molecular interaction parameters between carbon dioxide and nitrous oxide was used to infer the effect of phenolate concentration on the diffusivity from corresponding measurements with nitrous oxide. In order to determine

the diffusivities of nitrous oxide in aqueous solutions of sodium phenoxide with various concentrations, the physical absorption was carried out in the laminar liquid-jet.

EXPERIMENTAL RESULTS AND DISCUSSION

Physico-chemical properties

The results of the solubility of nitrous oxide in aqueous phenolate solutions of various concentrations are listed in Table 1. In view of the correlation by van Krevelen and Hoftyzer[5]:

$$\log\frac{\alpha}{\alpha_w} = -KC_{B0} \tag{1}$$

$$K = x_g + x_a + x_c \tag{2}$$

, the value of x_a for $C_6H_5O^-$ was determined to be 0.4084. Here the values of x_g and x_c for N_2O and Na^+ were taken to be -0.2141 and -0.0183, respectively from the measurements by Onda et al.[6]

Table 1. Solubilities of nitrous oxide in aqueous solutions of sodium phenoxide at 1 atm and 25℃.

Sodium phenoxide concentration [mol/1]	Bunsen absorption coefficient α [－]
0	0.551
0.630	0.435
1.13	0.362
1.75	0.270

From physical absorption data obtained in a laminar liquid-jet, diffusivities of nitrous oxide in aqueous solutions of sodium phenoxide of various concentrations were calculated by

$$Q_A = 4C_{Ai}\sqrt{D_A v h} \times 10^{-3} \tag{3}$$

, The values of nitrous oxide diffusivity are presented in Table 2. The reduction of the diffusivity of carbon dioxide in an aqueous phenolate solution was assumed same as observed reduction in nitrous oxide diffusivity.

Table 2. Diffusivities of nitrous oxide in aqueous solutions of sodium phenoxide derived from physical absorption data with a laminar liquid-jet at 1 atm and 25℃.

Sodium phenoxide concentration [mol/1]	Diffusivity of nitrous oxide [cm²/sec]
0	1.78×10^{-5}
0.567	1.66×10^{-5}
1.13	1.48×10^{-5}
1.75	9.92×10^{-6}

Chemical absorption

When carbon dioxide is absorbed into an aqueous phenolate solution, it reacts according

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to the overall reaction:

$$CO_2 + 2C_6H_5ONa + H_2O \rightarrow 2C_6H_5OH + Na_2CO_3 \qquad (4)$$
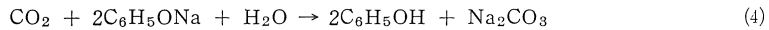
to form phenol and sodium carbonate. Its reaction rate constant is conventionally evaluated from the absorption rates with the wetted wall column under presumably fast reaction regime:

$$Q_A = \pi dh C_{Ai} \sqrt{D_A k C_{BO}} \times 10^{-3} \qquad (5)$$

Here, kinematically it is assumed to be of the irreversible second order with respect to the two reactants. Equation (5) is valid under $\phi > 3$ and $\sqrt{M} \ll q_B$. Application of eqn. (5) to observed absorption rates under the fast-reaction regime with estimates of D_A and C_{Ai} gives values of the reaction rate constant, which are listed in Table 3. In the same table, estimated values of D_A and C_{Ai} are given as well.

Table 3. Reaction rate constants from chemical absorption data with a wetted wall column under the fast reaction regime at 25°C

C_{BO} mol/1	$C_{Ai} \times 10^2$ mol/1	$D_A \times 10^5$ cm²/sec	k 1/mol sec
0.934	2.39	1.71	19.1
1.48	1.95	1.43	21.2

$(k)_{av} = 20.2$

Experimental results for chemical absorption with the liquid-jet and the wetted wall column are shown in Fig. 1 as a plot of enhancement factor ϕ_A vs. reaction-diffusion modulus $\sqrt{M}$. Experimental absorption rates and contact times are converted into the enhancement factors and reaction-diffusion moduli, using estimates of C_{Ai}, D_A and k as described. The solid line represents the penetration theory solution for gas obsorption accompanied by the first-order reaction. Every experimental point in the region of $\sqrt{M} < 3$ obtained from the liquid-jet and wetted wall column absorbers coincides well with the theoretical prediction.
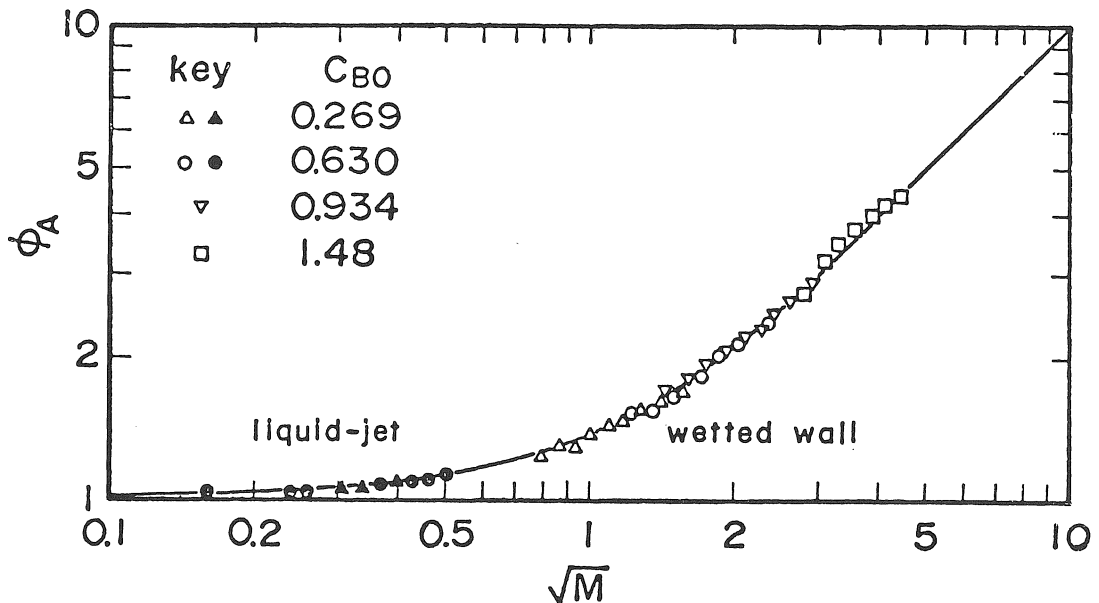
Fig. 1. Experimental enhancement factors with the liquid-jet and the wetted wall column.

To check the validity of the proposed reaction kinetics and to investigate the effect of the liberation of phenol on the absorption rate, the absorption process was observed at various stages of conversion using the batch stirred tank absorber. Experimental rate of absorption into each batch of absorbent was converted into the enhancement factor, using estimates of C_{Ai} and k_L^o and plotted against conversion X_A in Fig. 2. The value C_{Ai} was estimated by the correlation of solubility of gases in aqueous solutions of mixed salts proposed by Onda et al.[7] The liquid-side mass transfer coefficient under non-reacting conditions, k_L^o, was obtained from measurements in previous work[4] to be $1.70 \times 10^{-3} \times (D_A/D_{CO_2 H_2 O})^{2/3}$ cm/sec
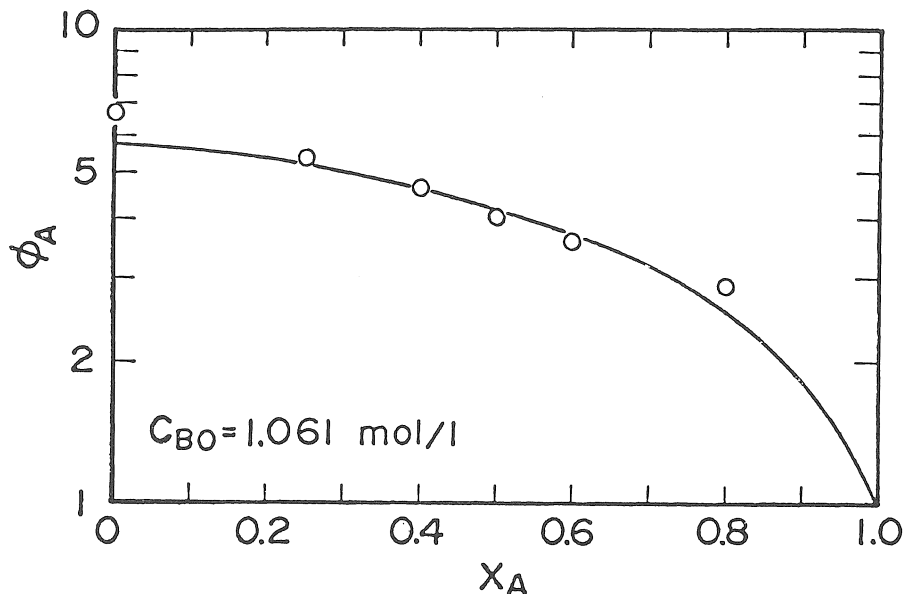

Fig. 2. Experimental enhancement factors with the stirred tank absorber.

at 105 rpm. The solid curve in Fig. 2 shows the film-theory prediction[8]. The values of diffusivity of sodium phenoxide in the aqueous solutions of various concentrations required in the calculation of the theoretical line were determined by assuming the relationship $D\mu/T = a$ constant, where μ is the viscosity of the solution. The relevant value of diffusivity in water is assumed to be equal to the corresponding value of phenol. The viscosities of the various solutions were determined with the standard Ostwald viscometer. A series of experimental points agree well with the solid line in view of uncertainty in phsico-chemical properties. In this run, the initial concentration of sodium phenoxide at $X_A = 0$ is 1.061 mol/1 that is about half of the concentration in the previous work[2]. Thus, there is no enhancement in the absorption rate due to the liberation of phenol from reaction mixture observed at the conversion close to 0.8.

CONCLUSION

The absorption of carbon dioxide in aqueous solutions of sodium phenoxide was carried out over a wide range of contact time. The absorption data with a wetted wall column under the fast-reaction regime gave the rate constant of the second-order reaction as 20.2 1/mol sec. The experimental data with three different types of absorbers (laminar liquid-jet, wetted

wall column and stirred tank absorber) were satisfactorily predicted by the theory of absorption with the second-order reaction, using measured physico-chemical properties and derived reaction rate constant.

NOMENCLATURE

C	concentration in liquid phase mol/l
D	molecular diffusivity in liquid phase cm^2/sec
d	diameter of wetted wall cm
h	height of jet or height of wetted wall cm
K	salting-out parameter l/mol
k	second-order reaction rate constant l/mol sec
k_L	liquid-side mass transfer coefficient cm/sec
M	$=\pi k C_{B_0} t/4$, reaction-diffusion modulus
Q	rate of gas absorption mol/sec
q_B	$=C_{B_0}/\nu C_{Ai}$
T	absolute temperature °K
t	gas-liquid contact time sec
v	liquid flow rate cm^3/sec
X	conversion
x_g, x_a, x_c	contribution of gas, anion and cation to K, respectively l/mol

Greek symbols

α	Bunsen absorption coefficient cm^3 of gas/cm^3 of solution
μ	viscosity of solution g/cm sec
ν	stoichiometric coefficient
ϕ	enhancement factor

Subscripts

A	dissolved gas A (CO_2)
B	liquid reactant B (C_6H_5ONa)
i	gas-liquid interface
w	water
0	initial value

Superscript

o	without chemical reaction

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