R&D NOTES

Kinetics of the Reaction of Carbon Dioxide with Aqueous 2-Piperidineethanol Solutions

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Sterically hindered amines have been proposed recently as attractive solvents for acid gas purification, since they have not only greater capacity for CO_2 but also a low tendency to form carbamate and an appreciable absorption rate for CO_2 (Sharma, 1965; Sartori and Savage, 1983; Savage et al., 1984; Say et al., 1984). The advantages of sterically hindered amines result from the bulkiness of the substituent attached to the amino group which causes an increased cyclic capacity and a decreased energy consumption in industrial operations. 2-piperidineethanol (2-PE) is a secondary amine in which the amino group is not only attached to a naphthenic ring group but also sterically hindered by a hydroxyethyl group that is connected to the α carbon atom of the cyclic system. It has been used for the bulk removal of CO_2 or the selective removal of H_2S (Goldstein et al., 1986).

Little information on 2-PE is available. Shen et al. (1991) investigated the kinetic rate of CO_2 in aqueous 2-PE solutions at 40°C within the amine concentration range 0.2–1.0 kmol/m^3. Their results showed that the reaction of CO_2 in aqueous 2-PE solutions is first-order with respect to both CO_2 and the amine. The second-order forward rate constant at 40°C was found to be 195 m^3/(kmol·s), which is much lower than that of 2-amino-2-methyl-1-propanol (AMP). Xu et al. (1992) presented the physicochemical properties of 2-PE and its aqueous solutions over a wide range of temperature and concentration. They found that the value of pKa for 2-PE at 25°C is 10.14, which is higher than that of AMP (the pKa of AMP is 9.694).

The aim of this work is to investigate the kinetic rate of absorption of CO_2 in aqueous 2-PE solutions using a stirred-cell absorber. The reaction mechanism and the kinetic order with respect to both the reactants CO_2 and 2-PE are studied within the amine concentration range of 0.25–2.5 kmol/m^3, over the temperature range from 10–40°C.

Reaction Mechanism

The main reaction is to form the carbamate even though there are several parallel and series reversible reactions simultaneously occurring in the solution. This reaction can be described by the zwitterion mechanism:

$$R_2R_1\mathrm{NH} + \mathrm{CO_2} \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} R_2R_1\mathrm{NH^+COO^-} \tag{I}$$

$$R_2R_1\mathrm{NH^+COO^-} + B \underset{k_{-b}}{\overset{k_b}{\longleftrightarrow}} R_2R_1\mathrm{NCOO^-} + B\mathrm{H^+} \tag{II}$$

Based on this mechanism, apart from the amine, water and hydroxyl ions can also contribute to the deprotonation of the zwitterion in aqueous solutions. At the same time, the carbamate will be hydrolyzed into the bicarbonate and 2-PE, that is:

$$R_2R_1\mathrm{NCOO^-} + \mathrm{H_2O} \underset{k_{-3}}{\overset{k_3}{\longleftrightarrow}} R_2R_1\mathrm{NH} + \mathrm{HCO_3^-} \tag{III}$$

Generally, the concentration of the zwitterion is considered to be in a pseudo-steady state, and the deprotonation process by various kinds of bases should be taken into account (Danckwerts, 1979). As a consequence, the CO_2 absorption rate by aqueous 2-PE solutions can be described as follows:

$$r_{CO_2} = \frac{[CO_2][R_2R_1NH]}{\dfrac{1}{k_1} + \dfrac{k_{-1}}{k_1 \, \Sigma \, k_b[B]}} \tag{1}$$

From Eq. 1, there are two limiting cases. If the term $k_{-1}/\Sigma\, k_b[B] \ll 1$, which indicates that the zwitterion is deprotonated relatively fast in comparison with the reversion rate of CO_2 and amine, Eq. 1 is simplified to Eq. 2 which was used by Shen et al.:

$$r_{CO_2} = k_1[CO_2][R_2R_1NH] \tag{2}$$

On the other hand, if $k_{-1}/\Sigma\, k_b[B] \gg 1$ and also the rate contributed by the hydroxyl ion and water may be neglected compared with the $k_{AM}[AM]$, Eq. 1 becomes an overall third-order kinetics equation:

$$r_{CO_2} = \frac{k_1 k_{AM}}{k_{-1}}\,[CO_2][R_2R_1NH]^2 \tag{3}$$

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Experiment and Methods

A pressure decrease method similar to that presented by Laddha and Danckwerts (1981) and further developed by Blauwhoff et al. (1984) was applied to measure the kinetic constants of physical or chemical absorption of gases in the aqueous 2-PE solutions. More detailed information about the experiments was presented by Xu et al. (1991). The reaction conditions of the experiments were selected in such a way that the absorption process occurred in the "fast pseudo-first-order reaction regime" ($3 \ll Ha \ll Ei$). Here,

$$Ha = \sqrt{k_{ov} D_{CO_2}}/k_L \tag{4}$$

$$Ei = \sqrt{\frac{D_{CO_2}}{D_{AM}}} + \sqrt{\frac{D_{AM}}{D_{CO_2}}}\,\frac{[AM]}{\nu_{AM}}\,\frac{H_{CO_2}}{P_{CO_2}} \tag{5}$$

$$k_{ov} = k_{app} + \overset{*}{k}_{OH^-}[OH^-] \tag{6}$$

where $\overset{*}{k}_{OH^-}$ was obtained from Pinsent et al. (1956). Under these conditions, the absorption rate per unit area and time is given by:

$$J_{CO_2} = \frac{P_{CO_2}}{H_{CO_2}}\sqrt{D_{CO_2} k_{ov}} \tag{7}$$

If the initial pressure is very low, the loading of CO_2 in the aqueous solution is so small that the equilibrium pressure of CO_2 contributed by the CO_2 in the solution may be ignored, and the absorption rate can be calculated by:

$$-\frac{V_g}{RT}\left(\frac{dP_{CO_2}}{d\tau}\right) = \left(\frac{P_{CO_2}}{H_{CO_2}}\right)\cdot a \cdot \sqrt{D_{CO_2} k_{ov}} \tag{8}$$

The ln P_{CO_2} vs. τ data were correlated by the method of least squares to obtain a value of k_{ov}, in which the concentrations of [AM] and $[OH^-]$ are the average concentrations. The relative deviations of the CO_2 partial pressure between the experimental data and the correlated values are less than 5%.

The hydroxyl ion concentration in the bulk solution depends on the concentration of free amine and the protonation constant of water as well as that of 2-PE (Astarita et al., 1983); they were obtained from Perrin (1965) and Xu et al. (1992).

If only physical absorption is involved, the rate equation (Eq. 8) can be simplified to the following equation:

$$\frac{V_L}{H_m}\ln\left(\frac{P\cdot H_m - P^o}{P^o(H_m-1)}\right) = k_L^o \cdot a \cdot \tau \tag{9}$$

$$H_m = \frac{RTV_L}{HV_g} + 1 \tag{10}$$

Here P is the gas pressure at time τ, and P^o is the initial gas pressure. The physical mass-transfer coefficient in the liquid phase for this apparatus can also be predicted by the following equation:

$$Sh = 0.138\, Re^{0.70} Sc^{0.5} \tag{11}$$

The physical mass-transfer coefficient of N_2O in 2-PE solutions was experimentally measured, and therefore, the diffusivities of N_2O in the solutions could be obtained from Eq. 11. The N_2O analogy method presented by Laddha et al. (1981) was adopted in this work, and the analogy parameter for the aqueous solution was taken from Versteeg and van Swaaij (1988a).

The density and viscosity of aqueous 2-PE solutions and the solubility of N_2O in the aqueous solutions for each temperature and concentration of amine involved in the above calculation were directly obtained from the regression equations presented by Xu et al. (1992).

The reagent-grade 2-PE with a purity of 95% was obtained from Aldrich Chemical Company. After the solvent was distilled at reduced pressure, the purity of the distilled 2-PE was higher than 99.5%, as analyzed by gas chromatography. The aqueous 2-PE solutions were prepared from the purified 2-PE and distilled water and stored under a nitrogen atmosphere. The N_2O and CO_2 used in this experiment were supplied by Union Carbide Canada Limited with a minimum purity of 99.8% and 99.99%, respectively.

Results and Discussion

The diffusivity data of N_2O in aqueous 2-PE solutions have to be measured to interpret the kinetic experiments. The experimental determination of the diffusivity of N_2O was carried out by the stirred-cell reactor. The diffusivities of N_2O in aqueous 2-PE solutions over a wide range of amine concentrations up to 40 wt. % at 20 and 40°C were obtained using Eqs. 9-11. The experimental results in Table 1 are correlated for convenient use.

Preliminary experiments showed that a stirring speed of the impeller between 70–95 rpm did not affect the absorption rate of CO_2 in the solutions. The reaction is dominated by the forward reaction in the initial period of the reaction, although it is reversible and complex. The Hatta numbers obtained from this work range from 16.7 to 127.4, which show that the reaction of CO_2 in aqueous 2-PE solutions takes place in the fast pseudo-first-order reaction regime.

The apparent kinetic rate constants of CO_2 in the aqueous 2-PE solutions determined in the range of amine concentrations from 0.25 to 2.5 kmol/m^3 and over the temperature range from 10 to 40°C are shown in Table 2 and Figure 1 for comparison with that of CO_2 in aqueous AMP solutions. It shows that the apparent kinetic rate constant of CO_2 in aqueous 2-PE solutions increases with the increase of the concentration of 2-PE and the reaction temperature. However, the apparent

Table 1. Diffusivity of N_2O in Aqueous 2-PE Solutions

Conc. of 2-PE wt. %	D_{N_2O}, 10^9 m^2·s^{-1} 20°C	40°C
0.0	1.56*	2.61*
5.0	1.26	1.98
13.0	0.98	1.58
20.0	0.81	1.42
30.0	0.72	1.24
40.0	0.64	1.18

*Obtained from Versteeg and van Swaaij (1988a).

Table 2. Kinetic Data for the Absorption of CO_2 in Aqueous 2-PE Solutions

Temp. K	[AM] kmol/m^3	[H_2O] kmol/m^3	k_{app} 1/s
283	0.251	54.064	48.9
283	0.380	52.952	75.7
283	0.611	51.404	108.9
283	0.990	48.789	214.3
283	1.457	45.501	300.6
283	1.981	42.116	412.9
283	2.476	38.637	515.7
293	0.250	53.864	94.3
293	0.380	52.831	124.3
293	0.606	51.264	248.6
293	0.995	48.627	408.6
293	1.471	45.318	591.4
293	1.948	41.916	791.4
293	2.443	38.428	1,068.6
303	0.249	53.664	169.7
303	0.376	52.952	257.1
303	0.600	51.093	407.9
303	0.979	48.442	712.9
303	1.399	45.119	1,096.6
303	1.922	41.709	1,345.7
303	2.419	38.271	1,902.4
313	0.246	53.464	297.1
313	0.369	52.474	421.4
313	0.597	51.264	785.7
313	0.975	48.627	1,108.1
313	1.439	44.902	1,857.1
313	1.924	41.491	2,420.4
313	2.400	38.001	3,127.1

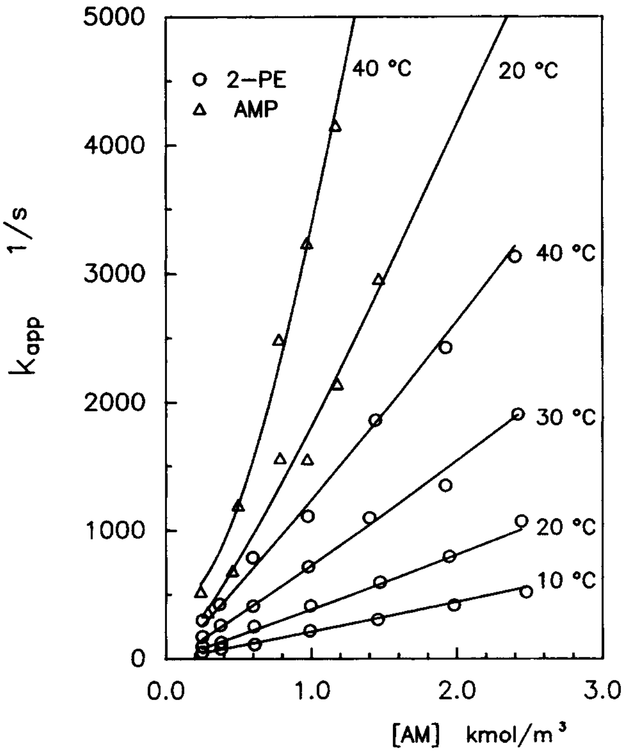

Figure 1. Apparent rate of reaction of CO_2 with aqueous 2-PE and AMP solutions.

kinetic rate constant of CO_2 in aqueous 2-PE solutions is lower than that of CO_2 in aqueous AMP solutions at the same temperature and amine concentration, even though the value of pKa of 2-PE is higher than that of AMP.

According to the Brønsted relationship between the secondary rate constant for the formation of the zwitterion and the dissociation constant of the alkanolamine presented by Versteeg and van Swaaij (1988b), the kinetic rate constant of 2-PE should be larger than that of AMP. In fact, the experimental results in this case are the opposite. This means that the Brønsted relationship is insufficient to describe the relationship between the rate constant for the formation of the zwitterion and the pKa value of amine, since the organic-base solvent cannot be completely characterized by a single parameter such as the pKa (Chakraborty et al., 1986). In this case, the structure of 2-PE in which the amino group is sterically hindered by a hydroxyethyl group and fastened to the naphthenic ring affects both the dissociation of the amine and the reaction rate of CO_2 in the solutions.

If the dissociation constant of 2-PE is only considered as the criterion of how many hydroxyl ions formed in the aqueous 2-PE solution, it may not be an important factor for the absorption process of CO_2, in that the concentration of hydroxyl ion in the solution is quite low. It was also found that the effect of the zwitterion deprotonated by the hydroxyl ion based on reaction II could be neglected, if the zwitterion mechanism was considered in the reaction (Versteeg and Oyevaar, 1989). Therefore, the forward apparent kinetic rate constant of the reaction CO_2 in aqueous 2-PE solutions can be simplified from Eq. 1:

$$k_{app}=\frac{[AM]}{\frac{1}{k_1}+\frac{k_{-1}}{k_1k_{H_2O}[H_2O]+k_1k_{AM}[AM]}} \tag{12}$$

According to Eq. 12 and the experimental results in Table 2, the second-order reaction constant and the two constant groups individually calculated at each temperature are presented in Table 3 and correlated as a function of temperature over the experimental range by a nonlinear regression method. All deviations from the regression are less than 6%.

$$k_1=4.111\times10^{10}\cdot\exp\left(-\frac{44{,}621}{RT}\right) \tag{13}$$

$$\frac{k_1k_{H_2O}}{k_{-1}}=1.011\times10^{9}\cdot\exp\left(-\frac{44{,}206}{RT}\right) \tag{14}$$

$$\frac{k_1k_{AM}}{k_{-1}}=4.921\times10^{10}\cdot\exp\left(-\frac{41{,}695}{RT}\right) \tag{15}$$

Table 3. Kinetic Constants of 2-PE Solutions

Temp. K	k_1 m^3/kmol·s	$k_1k_{H_2O}/k_{-1}$ m^6/kmol^2·s	k_1k_{AM}/k_{-1} m^6/kmol^2·s
283	243	7.08	1,020
293	448	13.39	1,764
303	861	24.41	3,205
313	1,468	42.76	5,521

From Table 3, the second-order reaction constant at 40°C is 1,468 $m^3/kmol \cdot s$, which is larger than that found by Shen et al. (1991), 196 $m^3/kmol \cdot s$, in their laboratory wetted-wall column. These values, however, do not have the same meaning although their units are the same, since Shen et al. simplified the zwitterion mechanism and used only the first-order equation with respect to both CO_2 and 2-PE to treat their experimental results. If the second-order rate constant in this work is also correlated using the method of Shen et al., its value is 1,207 $m^3/kmol \cdot s$ at 40°C with an absolute error as high as $\pm 13\%$, which is still larger than the value of Shen et al. It clearly shows that the apparent kinetic rate of CO_2 in aqueous 2-PE solutions is affected not only directly by the protonation rate to free amine, but also by the zwitterion deprotonation rate that depends on the concentrations of water, amine, and other species.

The difference between the second-order rate constants at the same temperature obtained by Shen et al. (1991) and this work may first result from the purity of 2-PE, since commercial 2-PE generally has only a purity of 95 wt. %. This material has to be purified before use in a kinetic reaction process, because traces of impurities may have a very significant effect on the kinetic rate. Secondly, the aqueous solution may obtain CO_2 from the air prior to the start of an experiment. Since the initial CO_2 loading affects the absorption rate of CO_2, in this work the aqueous 2-PE solutions prepared for use in measuring the kinetic rate were kept under an atmosphere of nitrogen. The third reason may be the different apparatus and property values of the solutions used by different workers, which can result in a different conclusion.

For the sterically hindered amines, the apparent kinetic rate constants of 2-PE are dramatically lower than those of AMP, and the apparent activation energy of 2-PE according to the secondary rate constants is 44.6 kJ/mol, which is much higher than that of AMP, 23.6 kJ/mol. This means that the reaction of CO_2 with the aqueous 2-PE solutions is not as fast as that with AMP.

Conclusions

The reaction of CO_2 in aqueous 2-PE solutions can be described as the zwitterion mechanism, although this reaction includes some parallel and series reactions occurring simultaneously. When the loading of CO_2 in the solution is low, the reaction rate belongs to the fast pseudo-first-order regime. The kinetic rates of CO_2 in aque[illegible] 2-PE solutions can be modeled well by this mechanism wit[illegible] deviation of 6%.

The second-order reaction rate constants and other kinetic group constants obtained from these experimental results are correlated as an exponential function of temperature. The apparent activation energy for the secondary reaction rate constant is 44.6 kJ/mol, which is higher than that of AMP. Compared with other primary or secondary alkanolamines, 2-PE has lower apparent kinetic rate constants at the same concentration of the free amine and temperature because of its special molecular structure.

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Notation

a = interfacial area of gas in contact with liquid, m^2
AM = amine
B = base
d = diameter of impeller, m
D = diffusion coefficient, m^2/s
Ei = instantaneous enhancement factor for mass transfer for CO_2
H = Henry's coefficient, $kPa \cdot m^3/kmol$
H_a = Hatta number defined by Eq. 4
J = molar flux, $kmol/(m^2 \cdot s)$
k_i = forward reaction rate constant for reaction i
k_{-i} = reverse reaction rate constant for reaction i
k_L^o = liquid-phase mass-transfer coefficient, m/s
k_{OH}^* = reaction rate constant for CO_2 hydration, $m^3/(kmol \cdot s)$
K_p = dissociation constant of amine ($K_p = [AMRH][H^+]/[AMRH_2^+]$), $kmol/m^3$
K_w = protonation constant of water, ($K_w = [H^+][OH^-]$), $kmol^2/m^6$
N = stirring speed, 1/s
P = pressure, kPa
r = reaction rate, $kmol/(m^3 \cdot s)$
R = molar gas constant, 8.3145 $J/(mol \cdot K)$
Re = Reynolds number, $d^2 N\rho/\mu$
Sc = Schmidt number, $\mu/(\rho D)$
Sh = Sherwood number, dk_L^o/D
T = temperature, K
V_g = gas-phase volume in the stirred cell, m^3
V_L = liquid-phase volume in the stirred cell, m^3
[ ] = concentration, $kmol/m^3$

Greek letters

μ = viscosity, 10^{-3} $Pa \cdot s$
ν = stoichiometric coefficient
ρ = density, kg/m^3
τ = reaction time, s

Subscripts

app = apparent reaction rate constant
AM = amine for zwitterion deprotonation
b = base for zwitterion deprotonation
CO_2 = carbon dioxide
H_2O = water for zwitterion deprotonation
N_2O = nitrous oxide
ov = overall reaction rate
OH^- = hydroxyl ion

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