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Kinetic of CO_2 absorption and carbamate formation in aqueous solutions of diethanolamine

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Abstract−The absorption rates of CO_2 into aqueous solutions of Diethanolamine (DEA) with varying concentrations from 0.2 to 4 M and temperature range from 293 to 323 K were measured by using a laboratory stirred reactor. The CO_2 partial pressure was varied in a range that the reaction would occur in pseudo first order regime. Experimental data were analyzed and the kinetic parameters associated with the reaction were determined. The activation energy for the deprotonation of the intermediate zwitterion was estimated at about 11.4 kcal/mol. The contribution of carbamate formation to the overall absorbed CO_2 was experimentally evaluated and found to be of the order of 100%.

Key words: Diethanolamine, Carbon Dioxide, Carbamate, Absorption Kinetics

INTRODUCTION

The removal of acid gases such as CO_2 and H_2S from natural and refinery gases is an important industrial process. The use of alkanolamine-based solvents such as MEA, DEA, and MDEA is still the choice in gas treating technology. The design and analysis of separation processes involving aqueous solutions of such species require accurate knowledge on the kinetics of the reactions involved.

Most investigators agree that the reaction order is unity with respect to CO_2. The order of the reaction with respect to DEA concentration is still under speculation with reported values varying from one to two. These discrepancies may be related to the different reaction mechanisms being proposed for the interpretation of the experimental data. In addition, the experimental techniques used to generate the kinetic data may also have contributed to the observed differences. Furthermore, studies concerning the variation of the reaction rate constant with temperature are still insufficient. Blanc and Demarais [1] measured the kinetics of the reaction at a temperature range 293-333 K for amine concentration varying from 0.005 to 4 mol/*l*. However, they used a non-zwitterion based mechanism to interpret their data. Rinker et al. [2] studied a wider temperature range of 293-343 K and amine concentration from 0.25 to 2.8 mol/*l*. Blauwhoff et al. [3], by applying the Zwitterion mechanism originally proposed by Caplow [4] and reintroduced by Danckwerts [5], showed that most of the previous works could be understood according to this mechanism. Versteeg et al. [6] concluded that at 298 K the kinetics of DEA are well established and in line with the Zwitterion mechanism. However, the influence of temperature is scarcely correctly studied, which makes additional contributions still needed for a better understanding of the reaction kinetics since most of the published work does not include raw data. This makes the analysis of the available kinetic data using different mechanisms a tedious, if not impossible, task.

The reaction of carbon dioxide with diethanolamine is one of the most extensively studied in CO_2-alkanolamine systems, and despite the importance of the carbamate-forming reactions, reliable assessments of its contribution to the overall absorbed CO_2 are not readily available in the literature. The lack of experimental data on carbamate formation in the literature is mainly attributed to the difficulty in measuring the carbamate ion concentration accurately.

In this work, additional data on kinetics of the reaction between CO_2 and DEA in aqueous solutions are presented. The absorption rate of CO_2 into aqueous DEA was determined at different pressures and amine concentrations by using a laboratory stirred cell reactor. The temperature was chosen in such a way to cover a range of typical industrial absorption columns that is 293 to 323 K. In addition, the contribution of the carbamate formation to the overall absorbed CO_2 was quantified experimentally.

THEORETICAL

1. Reaction Mechanism

Different reaction mechanisms were proposed to analyze the absorption data of CO_2 in aqueous DEA solutions. The generally accepted mechanism is the one originally proposed by Caplow [7]. This mechanism involves the formation of an intermediate zwitterion followed by the removal of a proton by a base B. As a result, carbamate ion is formed. For the secondary amine DEA, its reaction with CO_2 can be described as follows:

$$CO_2 + 2DEA \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} DEACOO^- + DEAH^+ \tag{1}$$

The formation of carbamate proceeds as follows:

- Formation of zwitterion

$$CO_2 + DEA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} DEAH^+COO^- \tag{2}$$

- Removal of the proton by a base B

$$DEAH^+COO^- + B \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} DEACOO^- + BH^+ \tag{3}$$

Where the base B, could be the amine itself water molecules, or

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hydroxyl ions. In aqueous solutions, the corresponding reactions are as follows:

$$\mathrm{DEAH^{+}COO^{-}+DEA\xrightarrow{k_{DEA}}DEACOO^{-}+DEAH^{+}} \tag{4}$$

$$\mathrm{DEAH^{+}COO^{-}+H_2O\xrightarrow{k_{H_2O}}DEACOO^{-}+H_3O^{+}} \tag{5}$$

$$\mathrm{DEAH^{+}COO^{-}+OH^{-}\xrightarrow{k_{OH^{-}}}DEACOO^{-}+H_2O} \tag{6}$$

Assuming quasi-steady state condition for the zwitterion concentration, the overall forward reaction rate is given by the following relationship:

$$\mathrm{R}_{CO_2\text{-}DEA}=-\frac{\mathrm{k_2[CO_2][DEA]}}{1+\dfrac{\mathrm{k_{-1}}}{(\mathrm{k}_{H_2O}[\mathrm{H_2O}]+\mathrm{k}_{OH^-}[\mathrm{OH^-}]+\mathrm{k}_{RR'NH}[\mathrm{DEA}])}} \tag{7}$$

Or in a general form

$$\mathrm{R}_{CO_2\text{-}DEA}=-\mathrm{k_2[CO_2][DEA]}\Big/\left(1+\frac{\mathrm{k_{-1}}}{\sum \mathrm{k}_b[\mathrm{B}]}\right) \tag{8}$$

Beside the reaction between CO_2 and DEA to form carbamate, other parallel reactions take place in the aqueous medium. The first reaction to be considered is the CO_2 hydration according to the following scheme:

$$\mathrm{CO_2+H_2O \rightleftarrows HCO_3^{-}+H^{+}} \tag{9}$$

This reaction obeys a first order law with respect to CO_2 with a rate constant of $k_{H_2O}=0.026\ s^{-1}$ at 298 K [8]. Due to its smaller rate, its contribution to the overall reaction rate is insignificant and is usually neglected in the overall rate expression [9]. The other reaction, which is considered important, is the bicarbonate formation as shown by the following equation:

$$\mathrm{CO_2+OH^{-} \rightleftarrows HCO_3^{-}} \tag{10}$$

The forward rate of reaction firstly given by Pinsent et al. [8] is described as follows:

$$\mathrm{R}_{CO_2\text{-}OH^-}=-\mathrm{k}^{*}_{OH^-}[\mathrm{CO_2}][\mathrm{OH^-}] \tag{11}$$

Where,

$$\mathrm{Log_{10}k^{*}_{OH^-}=13.635-2895/T\ \ m^3\cdot kmol^{-1}\cdot s^{-1}} \tag{12}$$

Taking into account Eqs. (7) and (11), the net effect of reactions involved in CO_2 absorption by an aqueous solution of DEA becomes

$$\mathrm{R}_{CO_2}=\mathrm{R}_{CO_2\text{-}DEA}+\mathrm{R}_{CO_2\text{-}OH^-} \tag{13}$$

Thus,

$$\mathrm{R}_{CO_2}=-\left(\begin{array}{l}\dfrac{\mathrm{k_2[CO_2][DEA]}}{1+\dfrac{\mathrm{k_{-1}}}{(\mathrm{k}_{H_2O}[\mathrm{H_2O}]+\mathrm{k}_{OH^-}[\mathrm{OH^-}]+\mathrm{k}_{RR'NH}[\mathrm{DEA}])}}\\ +\mathrm{k}^{*}_{OH^-}[\mathrm{CO_2}][\mathrm{OH^-}]\end{array}\right) \tag{14}$$

In this case, the overall reaction rate can be presented by the following:

$$\mathrm{k}_{ov}=\mathrm{k}_{app}+\mathrm{k}_{OH^-}[\mathrm{OH^-}] \tag{15}$$

Where k_{app} is the apparent rate of the reaction calculated as follows:

$$\mathrm{k}_{app}=\frac{[\mathrm{DEA}]}{\dfrac{1}{\mathrm{k_2}}+\dfrac{1}{\dfrac{\mathrm{k_2k}_{H_2O}}{\mathrm{k_{-1}}}[\mathrm{H_2O}]+\dfrac{\mathrm{k_2k}_{OH}}{\mathrm{k_{-1}}}[\mathrm{OH^-}]+\dfrac{\mathrm{k_2k}_{DEA}}{\mathrm{k_{-1}}}[\mathrm{DEA}]}} \tag{16}$$

2. Physico-Chemical Properties

Direct determination of these parameters is not possible as CO_2 reacts in the liquid phase. Hence, the use of N_2O analogy has been the common choice among investigators. Laddha et al. [10] demonstrated the existence of proportionality between the solubility (and the diffusivity) of CO_2 and N_2O according to the following relationships:

$$\mathrm{H}_{CO_2}=\mathrm{H}_{N_2O}(\mathrm{H}_{CO_2}/\mathrm{H}_{N_2O})_{in\ water} \tag{17}$$

$$\mathrm{D}_{CO_2}=\mathrm{D}_{N_2O}(\mathrm{D}_{CO_2}/\mathrm{D}_{N_2O})_{in\ water} \tag{18}$$

2-1. Solubility

Solubilities and in water were estimated by using the correlations of Versteeg and Van Swaaij [11]:

$$\mathrm{H}_{CO_2}=2.82\cdot 10^{6}\exp(-2044/\mathrm{T}) \tag{19}$$

$$\mathrm{H}_{N_2O}=8.55\cdot 10^{6}\exp(-2284/\mathrm{T}) \tag{20}$$

In a similar way to the work of Snijder et al. [12], the available solubility data of N_2O in aqueous DEA solutions summarized in Table 1 were compiled in a single relationship that takes into account the effects of both temperature and amine concentration, C_{DEA}, as follows:

$$\mathrm{H}_{N_2O\text{-}DEA}=\exp\left(14.94314-\frac{1966.5}{\mathrm{T}}+0.037972\mathrm{C}_{DEA}\right) \tag{21}$$

The range of validity of this equation is $288<T<353$ K and $0<C_{DEA}<3.6$ mol/*l* with an overall average absolute deviation of 0.1% and a maximum deviation of 12.4%.

2-2. Diffusivity

The diffusivities of CO_2 and N_2O in water were estimated from the work of Versteeg et al. [13] according to the following relationships:

$$\mathrm{D}_{CO_2}=2.35\cdot 10^{-6}\exp(-2119/\mathrm{T})\mathrm{m^2\cdot s^{-1}} \tag{22}$$

$$\mathrm{D}_{N_2O}=5.07\cdot 10^{-6}\exp(-2371/\mathrm{T})\mathrm{m^2\cdot s^{-1}} \tag{23}$$

Table 1. Solubility of N_2O in DEA aqueous solutions

Temperature (K)	Concentration (mol /*l*)	Reference
303-333	0-3.64	Littel et al. [25]
298	0-3.081	Sada et al. [26]
298	0-3.081	Sada et al. [27]
288-303	0-3.116	Haimour [28]
293-353	0-2.88	Rinker and Sandall [29]
303-313	0.5-3.0	Tsai et al. [30]
298	0-2.53	Oyvaar et al. [31]
298	0-3.08	Versteeg and Van Swaaij [11]
298	0-8.55	Versteeg and Oyvaar [32]
298	0-2.389	Versteeg et al. [33]
298	0.96-3.84	Browning and Weiland [34]
298	0.5-2.0	Laddha et al. [10]
303-313	2.88	Li and Lee [35]

For the diffusivity of N_2O in alkanolamine solutions, the modified Stokes-Einstein equation was used as follows [13].

$$(D^{0.8}_{N_2O})_{am\text{-}sol} \qquad (D^{0.8}_{N_2O})_{water} \tag{24}$$

Where, μ is the viscosity of the solution and D_{N_2O} is the diffusivity of N_2O in water.

2-3. Diffusivity of DEA in DEA Solutions

Snijder et al. [12] used the Taylor dispersion technique [14] to measure diffusion coefficients of several aqueous alkanolamines including DEA. They established a specific correlation relating the diffusion coefficient to the temperature and the amine concentration was given according to the following relationship:

$$D_{DEA\text{-}DEAsol} = \exp(-13.268 - 2287.7/T - 19.699 \cdot 10^{-5} C_{DEA}) \tag{25}$$

2-4. Viscosity

To estimate the viscosity of the amine solution, the correlation developed by Glasscock et al. [15] was used in this work as follows:

$$\mathrm{Ln}\mu = B_1 + \frac{B_2}{T} + B_3 T \tag{26}$$

The viscosity of water at different temperatures was taken from the Handbook of Chemistry and Physics [16].

2-5. Density

The density, d, of the amine solution was estimated with the following correlation where the solvent is water and pure amine is taken as solute:

$$d = \frac{997.1 + 0.01189 C_{DEA} 1000}{1000} \tag{27}$$

Where, C_{DEA} is the concentration of the amine solution.

3. Kinetics of Absorption with Chemical Reaction

The theory of gas-liquid reaction is well-established [17]. Only the necessary points to analyze the experimental results will be highlighted.

For a chemical reaction between a gaseous constituent A and a liquid reactant B in an aqueous solution to yield a product P;

$$A + B \xrightarrow{k_1} P \tag{28}$$

The rate of the reaction, R, obeys the relationship

$$R_A = -\frac{dC_A}{dt} = \frac{dP}{dt} = k_1 C_A C_B \tag{29}$$

Where C_A, C_B are the concentrations of components of A and B, respectively, and k_1 is the overall reaction rate constant. The molar flux of constituent A being transferred per unit time in a volume of liquid, dv, trough an interfacial area, a, is given by:

$$R_A = \frac{dR_A}{adv} = k_L C_i E \tag{30}$$

Where k_L is mass transfer coefficient in the liquid phase, C_i is the concentration and E is the enhancement factor. Eq. (30) is only valid with the assumptions that there is no resistance to mass transfer in the gas phase and the bulk liquid is initially free from A. According to Whitman [18], the mass transfer coefficient, k_L, in the film model is given by the following expression:

$$k_L = R_A/(C^i_A - C^b_A), \tag{31}$$

In this case, C^i_A, C^b_A are the concentrations of A at the interface and in the liquid bulk, respectively.

Danckwerts [17] analyzed the relationship between the enhancement factor, E, and the Hatta number [19], Ha, defined as

$$Ha = \left(\frac{2}{m+1} D_a k_{mn} (C^*_A)^{m-1} C^n_B\right)^{1/2} \Big/ k_L \tag{32}$$

Where C^*_A is the concentration of the gas at interface given by Henry's law:

$$C^*_A = \frac{P_A}{H_A} \tag{33}$$

Where H_A is Henry's constant and C_B is the concentration of component B in the liquid. He concluded that three different reaction zones could be identified:

- First zone is where E has a value close to 1 and corresponds to the slow reaction regime.
- Second zone in which E is approximately equal to Ha and the reaction is moderately fast. This zone is considered in pseudo m-nth order regime where the kinetics of a chemical reaction can be determined by measuring the flux of the absorbed gas.
- Third zone corresponds to the instantaneous reaction regime where the instantaneous enhancement factor is given by

$$E_i = \left(\frac{D_A}{D_B}\right)^{1/2} + \left(\frac{D_B}{D_A}\right)^{1/2} \frac{C_B}{zC^*_A} \tag{34}$$

The region of pseudo m-nth order is characterized as satisfying the condition [20]:

$$3 < E = H_a << E_i \tag{35}$$

The specific absorption rate can be expressed as:

$$R_A = \left(\frac{P_A}{H_A}\right)^{m+1/2} \left(\frac{2}{m+1} D_A k_{mn} C^n_B\right)^{1/2} \tag{36}$$

In case the resistance to mass transfer in the gas phase is not negligible, the specific absorption rate is given as follows:

$$\frac{P_A}{R_A} = \frac{1}{k_g} + \frac{H_A}{\sqrt{\frac{2}{m+1} k_{mn} D_A C^{m-1}_i C^n_B}} \tag{37}$$

Similarly, using Eq. (36) the overall reaction rate can be calculated as follows:

$$k_{ov} = k_{mn} = (R_A H^{m+1/2}_A / P^{m+1/2}_A D^{0.5}_A)^2 \tag{38}$$

EXPERIMENTAL

1. Materials

The chemicals used in the investigation were diethanolamine 99% assay obtained from Riedel deHaën, commercially available carbon dioxide of 99.99% purity and 99.999% Nitrogen and Reagecon standard 1 M aqueous NaOH and 1 M HCl solutions. All these chemicals were used as received. Distilled water was used as solvent throughout the experiment.

2. Experimental Set-up

The experimental set-up used in this work is described by Ben-

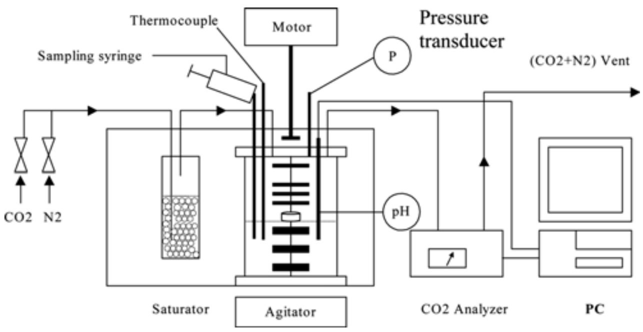

Fig. 1. Schematic diagram of the experimental set up.

amor and Aroua [21]; a schematic diagram is shown in Fig. 1. The main component of the system is a 10 cm internal diameter, double-jacketed stirred cell reactor. The total volume of the reactor is about 1,800 cm^3 with an active interface area, a, of 76.93 cm^2. The temperature in the reactor was measured with a J type thermocouple to within ±0.5 ^{o}C. Other accessories fitted to the reactor include a pressure transducer and syringe used for sample withdrawal. A Metrohm^R 716 DMS autotitrator automatically controlled with the Tinet^R 2.4 software was also available for analysing the liquid samples.

3. Experimental Procedure

For a typical run, 600 ml of amine solution was charged into the reactor, stirred and maintained at the preset temperature for about 10 minutes. Nitrogen was passed through the reactor to purge out any possible contaminant gas in the reactor. The experiment began by flowing into the reactor the reaction gas containing the desired proportions of CO_2 and N_2. The reaction gas flow rates were controlled by using factory calibrated 5080E series Brooks® mass flow controllers. Before entering the reactor, the reaction gas was passed through a water saturator maintained at the same temperature as that of the reactor. Exhaust gas from the reactor was fed to Rosemount® infrared CO_2 analyzer model 880A to determine CO_2 concentration in the outlet stream, which was recorded every 30 seconds. The analyzer was linked to a computerized data acquisition system using Daxpert® hardware and software. Throughout the experiment, the liquid was stirred constantly at 3.5 rpm. Under these conditions, a non-rippling gas-liquid interface was obtained. To determine the variations of carbamate concentration in the liquid, an aliquot sample of about 5 ml was taken at 5 min intervals and analyzed by using the titration technique described by Haji-Sulaiman. et al. [22]. At the end of each run, a liquid sample was immediately removed from the reactor for further analysis to determine the total gas loading and the amine final concentration.

RESULTS AND DISCUSSION

1. Determination of Amine Concentration

The concentration of DEA, C_{DEA}, in the solution was checked at the beginning and at the end of each run by using 1 M HCl standard solution. In all cases, the discrepancy between the initial and the final amine concentration was found to be less than 3%. Thus, the assumption of constant total amine concentration throughout the experiment was justified.

Table 2. Experimental data for the reaction CO_2-DEA at 293 K

DEA (mol/*l*)	P_{CO_2} (kPa)	$R_{CO_2}\times 10^6$ kmol/m$^2\cdot$s	k_{ov} (s^{-1})	$k_{ov\text{-}aver}$ (s^{-1})
0.2	1.53	0.147	46.94	48.1
	1.70	0.154	41.41	
	1.52	0.158	54.69	
	1.69	0.170	51.41	
	1.87	0.188	50.98	
	2.26	0.218	46.92	
	2.83	0.266	44.76	
0.5	4.81	0.969	227.95	212.4
	6.31	1.212	206.65	
	8.02	1.502	196.74	
	1.41	0.297	249.82	
	1.58	0.312	219.64	
	2.13	0.388	186.48	
	3.56	0.671	199.96	
1	11.97	3.368	536.46	545.1
	8.69	2.495	559.09	
	5.81	1.610	521.09	
	4.31	1.245	566.62	
	8.87	2.401	494.54	
	7.29	2.021	520.40	
	2.47	0.717	573.82	
	2.01	0.543	497.93	
	1.64	0.483	593.02	
	1.33	0.392	587.89	
2	10.90	4.072	1477.32	1835.7
	7.72	3.021	1623.35	
	1.47	0.687	2301.09	
	2.24	1.015	2166.39	
	3.08	1.279	1822.69	
	3.88	1.517	1623.12	
4	10.87	4.032	3823.35	4368.4
	9.22	3.594	4217.30	
	7.71	3.042	4320.79	
	6.17	2.648	5112.05	

2. Reaction Kinetics

The CO_2 absorption data into aqueous solutions of DEA were analyzed to determine the kinetics parameters associated with the reaction. The experimental data at different temperatures, pressures and amine concentrations are given in Tables 2-5. The CO_2 absorption flux per unit of time and surface, R_{CO_2}, is calculated as follows: $R_{CO_2}=J_{CO_2}/a$, where a is the gas-liquid contact area. The instantaneous absorption flux per unit of time, J_{CO_2}, is given by; $J_{CO_2}=CO_{2,out}-CO_{2,in}$ where, $CO_{2,in}$, and $CO_{2,out}$ are the amount of CO_2 fed into the reactor and that in the outlet stream, respectively. The CO_2 loading, α, is calculated from the total CO_2 in the solution, $CO_{2,tot}$, during the reaction holding time, t_r, and the volume of the solution, V_{sol}, and free amine concentration, C_{DEA}, according to the following relationship: $\alpha=CO_{2,tot}\cdot 1000/V_{sol}C_{DEA}$. The total CO_2 absorbed by the amine solution is given by $CO_{2,tot}=\sum_{t=0}^{t=t_r} J_{CO_2}$.

Table 3. Experimental data for the reaction CO_2-DEA at 303 K

DEA (mol/*l*)	P_{CO_2} (kPa)	$R_{CO_2}\times10^6$ kmol/m^2·s	k_{ov} (s^{-1})	$k_{ov\text{-}aver}$ (s^{-1})
0.2	1.66	2.03	87.1	73.9
	1.87	1.88	59.0	
	2.23	2.64	81.8	
	2.80	3.02	67.7	
0.5	1.52	3.87	420.8	342.6
	2.08	4.55	310.0	
	2.60	5.58	296.9	
1	1.25	4.97	1228.5	1114.8
	1.41	5.26	1082.0	
	1.55	5.91	1124.3	
	1.91	6.66	939.7	
	3.10	12.56	1270.6	
	3.93	14.44	1043.3	
2	1.27	7.05	3620.6	3232.5
	1.43	7.40	3114.6	
	1.71	9.18	3349.5	
	2.19	10.83	2845.5	
4	1.23	7.16	9649.6	9592.9
	1.36	7.93	9689.6	
	1.62	9.83	10423.3	
	2.09	11.50	8608.9	

Table 4. Experimental data for the reaction CO_2-DEA at 313 K

DEA (mol/*l*)	P_{CO_2} (kPa)	$R_{CO_2}\times10^6$ kmol/m^2·s	k_{ov} (s^{-1})	$k_{ov\text{-}aver}$ (s^{-1})
0.2	1.64	2.36	138.9	144.6
	1.80	2.76	157.6	
	2.16	3.43	167.8	
	2.76	3.60	114.3	
0.5	1.32	4.03	681.7	572.8
	1.47	4.41	657.6	
	1.64	4.72	607.9	
	2.02	5.22	489.6	
	2.56	6.16	427.1	
1	1.27	4.76	1247.1	1395.8
	1.36	5.89	1674.6	
	1.50	6.55	1674.6	
	1.88	7.10	1270.5	
	2.35	8.79	1270.5	
	3.19	11.50	1270.5	
	3.91	14.81	1362.9	
2	1.05	7.45	6419.0	5108.6
	1.24	7.37	4510.3	
	1.32	8.78	5626.7	
	1.65	9.94	4628.7	
	2.09	12.17	4358.1	
4	1.1	8.30	15513.9	12933.3
	1.6	10.69	13800.3	
	2.0	12.73	11899.4	
	2.7	16.41	10519.7	

Table 5. Experimental data for the reaction CO_2-DEA at 323 K

DEA (mol/*l*)	P_{CO_2} (kPa)	$R_{CO_2}\times10^6$ kmol/m^2·s	k_{ov} (s^{-1})	$k_{ov\text{-}aver}$ (s^{-1})
0.2	1.47	2.22	175.3	
	1.61	2.68	211.5	
	1.78	2.98	213.1	187.8
	2.19	3.09	151.4	
0.5	1.33	3.92	724.1	
	1.47	4.41	746.3	668.4
	1.64	4.83	729.2	
	2.05	4.88	473.8	
1	1.19	5.70	2251.4	
	1.35	6.00	1944.7	
	1.49	6.66	1957.2	1965.5
	1.83	7.65	1708.6	
2	1.08	7.15	6187.6	
	1.20	7.89	6074.5	5866.7
	1.33	8.67	5956.2	
	1.64	10.05	5248.7	
4	1.05	7.15	13983.6	
	1.15	8.20	15469.1	
	1.27	9.09	15557.8	14615.2
	1.57	10.48	13450.3	

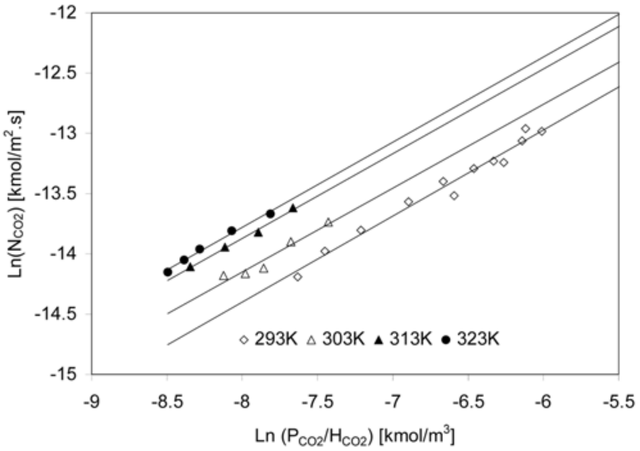

Fig. 2. Reaction order with respect to CO_2 for DEA 2 M at different temperatures.

The order of the reaction with respect to CO_2 was determined by plotting $\ln R_{CO_2}$ versus $\ln(P_{CO_2}/H_{CO_2})$ at different temperatures, and DEA concentrations are shown in Figs. 2 and 3. It is evident that linear variations of R_{CO_2} with P_{CO_2}/H_{CO_2} (on log-log plot) are obeyed in both graphs. From the slopes, it was found that the order of the reaction with respect to CO_2 is equal to one. This finding is in agreement with the conclusion reported in the literature regarding the order of the reaction with respect to CO_2.

To determine the reaction order with respect to amine concentration, substituting m=1, Eq (36) reduces to $\ln((R_{CO_2}H_{CO_2})^2/D_{CO_2}P^2_{CO_2})=\ln k_{mn}+n\ln C_B$. Thus, a plot of $\ln((R_{CO_2}H_{CO_2})^2/D_{CO_2}P^2_{CO_2})$ versus $\ln C_B$ would generate straight lines with slopes equal to n as shown in

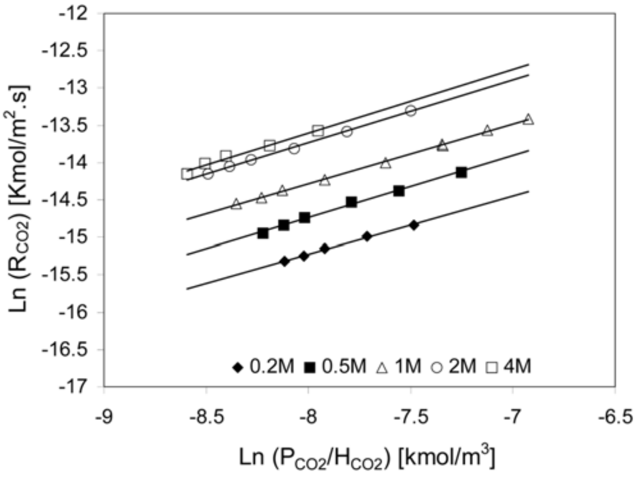

Fig. 3. Reaction order with respect to CO_2 at 323 K for different concentrations.

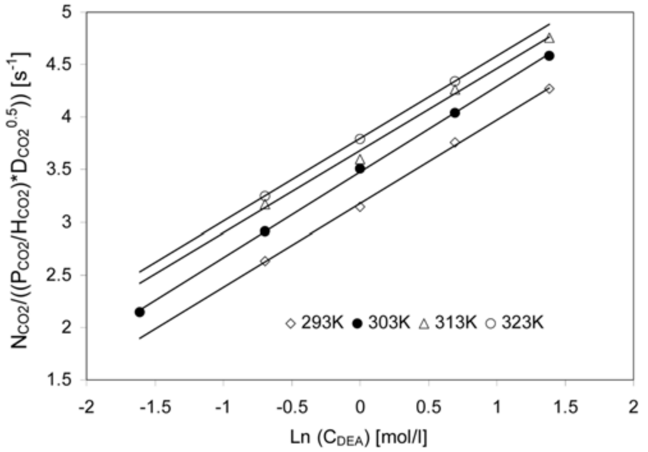

Fig. 4. Reaction order with respect to DEA concentration at different temperatures.

Fig. 4. Evaluation of the different slopes revealed that the value on n varies from 0.72 to 0.8, indicating a reaction order varying between one and two. This result suggests that the reaction scheme does not involve a direct reaction with DEA but proceeds through a specific mechanism. Thus, the application of a reaction mechanism, such as that of the zwitterion, to analyze the result is justified.

Taking the reaction order with respect to CO_2, equals to 1, the overall reaction rate, k_{ov}, is given by Eq. (38). To verify the reaction regime, values of Hatta number were calculated by using Eq. (32) and assuming a reaction order with respect to DEA equals 1.5. Mass transfer coefficient was obtained from a previous work [21]. All results with Hatta number less than two were discarded.

Considering Eqs. (15), (12) and (38), values of k_{app} at different temperatures were evaluated and presented in Table 6. By fitting the obtained k_{app} values to Eq. (16), all terms in the denominator, including k_2, were generated by using a non-linear regression technique based on Marquard-Lambda method. The fitted values of the kinetic constants are summarized in Table 7. The species concentrations in the solution required to fit Eq. (16) were estimated by using a VLE model developed by Benamor and Aroua [23].

Table 6. Apparent rate of the reaction between CO_2 and DEA at different temperatures and amine concentrations

Temp. (K)	DEA (kmol/m^3)	$k_{ov\text{-}aver}$ (s^{-1})	$k_{app\text{-}ave}$ (s^{-1})
293	0.2	48.2	45.1
	0.5	211.2	208.9
	1	540.2	537.5
	2	1835.7	1812.3
	4	4368.4	4356.2
303	0.2	73.9	59.0
	0.5	342.6	318.0
	1	1114.7	1066.7
	2	3232.5	3172.2
	4	9592.9	9518.4
313	0.2	144.6	111.6
	0.5	572.8	519.6
	1	1395.8	1290.1
	2	5108.5	4984.3
	4	12933.3	12758.1
323	0.2	187.8	122.0
	0.5	668.4	559.8
	1	1965.4	1813.0
	2	5866.7	5577.2
	4	14615.2	14262.4

Table 7. Fitted values of kinetic constants for the reaction between DEA and CO_2

Temp. (K)	k_2 (m^3/mole·s)	$k_2k_{H_2O}/k_{-1}\times10^6$ (m^6/mole^2·s)	$k_2k_{RR'NH}/k_{-1}\times10^4$ (m^6/mole^2·s)	$k_2k_{OH^-}/k_{-1}$ (m^6/mole^2·s)
293	4.18	3.14	3.54	$0.156.10^{-4}$
303	7.37	6.57	6.76	$27.57.10^{-2}$
313	14.63	11.72	13.22	$1.06.10^{-2}$

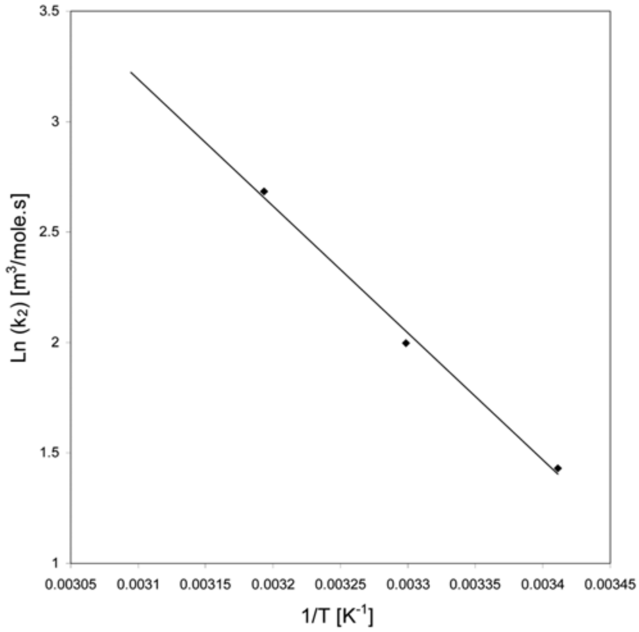

Fig. 5. Arrhenius plot for the reaction of CO_2 with DEA.

Table 8. Contribution of carbamate ion to the overall absorbed CO_2 in 0.5 M DEA solution

P_{CO_2} (kPa)	Time (min)	Loading (mol CO_2/mol amine)	Carbamate (mol CO_2/mol amine)	Carbamate/Loading (%)
17.1	10	0.024	0.024	96.8
	15	0.036	0.04	109.8
	20	0.049	0.056	114.0
	25	0.063	0.072	113.3
	30	0.077	0.086	111.2
14.2	10	0.020	0.02	98.0
	15	0.031	0.034	106.8
	25	0.053	0.056	105.6
	30	0.064	0.068	104.4
10.1	10	0.017	0.014	85.4
	15	0.026	0.028	112.0
	20	0.035	0.036	103.1
	25	0.044	0.046	103.8
	30	0.054	0.056	102.7
8.1	10	0.015	0.014	89.9
	15	0.023	0.024	106.7
	20	0.031	0.032	100.7
	25	0.039	0.042	108.1
	30	0.048	0.048	100.1
6.3	10	0.013	0.012	97.1
	15	0.020	0.02	101.8
	20	0.027	0.028	100.5
	25	0.035	0.036	102.8
	30	0.042	0.046	106.3
4.5	10	0.011	0.012	104.4
	15	0.017	0.018	106.6
	20	0.023	0.024	105.8
	25	0.029	0.03	104.0
	30	0.036	0.038	106.3
		Average (%)		103.7

Table 9. Contribution of carbamate ion to the overall absorbed CO_2 in 1 M DEA solution

P_{CO_2} (kPa)	Time (min)	Loading (mol CO_2/mol amine)	Carbamate (mol CO_2/mol amine)	Carbamate/Loading (%)
16.7	10	0.016	0.014	84.5
	15	0.024	0.022	91.2
	20	0.033	0.032	96.1
	25	0.042	0.041	96.6
	30	0.051	0.050	96.7
12.4	10	0.017	0.017	101.3
	15	0.026	0.029	113.3
	20	0.035	0.040	114.2
	25	0.044	0.050	113.9
	30	0.054	0.061	113.5
8.8	10	0.013	0.012	90.0
	15	0.020	0.021	102.9
	20	0.027	0.028	102.2
	25	0.034	0.036	104.5
	30	0.042	0.044	105.7
7.3	10	0.011	0.008	69.4
	15	0.017	0.014	84.6
	20	0.023	0.022	96.5
	25	0.029	0.029	100.4
	30	0.035	0.036	100.9
		Average (%)		98.9

3. Activation Energy

The effect of temperature on the reaction rate constant, k_2, was assessed by using an Arrhenius plot for the fitted values of k_2 as shown in Fig. 5. From the line of $\ln(k_2)$ versus $\ln(1/T)$, a negative slope having a value of 5742 equals to $-E_a/R$ was obtained. From which, the activation energy, E_a, could be estimated 11.42 kcal/mol. It should be noted here that the value of k_2 at 323 K was not taken into account in this plot as it exhibits a low value; this can be explained by the effect of the reverse reaction at 323 K having a pronounced impact on the overall reaction rate constant. Thus, the obtained values of k_2 using the approximate analytical solution do not represent its true value; a numerical solution is more appropriate in this case to take into account the effect of the reverse reaction. The temperature dependency of the rate constant k_2 was correlated as follows: $k_2=1.31\cdot10^9\exp(-5742/T(K))$

4. Comparison with the Literature

A strict comparison between the results of this work and those published in the open literature is not possible as they were obtained under different conditions using different optimization techniques. The use of different optimization techniques to generate the reaction rates constants may yield different values, especially if inappropriate weightings for the influence of each species are used. However, the values obtained from this work compare favorably in the order of magnitude with most of the values reported in the literature as shown in Table 12. These results confirm the conclusion that the zwitterions deprotonation rate constants increase with the increasing basicity of the deprotonating base as pointed out by Little et al. [25]. Comparing the value of the activation energy with those reported in the literature shows a good agreement, which can make a similar conclusion.

Table 10. Contribution of carbamate ion to the overall absorbed CO_2 in 2 M DEA solution

P_{CO_2} (kPa)	Time (min)	Load (mol/mol)	Carbamate (mol/mol)	Carba/Load (%)
15.1	10	0.023	0.023	101.3
	15	0.035	0.037	105.1
	20	0.047	0.049	104.1
	25	0.060	0.063	104.7
	30	0.074	0.076	103.7
11.3	10	0.019	0.019	102.2
	15	0.030	0.031	104.0
	20	0.042	0.042	102.0
	25	0.052	0.054	102.7
	30	0.065	0.066	101.8
8.0	10	0.016	0.017	105.8
	15	0.025	0.027	105.5
	20	0.034	0.036	104.8
	25	0.043	0.045	103.8
	30	0.053	0.054	102.6
6.7	10	0.013	0.013	102.1
	15	0.020	0.020	103.2
	20	0.027	0.027	102.1
	25	0.034	0.034	101.4
	30	0.041	0.041	99.4
5.4	10	0.010	0.009	94.9
	15	0.015	0.014	93.6
	20	0.020	0.019	95.1
	25	0.026	0.025	96.1
	30	0.032	0.031	97.4
4.3	10	0.007	0.007	100.4
	15	0.011	0.010	93.0
	20	0.015	0.014	93.6
	25	0.019	0.018	95.3
	30	0.024	0.022	93.3
Average (%)				100.5

5. Carbamate Concentration

To establish the significance of carbamate formation in the reaction, the concentration of carbamate in the loaded solution was determined by using the titration technique described by Haji-Sulaiman et al. [24]. The analysis was performed on aliquot sample of 5 ml taken from the reactor and titrated with a solution of 0.05 N NaOH with the computer-controlled metrohm 716 DMS titrino autotitrator. The volume of NaOH, V_{NaOH}, required to neutralize the acidic species in the solution was determined from the first derivative of the titration curve. In this case, only the bicarbonate, the protonated amine ions and the free CO_2 will react with the hydroxide ions. Thus, the concentration of carbamate, $[DEACOO^-]$, can be related to the

Table 11. Contribution of carbamate ion to the overall absorbed CO_2 in 4 M DEA solution

P_{CO_2} (kPa)	Time (min)	Load (mol/mol)	Carbamate (mol/mol)	Carba/Load (%)
15.3	10	0.004	0.005	104.9
	15	0.007	0.007	104.7
	20	0.010	0.010	103.5
	25	0.013	0.013	101.8
	30	0.016	0.017	102.9
11.1	10	0.004	0.004	107.9
	15	0.006	0.007	103.0
	20	0.009	0.009	99.5
	25	0.012	0.013	101.2
	30	0.015	0.016	101.6
9.4	10	0.003	0.004	104.1
	15	0.006	0.006	99.3
	20	0.008	0.008	98.4
	25	0.011	0.011	99.0
7.9	10	0.003	0.003	100.7
	15	0.005	0.005	96.4
	20	0.007	0.007	97.3
	25	0.010	0.010	101.3
	30	0.012	0.013	103.1
6.3	10	0.003	0.003	97.0
	15	0.004	0.004	96.1
	20	0.006	0.006	96.7
	25	0.008	0.009	101.1
	30	0.010	0.011	102.4
Average (%)				100.9

Table 12. Comparison between the fitted values of kinetic constants for the reaction between DEA and CO_2

Reference	Temp. (K)	k_2 (m^3/mole·s)	$k_2k_{H_2O}/k_{-1}\times10^6$ ($m^6/mol^2\cdot s$)	$k_2k_{RR'NH}/k_{-1}\times10^4$ ($m^6/mole^2\cdot s$)	$k_2k_{OH^-}/k_{-1}$ ($m^6/mole^2\cdot s$)
This work	293	4.18	3.14	3.54	$0.156.10^{-4}$
This work	303	7.37	6.57	6.76	$27.57.10^{-2}$
This work	313	14.63	11.72	13.22	$1.06.10^{-2}$
Laddha et al. [10]	298	1.14	-	12.0	-
Blauwhoff et al.[3]	303	>7.3	3.7	4.8	$8.52.10^{-6}$
Sada et al. [36]	298	1.1	-	13.2	-
Versteeg and Oyevaar [32]	298	3.24	1.7	7.1	-
Little et al. [25]	303	4.36	8.5	13.0	-
	318	7.31	18.2	13.6	-
	333	∞	4.3	13.1	-

CO_2 loading, α, and the concentration of NaOH, B, by the relationship: $[DEACCOO^-]=2\alpha[C_{DEA}]_t-B$, experimental results are shown in Tables 8-11. Analysis of these results revealed that the total contribution of carbamate to the overall absorbed CO_2 has an average of 101% with a maximum deviation of 11.1%. This shows that carbamate ion is the only product of the reaction and contributions of free CO_2 and bicarbonate ion to the overall absorbed CO_2 is negligible. This reaffirms the observation made by the authors CO_2-DEA-H_2O species concentration profile based on their VLE model [23], where they concluded that at low CO_2 partial pressure, carbamate is the only product of the reaction.

CONCLUSIONS

Additional data on the kinetics of the reaction between CO_2 and aqueous solutions of diethanolamine (DEA) were reported at 293, 303, 313, and 323 K and varying carbon dioxide partial pressures with amine concentrations varied from 0.2 M to 4.0 M. The reaction between CO_2 and DEA can be interpreted by using the zwitterion mechanism proposed by Caplow [7]. The order of the reaction with respect to DEA is found to vary between one and two, which is in accordance with the proposed mechanism. However, the range of validity of each order and the intermediate zone could not be established. The deprotonation rate constant for DEA-zwitterion was evaluated at 293, 303 and 313 K. However, due to the limitations of the absorption technique used in this work, its value at 323 K was found not to be in line with the values obtained at lower temperatures. This is mainly due to the fact that the reaction is very fast and the effect of the reversible reaction assumed negligible in the Danckwerts model [17] is not verified. Thus, the condition of pseudo first order reaction regime is not fulfilled at this temperature. The activation energy of the intermediate zwitterions deprotonation rate constant is estimated at about 47.74 kJoule/mol, which is in line with most published results. The temperature dependency of the rate constant, k_2, can be estimated with the following relationship: $k_2=1.31\cdot10^9\exp(-5742/T(K))m^3\cdot mol^{-1}\cdot s^{-1}$. Furthermore, the contribution of carbamate ion to the overall absorbed CO_2 was experimentally determined and found to be of the order of 100%, indicating that carbamate is the only product of the reaction.

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NOMENCLATURE

C_i : concentration of components i [mol/l]
C_A^* : concentration of the gas at the interface [mol/l]
D_i : diffusion coefficient of component i [m^2/s]
E_i : instantaneous enhancement factor [-]
Ha : Hatta number [-]
H_i : solubility of component i [Pa·m^3/mol]
J_{CO_2} : instantaneous absorption flux per unit of time [mol/s]
P_i : partial pressure of component i [kPa]
R_{CO_2} : absorption flux per unit of time and surface [mol/m^2·s]
a : gas-liquid contact area [m^2]
d : density [kg/l]
k_{H_2O} : CO_2 hydration rate constant [s^{-1}]
$k^*_{OH^-}$: bicarbonate formation rate constant [s^{-1}]
k_{ov} : overall reaction rate constant [s^{-1}]
k_{app} : apparent reaction rate constant [s^{-1}]
k_L : liquid mass transfer coefficient [m/s]
m : reaction order with respect to CO_2 [-]
n : reaction order with respect to amine [-]
μ : viscosity [cp]

REFERENCES

1. C. Blanc and G. Demarais, *Int. Chem. Eng.*, **24**(1), 43 (1984).
2. E. B. Rinker, S. S. Ashour and O. C. Sandall, *Ind. Eng. Chem. Res.*, **35**, 1107 (1996).
3. P. M. M. Blauwhoff and W. P. M. Van Swaaij, *Chem. Eng. Sci.*, **38**, 1411 (1983).
4. M. Caplow, *J. Am. Chem. Soc.*, **90**, 6795 (1968).
5. P. V. Danckwerts, *Chem. Eng. Sci.*, **34**, 443 (1979).
6. G. F. Versteeg, L. A. Van Dijck and W. P. M. Van Swaaij, *Chem. Eng.*, **144**, 113 (1996).
7. M. Caplow, *J. Am. Chem. Soc.*, **90**, 6795 (1968).
8. B. R. W. Pinsent, L. Pearson and F. G. W. Roughton, *Trans. Faraday Soc.*, **52**, 1512 (1956).
9. P. M. M. Blauwhoff and W. P. M. Van Swaaij, *Chem. Eng. Sci.*, **38**,

1411 (1983).

10. S. S. Laddha, J. M. Diaz and P. V. Danckwerts, *Chem. Eng. Sci.*, **36**, 229 (1981).
11. G. F. Versteeg and W. P. M. Van Swaaij, *J. Chem. Eng. Data.*, **33**, 29 (1988).
12. E. D. Snijder, M. J. M. Riele, G. F. Versteeg and W. P. M. Van Swaaij, *J. Chem. Eng. Data.*, **38**, 475 (1993).
13. G. F. Versteeg, L. A. J. Van Dijck and W. P. M. Van Swaaij, *Chem. Eng. Sci.*, **144**, 113 (1996).
14. F. R. S. Taylor, *Proc. R. Soc. London.*, **A219**, 186 (1953).
15. D. A. Glasscock, J. E. Critchfield and G. T. Rochelle, *Chem. Eng. Sci.*, **46**, 2829 (1991).
16. Handbook of Chemistry and physics 83rd Edition (2003).
17. P. V. Danckwerts, *Gas liquid reaction*, Mcgraw-Hill, New York (1970).
18. W. G. Whitman, *Chem. Met. Engng.*, **29**, 146 (1923).
19. S. Hatta, *Technol. Repts.*, Tohoku Imp University, **9** (1928).
20. C. Alvarez-Fuster, N. Midoux, A. Laurent and J.-C. Charpentier, *Chem. Eng. Sci.*, **35**, 1717 (1980).
21. A. Benamor and M. K. Aroua, *Korean J. Chem. Eng.*, **24**, 16 (2007).
22. M. Z. Haji-Sulaiman, M. K. Aroua and A. Benamor, *Trans IChemE.*, **76**, Part A, 961 (1998).
23. A. Benamor and M. K. Aroua, *Fluid Phase Equilibria.*, **231**, 150 (2005).
24. M. Z. Haji-Sulaiman, M. K. Aroua and M. I. Pervez, *Gas. Sep. Pur.*, **10**, 13 (1996).
25. R. J. Little, G. F. Versteeg and W. P. M. Van Swaaij, *Chem. Eng. Sci.*, **47**, 2037 (1992).
26. E. Sada, H. Kumazawa and M. A. Butt, *J. Chem. Eng. Data*, **22**, 277 (1977).
27. E. Sada, H. Kumazawa and M. A. Butt, *Chem. Eng. Sci.*, **31**, 839 (1976).
28. N. Haimour, *J. Chem. Eng. Data*, **35**, 177 (1990).
29. E. B. Rinker and O. C. Sandall, *Chem. Eng. Com.*, **144**, 85 (1996).
30. T.-C. Tsai, J.-J. Kho, M.-H. Wang, C.-Y. Lin and M.-H. Li, *J. Chem. Eng. Data*, **45**, 341 (2000).
31. M. H. Oyvaar, R. W. J. Morssinkhof and K. R. Westerterp, *J. Chem. Eng. Data*, **34**, 77 (1989).
32. G. F. Versteeg and M. H. Oyevaar, *Chem. Eng. Sci.*, **44**, 1264 (1989).
33. G. F. Versteeg, P. M. Blauwhoff and W. P. M. Van Swaaij, *Chem. Eng. Sci.*, **42**, 1103 (1987).
34. G. J. Browning and R. H. Weiland, *J. Chem. Eng. Data*, **39**, 817 (1994).
35. M. H. Li and W. C. Lee, *J. Chem. Eng. Data*, **41**(3), 551 (1996).
36. E. Sada, H. Kumazawa, Z. Q. Han and M. A. Butt, *AIChE J.*, **31**, 1297 (1985).