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SEPARATIONS

Absorption of Carbon Dioxide at High Partial Pressures in Aqueous Solutions of Di-isopropanolamine

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The process of carbon dioxide (CO_2) absorption is analyzed at high partial pressures, in aqueous solutions of di-isopropanolamine (DIPA). The experiments were performed in a stirred tank reactor with a planar and known interfacial area. The variables considered were the DIPA concentration (within a range of 0.0413−1.90 kmol/m^3) and the temperature (within an interval of 288−313 K). From the results, we deduce that the absorption process occurs in a moderately fast reaction regime with a second-order kinetic for the amine and a first-order kinetic for the CO_2. The reaction rate constant for each process was calculated and correlated as a function of temperature.

1. Introduction

Two aspects may underscore the importance of the use of alkanolamines. First, from an industrial standpoint, the application of alkanolamine solutions to gaseous currents that have impurities from acidic gases (e.g., CO_2, H_2S) is a process of great importance that, for the requirements of the industry itself, are habitually used, as in the case of the production processes of natural gas, hydrogen purification, treatment of refinery gas, production of synthesis gas, etc. Second, to satisfy the Kyoto Accords for the year 2012 (and thereby preserve the environment for future generations), the governments of the different countries must establish suitable guidelines to reduce the emission of gases that cause the greenhouse effect, which, as in the case of CO_2, are contributing to climatic change. In this way, national plans for CO_2 emissions should be developed to encourage companies to invest in new technologies that pollute less and meet the CO_2-emission quotas that are permitted by the different industrial sectors. In this sense, the purification of the gaseous effluents by alkanolamine has proven especially useful.

Industrial CO_2 removal by absorption processes use aqueous and organic alkanolamine solutions. In principle, it is necessary to differentiate between primary, secondary, and tertiary alkanolamines. The most common alkanolamines used in industry are monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), di-isopropanolamine (DIPA), triethanolamine (TEA), and methyldiethanolamine (MDEA). A recent advancement in gas-treatment technology is the application of sterically hindered amines, examples of which are primary 2-amino-2-methyl-1-propanol (AMP) or secondary 2-methyl-amino-ethanol (MAE) and 2-ethyl-amino-ethanol (EAE). These amines offer higher absorption capacity, absorption rate, and selectively lower corrosive behavior, so that they can be used at high concentrations and the stripping energy requirements can be reduced, compared to those of the conventional absorption processes using MEA and DEA as absorbents[1] (20% less than required for MEA). Recently, different research groups have studied the absorption of acidic gases in blended amines that have specific advantages over the use of single amines.[2−5]

Most of the aforementioned amines have been widely studied, in relation to their kinetics at low pressures; however, there is no information about their behavior at high partial pressures of carbon dioxide (CO_2).

In any case, the chemistry of CO_2 reactions in the liquid phase in amine solutions is complex and not fully understood.[6,7] An idea of the complexity of these systems is conveyed by the reaction mechanisms of the primary and secondary alkanolamines. In this scheme, a high number of different reaction can be involved and, in the liquid phase, almost nine compounds and ionic species can coexist:[8] $R'RNH$, $R'RNH_2^+$, $RNCOO^-$, CO_2, HCO_3^-, $CO_3^=$, OH^-, H^+ (or H_3O^+), and H_2O, where R and R′ are the radicals $-CH_2-CH_2OH$ or $-H$; this implies the need to establish, in a rigorous way, for each amine, the reactions involved in the process, because knowledge of the kinetic of these reactions (different for primary, secondary, or tertiary amines, or if the medium is aqueous or organic) is indispensable for determining the absorption rates and, therefore, designing, materials of construction, and optimization of the industrial contactors of absorption in which these processes are performed.

In the present work, we analyze the absorption process of CO_2 at high partial pressures in aqueous solutions of DIPA and the kinetic aspects of the process.

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2. Experimental Section

The gas used in this work was CO_2 (99.98% SEO), with oxygen, water steam, and hydrocarbons as impurities; di-isopropanolamine (DIPA) was a Fluka product of nominal purity (>98%). Aqueous solutions of alkanolamine were prepared with distilled–deionized water (resistivity of 18.2 MΩ cm).

The experiments were conducted in a stirred tank reactor that was operated in batches, with respect to the gas–liquid phases, having a planar interfacial area. The use of pure CO_2 enables the determination of the absorption rate at different points, using a soap-film meter, which allows the direct measurement of the CO_2 absorbed. The same experimental installation as that described in a previous work was used.[9] Volumes of 100 mL of the aqueous solutions of DIPA were used in the range of 0.0413–1.90 kmol/m^3. The temperature was set within the interval of 288–313 K. In all the experiments, the stirring rate in the reactor was 180 rpm, maintaining a flat interface area of 35.26 cm^2.

2.1. Physical and Transport Properties. Under the aforementioned conditions, the viscosity and density of the alkanolamine solutions were experimentally determined.

The calculation of the initial partial pressure of CO_2 (p_A) is given by

$$p_{\mathrm{A}} = P - p_{\mathrm{V}} \tag{1}$$

where the CO_2 impurities were not considered.

To determine the solubility of CO_2 in aqueous solutions of DIPA, we used the Danckwerts relationship,[10] using eqs 2 and 3 within the temperature intervals of 288–298 K and 303–313 K, respectively:

$$\mathrm{He} = 10^{(5.3+0.035C_{\mathrm{Bo}}-1140/T)} \tag{2}$$

$$\mathrm{He} = 10^{(5.3+0.026C_{\mathrm{Bo}}-1140/T)} \tag{3}$$

The water viscosities (μ_{w}) and alkanolamine solutions (μ_{B}) were measured using a capillary viscosimeter; the former were determined in a previous work at the assayed temperatures.[11]

The diffusion coefficients of CO_2 in aqueous solutions of DIPA ($D_{\mathrm{CO_2}}$) were determined using the relationships of Sada et al.,[12] Versteeg and van Swaaij,[13] and the modified Stokes–Einstein relationship:

$$\frac{D_{\mathrm{CO_2}}}{D_{\mathrm{CO_2,w}}} = \frac{D_{\mathrm{N_2O}}}{D_{\mathrm{N_2O,w}}} \tag{4}$$

where

$$D_{\mathrm{CO_2,w}} = 2.35 \times 10^{-6}\, \mathrm{e}^{-2119/T} \tag{5}$$

$$D_{\mathrm{N_2O,w}} = 5.07 \times 10^{-6}\, \mathrm{e}^{-2371/T} \tag{6}$$

$$D_{\mathrm{N_2O}}\mu_{\mathrm{B}}^{\gamma} = D_{\mathrm{N_2O,w}}\mu_{\mathrm{w}}^{\gamma} \tag{7}$$

The value of γ in eq 7 was evaluated using the diffusion coefficient of N_2O in aqueous solutions of different alkanolamines.[12]

The diffusion coefficient of the alkanolamine in the liquid phase (D_{B}) was calculated by means of the empirical relationship of Wilke and Chang:[14]

$$D_{\mathrm{B}} = 2.16 \times 10^{-15}\left(\frac{T}{\mu_{\mathrm{B}}}\right) \tag{8}$$

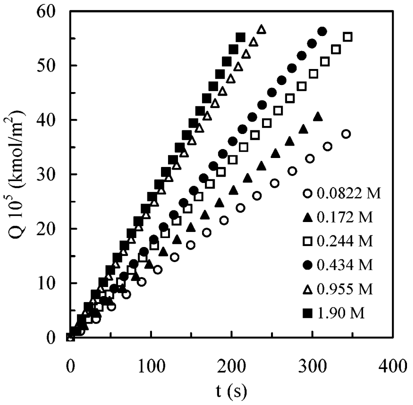

Figure 1. CO_2 absorbed per unit of surface and time in the experiments with di-isopropanolamine (DIPA) at 293 K.

2.2. Analytical Methods. The initial concentration of the amine was determined by titration with a HCl solution, using methyl orange as the indicator. The CO_2 concentration in liquid was determined by standard titration methods. An excess of NaOH and of $BaCl_2$ were added to the liquid sample, and the excess of NaOH was titrated with HCl solution, using an aqueous solution of blue thymol 0.04% as the indicator.

3. Results and Discussion

The flow density (N_{A}) values were calculated assuming that the gas follows ideal behavior, using the following expressions:

$$N_{\mathrm{A}} = \frac{n'}{A} = \frac{PQ'}{RTA} \tag{9}$$

The value of the volumetric flow (Q') coincided with the value of the slope of the straight lines resulting from the representation of the CO_2 volume absorbed against time for each experiment, and the determinations were made using the linear-regression method of the experimental results. For example, Figure 1 offers graphic representation of the CO_2 absorbed per unit of surface against time in the experiments conducted at 293 K. The operating temperature and partial pressure of the gas were maintained constant, while the initial concentration of di-propanolamine (DIPA) was varied in the range of 0.082–1.9 kmol/m^3. In the absorption experiments with pure CO_2 in aqueous DIPA solutions, we analyzed the influence of the initial alkanolamine concentration and the operating temperature.

3.1. Absorption in DIPA Solutions. DIPA (represented as the formula NH–(CH_2–CHOH–CH_3)$_2$), as a secondary alkanolamine, has two functional groups (>NH) and (–OH) that can react with CO_2, following reactions 10 and 11. If we consider the aqueous and basicity characteristics of the absorbent solutions, reactions 12 and 13 can also be considered:

$$-\overset{|}{\mathrm{N}}\mathrm{H} + \mathrm{CO_2} \rightarrow -\overset{|}{\mathrm{N}}\mathrm{COO^-H^+} \tag{10}$$

carbamic acid derivative

$$-\mathrm{OH} + \mathrm{CO_2} \rightarrow -\mathrm{OCOO^-H^+} \tag{11}$$

carbonic acid derivative

$$\mathrm{CO_2} + \mathrm{H_2O} \rightleftarrows \mathrm{H_2CO_3} \tag{12}$$

$$\mathrm{CO_2} + \mathrm{OH^-} \rightleftarrows \mathrm{HCO_3}^- \tag{13}$$

Table 1. Flow Densities in the Absorption of Carbon Dioxide (CO_2) in Di-isopropanolamine (DIPA) Solutions

p_A (kPa)	C_{Bo} (kmol/m^3)	η	N_A ($\times 10^6$ kmol/m^2 s)	p_A (kPa)	C_{Bo} (kmol/m^3)	η	N_A ($\times 10^6$ kmol/m^2 s)
	$T = 288$ K				$T = 303$ K		
92.9	0.0865	0.48	1.10	89.9	0.0413	0.62	1.26
91.9	0.175	0.23	1.26	89.7	0.146	0.17	1.52
91.8	0.274	0.15	1.40	89.6	0.224	0.11	1.75
92.9	0.440	0.092	1.72	89.6	0.385	0.065	2.10
92.7	0.867	0.045	2.01	89.1	0.805	0.030	2.80
91.7	1.83	0.019	2.15	88.8	1.63	0.014	3.14
	$T = 293$ K				$T = 308$ K		
91.6	0.0822	0.43	1.13	88.2	0.0732	0.30	1.33
92.2	0.172	0.20	1.38	88.9	0.160	0.14	1.61
92.1	0.244	0.14	1.61	87.9	0.224	0.088	1.86
91.2	0.434	0.078	1.83	87.2	0.384	0.055	2.48
91.5	0.955	0.034	2.39	87.1	0.825	0.025	2.93
90.6	1.90	0.016	2.63	87.2	1.68	0.012	3.68
	$T = 298$ K				$T = 313$ K		
91.2	0.0567	0.53	1.12	86.2	0.0647	0.30	1.50
91.5	0.145	0.21	1.28	86.4	0.122	0.16	1.81
91.2	0.224	0.13	1.60	85.7	0.193	0.095	2.11
91.0	0.400	0.073	2.08	86.5	0.363	0.051	2.68
90.9	0.874	0.032	2.41	85.5	0.791	0.022	3.43
90.5	1.90	0.014	2.72	85.4	1.53	0.011	3.99

However, the bicarbonate formation is considered negligible against the carbamic acid formation. The extent to which any of the above reactions occur is dependent on their kinetic constants, the alkanolamine concentration, and the OH^- ion present; therefore, the relative quantities of CO_2 and DIPA are determinant in the formation of the derivative of carbamic acid. Thus, if the carbonation ratio (η) is <0.5, the main formed product is the derivative of the carbamic acid:[15]

$$CO_2 + R_2NH \rightarrow R_2NCOO^- + R_2NH_2^+ \qquad (14)$$

whereas if $\eta \geq 0.5$, the conversion of carbamate into bicarbonate can occur:[15]

$$R_2NCOO^- + 2H_2O + CO_2 \rightarrow R_2NH_2^+ + 2HCO_3^- \qquad (15)$$

In almost all experiments performed in this work, except when $T = 298$ K ($C_{Bo} = 0.057$ kmol/m^3) and $T = 303$ K ($C_{Bo} = 0.041$ kmol/m^3), the carbonation ratio was <0.5 (Table 1), which, in agreement with Astarita et al.,[15] indicates that the carbamate was the product of the reaction between the CO_2 and DIPA, and the mechanism would be that indicated by reactions 16, 17, and 18.

$$CO_2 + R_2NH \rightarrow R_2NCOOH \qquad (16)$$

$$R_2NCOOH \rightarrow R_2NCOO^- + H^+ \qquad (17)$$

$$R_2NH + H^+ \rightarrow R_2NH_2^+ \qquad (18)$$

Table 1 lists the values of N_A, the partial pressure, and the carbonation ratio corresponding to each of the initial DIPA concentrations assays.

On the other hand, the influence of pH in reaction 11 is very important, and, according to Astarita et al.,[15] this reaction is possible only at pH ≥ 11. At pH <10, the formation of the carbonic acid derivative can be considered to be negligible.

The pH values measured during the absorption process in all the experiments of the di-isopropanolamine solutions at the beginning of the experiments indicate that the pH was between 9.6 for the lower concentrations and 11.1 for the higher ones. On the basis of the results found, the main reaction can be considered to be the formation of the carbamic acid derivative for all the temperatures and concentrations assayed, whereas reaction 11 could only occur for the highest concentration and during the initial instants.

It should be indicated that, because of the basic character of DIPA, the reaction with the CO_2 caused the concentration of the alkanolamine to diminish over time, with a concomitant fall in the pH of the solution, as reflected in Figure 2a, which also shows that the initial pH increased with the concentration for the different experiments of the $T = 293$ K series.

For the entire range of temperatures and concentrations assayed, the pH values of the aqueous solutions of alkanolamine were correlated with the initial concentration of DIPA, as shown in the representation of

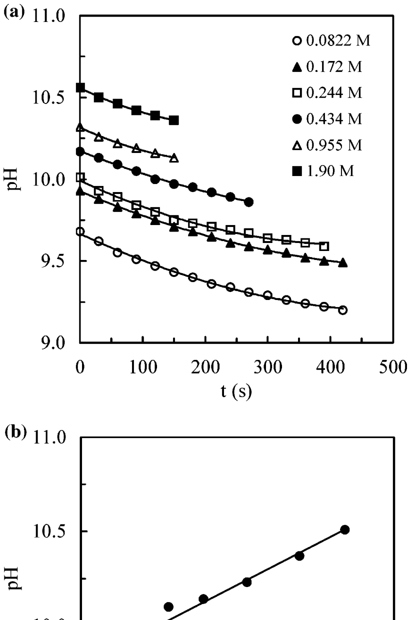

Figure 2. (a) Variation in pH of the DIPA solution with time, over the absorption process at 293 K at corresponding concentrations. (b) Variation in pH with the DIPA concentration at 313 K.

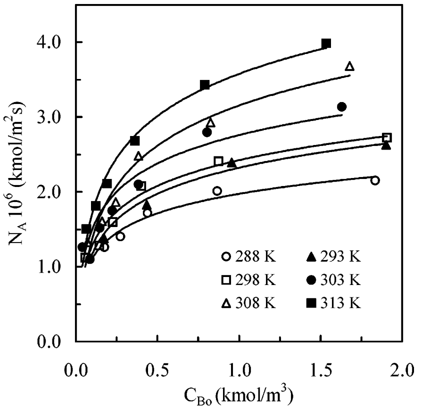

Figure 3. Variation in N_A with the DIPA concentration at the temperatures indicated.

Figure 2b, for the 313 K series, reflecting a linear relationship according to eq 19, resulting in similar fits for the rest of the temperatures assayed:

$$\mathrm{pH} = 0.428 \log C_{Bo} + 10.4 \tag{19}$$

3.2. Reaction Regimen. For the determination of the reaction regimen, representations were made of values of the flux density N_A against the amine concentration C_{Bo}, as shown in Figure 3, where no linear relationship was appreciated. This fact, in principle, rules out the idea of an instantaneous reaction regimen for all the concentrations and temperatures assayed.

Assuming that the carbonation ratio is <0.5 and that the reaction occurs by means of a second-order mechanism, we can apply the criterion of Astarita et al.,[15] referring to the fast-reaction regime (eq 20):

$$N_A = C_A^* \sqrt{D_A k C_{Bo}} \tag{20}$$

This requires previous knowledge of the kinetic constant of the reaction, and in the absorption process with DIPA, the literature shows disagreement on the correct value of k at the same temperature. In this sense, Danckwerts and Sharma,[16] at 298 K, determined a value of 400 m^3 kmol^{-1} s^{-1} for a first-order kinetic, with respect to DIPA. Using a stirred contactor at the same temperature, Groothuis[17] and Versteeg and van Swaaij[18] proposed values of 450 and 2700 m^3 kmol^{-1} s^{-1}, respectively. Meanwhile, Blauwhoff et al.,[19] for a kinetic of pseudo-first order (1.6−1.8 with respect to the alkanolamine) operating with pure CO_2 in a stirred contactor, have determined a value of 2440 m^3 kmol^{-1} s^{-1}.

From these differences, it can be stated that the kinetic of the absorption processes is not fully established. In relation to the CO_2−DIPA system, a reaction order of 2, with respect to DIPA, and a two-step mechanism that considers "zwitterion" formation is proposed. This mechanism was initially proposed by Caplow,[20] reintroduced afterward by Danckwerts,[21] and currently is widely accepted.[22] The first step of the mechanism is the "zwitterion" formation CO_2−DIPA (R_2NH^+ COO^-), followed by a deprotonation of the "zwitterion" catalyzed by a base.

If we assume, as an initial hypothesis, the fast-reaction regime, the flux density N_A can be determined by the expression[23,24]

$$N_A = \sqrt{\frac{2}{m+1} D_A k_{m,n} {C_{Ao}}^{m+1} {C_{Bo}}^{n}} \tag{21}$$

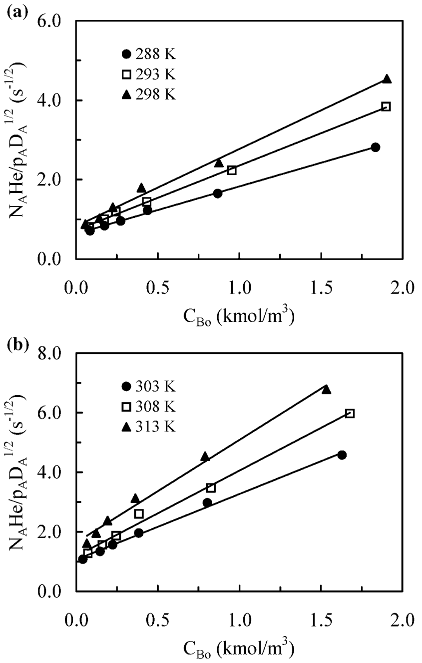

Figure 4. Study of reaction regime for DIPA.

with an order m, with respect to the CO_2, and an order n, with respect the alkanolamine.

Under the assumption that the order of the reaction is one with respect to CO_2 in the absorption with secondary alkanolamines, eq 21 is reduced to

$$N_A = C_{Ao} \sqrt{D_A k_{1,n} {C_{Bo}}^{n}} \tag{22}$$

3.3. Kinetic Parameters. The CO_2 absorption by aqueous DIPA solutions was considered to have occurred under practically isothermal conditions, given that the increase of temperature in the solution was <0.2 K during the absorption and could be neglected.

Assuming a fast-reaction regime with a second-order kinetic, with respect to the alkanolamine, and a first-order kinetic, with respect to the CO_2, we can express eq 22 in the following way:

$$N_A = C_{Bo} C_{Ao} \sqrt{D_A k_{1,2}} \tag{23}$$

If we consider that C_{Ao} is the CO_2 concentration in equilibrium with the gaseous phase, C_{Ao}^*, this can be evaluated by Henry's law ($p_A = He C_{Ao}^*$), leading to

$$N_A = C_{Bo} \left(\frac{p_A}{He}\right) \sqrt{D_A k_{1,2}} \tag{24}$$

and its subsequent ordering to eq 25:

$$\frac{N_A He}{p_A \sqrt{D_A}} = \sqrt{k_{1,2}}\, C_{Bo} \tag{25}$$

The application of eq 25 to the experimental results allows us to make the graphic representations of $N_A He/p_A \sqrt{D_A}$ vs C_{Bo} at all the concentrations and temperatures assayed, as shown in Figure 4a and b.

These representations reflect an acceptable linear relationship for each temperature, initially indicating that we would be operating in a fast-reaction regime, which would confirm the assumed reaction order. Nevertheless, we find the presence of ordinates at the origin

Table 2. Kinetics Constants in the CO_2−DIPA System

temperature, T (K)	$k_{1,2}$ (m^6 $kmol^{-2}$ s^{-1})	0.0	r^2
288	1.41	0.64	0.998
293	2.65	0.72	0.998
298	3.77	0.83	0.994
303	4.83	1.06	0.996
308	8.23	1.18	0.992
313	11.8	1.64	0.990

(0.0), which are not covered by eq 25 and could be ascribed to the experimental results themselves, fundamental to the determination of CO_2 solubility and the diffusion coefficient of CO_2 in the liquid phase.

The adjustment of the values by the least-squares method gives the kinetic constants $k_{1,2}$, as shown in Table 2.

From the $k_{1,2}$ values calculated for each temperature, we prepared the representation in Figure 5, revealing an acceptable linear relationship.

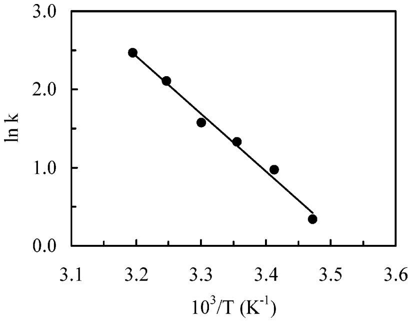

Figure 5. Variation of the kinetic constant with temperature for DIPA.

The application of the least-squares method enabled us to propose eq 26 for the kinetic constant, under the assumed initials of the reaction order, valid in the interval of temperatures in which we have operated:

$$\ln k_{1,2} = 26.0 - \frac{7360.5}{T} \tag{26}$$

From this equation, we can deduce an apparent activation energy, $(E_a)_{ap}$, of 59.9 kJ/mol. This result is higher than 41.8 kJ/mol, which is a value found at 298 K by Danckwerts and Sharma,[16] who operated their experiments under different conditions and considered a first-order reaction, with respect to the amine.

3.4. Hatta Number and Enhancement Factors. Using eq 27, we determined, following surface renewal theory, the instantaneous enhancement factor (E_i) for the range of concentrations and temperatures considered. Equations 1, 2, 3, and 4 and 8 were used to calculate p_A, He, D_A, and D_B, respectively.

$$E_i = \sqrt{\frac{D_A}{D_B}} + \frac{C_{Bo}He}{2p_A}\sqrt{\frac{D_B}{D_A}} \tag{27}$$

In addition, to confirm the reaction regime proposed, considering the expression for the kinetic constant established (eq 26) to be valid, and using the values for the individual liquid-phase mass-transfer coefficient (k_L) determined in previous works,[9] we calculated the value of the Hatta number (eq 28),

$$Ha = \frac{1}{k_L}\sqrt{\frac{2}{m+1}k_{m,n}D_A{C_A}^{m-1}\,{C_{Bo}}^{n}} \xrightarrow{m=1,\,n=2} Ha = \frac{1}{k_L}\sqrt{k_{1,2}D_A{C_{Bo}}^2} \tag{28}$$

as well as the term $\sqrt{1+Ha^2}$, for all concentrations and temperatures assayed.

Finally, using the expression of DeCoursey[25] (eq 29), we determined the enhancement factor, E:

$$E = -\frac{Ha^2}{2(E_i-1)} + \sqrt{\frac{Ha^4}{4(E_i-1)^2} + \frac{E_iHa^2}{E_i-1} + 1} \tag{29}$$

It should be emphasized that, in our case, for a fast-reaction regime, it happened that $E = Ha$, whereas, for a moderately fast-reaction regime $E = \sqrt{1+Ha^2}$. Table 3 presents the values of E, E_i, Ha, and $\sqrt{1+Ha^2}$ for all the experiments.

An analysis of the foregoing table indicates that, generally, for all the concentrations, the values of E and $\sqrt{1+Ha^2}$ had a tendency to be approximately equal, indicating a fast-reaction regime and reflecting greater

Table 3. Enhancement Factors (E and E_i) and the Hatta Number (Ha) in the DIPA Experiments

C_{Bo} (kmol/m^3)	E_i	Ha	E	$\sqrt{1+Ha^2}$	C_{Bo} (kmol/m^3)	E_i	Ha	E	$\sqrt{1+Ha^2}$
		T = 288 K					T = 303 K		
0.0865	2.27	0.17	1.01	1.01	0.0413	2.10	0.13	1.01	1.01
0.175	2.96	0.33	1.05	1.05	0.146	3.39	0.45	1.09	1.10
0.274	3.70	0.51	1.11	1.12	0.224	4.34	0.68	1.19	1.21
0.440	4.87	0.79	1.24	1.27	0.385	6.24	1.14	1.44	1.52
0.867	7.85	1.40	1.61	1.72	0.805	11.1	2.17	2.16	2.39
1.83	15.6	2.03	2.12	2.26	1.63	21.1	3.37	3.17	3.52
		T = 293 K					T = 308 K		
0.0822	2.34	0.17	1.01	1.01	0.0732	2.64	0.28	1.03	1.04
0.172	3.14	0.36	1.06	1.06	0.160	3.88	0.60	1.15	1.16
0.244	3.77	0.50	1.11	1.12	0.224	5.10	0.90	1.30	1.34
0.434	5.44	0.85	1.28	1.31	0.384	7.11	1.38	1.60	1.70
0.955	9.78	1.66	1.80	1.93	0.825	13.1	2.68	2.55	2.87
1.90	19.1	2.30	2.35	2.50	1.68	25.5	4.20	3.85	4.31
		T = 298 K					T = 313 K		
0.0567	2.19	0.14	1.01	1.01	0.0647	2.63	0.27	1.03	1.03
0.145	3.11	0.36	1.06	1.06	0.122	3.62	0.50	1.11	1.12
0.224	3.94	0.55	1.13	1.14	0.193	4.91	0.78	1.24	1.27
0.400	5.73	0.94	1.33	1.37	0.363	7.77	1.43	1.64	1.74
0.874	10.4	1.83	1.92	2.08	0.791	14.9	2.85	2.71	3.01
1.90	22.7	2.63	2.64	2.81	1.53	27.5	4.50	4.11	4.61

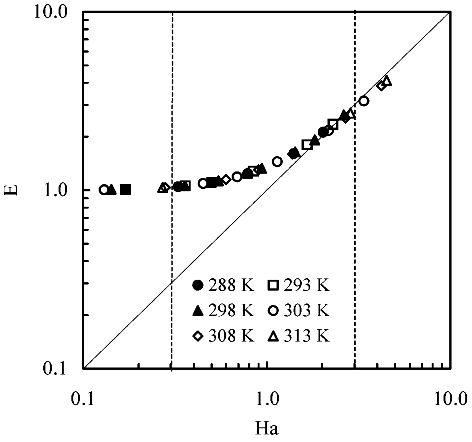

Figure 6. Variation of the enhancement factor (E) with the Hatta number (Ha) in the experiments of DIPA at the temperatures indicated.

coincidence as the operating temperature falls, with slight discrepancies at the highest concentrations.

In addition, except at the lowest concentration in the 288−303 K series, and at the highest concentration in the 303−313 K series, the expectation is fulfilled that

$$0.3 < Ha < 3$$

In agreement with the results of Charpentier,[23] the process of CO_2 absorption by aqueous DIPA solutions occurred in the moderately fast-reaction regime.

The representation of E vs Ha on logarithm coordinates shown in Figure 6 confirms the regimen indicated, showing that all the points that represent the higher concentrations and temperatures adjust acceptably to the bisector of the first quadrant for the entire range of temperatures and concentrations.

4. Conclusion

The rates of absorption of carbon dioxide (CO_2) in aqueous solutions of di-isopropanolamine (DIPA) were measured in the temperature range of 288−313 K, using a stirred tank reactor with a plane gas−liquid interface. The absorption rate data under the moderately fast-reaction regime were analyzed by chemical absorption theory to clarify the kinetics of CO_2 and DIPA. The reaction has been determined to be second-order, with respect to the amine. The values of the rate constant have been determined to be 1.41, 2.65, 3.77, 4.83, 8.23, and 11.8 $m^6\ kmol^{-2}\ s^{-1}$ at 288, 293, 298, 303, 308, and 313 K, respectively, within the amine concentration range of 0.0413−1.90 $kmol/m^3$. The apparent activation energy for the CO_2−DIPA reaction has been determined to be 59.9 kJ/mol.

Nomenclature

Symbols

A = interfacial area (m^2)
C_{Ao} = initial concentration of component A (CO_2) ($kmol/m^3$)
C_A^* = concentration of component A (CO_2) in equilibrium with the gaseous phase ($kmol/m^3$)
C_{Bo} = initial concentration of amine in the aqueous phase ($kmol/m^3$)
D_A = diffusion coefficient of component A in the aqueous alkanolamine solution (m^2/s)
D_B = diffusion coefficient of alkanolamine in the liquid phase (m^2/s)
D_{CO_2} = diffusion coefficient of CO_2 in the aqueous alkanolamine solution (m^2/s)
$D_{CO_2,w}$ = diffusion coefficient of CO_2 in water (m^2/s)
D_{N_2O} = diffusion coefficient of N_2O in the alkanolamine solution (m^2/s)
$D_{N_2O,w}$ = diffusion coefficient of N_2O in water (m^2/s)
E = enhancement factor (dimensionless)
$(E_a)_{ap}$ = apparent activation energy (kJ/mol)
E_i = instantaneous-enhancement factor (dimensionless)
Ha = Hatta number (dimensionless)
He = Henry's law constant (kPa m^3/kmol)
k = reaction rate constant
k_L = liquid-phase mass-transfer coefficient (m/s)
m = order of reaction with respect to CO_2
n = order of reaction with respect to amine
n' = absorption rate of CO_2 (kmol/s)
N_A = absorption rate per unit interfacial area of component A (CO_2) (kmol m^{-2} s^{-1})
0.0 = ordinates at the origin in Figure 4b
p_A = partial pressure of component A (CO_2) (kPa)
P = total pressure (kPa)
p_v = vapor pressure of the water (kPa)
Q' = volumetric flow rate of absorbed CO_2 (m^3/s)
r^2 = lineal regression coefficient
R = gas constant (kPa m^3 K^{-1} $kmol^{-1}$)
t = time (s)
T = temperature (K)

Greek Letters

γ = constant defined in eq 7
η = carbonation ratio (mol CO_2/mol of amine)
μ_B = viscosity of the solution amine (Pa s)
μ_w = viscosity of the pure water (Pa s)

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