Kinetics of Carbon Dioxide Absorption into Aqueous Glucosamine Solutions

Diego Gómez-Díaz and José M. Navaza
PF&PT Research Team, Dept. of Chemical Engineering, ETSE, University of Santiago de Compostela,
Santiago de Compostela, Galicia, Spain

DOI 10.1002/aic.11354

Chemical reaction kinetics of carbon dioxide with aqueous solutions of D *(+) glucosamine hydrochloride (2-amino-2-deoxy-*D*-glucose hydrochloride) has been studied using a stirred tank reactor with a planar interfacial area. The operational variables considered in this work have been the glucosamine concentration and the reaction temperature. Specific absorption rates have been obtained and different correlations have been employed to estimate physicochemical properties of carbon dioxide in glucosamine aqueous solutions. Results indicate that the absorption process occurs in a moderately fast reaction regime with a first-order kinetic for amine and carbon dioxide. The reaction rate constant was calculated and correlated as a function of temperature.*
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Keywords: absorption, reaction kinetics

Introduction

Carbon dioxide is a very important greenhouse gas that is emitted by several industrial processes. Carbon dioxide accompanying natural gas necessitates carrying out different cleaning operations for its later use. Recent methods for carbon dioxide capture, separation, and sequestration, involve different options such as physical and chemical absorption (and adsorption), membranes separations, mineralization, etc.

The use of aqueous solutions of amines in gas-liquid reactors (stirred tanks, bubble and packed columns, air-lift, etc) for the capture of acid gases (mainly carbon dioxide) is a common procedure that is adopted in numerous industrial processes and has been the aim of a great number of research studies during the last decades.[1]

Currently, aqueous alkanolamines solutions based on monoethanolamine, diethanolamine, 2-dipropanolamine, and methyldiethanolamine are most commonly used in industry. These amines have shown fast regimes of absorption accompanied by a chemical reaction, which has a high importance as regards the aim of capturing higher quantities of carbon dioxide, as well as the scale-up of operation units. The most recent research studies are also related to the development and testing of new reagents and/or amines to capture carbon dioxide,[2] as well as the use of blends of different amines[3,4] with the aim of achieving a certain enhancement in pollutant gas capture, due to their combined action. For these reasons, it is important to determine kinetic data for these kinds of reactions with the aim of understanding the behaviour of different amines or blends when reacting with the carbon dioxide present in a gas stream, so that we can calculate the capture efficiency or the geometrical characteristics[5] to design gas-liquid contactors.

This work introduces a new amine (2-amino-2-deoxy-D-glucose, called glucosamine) to capture carbon dioxide. This substance has been explored for the removal process by absorption of carbon dioxide from the environment. Moreover, it could be a highly interesting compound for its use in carbon dioxide capture procedures by means of absorption accompanied by a chemical reaction.

Glucosamine could be a highly interesting reagent because of its special characteristics in relation to the safety requirements with negligible negative effects upon equipment maintenance. Moreover, the treatment of exhaust aqueous solutions of glucosamine is also easier than other amines employed in carbon dioxide absorption. Because of these

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Correspondence concerning this article should be addressed to J. M. Navaza at eqnavaza@usc.es.

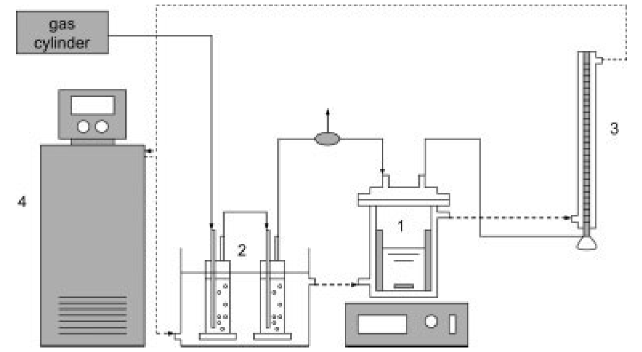

Figure 1. Experimental set-up for kinetic studies of gas-liquid systems.

interesting characteristics, the present work aims to determine the mechanism of the absorption accompanied by chemical reaction between carbon dioxide and glucosamine, the absorption with a chemical reaction regime, and the kinetic parameters (reaction orders and kinetic constant).

Experimental Section

Commercial grade CO_2 gas of 99.998% purity, supplied by Carburos Metálicos, (Spain) was used in this work. Glucosamine hydrochloride of 99% purity was obtained from Fluka (USA). Aqueous solutions of glucosamine were prepared with double distilled water.

Glucosamine hydrochloride is acidic in aqueous solution and inhibits the reaction between the carbon dioxide absorbed in the liquid phase and the amine. To overcome this, the hydrochloride on glucosamine can be neutralized by adding stoichiometric amount of sodium chloride.

The experiments were conducted in a stirred cell (1) having a planar interfacial area working in batches as regards both phases (see Figure 1). Four baffles have been placed in its internal wall to improve the mixing and prevent vortex formation during stirring. The gas to be absorbed, carbon dioxide, was passed through two humidifiers (2) to prepare the gas phase. This procedure removed other resistance to mass transport and allowed only the evaluation of the liquid phase resistance to the gas transfer. Water was placed into the "humidifiers." A soap flow-meter (3) was used to determine the absorption rate of carbon dioxide by the absorption accompanying the chemical reaction produced by the glucosamine present in the liquid phase. The absorption rate was measured by analysing the movement (produced by the consumption of carbon dioxide) of the soap film along the calibrated glass tube. The absorption processes have been carried out at different temperatures (7–55°C) by connection of humidifiers, stirred cell and flow-meter to a thermostat-cryostat (4).

Results and Discussion

The kinetics of reaction between carbon dioxide and glucosamine absorbed in water was studied by employing gas phase absorption data. The flow densities were calculated assuming that the gas phase follows an ideal behaviour, taking previous studies into account.[6]

Carbon dioxide flow density was calculated by means of experimental data corresponding to the absorbed quantity of carbon dioxide along the operation time. Figure 2 shows the experimental results, which were obtained in relation to the flux density determined for the liquid phases employed in this work. Experimental data shows a linear trend in all cases in the studied operation time range, and this kind of behaviour allows the use of experimental data for kinetic studies. The slope of the linear plot shown in Figure 2 allows the calculation of the absorption volumetric flux at different operation conditions. Similarly, results from Figure 2 indicate that there is certain influence of initial glucosamine concentration in the liquid phase upon the carbon dioxide absorption rate or upon the slope of linear fits. This observation confirms the existence of chemical reaction in the liquid phase of carbon dioxide with glucosamine.

Glucosamine is a primary amine that includes two functional groups: amino (NH_2) and hydroxyl (OH), like different alkanolamines employed by several researchers.[7] The presence of both functional groups is interesting because, in different situations, the reaction between absorbed carbon dioxide and these functional groups can take place by means of the reactions shown in Eqs. 1 and 2.

$$—NH_2 + CO_2 \rightarrow —NH_2^+\ COO^- \qquad (1)$$

$$—OH^- + CO_2 \rightarrow —OCOO^-\ H^+ \qquad (2)$$

This latter reaction (Eq. 2) may take place in a basic solution at pH values higher than 11, but at low pH values the reaction to produce carbonic acid can be considered negligible.[8] In the present work, the initial pH of glucosamine aqueous solutions has shown values lower than 11. Therefore, only the reaction shown in Eq. 1 (carbamic formation) must be taken into account. Also, the product of this reaction is very unstable due to the alkyl group attached to the amine, and these results in a fast hydrolysis reaction with bases such as water, amine or hydroxyl ions can contribute to the deprotonation of the zwitterions.[9]

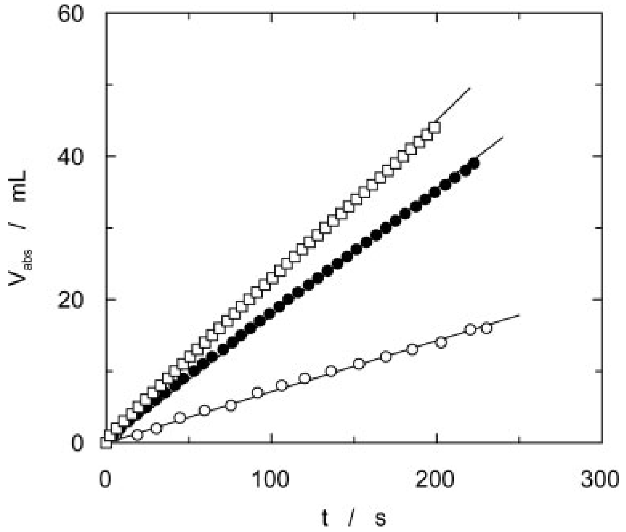

Figure 2. Carbon dioxide absorption along operation time for aqueous solutions of glucosamine at 25°C.

(○) C_{Bo} = 0 mol L^{-1}; (●) C_{Bo} = 0.1 mol L^{-1}; (□) C_{Bo} = 0.3 mol L^{-1}.

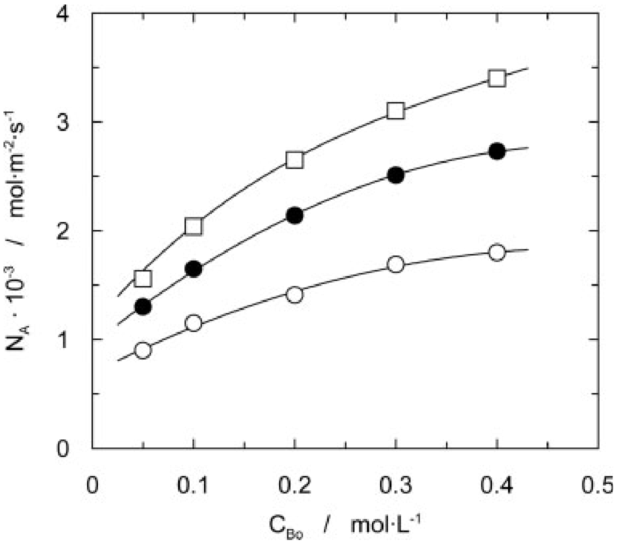

Figure 3. Influence of glucosamine initial concentration upon carbon dioxide flow density at (○) T = 7°C, (●) T = 25°C, and (□) T = 45°C.

The reaction between carbon dioxide and amine involves different parallel chemical reactions, such as the reaction between this gas and hydroxyl ions (bicarbonate formation) and water (carbonic acid formation). However, the influence of these reactions under the conditions employed in the present work could be considered negligible.[2] As regards the carbonic acid formation and reaction, it is very slow and it must be considered of no influence on the system studied.[10] The other parallel reaction abovementioned between carbon dioxide and hydroxyl ions could be negligible due to the low hydroxyl ions concentration in the system, such as different studies have proved.[11] On the basis of conclusions reached by different studies (i.e., Astarita et al.[8]), which indicate that carbamic reaction is the mechanism of reaction between carbon dioxide and amines when the carbonation relationship (moles of carbon dioxide/moles of amine) is lesser than 0.5, we could develop the analysis of our experimental results using this hypothesis, that is in agreement with results based on pH measurements ($<$11), previously commented.

According to other studies,[8] a value of carbonation ratio lesser than 0.5 indicates that the reaction takes place by means of a second-order mechanism with three possible regimes: physical absorption, fast-reaction and instantaneous regime. Since the glucosamine concentration is high in the liquid phase and implies values of $C_{Bo}/C_{Ao} \gg 1$, the physical absorption regime must be ruled out, so it is necessary to analyse the instantaneous and fast-reaction regimes.

An instantaneous regime relates carbon dioxide flow density (N_A) with initial glucosamine concentration with a linear trend. Figure 3 shows this relation, which indicates that this regime does not govern the reaction mechanism.

The latter regime (fast-reaction) allows the calculation of the carbon dioxide flow density by means of Eq. 3,[12] taking into account that the reaction order, as regards the carbon dioxide when reacting with aqueous solutions of primary amines, is one.[13]

$$N_A = C_{Ao}\sqrt{D_A k_{1,n} C_{Bo}^n} \tag{3}$$

where C_{Ao} and C_{Bo} are the initial concentrations of carbon dioxide and glucosamine in the liquid phase, D_A is the gas diffusivity in glucosamine aqueous solutions and $k_{1,n}$ is the overall reaction rate constant.

The diffusion coefficient corresponding to carbon dioxide in aqueous solutions of glucosamine was calculated employing the expression shown in Eq. 4.[14,15]

$$D_A = D_{A,w}\left(\frac{\eta_w}{\eta}\right)^{0.8} \tag{4}$$

where $D_{A,w}$ is the diffusivity of carbon dioxide in pure water, η_w and η are the viscosity of pure water and aqueous solutions of glucosamine, respectively. The value of carbon dioxide diffusivity in pure water was determined employing the expressions proposed by different studies.[12,16] On the other hand, the water viscosity and glucosamine aqueous solutions have been obtained from literature.[17]

Diffusivity values calculated by means of Eq. 4 are quite similar to literature data of carbon dioxide diffusivity in aqueous solutions of glucose,[14] which has a very similar structure to glucosamine.

The initial carbon dioxide concentration in the liquid phase must coincide with the concentration in equilibrium in gas phase. This parameter could be replaced in Eq. 3 employing Henry's law. These considerations allow us to obtain the linearized expression shown in Eq. 5 to fit experimental data as well as to calculate the reaction order corresponding to glucosamine:

$$\log\left(\frac{N_A^2 He^2}{P_A^2 D_A}\right) = \log\,(k_{1,n}) + n\log(C_{Bo}) \tag{5}$$

where He is Henry's constant and P_A is the carbon dioxide partial pressure.

Figure 4 shows the results obtained after using Eq. 5 to fit the experimental results obtained in the present work. These

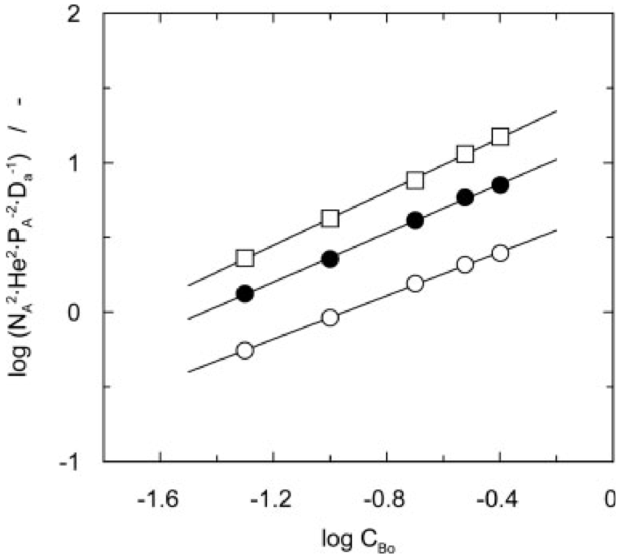

Figure 4. Experimental data fitted with Eq. 5 for kinetic parameters and mechanism determination. (○) T = 15°C, (●) T = 35°C, and (□) T = 55°C.

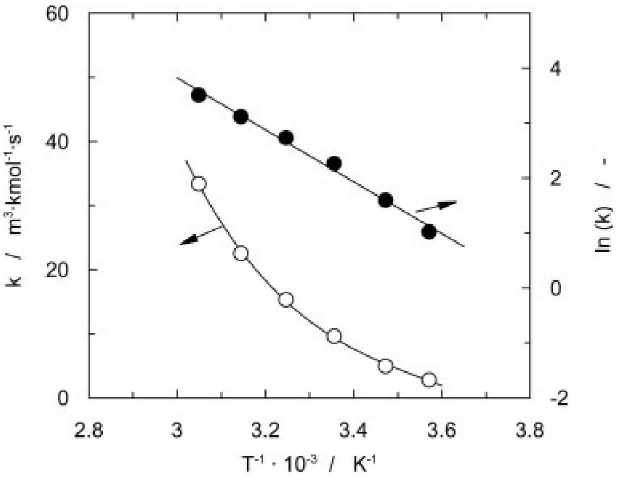

Figure 5. Influence of temperature upon kinetic constant for carbon dioxide + glucosamine reaction.

results indicate a good agreement between the experimental data and the linear fits of Eq. 5 under de operation conditions employed in this work.

Linear fits of the experimental data (i.e., in Figure 4) have been used to calculate the reaction order regarding the glucosamine, as well as the value of the kinetic constant employing the intercept with the origin. The slope of linear fits obtained at different temperatures contributes values close to 1. This is the reaction order corresponding to glucosamine, being in agreement with previous studies of chemical absorption of carbon dioxide with other primary amines.[18]

In relation to kinetic constant, a value of 10.14 $m^3\ kmol^{-1}\ s^{-1}$ was determined when the chemical absorption is performed at 25°C. This value is quite similar to literature values for other carbon dioxide + amine reaction.[19] The influence of temperature upon the value of the kinetic constant for the reaction studied in the present work has been analysed. Figure 5 shows the behaviour observed that is so common in this kind of studies. An increase in temperature also produces an increase in the value of the kinetic constant. Experimental values have been fitted using an Arrhenius type equation to calculate the pre-exponential factor and the activation energy. Eq. 6 shows the calculated values for both parameters.

$$\ln k = 17.8 - \frac{4716.9}{T} \tag{6}$$

The value determined for the activation energy (47.6 kJ mol^{-1}) is close to values obtained for this parameter for other reactions between carbon dioxide and amines, such as MEA, MIPA and AP.[20] This value for the activation energy is close to literature data for other systems, even though our value is slightly higher than the previously commented systems. So, based on previous studies,[20] this result can be attributed to certain steric impediment for carbon dioxide – glucosamine reaction.

The Hatta number (*Ha*) and enhancement factor (*E*) have been calculated with the aim of confirming the reaction regime supposed (fast reaction) at the beginning of the results and discussion section. Eq. 7 has been employed to determine the Hatta number.

$$Ha = \sqrt{\frac{k\ C_{\mathrm{Bo}}\ D_{\mathrm{A}}}{k_{\mathrm{L}}^2}} \tag{7}$$

where k_{L} is the liquid phase mass transfer coefficient.

In the case of the enhancement factor, the expression shown in Eq. 8 has been employed to calculate the value of this parameter, based on the value of carbon dioxide flux density.

$$E = \frac{N_{\mathrm{A}}}{k_{\mathrm{L}}\ C_{\mathrm{A}}^*} \tag{8}$$

Equations 7 and 8 include in their expressions the value of mass transfer coefficient corresponding to liquid phase, k_{L}. This parameter has been determined employing pure water as liquid phase because the influence of the glucosamine (on the concentration range employed in this work) upon the liquid phase viscosity is lower.[17]

In addition, the instantaneous enhancement factor has been calculated employing Eq. 9.

$$E_i = 1 + \frac{D_{\mathrm{B}}}{D_{\mathrm{A}}}\frac{C_{\mathrm{Bo}}}{C_{\mathrm{A}}^*} \tag{9}$$

The diffusion coefficient for glucosamine (D_{B}) in aqueous solution has been calculated by means of the Wilke-Chang equation[21] modified by Hayduk and Laudie.[22]

Table 1. Hatta Number, Enhancement Factor, and Instantaneous Enhancement Factor

T (°C)	C_{Bo} (mol L^{-1})	*E*	*Ha*	E_{i}	$\sqrt{1+Ha^2}$
7	0.05	1.05	0.83	1.43	1.30
7	0.1	1.34	1.16	1.87	1.54
7	0.2	1.64	1.62	2.80	1.90
7	0.3	1.97	1.95	3.78	2.19
7	0.4	2.09	2.13	5.13	2.36
15	0.05	1.15	0.92	1.47	1.36
15	0.1	1.54	1.29	1.96	1.63
15	0.2	1.96	1.78	3.01	2.05
15	0.3	2.23	2.15	4.13	2.37
15	0.4	2.36	2.40	5.45	2.60
25	0.05	1.34	1.04	1.53	1.45
25	0.1	1.70	1.46	2.07	1.77
25	0.2	2.20	2.02	3.24	2.26
25	0.3	2.58	2.43	4.51	2.62
25	0.4	2.81	2.74	5.88	2.92
35	0.05	1.36	1.09	1.57	1.48
35	0.1	1.75	1.52	2.17	1.82
35	0.2	2.28	2.11	3.43	2.33
35	0.3	2.67	2.52	4.83	2.71
35	0.4	2.92	2.85	6.30	3.02
45	0.05	1.38	1.14	1.61	1.52
45	0.1	1.81	1.59	2.26	1.88
45	0.2	2.35	2.21	3.61	2.43
45	0.3	2.75	2.63	5.15	2.82
45	0.4	3.02	2.97	6.78	3.14
55	0.05	1.31	1.19	1.66	1.55
55	0.1	1.75	1.65	2.37	1.93
55	0.2	2.31	2.30	3.83	2.51
55	0.3	2.74	2.73	5.53	2.91
55	0.4	3.04	3.06	7.40	3.22

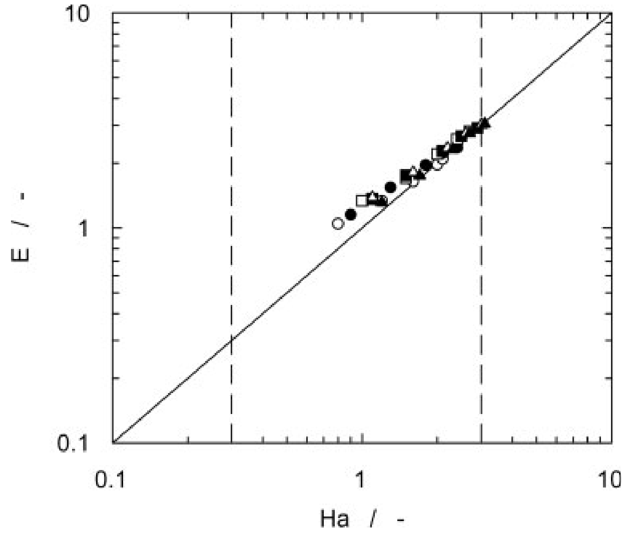

Figure 6. Relation between enhancement factor and Hatta number.
(○) T = 7°C; (●) T = 15°C; (□) T = 25°C; (■) T = 35°C; (△) T = 45°C; (▲) T = 55°C.

$$D_B = \frac{7.4 \times 10^{-8}\sqrt{\varphi_w M_w T}}{\eta_w V_B^{0.6}} \qquad (10)$$

where M_w is molecular weight of water, T is temperature, η_w is the viscosity of water, V_B is the molar volume of glucosamine, and φ_w is the solvent (water) association factor with a value of 2.26.[2]

Table 1 summarises the calculated values for previously commented parameters related to the chemical reaction between carbon dioxide and glucosamine. We can observe in this table that the values of Hatta number take values in all cases into the interval established by Eq. 11, which match the characteristics of a moderately-fast reaction.

$$0.3 < Ha < 3 \qquad (11)$$

Figure 6 shows the relation between the enhancement factor and Hatta number in logarithmic coordinates. This plot shows that the enhancement factor experimental data are higher than the bisector. Therefore, an instantaneous reaction regime for the absorption accompanying with chemical reaction between carbon dioxide and glucosamine is ruled out. Also, the experimental points corresponding to experiments with high glucosamine concentration in the liquid phase fit in an acceptable way the bisector of this representation. In the case of a fast reaction regime the relation between enhancement factor and Hatta number is $E = Ha$, whereas for a moderately-fast reaction regime the relation is $E = \sqrt{1 + Ha^2}$. The values for these parameters shown in Table 1 indicate that there is a relation corresponding to a moderately-fast reaction regime. Figure 6 also shows that the values of Hatta number for all the experimental conditions employed in this work are included in the range shown in Eq. 11.

Conclusions

A new amine has been employed to capture carbon dioxide by chemical absorption. The rates of carbon dioxide absorption in aqueous solutions of glucosamine were measured in the temperature range of 280–328 K using a stirred cell reactor with planar interface. The absorption rate experimental data and the chemical absorption theory have determined the existence of a moderately fast-reaction regime between the carbon dioxide and the glucosamine. They have also determined that the reaction order as regards glucosamine is one. The influence of the temperature upon the rate constant has been analysed and the activation energy was calculated and compared with previous studies that confirms a certain steric impediment for the reaction.

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Manuscript received July 10, 2007, and revision received Sept. 26, 2007.