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Kinetics of chemical absorption of carbon dioxide into aqueous calcium acetate solution

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Abstract

Increasing energy demand in the world leads to more electricity generation mainly at fossil fuel power plants. Greenhouse gases are thus produced and mostly emitted to the atmosphere directly, resulting in global warming and climate change. Carbon dioxide is believed to be a main pollutant among greenhouse gases responsible from global warming. Conventional systems using mostly amine solutions to capture carbon dioxide at the source have some disadvantages, and alternatives are constantly being searched. In this work, a benign system of aqueous calcium acetate solution was investigated for this purpose. Calcium acetate is easy to produce, relatively cheap, environmentally friendly, nonhazardous, and noncorrosive. These properties make it a great alternative for use in capturing carbon dioxide. This absorption process is accompanied by chemical reaction. Therefore, the reaction kinetics needs to be investigated before its use in absorbers. A stirred cell reactor was used in the experiments using aqueous calcium acetate solution of different concentrations (2-20% w/w) and different carbon dioxide concentrations in gas mixtures (4.5-100% v/v dry carbon dioxide) at temperatures ranging from 286 to 352 K. The Gibbs free energy change for the overall reaction between carbon dioxide and aqueous calcium acetate solution was found to be –2.75 kJ/mol that shows the reaction is exergonic and occurs spontaneously. It was also found out that the reaction is pseudo–first order with respect to carbon dioxide which was also proven by calculating the Hatta number. Activation energy and Arrhenius (frequency) constant were also determined experimentally.

KEYWORDS
absorption, calcium acetate solution, carbon dioxide, reaction kinetics, stirred cell

Nomenclature: C, concentration, mol/m^3; d_r, inner diameter of the reactor, m; D, diffusion coefficient, m^2/s; E, enhancement factor; E_a, activation energy, J/mol; $h_{ion/gas}$, ion/gas specific parameter, m^3/kmol; H, Henry's law constant, Pa·m^3/mol; Ha, Hatta number; k_L^o, liquid side physical mass transfer coefficient, m/s; k_o, Arrhenius (frequency) constant, m^3/mol·s; m, dimensionless solubility; P, pressure, Pa, atm, mmHg; r_f, film volume–based reaction rate, mol/m^3.s; r_s, interfacial area–based reaction rate, mol/m^2·s; R, gas constant, Pa·m^3/mol·K; T, temperature, K; V, volume, m^3; x, weight percentage of solution; y, molar fraction; δ, film thickness, m; $\mathcal{H}_s$, saturation humidity, kg water/kg dry gas; $\mathcal{W}$, change in moles of gas, mol/s; ψ, Thiele modulus.

1 | INTRODUCTION

The emission of greenhouse gases (GHG) to atmosphere to fulfill the energy demand throughout the world has become one of the most important challenges for the past decades. Carbon dioxide is accepted as the most threatening gas among all GHG because of its shielding effect on solar radiation and a continuous increase of its concentration in atmosphere in the past decades, and carbon dioxide emissions are need to be reduced by 25% until 2030 and by 100% until 2070 to limit global warming to just below 2°C.[1–5] The major sources of anthropogenic carbon dioxide emission are point sources, like power plants where fossil fuels (coal, petroleum and natural gas) are being used to generate electricity. Regarding the energy scenarios, the use of fossil fuels will be continued for at least 80 more years and the increasing demand in energy is going to be compensated by using renewable energy sources within this period of time.[1,2,6] Hence, production of GHG in fossil fuel power plants or other industrial plants will continue to be one of the problems that industry and scientist must focus at in the near future.

The solution to decelerate global warming is to control the emission of GHG, especially carbon dioxide. For this purpose, carbon dioxide is needed to be separated from the rest of the flue gas and new units are needed in plants to store it or compress it to send to other units. The most expensive part of carbon dioxide capture and sequestration systems is the capturing of carbon dioxide. In the design of the new power plants, it is important to consider whether there will be additional carbon capture and storage (CCS) facilities or carbon capture and utilization (CCU) processes. Adding these units to existing power plants or to new power plants will increase the capital investment as well as the operating costs, which will result in higher unit price for the energy. Because of the strict regulations and the points mentioned, the technical and economical enhancement of CCS or CCU units and finding novel chemicals that can capture carbon dioxide with high efficiency are among the most important research topics nowadays.[7]

Generally, capturing carbon dioxide can be classified into four techniques as postcombustion, precombustion, oxycombustion, and chemical looping combustion systems. Postcombustion separation is capturing carbon dioxide from flue gases formed as a result of combustion of the fuel with air. The precombustion technique is about capturing carbon dioxide from syngas before using it as a fuel. In oxycombustion processes, the oxygen in the air is separated from nitrogen and oxygen is used to combust the fuel so that the flue gas is essentially carbon dioxide. Carbon dioxide also forms as a result of combustion with oxygen transported via a metal oxide and capturing carbon dioxide in such cases is known as a chemical-loop combustion system. Among these four techniques, the most readily applicable one seems to be postcombustion systems,

since it is retrofittable to existing plants. There are several subtechniques like absorption, adsorption, cryogenic separation, and membrane separation that are adaptable for the main four separation processes (Figure 1). Among all techniques, the most applicable process for capturing carbon dioxide is accepted to be postcombustion absorption.[8] Retrofitting existing power plants and adding absorption units seems to be the most convenient and economic option.[9]

Many solvents have been tried and are being used in commercial processes for physical absorption of carbon dioxide such as methanol in the Rectisol processes, dimethyl ether of polyethylene glycol (DMPEG) in the Selexol process, *n*-methyl-2-pyrrolidone (NMP) in the Purisol process, propylene carbonate in the Fluor process. Amine solutions such as monoethanolamine (MEA) and diethanolamine (DEA) are used for chemical absorption with or without additives as reaction accelerators. In addition, various ionic liquids are being investigated as potential solvents.

Considering the current physical absorption processes developed for carbon dioxide removal, cooling to low temperatures (233-213 K) due to the low boiling point of solvents, high operational costs are required. Some have high CO_2 selectivity but low capacity.[13] Some require high operating pressures (2.07-13.8 MPa) to achieve efficient performance. In addition, the high viscosity of the solvent used in some processes (0.0058 Pa·s at 298 K) results in a low mass transfer rate in the absorption column.[14] Moreover, some solvents have high vapor pressures, resulting in high solvent losses. High vapor pressure also leads to difficulties in solvent regeneration. Some solvents are very expensive and become unstable at high temperature (338 K and above).

Chemical absorption of carbon dioxide is mostly preferred because compared to other postcombustion capture techniques it has higher capture capacity and is more efficient.[11,15,16] Chemical absorption systems are being used in ammonia plants used for food applications since 1930s. Although it is commercially known, the application in power plants is very rare. Currently, amine solutions, ammonia, and solutions like potassium carbonate are popular and mostly used in existing postcombustion carbon dioxide chemical absorption systems.[11] In these systems, carbon dioxide is captured by continuous stripping systems. The overall system consists of an absorber and a desorber. In the absorption process, carbon dioxide gives a reversible reaction with an alkali solution. The temperature and pressure of absorption unit is generally between 30 and 60°C and 1–2.24 atm, respectively. In the desorber process, which is operated generally at 120°C and 1 atm, carbon dioxide is separated from the solution. The separated pure carbon dioxide is sent to a compression unit for storage or utilization. The regenerated and recycled solution is sent back to the absorber. In the desorption process, high energy is needed to ensure that the temperature of the solution is raised to required values and essential driving force is
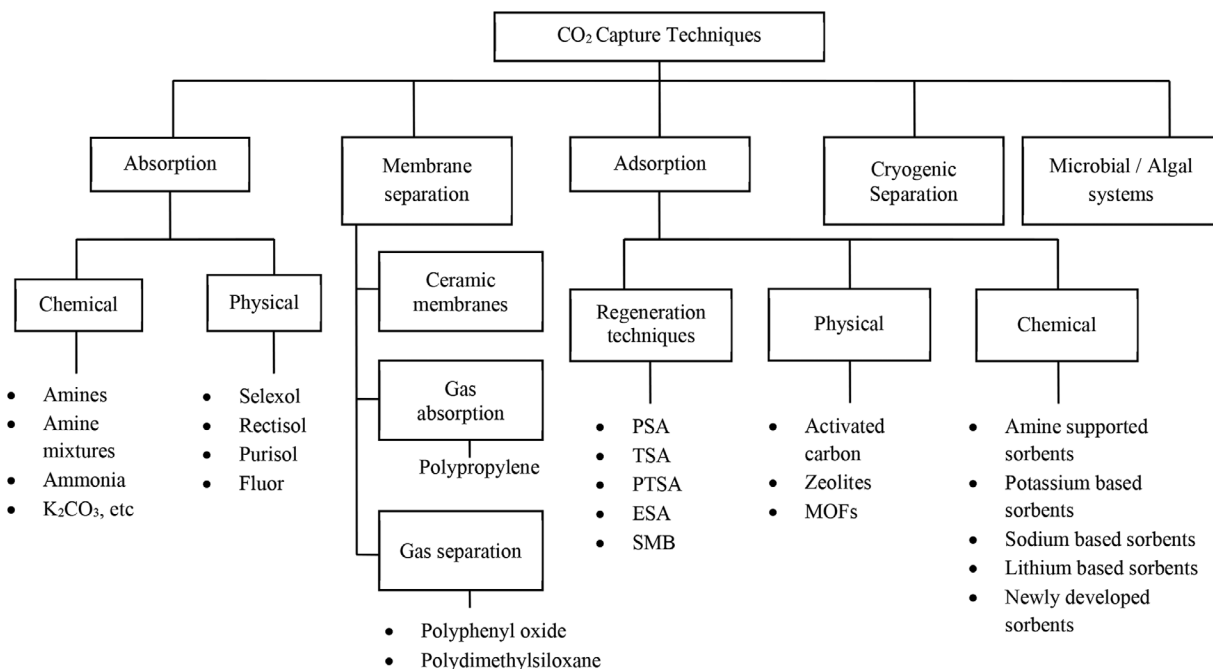
FIGURE 1 Postcombustion carbon dioxide capture techniques[10–12]

obtained. Moreover, high pressure needed in the absorption process leads to high-energy cost.[15]

MEA, DEA, diisopropanol amine, and methyldiethanol amine (MDEA) are the most used alkanolamine solutions in chemical absorption systems.[17–20] MEA is the most used amine solutions among others. Besides, additive agents are used with these solutions to speed up the process.[21,22] Piperazine, carbonates, and ionic liquids are used and researched for carbon dioxide absorption all by themselves or with some activating additives.[11]

When chemical absorption processes are considered, the solvent regeneration requires very high energy. For all these reasons, it is admitted that the commercially available processes have certain disadvantages and there is still need to develop alternative solvents.[23–26] The new solvents that may have potential in carbon dioxide capture should not be expensive, should be recoverable for reuse, should not be very volatile, should not require high energy in absorption and recovery steps, and should not harm the environment.[27–29]

With this purpose, a novel investigation of capturing carbon dioxide using aqueous calcium acetate solution was done in this work. Calcium acetate ($Ca(CH_3COO)_2$) is a benign good alternative to solutions that are currently being used in conventional systems regarding its chemical and physical properties. Calcium acetate is very easy and relatively cheap to produce, and it is environmentally friendly. It is not hazardous and not corrosive. It enables to operate the absorption unit at atmospheric pressure. It is possible to regenerate the loaded solution by using simple techniques and to use the solution again in absorption unit.[10] Since carbon dioxide undergoes reaction in aqueous calcium acetate solution, there is no need

to change pressure or temperature to strip carbon dioxide from used solution in a regeneration unit. This is a great advantage since it decreases a significant amount of need in energy in an absorption/regeneration unit.

To the best our knowledge, there is no information available on the use of aqueous calcium acetate solution for carbon dioxide capture. Since the absorption of carbon dioxide into calcium acetate solution is absorption with chemical reaction, the reaction kinetics was first investigated together with the thermophysical properties of the aqueous solution in this first study.[12]

2 | MATERIALS AND METHODS

First, solubility of carbon dioxide in calcium acetate solution was to be considered to determine the liquid side interfacial concentration. Then, reaction kinetics was investigated. A stirred cell was used in the experiments. The method is outlined below.

2.1 | Calculation of Henry's law constant for the aqueous calcium acetate solution-CO_2 system

Physical solubility of carbon dioxide in aqueous solutions is known to be very small. Henry's law is applicable for dilute systems:

$$\bar{P}_A = H_A C_A \qquad (1)$$

Here, $\bar{P}_A$ is the partial pressure of component A (carbon dioxide), C_A is its concentration in liquid, and H_A is the Henry's law constant.[30] For the absorption system of calcium acetate and carbon dioxide, it is needed to calculate the Henry's law constant; since, to the best knowledge of the authors, there is not any information about this in the literature.

For the absorption systems with a chemical reaction in salt solutions, it is not possible to measure the solubility of gas in the solution experimentally as done for physical systems.[31] Using the method originally proposed by Setschenow and improved by van Krevelen and Hoftijzer, it is however possible to calculate the solubility in electrolyte solutions.[32,33] In this method, the Henry's law constant of gas in solutions is correlated with that in water with the relation given below[31]:

$$\log_{10}\left(\frac{H}{H^o}\right) = hI = (h_+ + h_- + h_G)\left(\frac{1}{2}\right)\Sigma\left(c_i z_i^2\right).$$ (2)

Here, H^o is the Henry's law constant of solute in water, I is the ionic strength, c_i is the concentration of ions with z_i valence, and h represents the specific parameters of positive and negative ions and solute.[34] Although this method is widely used in the literature,[35–38] the data on specific parameters of the ions are limited in the literature. This method was improved to relate the solubility of gases in salt solutions to a salt concentration directly as given below[39]:

$$\log\left(\frac{C_{G,0}}{C_G}\right) = KC_s.$$ (3)

Here, $C_{G,0}$ and C_G are the solubility of gaseous solute in water and solution, respectively, C_s is the molar concentration of salt solution. K, the Setschenow constant, is a parameter that differs for the solute and salt solution and can be used for solutions involving one salt or more[40]:

$$K = \Sigma\left(h_i + h_G\right)n_i.$$ (4)

Weisenberg and Schumpe[41] investigated the solubility of gases at different temperatures. They concluded that for the temperatures between 273 and 363 K the specific parameter of gas (h_G) shows a linear difference. Regarding this, the dependence of specific gas parameter relation is given below:

$$h_G = h_{G,0} + h_T(T - 298.15).$$ (5)

Here, $h_{G,0}$ is the gas-specific parameter value at 298.15 K, h_T is the contribution of temperature to specific parameter of gas, and T is the temperature in K. The constants for this work are given in Table 1. As seen from the table, for the anion-specific parameter, the value of a carboxyl group is used. For similar groups, it is possible to use the same value.[31]

Using this approach, collocation of the relations given above yields Henry's law constant for carbon dioxide in calcium acetate solution as

$$H_{CO_2}^{Ca(CH_3COO)_2} = \frac{H_{CO_2}^{H_2O}}{10^{\left(C_s\left(0.1543+\left(-0.0172-0.338\times10^{-3}(T-298.15)\right)\right)+2C_s\left(-0.0089+\left(-0.0172-0.338\times10^{-3}(T-298.15)\right)\right)\right)}}.$$ (6)

Here, C_s is the concentration of calcium acetate solution in kmol/m³ and T is temperature in K. The Henry's law constant for CO_2 in water ($H_{CO_2}^{H_2O}$) can be calculated using the equation given below.[42,43] Henry's law constant and temperature are in Pa·m³/mol and K, respectively.

$$H_{CO_2}^{H_2O} = 100\, e^{\left(-\frac{2625}{T}+12.2\right)}.$$ (7)

Also, solubility of carbon dioxide in calcium acetate solution can be directly expressed as

$$C_{CO_2} = \frac{C_{CO_2,0}}{10^{\left(C_s\left(0.1543+\left(-0.0172-0.338\times10^{-3}(T-298.15)\right)\right)+2C_s\left(-0.0089+\left(-0.0172-0.338\times10^{-3}(T-298.15)\right)\right)\right)}}.$$ (8)

2.2 | The rate of reaction of carbon dioxide with calcium acetate

Considering the overall reaction between CO_2 and $Ca(CH_3COO)_2$

$$CO_2 + Ca(CH_3COO)_2 + H_2O \rightarrow 2CH_3COOH + CaCO_3,$$ (9)
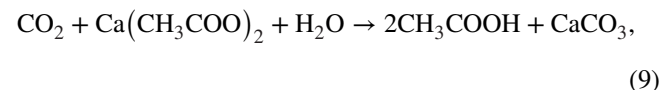
the reaction rate can be written as

$$r = kC_{CO_2}^m C_{Ca(CH_3COO)_2}^n.$$ (10)

A parametric study was needed to determine the orders of reactants, reaction rate constant, the activation energy, and the frequency factor.

TABLE 1 System-relevant parameter values for Henry's law coefficient calculation

Ion/gas-specific parameters	Parameter definition	Parameter values
$h_{Ca^{2+}}$,	Ion-specific parameter	0.1543 [Ref. 39]
$h_{\emptyset CH_2COO^-}$, $m^3/kmol$	Ion-specific parameter*	−0.0089 [Ref. 39]
$h_{CO_2^0}$, $m^3/kmol$	Gas-specific parameter	−0.0172 [Ref. 41]
h_{T,CO_2}, $m^3/kmol \cdot K$	Temperature contribution to a gas-specific parameter	-0.338×10^{-3} [Ref. 41]

*Adopted to acetate ion because of similarity.[31]

To start with, experiments with different concentrations of aqueous calcium acetate solution were made at constant temperature with constant carbon dioxide concentration in gas to determine the order of calcium acetate solution concentration (n). Second, the order of carbon dioxide (m) was investigated at constant temperature and calcium acetate solution concentration. Finally, by doing experiments at different temperatures and constant concentration of calcium acetate solution and carbon dioxide, the frequency factor and the activation energy of the reaction were determined.

The setup shown in Figure 2 is used in the experiments. The reactor cell is made up of Pyrex glass. In experiments, a liquid chamber of the cell was filled with calcium acetate solution and the rest was filled with the gas used (pure CO_2 or CO_2-N_2 mixture). The gas rates were adjusted by gas mass flow controllers (Cole-Parmer model GZ 32907-63). The solution in the cell was stirred with a magnetic stirrer (VELP Scientifica ARE heating magnetic stirrer) slowly without any disturbance at the surface area to obtain a homogeneous concentration and a constant mass transfer area. While, with a pressure transmitter (HK Instruments DPT-R8), it was possible to measure the decrease in the pressure of the gas in the cell and with a data recorder (Ordel UDL100), the log of decrement of pressure per second was saved. Using the values of pressure decrement, reaction rates were calculated for every experiment.

A typical data for pressure decrement is shown in Figure 3. The reaction rate can be obtained from the slope:

$$\mathcal{W} = -\frac{V_G}{zRT}\frac{dP}{dt}. \tag{11}$$

The right-hand side of this equation shows the difference in moles of carbon dioxide at a gas chamber due to pressure decrement with respect to time. V_G is the volume of gas in m^3. dP/dt is the slope read from a graph, T is the temperature in K, R is the gas constant (8.31434 $Pa \cdot m^3/mol \cdot K$), and z is the compressibility factor.

The reaction rate based on the interfacial area can be calculated by the equation given below:

$$r_S = \frac{\mathcal{W}}{A} = \frac{\mathcal{W}}{\pi d_r^2/4}. \tag{12}$$

Here, r_s is the interfacial area–based reaction rate (mol/$m^2 \cdot$s) and d_r (m) is the inner diameter of the reactor.

The chamber was purged with gas long enough in every experiment to ensure the desired gas composition in the cell. The temperature of the gas was maintained at the reaction temperature and was sent to the chamber after passing through three humidifiers to ensure its saturation with water vapor and to prevent interference due to vaporization of the water inside the reactor cell during the experiment. The concentration of the gas had changed when it passed through the humidifiers. The following humidity of saturation expression was used to correct the concentration of the solute carbon dioxide in gas saturated with water vapor[44]:

$$\mathcal{H}_s = \frac{MW_{water} P_{water}^o}{MW_{gas}\left(P_{atm} - P_{water}^o\right)}. \tag{13}$$

Here, $\mathcal{H}_s$ is saturation humidity in kg water/kg dry gas and P_{water}^o is the vapor pressure of water. The vapor pressure of water was calculated by using the Antoine equation:

$$P_{water}^o = e^{\left(18.3036 - \left(\frac{3816.44}{-46.13+T}\right)\right)}. \tag{14}$$

In this equation, temperature and vapor pressure are in terms of K and mmHg, respectively.[30]

The water/solution in the liquid chamber was stirred slowly without disturbing the surface. So there was not any vortex formation, and the interfacial area did not change during the experiments. The volume of the liquid and gas in the cell was measured carefully in every experiment. The atmospheric pressure was also measured during experiments.

Although the conditions of the experiments were close to that of ideal gas, the compressibility factor (z) of the gas inside the reactor was also considered in the calculations. The compressibility factors were calculated using the Peng-Robinson model for gases saturated with water vapor at the temperature interval of the performed experiments.[45,46]

2.2.1 | Effect of concentration of calcium acetate on reaction kinetics

To investigate the effect of concentration of calcium acetate solution, experiments were performed at constant temperature and constant carbon dioxide concentration. For these experiments, pure carbon dioxide gas was used and temperature was kept constant at 293.15 ± 0.5 K. The concentration of the bulk aqueous calcium acetate solution was changed in the
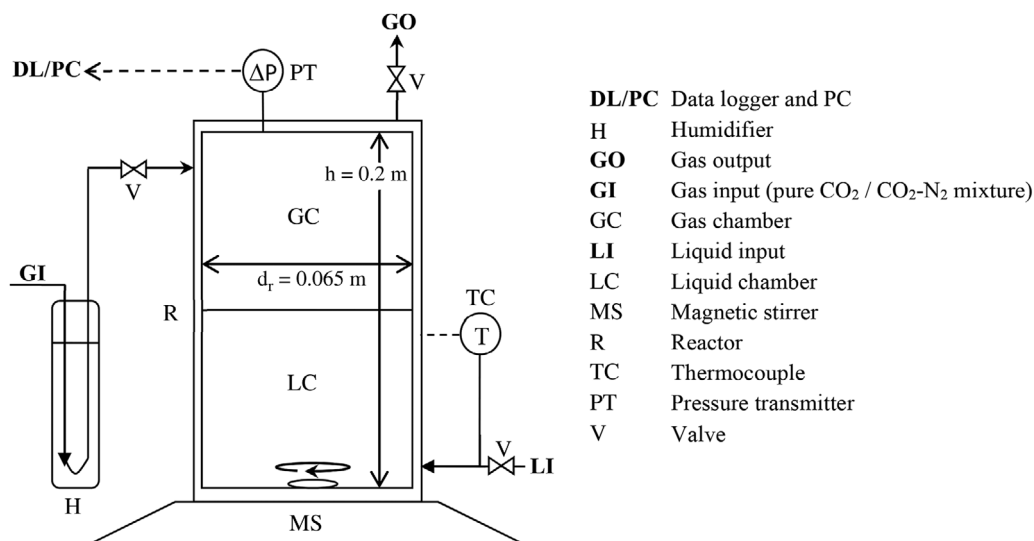
FIGURE 2 The schematic diagram of the experimental setup for determination of reaction kinetics
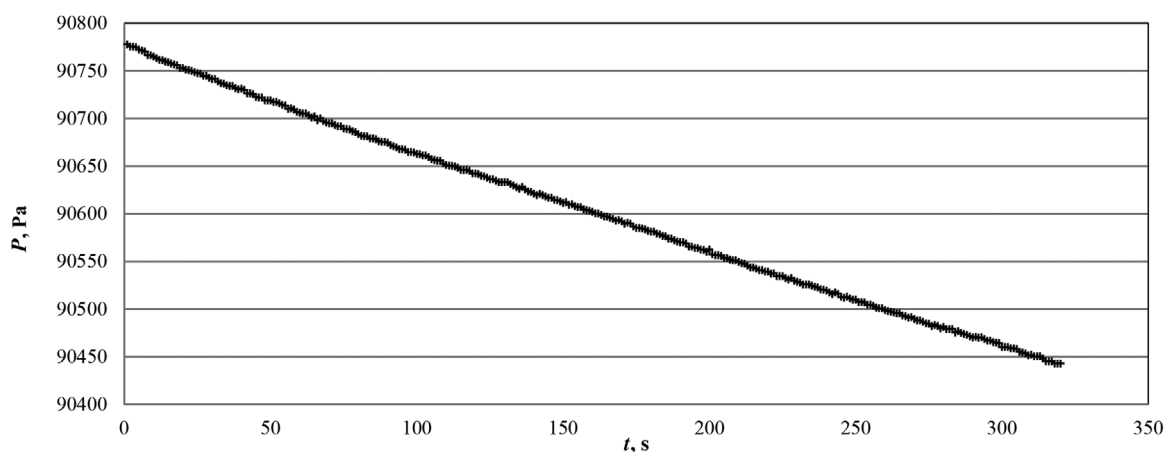

FIGURE 3 Sample pressure decrement data set—obtaining the trend line for the calculations; slope = −1.0398

range from 0.1 to 1.14 M (ie, approximately between 2 and 20 wt%). The reason for choosing the maximum concentration as 1.14 M (or approximately 20%) is that the solubility of calcium acetate is 26 g/100 g solution at 298.15 K.[47–50] The concentrations of aqueous calcium acetate solutions with the indicated solubility limitation were arranged as 2.00, 4.01, 6.02, 8.00, 10.01, 15.01, and 20.01% w/w (or 113.7, 227.5, 341.9, 454.3, 568.4, 851.8, and 1135.6 mol/m^3, respectively), and experiments for all concentration values were repeated three times. For all experiments, a reaction rate was calculated and the effect of concentration of calcium acetate solution on the kinetics of reaction was obtained.

2.2.2 | Effect of concentration of carbon dioxide on reaction kinetics

To investigate the effect of the concentration of carbon dioxide, the experiments were performed at constant temperature (293.15 ± 0.5 K)) and the concentration of calcium acetate

solution was kept the same (as 342 mol/m^3 or 0.342 M or 6% w/w) for all experiments in this part. The carbon dioxide concentration in a gas mixture (with N$_2$) was selected in the range of 4–100 vol%. The gas mixtures were adjusted with electronic mass flow meters (Cole Parmer model GZ 32907-63) with an accuracy of ±0.8% of reading ±0.2% full scale; repeatability of ±0.2%).

Henry's law constants for carbon dioxide in calcium acetate solution were calculated for every gas mixture, and by using these constants the concentration of carbon dioxide at a liquid side of the interface was calculated by the following equation:

$$C_{CO_2,i} = \frac{C_{CO_2,gas}}{m} = \frac{C_{gas}\, y_{CO_2}}{m}. \tag{15}$$

Here, C_{gas}, is the total concentration (mol/m^3) of gas consisting of nitrogen, carbon dioxide, and water vapor and m is

dimensionless solubility, which is calculated with the equation given below:

$$m = \frac{RT}{H_{CO_2}^{Ca(CH_3COO)_2}}, \tag{16}$$

where R is a gas constant (8.31434 Pa·m³/mol·K), T is temperature (in K), and H is Henry's law constant for carbon dioxide in calcium acetate solution (in Pa·m³/mol).

Since the mean carbon dioxide concentration in liquid is proportional to the concentration at the interface (Appendix A in the Supporting Information), it is possible to find the exponent of carbon dioxide on a reaction rate by obtaining reaction rate (r_s) values for different $C_{CO_2,i}$ values.[51]

In this experimental phase, the carbon dioxide concentration in gas mixtures was adjusted as 4.5, 7, 8.6, 11.8, 15, 18.3, 22.7, 31.1, 40.1, 50, 59.9, 69.7, 81.7, 90.4, and 100 vol%. The incremental change of concentration in the range of 4-20% was kept relatively smaller due to its industrial importance, around 3% for natural gas-fired combustors and 14% for coal-fired combustors.[8,15]

2.2.3 | Reaction rate constant and effect of temperature on reaction kinetics

At steady-state conditions, the reaction rate in the liquid phase must be equal to the mass transfer across the interface. Experimental determination of the mass transfer at the interface could be done by monitoring the pressure decrease in the gas phase as outlined above. This was used to determine the exponents of carbon dioxide and calcium acetate concentrations in the rate expression. But, for the determination of the reaction rate constant, the concentrations should be estimated carefully, that is the important point here is that an average carbon dioxide concentration in a liquid must be considered when doing the reaction rate constant calculations. If the reaction was instantaneous, the CO_2 concentration at the liquid side of the interface would be practically zero and the reaction rate would be infinitely large. However, it is well known that this is not the case for CO_2 absorption unless very concentrated alkaline solution with very high pH values is used. Thus, mass transfer and chemical reaction take place simultaneously in the vicinity of the interface at the liquid side. The driving force for mass transfer of carbon dioxide is the difference between an equilibrium concentration at the interface and zero in the bulk liquid. On the other hand, the average CO_2 concentration is needed for reaction kinetic calculations. The average CO_2 concentration cannot be taken as dependent on the depth of the reaction vessel, which may vary from one experimental setup to another. The natural approach is then to use the same models as mass transfer theories use them for mass transfer with a chemical reaction. Since, among others, mostly a film model is used due to its simplicity, and it is also adapted in the present work.

2.3 | Film theory for absorption with a chemical reaction

As seen in Figure 4, the presence of a film is considered near an interfacial area between gas and liquid phases. Here within the film, the mass transfer mechanism is accepted as molecular diffusion. When the physical absorption of gas into liquid is considered, according to film theory, the flux inside this theoretical fictitious film with a thickness of δ can be calculated very easily.[30]

For dilute systems, flux of solute A (CO_2) can be written as

$$N_A = D_{AB} \frac{(C_{A,i} - C_{A,\infty})}{\delta}. \tag{17}$$

The dashed line in Figure 4 represents the linear concentration profile in physical absorption according to the film theory. The flux of physical absorption can also be written in terms of a physical mass transfer coefficient (k_L^o) as follows:

$$N_A = k_L^o (C_{A,i} - C_{A,\infty}). \tag{18}$$

Therefore, from Equations (15) and (16), the physical mass transfer coefficient is defined according to the film theory as

$$k_L^o = \frac{D_{AB}}{\delta}. \tag{19}$$

Direct experimental determination of the film thickness is not possible. But, this relation can be used to estimate δ if k_L^o is known.

The physical mass transfer coefficient (k_L^o) for the cell used in the experiments was determined using the O_2 desorption technique,[12] employing the same mixing rate and same liquid volume. Details of the method are given in Appendix B in the Supporting Information. After converting O_2 desorption results to CO_2, it was determined as

$$k_L^o = 6.815 \times 10^{-6} \text{ m/s}. \tag{20}$$

This is in good agreement with the literature.[51–54]

Uysal also calculated the diffusivity of CO_2 in calcium acetate solution (D_{AB}) using the Stokes-Einstein method and proposed the following equation, which is also used in the present work[12]:

$$D_{AB} = 1050.1 - 33.26 \, x_{Ca(CH_3COO)_2}) \times 10^{-9} \, e^{-\left(\frac{1895}{T}\right)}. \tag{21}$$

Using the interfacial area and film thickness, δ, volume of the fictitious film can be calculated. Thus, expression for the rate of reaction in terms of film volume, r_f (mol/m³·s) can be written as

$$r_f = \frac{\mathcal{W}}{A\delta} = \frac{r_s}{\delta}. \tag{22}$$
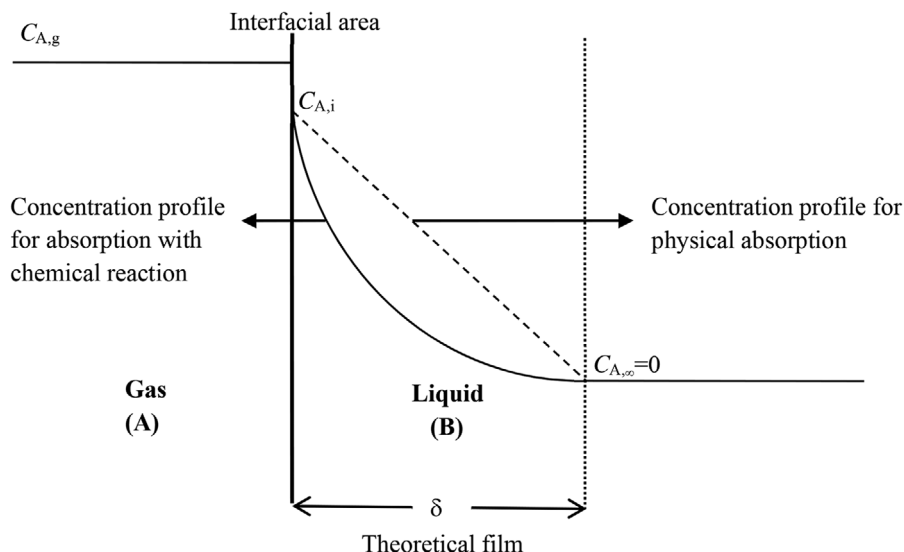
FIGURE 4 The change in the concentration in physical absorption and absorption with chemical reaction according to the film model for dilute systems

2.4 | Mean carbon dioxide concentration for chemical absorption within the film

As the solubility of CO_2 in aqueous solutions is very small and the concentration of liquid reactant is relatively much higher than the concentration of CO_2, it is generally accepted for chemical absorption of CO_2 that the reaction may be assumed as pseudo-first order. This was also confirmed for the present system as outlined below. Thus the reaction rate given by Equation (10) may be expressed in terms of an overall reaction rate constant. Basing on the film volume,

$$r_f = k_{ov} \, \bar{C}_{CO_2}. \tag{23}$$

The mean CO_2 concentration in the film is proportional to its interfacial concentration (Appendix A in the Supporting Information) as shown by the following equation:

$$\bar{C}_{CO_2} = C_{CO_2,i} \, \Lambda, \tag{24}$$

where

$$\Lambda = \left\{ \frac{1/\beta}{\sinh\beta} (\cosh\beta - 1) \right\} \tag{25}$$

$$\beta^2 = \frac{k_{ov}\delta^2}{D_{AB}}. \tag{26}$$

Here the difficulty arises due to the fact that the proportionality constant itself depends on k_{ov}. This was overcome by first assuming that

$$\bar{C}_{CO_2} = \frac{C_{CO_2,i} + C_{CO_2,\infty}}{2} = \frac{C_{CO_2,i} + 0}{2} = \frac{C_{CO_2,i}}{2},$$

and using it for the first calculation and repeating until the last two $\bar{C}_{CO_2}$ values are reasonably close, which did not require more than three trials.

2.5 | Reaction rate constant and the effect of temperature

The reaction rate expression (Equation 10) can be rewritten for the film using the mean carbon dioxide concentration to obtain reaction rate constants, k_f, for every experiment.

$$k_f = \frac{r_f}{\bar{C}_{CO_2}^m C_{Ca(CH_3COO)_2}^n}. \tag{27}$$

To find the Arrhenius (frequency) constant and activation energy values for this reaction rate constant, the effect of temperature on reaction was also investigated. In this part, experiments were performed using the same concentration of aqueous calcium acetate solution (342 mol/m^3 or 6% w/w) for all experiments and pure carbon dioxide was used for the gas phase. The temperature was changed between 286.15 and 351 K regarding the conventional flue gas temperatures for the carbon dioxide absorption process.

The instantaneous values of the interfacial carbon dioxide concentration at the liquid side were calculated by monitoring the pressure in the gas chamber,

$$C_{CO_2,i,t} = \frac{\bar{P}_{CO_2,t}}{H_{CO_2}^{Ca(CH_3COO)_2}}. \tag{28}$$

Here $C_{CO_2,i}$ is the interfacial concentration of carbon dioxide at the liquid side in terms of mol/m^3, and $\bar{P}_{CO_2,t}$ is the partial pressure (Pa) of carbon dioxide in the reactor at any time t. Since the gas was passed through a humidifier before

entering the reactor, the humidity values at every condition were calculated and taken into consideration in these calculations. The mean CO_2 concentration in the film, $\bar{C}^m_{CO_2,t}$, is then calculated as explained above, and Equation (29) was used to calculate the reaction rate constant at any time t.

$$k_{f,t} = \frac{r_f}{\bar{C}^m_{CO_2,t} \, C^n_{Ca(CH_3COO)_2}} \, . \tag{29}$$

By calculating the arithmetic mean of $k_{f,t}$ values obtained over the time of the experiment, a mean k_f value for that particular temperature was calculated.

Using reaction rate constant values for every experimental temperature and applying them to the Arrhenius equation, activation energy, E_a, and Arrhenius constant, k_0, can be calculated (Equation 30):

$$\ln k_f = \ln k_o - \frac{E_a}{RT}. \tag{30}$$

In the investigation of effect of temperature, because of doing the experiments at high temperatures not only the liquid was heated but all of the experimental setup including the piping was covered with a heating tape (Brisk heat thermolyne high temperature heavy insulated heating tapes BWH 101060L), and the heating tape was connected to a calibrated variac during the experiment. Thus, the evaporation of aqueous solution and a sudden decrease in temperature were prevented and correspondingly the errors in pressure readings were eliminated.

Regarding all these points, the experiments were performed at 17 different temperatures (286.65, 293.15, 294.85, 300.05, 308.65, 302.85, 308.65, 311.15, 314.95, 318.15, 323.25, 328.15, 333.35, 337.25, 338.15, 341.95, and 351.65 K), and the effect of temperature on a reaction was investigated.

3 | RESULTS AND DISCUSSION

3.1 | Results for the effect of the calcium acetate concentration on the reaction rate

A sample graph obtained by plotting pressure decrement values against time is given in Figure 3. From the figure, it was possible to calculate the dP/dt value for each experiment using the linear trend line obtained by regression. The reaction rates were calculated as explained in the preceding section, and the effect of concentration of calcium acetate solution on the reaction rate was investigated.

The final results for different calcium acetate concentrations are given in Figure 5, where r_s is plotted versus the calcium acetate concentration in the solution. It may be noted that $\mathcal{W}$ could as well be used instead of r_s for the purpose of examining the effect of the calcium acetate concentration. For

every aqueous calcium acetate concentration, three runs were performed and the average of them was used in the figure.

The results show that the rate of reaction is not affected by the calcium acetate concentrations. This was expected as the concentration of calcium acetate in the absorbing solution was in very much excess of the carbon dioxide concentration. Also, the concentration of carbon dioxide and thus the reaction rate was relatively so small that the amount and concentration of calcium acetate was not very much affected during the experiment. This outcome is in agreement with other studies on chemical absorption of carbon dioxide by various reactants in the literature.[51,55–57]

A mean value of reaction rate was 0.0312 mol/m²·s for the experimental conditions shown in Figure 5. Each experimental value was compared with this mean value, and the difference was very small as shown with 3% error bars.

3.2 | Results for the effect of the carbon dioxide concentration on the reaction rate

Following the method outlined before, experiments were performed with different carbon dioxide concentrations at a constant temperature ($T = 293.15$ K) and constant calcium acetate concentration ($C_{Ca(CH3COO)2} = 342$ mol/m³) to clarify the dependence of the reaction rate on the carbon dioxide concentration. The rate of reaction obtained in this set of experiments is plotted in Figure 6. The regression analysis with a regression coefficient of 0.9945 showed that the reaction rate has a first-degree dependence on the carbon dioxide concentration.

The results for the effects of carbon dioxide and calcium acetate concentrations (Figures 4 and 5) show clearly that the reaction in chemical absorption of carbon dioxide into the calcium acetate solution system has the same behavior as other chemical absorption systems, and it is pseudo-first order with respect to carbon dioxide.[51–53,58] Hence, the rate of reaction expression can be written as follows:

$$r_f = k C_{Ca(CH_3COO)_2} \bar{C}_{CO_2} = k_{ov} \bar{C}_{CO_2}. \tag{31}$$

3.3 | Results for the reaction rate constant and effect of temperature

The results of the experiments performed at different temperatures with pure carbon dioxide gas and the same calcium acetate concentration are given in Figure 7. The effect of temperature on chemical absorption systems is quite complicated. Mass transfer and chemical reaction take place simultaneously. As temperature increases, physical solubility of a gaseous solute in a liquid decreases. This results in a decrease in an interfacial concentration at the liquid side. The driving force for mass transfer is then affected and decreases, causing a decrease in a physical mass transfer rate. Moreover, as temperature increases, intrinsically carbon dioxide gas
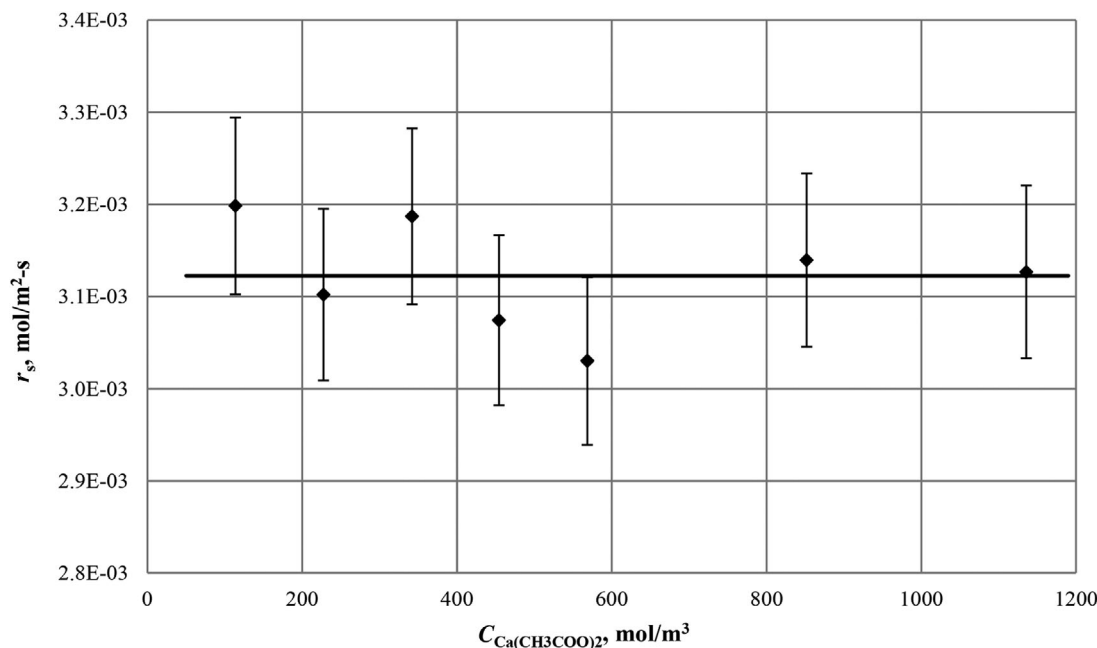
FIGURE 5 Rates of reaction for different calcium acetate solution concentrations at constant temperature ($T = 287.15$ K) and pure carbon dioxide (before humidifiers) (with 3% error bars)
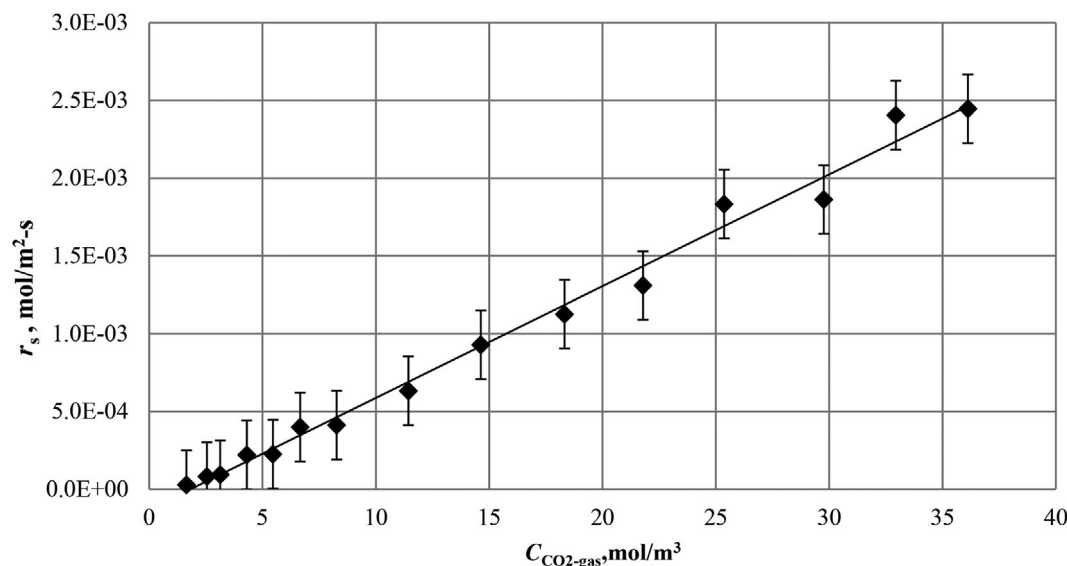

FIGURE 6 Rate of reaction values for experiments done with different carbon dioxide concentrations at constant temperature and constant calcium acetate solution concentration, verification of reaction being first order with respect to the carbon dioxide concentration (with 5% error bars)

entering the humidifiers, which were kept at the same temperature as the reactor cell, leaves with more water vapor to the cell since the saturation point increases according to the Clausius-Clapeyron relation and Antoine equation. This fact results in a decrease in the concentration of carbon dioxide in a gas mixture (y_{CO_2}) fed to the reactor. For this reason, the amount of carbon dioxide gas trapped in a cell decreases and consequently the liquid side interfacial concentration, which is in equilibrium with the gas phase, also decreases. On the other hand, the increase in temperature is expected to increase

the reaction rate. Thus, interference of these effects for chemical absorption systems requires special care, and accurate estimation of all the parameters needs to be made sensitively. In spite of all the care taken, some deviations in the experimental results are inevitable. This is also reflected in Figure 6, where logarithmic values of the reaction rate constant is drawn against $1/T$ values. Nevertheless, the regression analysis yielded the best-fit line to calculate activation energy from the slope and Arrhenius constant from the intercept. Activation energy and Arrhenius constant for this reac-
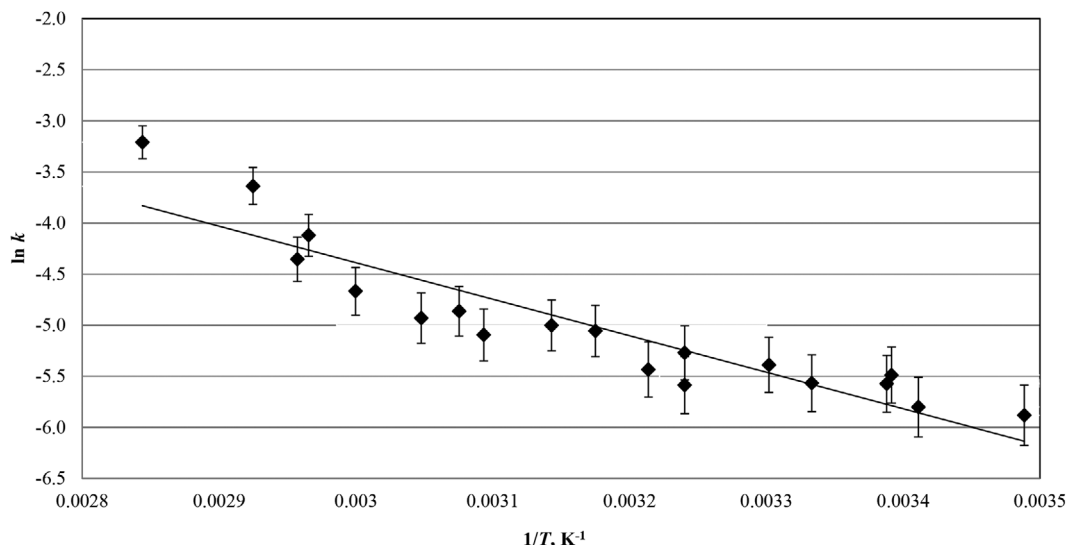
FIGURE 7 Results of the experiments performed at different temperatures with pure carbon dioxide gas (before humidifiers) and at the constant calcium acetate solution concentration (with 5% error bars)

tion were calculated as 29,762 J/mol (7.1085 kcal/mol) and 573.75 m³/mol·s, respectively (where the regression coefficient is 0.91961). With these values, the reaction rate constant in the rate expression as given in Equation (31) for this reaction can be written as

$$k = 573.75 \, e^{\frac{-29762}{RT}}. \tag{32}$$

In similar researches in the literature for other various reactants, the maximum temperature employed was 333 K.[51,55–57] In this work, the effect of temperature was investigated over a larger temperature range from 286 to 352 K. Along this temperature range, the reaction rate constant increased roughly three times with temperature.

To do calculations easily, use of the interfacial concentration and r_S may be preferred. In this case, r_S can be expressed as
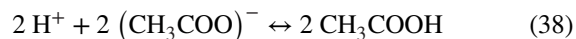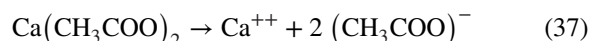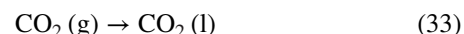
$$r_S = 0.2 \, e^{\frac{-29762}{RT}} \, C_{Ca(CH_3COO)_2} C_{CO_2,i}.$$

An assessment of the values for the reaction rate and rate constant obtained experimentally indicates that calcium acetate solution is an effective solvent to capture carbon dioxide by chemical absorption at atmospheric pressure and low temperatures. This eliminates the need for high temperature and pressure requirement for conventional systems. Elimination of high-temperature requirement also results in appreciable energy saving and less loss of solvent due to evaporation.

The effect of humidification of gas stream before entering the reactor on the Arrhenius constant and activation energy was also investigated. As stated before, the experiments were done using a stirred cell reactor, which is a widely used setup in such researches. Gas was saturated with water vapor at the reactor temperature before sending it to the reactor cell.[59–61]

This prevents evaporation or condensation of water vapor inside the reactor. Otherwise, it interferes with carbon dioxide absorption and pressure oscillations in the reactor cell become inevitable. One must carefully consider this effect when aqueous solutions of solvents are used. The effect of gas humidity on the carbon dioxide absorption rate was also checked, and a computational analysis was performed. It has been found that errors in mass transfer rates could be as high as 10% at low temperatures and 40% at high temperatures if prehumidification of the gas had not been made.

The steps of chemical absorption of carbon dioxide into calcium acetate solution can be postulated as follows:

$$CO_2 \, (g) \rightarrow CO_2 \, (l) \tag{33}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{34}$$

$$CO_2 \, (l) + \, OH^- \rightarrow \, HCO_3^- \tag{35}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{36}$$

$$Ca(CH_3COO)_2 \rightarrow Ca^{++} + 2 \, (CH_3COO)^- \tag{37}$$

$$2 \, H^+ + 2 \, (CH_3COO)^- \leftrightarrow 2 \, CH_3COOH \tag{38}$$

$$Ca^{++} + \, CO_3^{2-} \, \rightarrow CaCO_3. \tag{39}$$

Accordingly, the overall reaction for this system can be written as

$$CO_2 + Ca(CH_3COO)_2 + H_2O \rightarrow 2 \, CH_3COOH + CaCO_3. \tag{40}$$
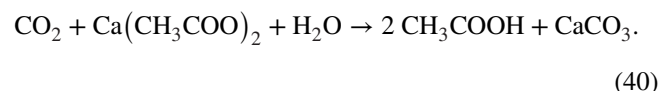
It may be worth to mention here that the Gibbs free energy change of the overall reaction was also calculated at standard conditions and was found as −2.75 kJ/mol.[62,63] This value

shows that this reaction is exergonic and occurs spontaneously without any addition of energy to the system. Also, in another similar study, this value is reported as –3.2 kJ/mol.[64]

3.4 | Validation of the reaction regime

A final note may be added here to elaborate the main conclusion that chemical absorption of carbon dioxide into calcium acetate solution is due to fast pseudo–first-order reaction with respect to carbon dioxide. The Thiele modulus and Hatta number (*Ha*) were calculated for this purpose.

The Thiele modulus is a dimensionless group used for mass transfer with a chemical reaction and is a measure of the effect of reaction with respect to the rate of diffusion in the system[65–67]:

$$\psi^2 = \frac{\text{Rate of reaction at the interface}}{\text{Rate of diffusion}}$$
$$= \frac{k_{ov} C_{CO_2,i} \, h}{D_{CO_2}^{Ca(CH_3COO)_2} \left(C_{CO_2,i} - C_{CO_2,L} \right) / h}, \quad (41)$$

where $C_{CO_2,L}$, is the carbon dioxide concentration in a bulk solution and h is the characteristic length. When carbon dioxide is transferred into the liquid, it gives a fast reaction with calcium acetate. Owing to its sudden consumption within the vicinity of the interface, the concentration of carbon dioxide in bulk liquid, $C_{CO_2,L}$, is zero. Rearranging Equation (44) regarding that the reaction is pseudo-first order and by defining the physical mass transfer coefficient considering the film theory and noting that $h = \delta$ film thickness, the Thiele modulus can be written as shown in Equation (45),[12,64,65]

$$\psi^2 = \frac{k_{ov} \, D_{CO_2}^{Ca(CH_3COO)_2}}{\left(k_L^0\right)^2}. \quad (42)$$

The square root of this equation is defined as the Hatta number.

$$Ha = \frac{\sqrt{k_{ov} \, D_{CO_2}^{Ca(CH_3COO)_2}}}{k_L^0} . \quad (43)$$

The Hatta number is a measure of the enhancement of absorption due to a chemical reaction with respect to physical absorption.[64] Here k_L^0 is the physical mass transfer coefficient (m·s^{-1}) and depends on the characteristics and hydrodynamics of the system. As stated earlier, investigation of the physical mass transfer coefficient of the used stirred cell reactor was done separately and it was found to be 6.812×10^{-6} m·s^{-1} [Ref. 12] at the experimental conditions of this work, which is in good agreement with other works in literature.[51–54] The diffusion coefficient of carbon dioxide was also inves-

tigated, and using the experimental results a correlation was developed[12]:

$$D_{CO_2}^{Ca(CH_3COO)_2} = \left(1050.1 - 33.26 \cdot x_{Ca(CH_3COO)_2} \right)$$
$$\times 10^{-9} \cdot e^{\left(\frac{-1895}{T} \right)}. \quad (44)$$

Here, x is the weight percentage of calcium acetate aqueous solution. Using these results, the Hatta number for every experiment of the present study was calculated and was found to vary in the range of 5–38. The average Hatta number was found as 13.

The enhancement factor, defined as the ratio of the mass transfer coefficient with a chemical reaction to the physical mass transfer coefficient, for the instantaneous regime is given by

$$E_\infty = \left(1 + \frac{D_{Ca(CH_3COO)_2} C_{Ca(CH_3COO)_2}}{\gamma_{CO_2} D_{CO_2}^{Ca(CH_3COO)_2} C_{CO_2,i}} \right) \sqrt{\frac{D_{CO_2}^{Ca(CH_3COO)_2}}{D_{Ca(CH_3COO)_2}}}, \quad (45)$$

and for the experimental conditions it was found as $E_\infty = 74.98$. If the Ha number is between $2 < Ha < 5E_\infty$, the reaction regime is defined as fast reaction. The instantaneous regime is for $Ha > 5E_\infty$. Therefore, these calculations show that the absorption of carbon dioxide into aqueous calcium acetate solution is in "fast pseudo–first-order regime."[31,51,55,56,61]

The concentration profiles for the absorption systems with a chemical reaction in the fast pseudo–first-order regime is depicted in Figure 8. The change in the concentration of bulk liquid is negligible due to the high concentration of the reactant in the absorbing liquid with respect to solute, that is, carbon dioxide, crossing the interface.

4 | CONCLUSIONS

In this work, the absorption of carbon dioxide into aqueous calcium acetate solution was investigated. The absorption in this system is with a chemical reaction so the reaction mechanism and kinetics were investigated. The reaction for carbon dioxide absorption with calcium acetate solution was found to be fast pseudo-first order like most of the carbon dioxide absorption processes with a chemical reaction. The Hatta number was calculated for every experiment and found to be greater than 2 and less than $5E_\infty$. This shows that the reaction is in the "fast pseudo–first-order regime." The activation energy and the Arrhenius (frequency) constant of the reaction were calculated as 29762 J/mol and 573.75 m^3/mol·s, respectively. Also, the Gibbs free standard energy change for the
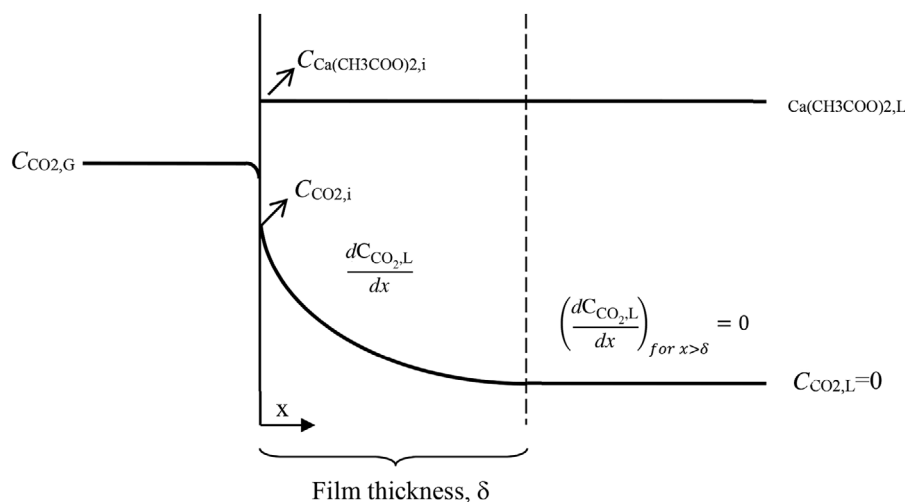
FIGURE 8 Gas and liquid concentration profiles for fast pseudo–first-order reaction in an absorption system

reaction was calculated as –2.75 kJ/mol. This study has been a good indicator to a benign process to capture carbon dioxide with calcium acetate solution, which is economical and environmentally friendly alternative to conventional solutions used in CCS or CCU systems.

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REFERENCES

1. IPCC Report, C C 2007: Mitigation. Contribution of Working Group III to the Forth Assesment Report of the Intergovernmental Panel on Climate Change; 2007.
2. IPCC Synthesis Report, Climate Change 2014: Synthesis Report. A report of the Intergovernmental Panel on Climate Change; 2014.
3. IEA (International Energy Agency). *Global energy and CO_2 status report* – 2017; March 2018.
4. IPCC. Special Report of Global Warming of 1.5°C; 2018.
5. PBL Netherlands Environmental Assessment Agency. Trends in global CO_2 and total greenhouse gas emissions-2017 report. The Hague, PBL Publication number: 24; 2017.
6. Metz B, Davidson O, Coninck H, Loos M, Meyer L. *Intergovernmental Panel on Climate Change (IPCC)–Carbon Dioxide Capture and Storage*. 1st ed. New York, NY: Cambridge University Press; 2005:19-37.
7. Smit B, Reimer JA, Oldenburg CM, Bourg IC. *Introduction to Carbon Capture and Sequestration*. The Berkeley Lectures on Energy, Vol 1. London: Imperial College Press; 2014.
8. Spigarelli BP, Kawatra SK. Opportunities and challenges in carbon dioxide capture. *J CO_2 Util*. 2013;1:69-87.
9. Herzog H, An introduction to CO separation and capture technologies. Cambridge, MA: MIT Energy Laboratory; 1999.
10. Rubin ES, Rao AB, A technical economic and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. Annual Technical Progress Report. Pittsburgh, PA: Carnegie Mellon University Center for Energy and Environmental Studies; 2002.
11. Mirzaei S, Shamiri A, Aroua MK. A review of different solvents, mass transfer and hydrodynamics for postcombustion CO_2 capture. *Rev Chem Eng*. 2015;31(6):1-41.
12. Uysal D. *Absorption of carbon dioxide with calcium acetate solution* [PhD thesis]. Gazi University Graduate School of Natural and Applied Sciences, Ankara; 2016 (in Turkish).
13. Weiss H. Rectisol wash for purification of partial oxidation gases. *Gas Sep Purif*. 1988;2:171-176.
14. Mohammed IY, Samah M, Mohamed A. Sabina G. Comparison of Selexol™ and Rectisol® technologies in an integrated gasification combined cycle (IGCC) plant for clean energy production. *Int J Eng Res*. 2014;3(12):742-744.
15. Zaman M, Lee JH. Carbon capture from stationary power generation sources: a review of the current status of the technologies. *Korean J Chem Eng*. 2013;30:1497-1526.
16. GCEP Technical Assessment Report. An assessment of carbon capture technology and research opportunities. GCEP Energy Assessment Analysis, Stanford University, Global Climate & Energy Project; 2005.
17. Davidson RM, Post-combustion carbon capture from coal fired plants—solvent scrubbing. CCC/125. London: IEA Clean Coal Centre; 2007.
18. Versteeg GF, van Dijk LAJ, van Swaaij WPM. On the kinetics between CO_2 and alkanolamines both in aqueous and nonaqueous solutions: an overview. *Chem Eng Commun*. 1996;144(1):113-158.
19. Kumar P, Hogendoorn J, Feron JA, Versteeg GF. Density, viscosity, solubility and diffusivity of N_2O in aqueous amino acid salt solutions. *J Chem Eng Data*. 2011;46(6):1357-1361.
20. ÖM D, U G, Topçu M, Uysal BZ, CO_2 absorption by aqueous monoethanolamine (MEA) in a bubble column. Paper presented at 18th International Congress of Chemical and Process Engineering, Prague, Czech Republic; 2008.
21. Kohl AL, Nielsen R. *Gas Purification*. 5th ed. Houston, TX: Gulf Publishing Co; 1997.
22. Aronu UE, Svendsen HF, Hoff KA. Investigation of amine amino acid salts for carbon dioxide absorption. *Int J Greenhouse Gas Control*. 2010;4(5):771-775.

23. Burr B, Lyddon L. A comparison of physical solvents for acid gas removal. *87th Annu Conv Proc*. 2008:100-113.

24. Kothandaraman A. *Carbon dioxide capture by chemical absorption: a solvent comparison study* [PhD thesis]. Cambridge, MA: Massachusetts Institute of Technology; 2010.

25. ÖM UDD, BZ U, Absorption of carbon dioxide into sodium metaborate solution using a bubble column. *Air Quality VIII Conference*. Arlington, Virginia; 2011.

26. Veawab A, Aroonwilas A, Chakma A, Tontiwachwuthikul P. Solvent formulation for CO_2 separation from flue gas streams. Regina, SK, Canada: Faculty of Engineering, University of Regina.

27. Resnik KP, Yeh JT, Pennline HW. Aqua ammonia process for simultaneous removal of CO_2, SO_2 and NO_x. *Int J Environ Technol Manag*. 2004;4:89-104.

28. Wang M, Lawal A, Stephenson P, Sidders J, Ramshaw C. Post-combustion CO_2 capture with chemical absorption: a state-of-art review. *Chem Eng Res Des*. 2011;89:1609-1624.

29. Feng Z, Cheng-Gang F, You-Ting W, Yuan-Tao W, Ai-Min L, Zhi-Bing Z. Absorption of CO_2 in the aqueous solutions of functionalized ionic liquids and MDEA. *Chem Eng J*. 2010;160:691-697.

30. Uysal BZ. *Principles and Applications of Mass Transfer*. 2nd ed. Ankara, Turkey: Gazi University Publications; 2003 (in Turkish).

31. Dankwerts PV. *Gas-Liquid Reactions*. New York, NY: McGraw Hill; 1970.

32. Setschenow M. Action de liacide carbonique sur les solutions dessel a acides forts: etude absortiometrique. *Ann Chim Phys*. 1892;25:226-270.

33. Van Krevelen DW, Hoftijzer PJ. Chimie et Industrie: numero Speciale du XXIe Congres International de Chimie Industrielle. *Bruxxels*. 1948.

34. Barett PVL. *Gas absorption on a sieve plate* [PhD thesis]. Cambridge, UK: Cambridge University; 1966.

35. Armenante PM, Karlsson HT. Salting-out parameters for organic acids. *J Chem Eng Data*. 1982;27:155-156.

36. Yasunishi A, Yoshida F. Solubility of carbon dioxide in aqueous electrolyte solutions. *J Chem Eng Data*. 1979;24(1):11-14.

37. Onda K, Sada E, Kobayashi T, Kito S, Ito K. Salting-out parameters of gas solubility in aqueous salt solutions. *J Chem Eng Jpn*. 1970;3(1):18-24.

38. Tasleem S, Durani S, Anwar M, Niaz M, Muzaffar K. Salting-out coefficients and activity coefficients of alkali and alkaline earth metals in aqueous and aqueous organic mixed solvents. *J Chem Soc Pakistan*. 2004;26(1):39-43.

39. Hermann C, Dewes I, Schumpe A. The estimation of gas solubilities in salt solutions. *Chem Eng Sci*. 1995;50(10):13-15.

40. Schumpe A, Deckwer WD. Estimation of O_2 and CO_2 solubilities in fermantation media. *Biotechnol Bioeng*. 1979;11:1075-1078.

41. Weisenberg S, Schumpe A. Estimation of gas solubilities in salt solutions at temperatures from 273 K to 363 K. *AIChE J*. 1996;42(1):298-300.

42. Licht SE, Weiland RH, Density and physical solubility of CO_2 in partially loaded solutions of MEA, DEA and MDEA. Paper No. 57f. Presented at the AICHE National Meeting, 1989: Houston.

43. Dang H, Rochelle GT. Carbon dioxide absorption rate and solubility in MEA/PZ/H_2O. *Sep Sci Technol*. 2003;38(2):337-357.

44. McCabe WL, Smith JC, Harriott P. *Unit Operations of Chemical Engineering*. 7th ed. New York, NY: McGraw-Hill; 2005.

45. Sandler SI. *Biochemical and Engineering Thermodynamics*. 4th ed. Hoboken, NJ: Wiley; 2006.

46. Li Y, Huang W, Zheng D, Mi Y, Dong L. Solubilities of CO_2 capture absorbents 2-ethoxyethyl ether, 2-butoxyethyl acetate and 2-(2-ethoxyethoxy)ethyl acetate. *Fluid Phase Equilibr*. 2014;370: 1-7.

47. Zhao HK, Zhang DS, Tang C, Jian PM, Yuan SH. Phase diagram of ternary calcium acetate–magnesium acetate–water system at 298 K, 313 K and 323 K. *J Phase Equilib Diff*. 2007;28(2): 1-171.

48. Apelblat A, Manzurola E. Solubilities of magnesium, calcium, barium, cobalt, nickel, copper and zinc acetates in water from $T = $ (278.15 to 348.15) K. *J Chem Thermodyn*. 1999;31:1347-1357.

49. Saury C, Boistelle R, Dalemat F, Bruggeman J. Solubilities of calcium acetates in the temperature range 0–100°C. *J Chem Eng Data*. 1993;38:56-59.

50. Seidell A. *Solubilities of Inorganic and Organic Compounds*. 2nd ed. New York, NY: Stanhope Press; 1919.

51. Kierzkowska-Pawlak H. Determination of kinetics in gas-liquid reaction systems. An overview. *Ecol Chem Eng*. 2012;19(2):175-196.

52. Hamborg ES. *Carbon dioxide removal processes by alkanolamines in aqueous organic solvents* [PhD thesis]. Groningen, the Netherlands: Wiskunde en Natuurwetenschappen aan de Rijksuniversiteit; 2011.

53. Zhang X, Bao D, Huang Y, Dong H, Zhang X, Zang S. Gas-liquid mass transfer properties in CO_2 absorption system with ionic liquids. *AIChE J*. 2014;60(8):2929-2939.

54. Portugal AF, Magalhães FD, Mendes A. Carbon dioxide absorption kinetics in potassium threonate. *Chem Eng Sci*. 2008;63:3493-3503.

55. Derks PWJ, Kleingeld T, van Aken C, Hogendoorn JA, Versteeg GF. Kinetics of absorption of carbon dioxide in aqueous piperazine solutions. *Chem Eng Sci*. 2006;61:6837-6854.

56. Darde V, Van Well WJM, Fosboel PL, Stenby EH, Thomsen K. Experimental measurement and modeling of the rate of absorption of carbon dioxide by aqueous ammonia. *Int J Greenhouse Gas Control*. 2011;5:1149-1162.

57. Luo X, Hartono A, Hussain S, Svendsen HF. Mass transfer and kinetics of carbon dioxide absorption into loaded aqueous monoethanolamine solutions. *Chem Eng Sci*. 2015;123: 57-69.

58. Van Swaaij WPM, Versteeg GF. Mass transfer accompanied with complex reversible chemical reaction in gas liquid systems: an overview. *Chem Eng Sci*. 1992;47:3181-3195.

59. Kumar PS, Hogendoorn JA, Versteeg GF. Kinetics of the reaction of CO_2 with aqueous potassium salt of taurine and glycine. *AICHE J*. 2003;49(1):203-213.

60. Blauwhoff PMM, Versteeg GF, van Swaaij WPM. A study on the reaction between CO_2 and alkanolamines in aqueous solutions. *Chem Eng Sci*. 1983;38(9):1411-1429.

61. Jiru Y, Eimer DA. A study of mass transfer kinetics of carbon dioxide in (monoethanolamine + water) by stirred cell. *Energy Proc*. 2013;37:2180-2187.

62. Perry RH, Green DW. *Perry's Chemical Engineers' Handbook*. 8 ed. New York, NY: McGraw-Hill; 2007.

63. Oelkers EH, Helgeson HC, Shock EL, Sverjensky DA, Johnson JW, Pokrovskii VA. Summary of the apparent standard partial molal Gibbs free energies of formation of aqueous species, minerals and gases at pressures 1 to 5000 bars and temperature 25 to 1000°C. *J Phys Chem Ref Data*. 1995;24(4):1401-1560.

64. Kakizawa M, Yamasaki A, Yanagisawa Y. A new CO_2 disposal process via artificial weathering of calcium silicate accelerated by acetic acid. *Energy*. 2001;26:341-354.

65. Bird RB, Stewart WE, Lightfoot EN. *Transport Phenomena*. 2nd ed. New York, NY: Wiley; 2007.

66. Fogler HS. *Elements of Chemical Reaction Engineering*. 4th ed. Massachusetts, MA: Pearson Education; 2006.

67. Astarita G. *Mass Transfer with Chemical Reaction*. Amsterdam, the Netherlands: Elsevier; 1967.

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