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Solubility Data of CO_2 in the MDEA+PZ Solvent: A Review of Experimental Data, Setups, and Procedures

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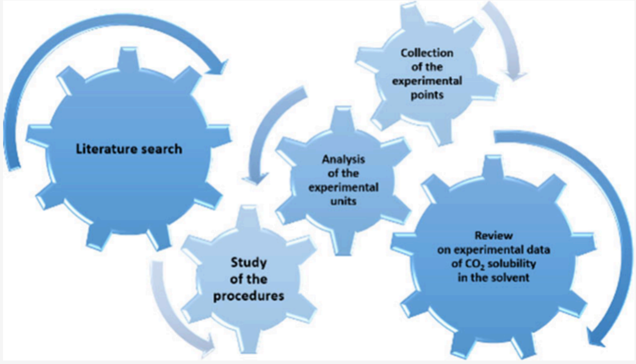
ABSTRACT: Chemical absorption is one of the most applied and efficient methods for CO_2 removal, and it is primarily employed in the processes related to the production of energy (natural gas, power plants, etc.). This work is the first review focusing on bibliographic research related to experimental data of CO_2 solubility in the MDEA+PZ aqueous solution, which is of interest for the CO_2 removal from several types of gaseous streams in important industrial and environmental processes. An in-depth review of the available experimental setups and procedures for collecting points of CO_2 solubility in the MDEA+PZ solvent is presented. The main methods to measure and compute the solubility of the acid gas in the solvent are analyzed, and the experimental points from all the sources are detailed and compared, considering different values of temperature, pressure, CO_2 loading, and composition of the solvent, as for the content of MDEA and that of PZ.



1. INTRODUCTION

Aqueous alkanolamine (amine) solutions have long been employed for the removal of acid gases from different types of gaseous streams. Methyldiethanolamine (MDEA) has gained significant industrial importance, with its use initially documented by Frazier and Kohl.[1] Despite relatively high capital costs and expensive solvents, the advantages of flexibility, ease of operation, and low energy expenditure have made it interesting both for new installations and for modifications to already existing plants. Being a tertiary amine, MDEA reacts slowly with CO_2 compared with primary and secondary amines. The use of aqueous amine blends of MDEA and a primary or a secondary amine was proposed by Chakravarty[2] to enhance the absorption rate of CO_2 while maintaining the advantages of using MDEA. Austgen et al.[3] report the CO_2 solubility in 2.0 M MDEA + 2.0 M MEA or DEA aqueous solution at 313 and 353 K for CO_2 partial pressures below 315 kPa. Li and Shen[4] and Shen and Li[5] measured the CO_2 solubility in aqueous blends of MDEA and MEA at the total amine concentration of 30% wt. Jou et al.[6] measured the CO_2 solubility in four aqueous mixtures of MDEA with MEA at temperatures from 25 to 120 °C for a range of CO_2 partial pressures from 0.001 to 19930 kPa. Solubility data for CO_2 in blends of 3.4 M MDEA + 0.8 M MEA or DEA and 2.1 M MDEA + 2.1 M MEA or DEA at temperatures from 343 to 453 K and CO_2 partial pressures from 100 to 3850 kPa were determined by Dawodu and Meisen.[7]

A step forward in the research on this topic has been the idea of adding a small amount of an accelerator to an aqueous solution of a tertiary amine, which has found widespread application in the selective or bulk removal of carbon dioxide from process gas streams.[8] The combination of the relatively high rate of reaction of carbon dioxide with the accelerator, usually a primary or secondary amine, and the low heat of reaction of CO_2 with the tertiary amine is the principle that is the basis of the use of these solvents. As a result, higher absorption rates in the absorber section and a low heat of regeneration of the solvent are obtained. Piperazine (PZ) is an activator commonly employed for MDEA, for which extensive VLE data are available across a wide range of aqueous PZ/MDEA mixtures. Formulations such as 7 m MDEA/2 m PZ and 5 m MDEA/5 m PZ are considered superior to the conventional 7 m MEA solvent for CO_2 capture. Compared to 7 m MEA, the MDEA/PZ blends are characterized by almost twice the capture capacity (~0.8 mol CO_2/kg amine + H_2O versus 0.47 mol CO_2/kg amine + H_2O) within the optimal operating range of ~0.5 and 5 kPa lean and rich CO_2 partial pressure, respectively.[9] They also show nearly twice the CO_2 absorption rate (~5.1 × 107 versus 3.1 mol/s·Pa·m^2)[9] at the nominal rich loading; significantly lower

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oxidative and thermal degradation rates, and 80−90% lower volatility (0.47 Pa MDEA and 0.30 Pa PZ versus 2.7 Pa MEA at 40 °C).[10] On the basis of a Scopus search considering the words "CO_2 MDEA PZ" in the sections "Abstract title, Abstract, Keywords", in the literature a total of 275 documents has been found, in detail 215 articles, 54 conference papers, 4 book chapters, and 2 reviews. The total number of documents confirms the relevance of the topic and the only two reviews focus on the amine degradation in CO_2 capture[11] and on recent advances in carbon dioxide capture and utilization with amines and ionic liquids.[12]

Similarly, a survey of the literature on Google Scholar using the keywords "CO_2 solubility in MDEA-PZ aqueous solutions" identified approximately 833 publications from 2015 to 2025. Some of these studies estimate the CO_2 solubility in MDEA/PZ blends using an artificial neural network (ANN) technique,[13,14] while others focus on the mass transfer and kinetics performance of the amine blend.[15−18] In addition, several works address the thermodynamic modeling of the VLE of the quaternary system (CO_2/H_2O/PZ/MDEA);[19−23] and others investigate thermophysical properties, such as heat of absorption, density, viscosity, refractive index, and surface tension.[24−26] Finally, some publications identified in the survey pertain to other chemical systems.[27−29] Among the various research directions identified, this work specifically focuses on the analysis of experimental data on the CO_2 solubility in the aqueous MDEA/PZ system.

Detailed knowledge on the thermodynamics of the system composed of CO_2 and the solvent is needed for a good understanding of the performances of the absorption and regeneration process[30] and for selecting the thermodynamic model to be used for process simulation.[31,32] To this aim, the experimental equilibrium data of CO_2+MDEA+PZ+H_2O are fundamental. Without them, this strongly nonideal system with chemical reactions occurring in the liquid phase could not be characterized.[33] Experimental measurements of the CO_2 solubility in the MDEA+PZ aqueous solvent have been available since 1998. However, a comprehensive review of all relevant sources on this topic is still lacking in the literature. This work aims to fill that gap by providing a thorough review, including a detailed description of the different experimental procedures and setups used to obtain the solubility data.

2. METHODOLOGY FOR THE REVIEW

For performing this review, a deep search of all the literature on the topic of the solubility of CO_2 in the MDEA+PZ aqueous solution was carried out. The sources found have been analyzed for the characteristics (temperature, pressure, and composition) of the collected points, for the experimental setup, and for the procedure.

All the research papers have been grouped on the basis of the experimental method employed for collecting the experimental data, and the units have been described in detail. Then, the procedure employed for obtaining the equilibrium values of CO_2 partial pressure and of CO_2 loading, defined as in eq 1, has been detailed for each source.

$$\text{CO}_2\text{ loading} = \frac{\text{mole fraction of apparent CO}_2}{\text{mole fraction of apparent MDEA} + \text{mole fraction of apparent PZ}} \qquad (1)$$

The methodology for analyzing the experimental points obtained from different literature sources and for validating them is based on the comparison of the data at the same temperature and similar concentrations of MDEA and of PZ. In particular, because different data at the same temperature and amine composition (of the solvent charged into the unit before the addition of CO_2) are not at exactly the same CO_2 loading and CO_2 partial pressure, a numerical comparison based on the evaluation of the Absolute Average Deviation % and on the Relative Average Deviation % could not be performed. Therefore, the comparison has been carried out by analyzing the trends of the CO_2 partial pressure as a function of the CO_2 loading and by graphically comparing them, as is usually done for this type of system.[34−36] In this way, the presence of some outliers could also be detected.

The analysis has been done for the same temperature and amine concentrations obtained from different sources, and for the same temperature and different amine concentrations from both the same and different sources.

3. SOURCES OF EXPERIMENTAL DATA

Several sources in the literature reporting the experimental data of the CO_2 solubility in aqueous mixtures of MDEA and PZ have been found and analyzed in detail.

- Xu et al.[37] studied the solubility data of CO_2 and saturated water vapor pressure over aqueous MDEA solutions and focused on the effect of PZ on the CO_2 loading and the equilibrium partial pressure of CO_2 in the MDEA aqueous solutions, with PZ concentrations from 0 to 0.515 M for an MDEA concentration equal to 4.28 M. They measured the CO_2 loading as a function of time at different pressures, temperatures, and MDEA concentrations. In addition, they collected PZ vapor pressure data in the PZ+MDEA+H_2O blend.
- Liu et al.[38] measured the solubility of carbon dioxide in aqueous mixtures of MDEA and PZ at temperatures from 303 to 363 K and at CO_2 partial pressures from 13.16 to 935.3 kPa, with MDEA concentrations between 1.53 and 4.77 M and PZ concentrations between 0 and 1.55 M.
- Kamps et al.[39] employed the experimental unit for measuring the solubility of CO_2 in about 2 molal MDEA and 2 molal PZ aqueous solutions at 353 K.
- Ali and Aroua[35] carried out a study on the solubility of CO_2 in aqueous solutions of PZ-activated MDEA for temperatures from 313 to 353 K and CO_2 partial pressures from 0.1 to 100 kPa, representative of the top of the industrial absorption columns and of systems involving flue gases at atmospheric pressure, as in power plants. The experiments were performed with an amine concentration (about 2 M) and a variable PZ concentration (from 0.01 to 0.1 M).
- Jenab et al.[40] and Vahidi et al.[41] collected experimental data of CO_2 solubility in aqueous solutions of MDEA and PZ, for concentrations ranging from 2 to 3 M (MDEA) and from 0.36 to 1.36 M (PZ), for temperatures between 313.15 and 343.15 K and for CO_2 partial pressures between about 30 and 3900 kPa.
- Bottger et al.[42] measured the CO_2 solubility in MDEA+PZ+H_2O solutions at temperatures from 313 to 393 K and pressures between 200 and 10000 kPa, with the molalities of MDEA and PZ in the solutions being 2.2 MDEA + 1.97 PZ, 4.22 MDEA + 2.01 PZ, and 7.83 MDEA + 2.07 PZ.

Table 1. Main Characteristics of the Collected Points for the System CO_2+MDEA+PZ+H_2O in Each Considered Source of Experimental Data Reported in the Literature—Part 1

	Liu et al.[38]	Kamps et al.[39]	Ali and Aroua[35]	Hosseini Jenab et al.[40]	Bottger et al.[42]	Vahidi et al.[41]
P_{CO2min} (kPa)	13.16	137.98	0.06	27.79	211.80	27.80
P_{CO2max} (kPa)	935.30	6358.59	95.78	3938.43	11841.24	3938.40
T_{min} [K]	303.15	353.14	313.15	313.15	313	313.15
T_{max} [K]	363.15	353.14	353.15	343.15	393.2	343.15
$MDEA_{min}$ [M]	1.35	1.43	1.8	2	1.58	2
$MDEA_{max}$ [M]	4.77	1.43	1.98	3	3.86	3
PZ_{min} [M]	0.17	1.43	0.01	0.36	1.02	0.36
PZ_{max} [M]	1.55	1.43	0.1	1.36	1.4	1.36
number of data	80	10	45	103	75	103

Table 2. Main Characteristics of the Collected Points for the System CO_2+MDEA+PZ+H_2O in Each Considered Source of Experimental Data Reported in the Literature—Part 2

	Derks et al.[34]	Speyer et al.[43]	Najibi and Maleki[44]	Dash and Bandyopadhyay[45]	Khan et al.[46]	Suleman et al.[47]
$P_{CO2\ min}$ (kPa)	0.25	0.11	26.3	0.09	200.00	98.58
$P_{CO2\ max}$ (kPa)	110.00	146.80	204.3	1426.82	4978.00	4086.22
T_{min} [K]	298	313.15	363.15	303	303.15	303.15
T_{max} [K]	323	393.15	423.15	333	333.15	343.15
$MDEA_{min}$ [M]	0.5	1.45	1.6	1.88	2.56	1
$MDEA_{max}$ [M]	4	4.13	3	4.15	2.56	2
PZ_{min} [M]	0.6	0.48	0.3	0.17	0.26	1
PZ_{max} [M]	1.5	2.25	0.7	0.69	0.26	2
number of data	84	149	71	196	21	42

- Derks et al.[8,34] reported experimental data related to the CO_2 solubilities and their corresponding partial pressures, pH, and conductivities, and some liquid speciation data obtained using NMR spectroscopy. The experiments were performed for temperatures ranging from 298 to 313 K and for CO_2 partial pressures between 0.25 and 110 kPa.
- Speyer et al.[43] complemented the experimental points for the high gas loading region collected by Bottger et al.[42] and focused on the measurements in the low gas loading region and partial pressures of CO_2 in between 0.1 and 150 kPa. The solubility was measured at three temperatures (313, 353, and 393 K) for CO_2 loadings ranging from 0.02 to 0.83, with a molality of MDEA and PZ in the aqueous mixture varied between 2 and 8 mol/kg_{water} and between 1 and 4 mol/kg_{water}.
- Najibi and Maleki[44] collected experimental data of the CO_2 solubility in aqueous solutions of MDEA and PZ for temperatures ranging from 363 to 423 K and pressures between 26.3 and 204.3 kPa, with an MDEA concentration from 1.6 to 3 M and a PZ concentration between 0.3 and 0.7 M.
- Dash and Bandyopadhyay[45] studied the solubility of carbon dioxide in PZ-activated aqueous solution of MDEA at temperatures from 303 to 333 K and at pressures between about 4 and 1435 kPa, considering MDEA mass fractions between 0.22 and 0.5 and PZ mass fractions between 0 and 0.08.
- Khan et al.[46] focused on the solubility of CO_2 in PZ-activated aqueous MDEA solution under high pressure, from 303.15 to 333.15 K and pressures from 200 to 5000 kPa, with a mass fraction of MDEA and PZ in the solution used for the absorption experiments equal to 0.3 and 0.03.
- Suleman et al.[47] studied the experimental loadings of carbon dioxide in the PZ+MDEA+H_2O solutions at pressures between 102.5 and 4110 kPa and for temperatures ranging from 303.15 to 343.15 K, with MDEA and PZ concentrations being 1 M (MDEA) + 1 M (PZ) and 2 M (MDEA) + 2 M (PZ).
- Xu[48] measured CO_2 solubility in 5 m MDEA/5 m PZ and 7 m MDEA/2 m PZ aqueous solutions between 383 and 433 K and CO_2 partial pressure ranging from 78 to 2054 kPa.
- Nguyen[10] investigated the amine volatilities and CO_2 solubilities in the same mixtures as Xu, but using a different apparatus. The experiments were conducted at atmospheric pressure and temperatures between 313.15 and 343.15 K.
- Bishnoi et al.[49] measured the carbon dioxide absorption in 0.6 M PZ/4 M MDEA solution in a wetted wall column (WWC) contactor for temperatures in between 295 and 343 K and CO_2 partial pressures from 0.015 to 61.1 kPa.
- Chen et al.[50] and Li[51] collected experimental data of the CO_2 solubility in aqueous solutions of 5 m MDEA/5 m PZ and 7 m MDEA/2 m PZ solutions for temperatures ranging from 283 to 373 K and CO_2 partial pressure between 0.046 and 28.21 kPa. The same WWC of Bishnoi has been employed for carrying out the experiments.
- Du[52] focused on the 2.5 m MDEA/2.5 m PZ solution at 313.15 K and CO_2 partial pressure between 0.183 and 5.91 kPa.
- Jalili et al.[53] measured CO_2 solubility and density of CO_2-loaded formulated aqueous solvents containing MDEA, PZ at temperatures of 303.15, 323.15, 343.15, and 363.15 K and CO_2 partial pressures of up to about 1000 kPa and CO_2 loadings below 0.9 mol CO_2 per total mole of amine. In a separate work, the CO_2 solubility of the same CO_2-saturated mixtures has also been measured at T = (313.15, 328.15, and 343.15) K and pressures of up to about 3000 kPa by using an isochoric saturation apparatus. A

Table 3. Main Characteristics of the Collected Points for the System CO_2+MDEA+PZ+H_2O in Each Considered Source of Experimental Data Reported in the Literature—Part 3

	Bishnoi and Rochelle[49]	Chen et al.[50]	Li[51]	Du[52]	Xu[48]	Nguyen[10]
$P_{CO2\ min}$ (kPa)	0.015	0.189	0.046	0.183	78	0
$P_{CO2\ max}$ (kPa)	61.1	28.21	8.26	5.91	2477	66.5
T_{min} [K]	295	313.15	283.15	313.15	373.15	313.15
T_{max} [K]	343	373.15	313.15	313.15	433.15	343.15
$MDEA_{min}$ [M]	4	2.55	2.55	1.69	2.41	2.59
$MDEA_{max}$ [M]	4	3.6	3.62	1.69	3.48	3.61
PZ_{min} [M]	0.6	1.01	1.03	1.69	0.95	1.01
PZ_{max} [M]	0.6	2.55	2.55	1.69	2.54	2.63
number of data	39	27	18	5	33	55

completely good consistency is observed between the two data sets obtained from the first and second experimental setups employed, the first one of which instantaneously measures and uses the density of CO_2-saturated solutions in the solubility calculations, and the second one that calculates the CO_2 solubilities using the density of the unloaded fresh solutions in the entire CO_2-loading regions.

Tables 1−4 show, for each considered source of experimental data reported in the literature, the minimum values and the maximum values of the partial pressure of CO_2, the temperature, the concentration of MDEA and of PZ, and the number of points for the system of CO_2+MDEA+PZ+H_2O.

Table 4. Main Characteristics of the Collected Points for the System CO_2+MDEA+PZ+H_2O in Each Considered Source of Experimental Data Reported in the Literature—Part 4

	Jalili et al.[53]	
$P_{CO2\ min}$ (kPa)	0	0
$P_{CO2\ max}$ (kPa)	989.2	2292.6
T_{min} [K]	303.15	313.15
T_{max} [K]	363.15	343.15
$MDEA_{min}$ [M]	1.93	0.614
$MDEA_{max}$ [M]	3.05	3.04
PZ_{min} [M]	0.35	0.36
PZ_{max} [M]	1.34	1.34
number of data	72	77

The experimental setup and the experimental procedure are detailed in Sections 3.1 and 3.2.

3.1. Experimental Setup. The solubilities of an acid gas, such as CO_2, in alkanolamine systems can be measured in a variety of apparatus that can be classified as static and dynamic, with or without analysis for vapor and liquid composition. In a static method, the system is closed and phase circulation is not provided, while mixing is guaranteed by agitation or rocking. After equilibrium has been reached, liquid and vapor samples can be withdrawn and analyzed; otherwise, mass balance and equations of state are exploited in order to compute partial pressure data. In a dynamic method, usually the vapor phase is circulated and equilibrium is attained in a shorter amount of time. Xu et al.[37] and Liu et al.[38] collected solubility data in an atmospheric pressure unit and in a high-pressure unit at the Research Institute of Chemical Technology, East China University of Science and Technology (Shanghai, People's Republic of China) following a static approach without sampling. The atmospheric-pressure apparatus is composed of a glass cell with an inside diameter equal to 70 mm and a height equal to 130 mm, stirred by a self-suction agitator. The aqueous solution inside the cell has a volume of about 200 cm^3. The high-pressure apparatus is a 500 mL stainless steel autoclave with a magnetic agitator. The laboratory at Universitat Kaiserslautern (Kaiserslautern, Germany) is provided with two different units for measuring the solubility of CO_2 into solvents, and both a static and a dynamic approach have been pursued according to the different authors.

Kamps et al.[39] and Bottger et al.[42] followed a special static method employing a 30 cm^3 thermostated high-pressure cell made of Hastelloy C4, provided with two sapphire windows. Two pressure transducers for pressures ranging from 4000−10,000 kPa are installed to determine the solubility pressure. Before and after each series of measurements, the transducers are calibrated with a high-precision pressure gauge. The maximum uncertainty in the pressure measurement is 0.1% of each transducer's maximum reading. Bottger et al.[42] further specify that the maximum uncertainty in the solubility pressure measurement comes from the intrinsic uncertainty of the pressure transducers (0.1% of the transducer's full scale), a further contribution of about 0.01 MPa from a small temperature drift inside the isolated (high-pressure) tubes filled with the solvent that connect the view cell with the pressure transducers, and the difference of the pressure transducer's readings before and after the last expansion step. The temperature is measured with an uncertainty lower than 0.1 K by two calibrated platinum resistance thermometers placed in the heating jacket of the cell. The temperature differences inside the thermostatting liquid in the annular jacket are smaller than the uncertainty of the temperature measurement because of the jacket insulation.[42] Dedicated density measurements exploiting a vibrating tube densimeter (VTD, model DMA 60/DMA 602 HAT, Anton Paar GmbH, Graz, Austria) with an uncertainty lower than about 0.001 g/cm^3 are exploited. The relative uncertainty of the mass of solvent and that of water in the view cell is about 0.14%. The relative uncertainty of the stoichiometric molality of CO_2 in the solvent is 1% at the lowest molality ($m_{CO2} \sim 2$ molal) and 0.3% at the highest molality ($m_{CO2} \sim 11$ molal). The solubility pressure is measured with two precise pressure transducers (WIKA GmbH, Klingenberg, Germany) with the full scale equal to 2.5 kPa and equal to 10,000 kPa, in connection with a mercury barometer (Lambrecht, Gottingen, Germany). All the pressure transducers are calibrated with a high-precision pressure balance (Desgranges & Huot, Aubervilliers, France) before and after each measurement series.

The unit employed by Speyer et al.[43] is based on headspace gas chromatography. The authors followed a dynamic approach with vapor sampling. A thermostated cell holder, a thermostated sample-valve holder containing a multiposition valve and the sampling system, two large 50 dm^3 buffer tanks, each one filled with high-purity N_2, and a gas chromatograph Agilent 6890, that is equipped with a capillary column (Alltech, type Heliflex ATQ, 30m, 0.32 mm I.D.), and a thermal conductivity detector, constitute the unit. In the experiments, eight sample cells, being stainless steel vials with a volume either equal to 11 cm^3 or equal to 30 cm^3, are partially filled to about 1/2 for the vial volume of 11 cm^3 or to about 3/4 for the vial volume of 30 cm^3 of the total volume with a liquid mixture of CO_2+MDEA+PZ+H_2O and mounted in the cell holder. The composition of the charged liquid mixture is known from its gravimetric preparation. The temperature is measured with a calibrated platinum resistance thermometer in the liquid bath that is used to control the temperature of the cell holder. The overall uncertainty of the temperature measurement is 0.1 K. During the equilibration, very small amounts of the volatile components evaporate into the vapor phase (headspace). The sample loop and each of the eight sample cells are connected by stainless steel capillaries with an inner diameter of 0.25 mm through a multiposition valve (Valco Instruments Co. Inc., type 2CSD16MWE-HC). Purging is done by exploiting the other eight positions of the multiposition valve. The multiposition valve and the sample valve are both operated pneumatically by an electronic controller. A high-precision pressure transducer (SchaferData-metrics, Langen, Germany, type 590A-1000T-2Q1-V1X-4D) is employed for the calibration.

The experimental unit considered in the work performed at the Department of Chemical Engineering, University of Malaya (Kuala Lumpur, Malaysia), is a stirred cell reactor where the amine solution and a flowing gas of CO_2 and N_2 of known composition are mixed together.[35] No additional details have been found.

The experiment at the Research Institute of Petroleum Industry, the National Iranian Oil Company, and Petroleum University of Technology (Tehran, Iran) is performed in a modified autoclave reactor, consisting of an electrically heated stainless steel cylindrical tank of one liter with a magnetically coupled stirrer on the top.[40] A static method without vapor and liquid sampling has been followed by the research groups. The unit is provided with valves for the liquid and the gas inlets and with a calibrated thermocouple inserted into the equilibrium cell, with an uncertainty of 0.1 K. The temperature is adjusted through a water bath, and a vacuum may be obtained with a vacuum pump. The pressure of the cylinder and gas container is measured by a calibrated pressure transmitter with an uncertainty of 0.70 kPa.[41]

A gas chromatograph (model 3800, Varian-Chrompack, Varian Inc., CA) equipped with a flame ionization detector (FID) and a 10 m × 0.5 mm DB-WAX capillary column analyzes the composition of the liquid. In addition, a high-pressure pycnometer had been made by the authors with 1/16 inch stainless steel tubing with high-pressure isolating valves for measuring the density.

The experimental setup and procedure employed by Derks et al.[8,34] at the University of Twente (Twente, The Netherlands) resemble those used by Kumar et al.[54] for another type of solvent. The authors considered two different setups for the experiments with diluted gas streams and for CO_2 partial pressures higher than 25 kPa. Both approaches are dynamic (involving circulation of the liquid phase), but continuous sampling of the vapor phase from the equilibrium cell is provided only for the experiments with diluted streams.

When dealing with diluted gas streams, the operation with respect to the liquid is always batch-wise, and with respect to the gas phase is continuous. A thermostated reactor of about 1.6 L, provided with a high-intensity gas-inducing impeller in the liquid phase and a propeller-type impeller in the gas phase, and with a digital pressure transducer and a thermocouple, is employed. During the continuous operation with respect to the gas phase, the inlet gas flows of both N_2 and CO_2 are controlled using mass flow controllers (Brooks Instr., type 5850). Prior to entering the reactor, the gas flows of N_2 and CO_2 are presaturated with an amine solution identical to the one in the reactor. After presaturation, the gas streams are mixed and fed to the bottom of the reactor using a sintered stainless steel sparger. The outlet gas flow of the reactor is continuously analyzed for determining the CO_2 content with an IR analyzer, type UNOR 610.

The setup for collecting the experimental data for CO_2 partial pressures higher than 25 kPa is a thermostated, vigorously stirred reactor of about 2 L, connected to a calibrated gas vessel. Both the reactor and the gas supply vessel are equipped with temperature and pressure indicators. The reactor is equipped with a vacuum pump to remove all of the inert gases from the setup and the dissolved gases from the amine solutions before starting the experiment.

To determine the pH and the conductivity, the reactor is connected to a calibrated gas vessel that is equipped with both a digital pressure transducer and a thermocouple. The presence of the gas vessel makes it possible to supply a given amount of pure CO_2 to the solution in the reactor. In addition, a sampling loop (total volume ca. 200 mL) is attached to the reactor for measuring the pH and the conductivity of the liquid during an experiment. In the sampling loop, a small liquid pump is installed and operated so that the average residence time inside the loop is lower than 60 s. All sampling loops are insulated to prevent heat losses; the returning liquid temperature is measured as a check. The actual measuring electrodes themselves are placed straight inside a small glass vessel within the loop. A Mettler DG 111-SC pH electrode, calibrated using standard buffer solutions with a known pH, measures the pH of the liquid. A Radiometer CDC 104 (nominal cell constant 1.0 cm^{-1}) type electrode connected to an analogous conductivity meter type CDM 2d is used to measure the conductivity of the solution.

Najibi and Maleki at the Petroleum University of Technology (Ahwaz, Iran) took advantage of a static approach without any sampling of the two phases at the equilibrium. The experimental setup of the Petroleum University of Technology (Ahwaz, Iran) consists of a stainless steel 316 cell with an inner volume equal to 250 cm^3, which can withstand pressures up to 5 MPa. The cell contents are stirred by a magnetic stirrer to facilitate reaching equilibrium. A bath of oil or water, depending on the required temperature, contains the cell, and the cell temperature is measured using a platinum resistance sensor (Pt100) inserted inside the cell. The pressure is measured using a Druck pressure transducer. The uncertainty for the temperature measurements is lower than 0.1 K, and for the pressure measurements, it is lower than 0.01 MPa. The solutions are prepared by the gravimetric method, employing a digital balance with an uncertainty of 0.0001 g.

A high-pressure stainless steel stirred equilibrium cell with a volume equal to 375×10^{-6} m^3, connected to a high-pressure stainless steel gas buffer vessel with a volume equal to 760×10^{-6} m^3, is employed at the Pandit Deendayal Petroleum University (Gujarat, India) and the Indian Institute of Technology

Kharagpur (Kharagpur, India). A static approach without sampling the vapor and liquid phases is performed. The liquid phase in the equilibrium cell is mixed by a magnetic stirrer. Both the cell and the gas buffer are equipped with platinum temperature sensors (Pt 100, JULABO, FRG) and PDCR 4010 (Druck, UK) pressure transducers in the pressure ranges 0−140, 0−700, 0−1400, and 0−2000 kPa with an accuracy equal to 0.75% of the full-scale, with digital pressure indicators (DPI 280, Druck, UK). The temperatures of the equilibrium cell and of the buffer vessel are controlled within 0.1 K of the desired temperature by a circulator temperature controller (F 32, JULABO, FRG). Precision pressure controllers (5866 series, Brooks Instruments, USA) with pressure ranges of 0−140, 100−700, and 700−1400 kPa, within an accuracy of 1% of the full-scale control the pressure of the cell. A vacuum pump (Indvac Model IV 50, India) is used to degas the solvent and to evacuate the equilibrium cell and the buffer vessel. The solvent mixture is prepared using a digital balance (Acculab ALC 210.4, accuracy of 0.0001 g).

The uncertainty of the loading is determined from the uncertainties in the temperature, pressure, volume, and molarity, being equal to 0.1 K, 0.75, 0.5, and 0.2%. The estimated uncertainty in the measured solubility with respect to the CO_2 loading is equal to 3 and 2% with respect to the partial pressure of CO_2.

The unit at the Department of Chemical Engineering, Universiti Teknologi PETRONAS (Perak, Malaysia), is a high-pressure vapor−liquid equilibrium apparatus composed of a high-pressure dual cell, described by Suleman et al.[47] A static approach without sampling is the chosen method for carrying out the experiments. The feed cell has a fixed volume of 620.0 mL, and the solubility cell has a fixed volume of 239.0 mL. The tubes connected to the feed cell have a total volume of 16.4 mL, and the ones connected to the solubility cell have a total volume of 15.7 mL. The combined volumes of the feed and solubility cell systems are 636.4 and 254.7 mL. Both of the cells are detachable and fully serviceable. Separate thermostated heaters are used to independently control the temperatures of the feed cell and of the solubility one. The LABview data acquisition software (National Instruments, Kuala Lumpur, Malaysia) is used to digitize and store the parametric measurements.

Khan et al.,[46] still at the Department of Chemical Engineering, Universiti Teknologi PETRONAS, employed a static approach but detailed that a SOLTEQ BP-22 high-pressure solubility cell is used, with a digital pressure indicator (Druck DPI 150) with an accuracy of 1.0 kPa for a pressure range of 0−10,000 kPa for measuring the pressure inside the vessels. The thermostatic water baths are employed to keep the temperature of pressure vessels within a 0.1 °C accuracy range, and the internal temperature of pressure vessels is taken with a digital thermometer (YOKOGAWA 7653) with a precision of 0.01 °C. All the chemicals are weighed on a Sartorius BSA224S-CW mass balance (Sartorius Stedim Malaysia, Kuala Lumpur, Malaysia (precision = 0.1 mg).[47]

Three experimental setups have been used to measure the CO_2 solubility in amine-based solutions at the University of Texas at Austin (Austin, Texas, USA).

The WWC has been extensively employed to evaluate the mass transfer coefficient and solubility of CO_2 in several amine systems.[49−52,55−59] Within the unit, an aqueous amine solution counter currently contacts a N_2/CO_2 gas stream over the surface of a stainless steel rod with a known geometry. The liquid solvent enters the WWC through the bottom of the metal rod, overflows at the top, forms a thin film on the outer surface of the tube, and exits from the bottom. The gas mixture (CO_2 and N_2) is introduced at the bottom of the reaction annulus through a single inlet port, and it flows upward, allowing absorption of the absorbing gas in the liquid film. The stainless steel tube has an exposed height of 9.1 cm and an outer diameter of 1.26 cm, and it is enclosed by a glass tube, resulting in a hydraulic diameter of 0.44 cm and a cross-sectional area for the gas flow of 1.3 cm^2. This contacting chamber is enclosed within a larger glass tube annulus filled with heating oil pumped from an external heat exchanger to control the temperature of the chamber. After contacting the gas phase, the solvent is pumped back to the liquid reservoir, forming a closed loop. The pump consists of a Micropump AC Drive (PN:83433, MOD:DP415A) and a Micropump head (PN:L27391, MOD:GA-T23.PKS.E, SER:903671001). A large solvent volume is required to provide a nearly constant loading during the experiments. Unlike the liquid solution, the gas is not recycled through the system. CO_2 and N_2 are mixed through mass flow controllers (Brooks Instr., type 5850E), and the resulting gas blend is saturated with water at the operating temperature upstream of the WWC using a jacketed bubbling saturator. A second bath is used to set the temperature at the saturator and employs water as the heating medium. The water-saturated gas then enters the WWC from the bottom, where the counter currently contacts the liquid, and mass transfer occurs. The gas exits from the top of the WWC, and it is sent to a water knockout (an Erlenmeyer flask placed in a beaker filled with ice), followed by a drying column containing Drierite anhydrous calcium sulfate, where the water vapor is removed from the gas. The dry gas is sent to the CO_2 analyzer for measuring the carbon dioxide concentration. A bypass line can be used to direct the saturated gas stream straight to the analyzer for the concentration measurement, bypassing the contacting chamber. The IR values obtained in bypass mode provide CO_2 concentration at the WWC inlet and are used as a calibration curve for the instrument since CO_2 concentrations are known via the mass flow controllers. The pressure in the WWC is adjusted using a valve on the gas outlet, and it is measured with a standard pressure gauge. By measuring the inlet and outlet concentration of CO_2 in the gas phase and applying a material balance over the gas phase in the WWC, the CO_2 absorption flux and the CO_2 equilibrium partial pressure can be experimentally determined.

A 500 mL stainless steel autoclave (ZipperClave, by Autoclave Engineers) and a static method without vapor sampling are the approaches followed by Xu.[48] The autoclave is equipped with a magnetic hollow shaft agitator with two impellers (~4.60 inch in length, adjustable, MAG075, MagneDrive II Series, by Autoclave Engineers) and a compressed air motor (2AM-NCC-16, by Gast), providing 100−2500 rpm as the agitation rate. The liquid and vapor phases are circulated by the agitator. The vapor enters from the top holes of the shaft and is spread from the bottom holes, which are under the bottom impeller (1 1/4 inch diameter). The mixing is improved by the top impeller, which is at about the interface of vapor and liquid, and by two baffle bars, which are placed in the autoclave during some tests. The Fuji Electric PXZ-4 PID temperature controller, with connection to a K-type thermocouple (±1.5 °C accuracy) placed inside the thermal well of the autoclave, controls the temperature. A 22 pressure transducer (Druck PTX 611, 0−30 bar absolute, ±2.4 kPa precision) is connected to a signal converter and a NI USB-6009 data logger to record data. The pressure indicator is calibrated by a dead weight pressure tester (S/N 19189/278, by Budenberg Volumetrics, INC.).

CO_2 solubility, together with amine volatility, has been measured in a 1 L stirred glass reactor coupled with a hot gas FTIR analyzer (Fourier transform infrared spectroscopy, Temet Gasmet Dx-4000) by Nguyen.[10] The FTIR unit has a 10 m gas cell path length with varying detection limits between 0.1 ppm and 60% vol+, depending on the absorption of the gas component analyzed within the range of 900−4200 cm^{-1} wavenumber. A dynamic approach with vapor sampling was selected to obtain the VLE data. A circulating heated dimethylsilicone oil in the outer reactor jacket, to and from the oil bath, is used to control the temperature of the reactor within ±0.1 °C. Thick insulation material provides insulation to the reactor. The temperature inside the reactor was measured with a digital thermometer to within ±0.1 °C. The reactor was maintained at ambient pressure by venting through a water seal. The room pressure was measured with a barometer to ±0.1 mm Hg.

As previously pointed out, Jalili et al.[53] employed two different experimental setups to perform the solubility measurements. Neither approach involved sampling of the liquid or vapor phases to determine the equilibrium composition. However, the first setup is dynamic in nature, as it includes liquid circulation within the measurement system. The first system consists of a main equilibrium cell (EC), a gas injection system (GIS), and a VTD. The EC is equipped with a side glass window (SW) to monitor solution foaming and to check the liquid level during the experiments. EC is double-wall-jacketed to enable water circulation from the water recirculation bath (WCB) to monitor the solution temperature in the cell. The EC temperature is controlled by a Lutron model TM-917 digital thermometer with a 0.01 K resolution using a PT-100 sensor. A Keller model PA-33X pressure transmitter sensor (P2) in the range of (0−2000) kPa with uncertainty within ±0.01% of the full scale was used to measure the pressure of the system. The GIS consists of a gas container (GC) with a constant known volume (VGC = 330 cm^3) equipped with a Keller model PA-33X pressure transmitter sensor (P1) in the (0−4000) kPa range with uncertainty within ±0.01% of the full scale. A high-pressure centrifuge pump (CP) is then used to circulate the gas-saturated liquid solution through the closed loop consisting of the VTD and the EC. The density of the solution is calculated using the equilibrium temperature and pressure of the EC and the oscillation period measured by VTD. The vibrating-tube densimeter (VTD) used is an Anton Paar model DMA HPM, equipped with a liquid jacket whose temperature is thermostated by water circulation from an external recirculating bath. The density-measuring cell comprises a U-shaped Hastelloy C-276 tube that is electronically excited to oscillate at its characteristic frequency, which is a function of the sample density. DMA HPM produces and measures the oscillation period as well as measuring the temperature. The instrument is connected to an interface module that communicates with an mPDS 2000 V3 evaluation unit (EU). The EU processes the raw measurement data (oscillation period, temperature, and pressure) and converts them into sample density values, according to the appropriate calibration equations. Distilled deionized water and nitrogen were used to calibrate the VTD density-measuring device in the (298.15−363.15) K temperature range, from atmospheric pressure up to about 7.0 MPa. The second setup does not consist of the centrifuge pump and densimeter, and the equilibrium cell is a high-pressure, double-walled (VEC = 130 cm^3) which exploits a magnetically driven stirring bar to facilitate equilibration. As in the other setup, the equilibrium cell is connected to the gas container (GC), and it is equipped with a graduated side glass. The temperature of the double-wall equilibrium cell, which is connected to a WCB (PMT Tamson model T 2500) with a temperature stability within ±0.05 K, is measured with a TI with a 0.01 K resolution using a Pt-100 sensor inserted into the cell. The CO_2 gas container (GC) is a (330 ± 3) cm^3 high-pressure SS-316 cylinder at ambient laboratory temperature. During the injection of CO_2 into the equilibrium cell (EC), the temperature of GC is measured by a Lutron model TM-917 digital thermometer. The temperature sensors were calibrated using a Testomodel 735 digital calibrator, equipped with a Pt1000 sensor. The type B uncertainty of 0.05 K was obtained for the Lutron thermometers. The equilibrium cell and the gas container pressures are measured using a KELLER model PA-33X pressure transmitter sensor in the range of 0−2 and 0−3 MPa, respectively, which are uncertain to within 0.05% of their full scale, as specified by the manufacturer. The calibration of the pressure sensors was carried out against a pneumatic dead weight gauge (DH. Budenberg model 550). The volumes of different compartments of the apparatus were measured using a calibrated bulb of known volume.

3.2. Experimental Procedure. The procedure experimentally employed in each reference is analyzed in this section.

3.2.1. Xu et al. The low-pressure test is carried out with a mixture of N_2 and CO_2 from cylinders with a purity of 99% that passes through a high-pressure regulator in order to keep the flow rate stable, then it is fed to a molecular sieve adsorber and metered by a soap film meter.[37] The total flow rate of the mixture gases is about 0.018 m^3/h during all the experiments. The mixture passes through a gas-mixture tube and is saturated at room temperature prior to being fed to the experimental cell. The mixture of gases is bubbled by a self-suction-type agitator. The partial pressure of CO_2 is regulated by adjusting the CO_2/N_2 ratio. The gas stream leaving the unit is cooled with water at ambient temperature, and the condensed water is recycled to the equilibrium cell. The outlet gas temperature is generally 0.2 °C above ambient. Moisture loss with the carrier gas is considered negligible in all experiments. To ensure attainment of equilibrium, the gas is bubbled through the liquid for at least 4 h prior to sampling the liquid phases. The concentration of CO_2 in the liquid phase is determined by acidifying the samples with an excess of sulfuric acid and measuring the evolved CO_2 volume using a graduated buret. As for the high-pressure tests, the solvent is charged into the autoclave, and then CO_2 gas with a purity of 99.9% is bubbled into the liquid solution and kept at a constant pressure. To ensure attainment of equilibrium, the system is kept for at least 6 h before sampling the liquid phase. In the vapor phase, the CO_2 is saturated with water vapor. The CO_2 content in the liquid phase is determined by adding excess $BaCl_2$ to precipitate the carbonate as $BaCO_3$. The precipitate is then washed and titrated with a standard 0.1 N HCl solution using a methyl orangexylene cyanol indicator, with the end point corresponding to a gray-green end point.

The experimental temperature is controlled to within 0.1 °C for both the low-pressure tests and the high-pressure tests.

3.2.2. Liu et al. The experimental procedure considered by Liu et al.[38] is similar to the one reported in Xu et al.;[37] the exception is the liquid CO_2 loading, which is measured by a volumetric analysis. The CO_2 partial pressure is calculated by subtracting the partial pressure of water from the total pressure of the system. Xu et al.[37] measured the equilibrium partial vapor pressure of water in aqueous 10−70 wt % MDEA solutions and concluded that Raoult's law can be employed to describe the equilibrium water partial pressure in an aqueous MDEA solution with an average deviation below 2.0%. Then they assumed that Raoult's law is also applicable to the MDEA+PZ+H_2O system. Xu et al. also studied the equilibrium partial pressures of MDEA and PZ in the MDEA+PZ+H_2O system, which were found to be extremely low. Therefore, compared with the CO_2 partial pressure, their partial vapor pressures are neglected with an error being lower than 1%.

3.2.3. Kamps et al. The aqueous solution is prepared in a storage tank by mixing a known amount of amine in pure water.[39] The molality of the amine in the aqueous solution is determined gravimetrically with a relative uncertainty smaller than 0.1%. The mass of the charged gas up to about 5 g is determined by weighing, with an uncertainty of 0.008 g. The volume of the aqueous solvent required to dissolve the gas is determined in each experiment. The mass of the solvent is calculated with a maximum relative uncertainty of 0.7% from its volume and a known density value, determined in different measurements with a VTD.

The unit is partially filled with a known amount of the aqueous solvent, and a known amount of gas is fed to the cell from a storage tank. Then, more solvent is added to the cell step by step by a calibrated high-pressure displacer until the gas is completely dissolved in the liquid phase. The amount of solvent charged to the cell is only slightly above the minimum amount needed to dissolve the gas completely. After equilibrium is attained, a small amount of the liquid mixture is withdrawn stepwise from the cell until the first very small stable bubbles appear. That pressure is considered to be the equilibrium pressure to dissolve the charged amount of the gas in the charged amount of solvent at the fixed temperature.

3.2.4. Ali and Aroua. The experiment, with MDEA (98.5% pure) and PZ (99.9% pure), is considered ended once equilibrium is achieved, as indicated by the constant pH value of the loaded solution.[35] CO_2 loading is measured using a methodology not detailed in the work.

To ensure the reliability of the experimental data, the total amine concentration is analyzed before and at the end of each run. The variation between the readings is less than 3%, though slightly higher variations of about 5% are obtained for experiments at low CO_2 partial pressure and high temperature, for which more than 20 h are needed to reach equilibrium, with the evaporation of water occurring. They added glycerin to the water bath and installed a condenser at the gas vent to reduce this issue. They mention that the measured variations also include the errors in the analysis that they estimated to be about 2%. On this basis, Ali and Aroua[35] concluded that, without introducing any significant errors, the total amine concentration in the solution remained constant throughout each experimental run.

3.2.5. Jenab et al. Absolute pressures below 13.3 Pa are generated in the unit.[40] Then, the cell is charged with 200 mL of liquid. The solution is prepared with deionized water, reagent-grade MDEA with a purity of 98.5%, and PZ with a purity higher than 99% and used without further purification. The temperature is then adjusted to the desired value through the external thermal bath. At a given temperature, with no other components added to the closed system, the liquid exists under its own vapor pressure. For determining the compositions at the equilibrium, Jenab et al.[40] considered the procedure by Park and Sandall.[60] In detail, a known quantity of CO_2 is introduced into the reactor from the gas container of a known volume. To determine this amount, the compressibility factor is calculated with the Peng−Robinson[61] Equation of State (several models were considered by the authors, and all provided analogous results with a maximum error of 1.2%). The calculated Z values for the range of pressure and temperature conditions of interest were compared with the values of density,[62] with an error lower than 0.5%. After transferring the CO_2 to the equilibrium cell, the stirrer is switched on, and equilibrium is attained (the authors report a time of about 30 min). Then, the equilibrium partial pressure of CO_2 is calculated as the difference between the total pressure and the vapor pressure of the solvent at the considered temperature. The number of moles of CO_2 in the gas phase is determined from the CO_2 partial pressure, the compressibility factor, and the gas-phase volume in the autoclave, corrected for the liquid volume change resulting from CO_2 dissolution. The pycnometer volume is measured at several temperatures and pressures, and gravimetric techniques are used to measure the density of loaded samples under the high-pressure conditions of the experiments. The moles of CO_2 in the liquid phase are then determined by subtracting the total moles of CO_2 in the gas phase at equilibrium from the total moles of CO_2 fed to the unit, and then the loading of the solvent at equilibrium can be defined.

The uncertainty of the moles of CO_2 in the gas phase is a function of the uncertainty in measuring the exact volume of the equilibrium cell and the density of the liquid samples. The errors in measurement are estimated by the authors, and then the uncertainties in the moles of dissolved CO_2 are estimated using a standard technique. Experiments were repeated at least three times, and accuracies better than 0.5% were obtained by the authors in all the volume and density measurement experiments.

3.2.6. Bottger et al. The procedure consists of measuring the pressure required to dissolve a precisely known amount of gas in a known amount of solvent that fills a high-pressure view cell.[42] The solvent mixtures are prepared gravimetrically. The experimental uncertainty of the stoichiometric molalities is less than 0.002 molal for MDEA and for PZ. The amount of mass of the solvent filled into the cell is calculated from the volume displacement in a calibrated spindle press (from which the solvent is charged into the cell) and the solvent density. The evacuated cell is charged with the solvent and the gas so that a homogeneous liquid phase exists at a pressure that is slightly above the solubility pressure. Then, very small amounts (volume expansion of about 0.012 cm^3) of the liquid mixture are withdrawn step by step until the first (very small) stable gas bubbles appear. The pressure at which degassing begins is defined as the solubility pressure of the mixture and is calculated as the arithmetic average of the pressures measured before and after the final withdrawal step. The mass of carbon dioxide in the view cell, ranging between 1.5 and 7 g, is determined gravimetrically by weighing the condenser (from which the cell is charged) before and after the charging process using a high-precision balance. The gravimetric uncertainties are about 0.01 g.

3.2.7. Vahidi et al. The experimental procedure is the same as described in Jenab et al.[40,41] Because of the low vapor pressure of pure MDEA and PZ in the temperature range considered, the authors neglected the partial pressure contributions of MDEA and PZ in the vapor phase, as done by Xu et al.[63] for the MDEA aqueous solution.

3.2.8. Derks et al. A known amount of PZ (with a purity of 99%) and MDEA (with a purity of 99%) are mixed with water and transferred to the unit, then the solution is degassed by applying a vacuum for a short while, and it stabilizes at the desired temperature, after which the vapor pressure is recorded.[34] Simultaneously, the gas supply vessel is filled with pure CO_2, and the initial pressure in this vessel is noted. The stirrer in the reactor is switched on, and a desired amount of CO_2 is fed from the gas supply vessel to the equilibrium cell. Then, the gas supply vessel is closed and time is waited to reach equilibrium, which is achieved in about 30 min and is considered to occur when the temperature, the pressure, the pH, and the conductivity measured in the sampling loop remain constant.

The total amount of CO_2 fed to the reactor is calculated by the initial and end pressure in the gas supply vessel, with the use of the ideal gas law, which is considered because the maximum pressure in the gas supply vessel never exceeds 4 bar in the tests by Derks.[8] The corresponding CO_2 loading of the solution is determined considering the difference between the initial pressure and the final pressure in the gas vessel.

For determining the corresponding partial pressure the method depends on whether the setup is operated in a batchwise or in continuous mode of operation during the experiment.[8,34]

When the equilibrium partial pressure of CO_2 is expected to be lower than 10 kPa, the setup is operated in continuous mode with respect to the gas phase. A gas flow consisting of N_2 and CO_2 is presaturated with the solvent and sent to the cell. The CO_2 concentration in the outgoing gas stream is measured by using an IR analyzer. The composition of the inlet gas stream is adjustable and controlled by two calibrated mass flow controllers. Once equilibrium is approached, a small sweep stream of pure N_2 gas is initially passed through the cell, and the CO_2 content of the outgoing gas stream is measured. The sweep stream is sufficiently small, and hence, the gas phase residence time is sufficiently large to ensure that the outgoing gas concentration is close to equilibrium. The mass flow controller regulating the CO_2 gas flow is then adjusted to this value so that the inlet gas composition matches the measured outlet composition. This procedure of tuning the CO_2 mass flow controller and the inlet composition to match the detected CO_2 concentration in the outlet is repeated until the IR analyzer signal becomes stable. At this point, usually attained within about 20−30 min, the inlet and outlet gas compositions coincide, and on this value the equilibrium composition of the gas can be determined.

When the equilibrium partial pressure of CO_2 is higher than 10 kPa, the CO_2 partial pressure could be calculated from the final pressure of the equilibrium cell considering the vapor pressure of the lean solution and assuming that the latter is not influenced by the CO_2 loading.

3.2.9. Speyer et al. CO_2 (4.5, volume fraction higher than 0.99995), MDEA with a mass fraction higher than 0.985 or higher than 0.99 depending on the supplier, and anhydrous PZ with a mass fraction higher than 0.99 are employed.[43] About 1400 mL of an aqueous solution of MDEA and PZ is gravimetrically prepared in an evacuated storage tank by dissolving known amounts of both amines in water (previously deionized, distilled, and degassed), then about 250 mL of this solution is transferred to a smaller storage tank previously evacuated with a volume of about 300 mL. Known amounts of carbon dioxide are added. The storage tank is weighed before and after the addition of CO_2 to determine the mass of dissolved CO_2. The storage tank is shaken for about 5 h and stored for at least another 24 h. After the equilibration, the cell is at first pressurized with nitrogen coming from a buffer tank to a constant pressure for 2 min. The sample loop is then filled from the vapor phase by connecting the vapor phase of the cell to another buffer tank, maintained at constant pressure. The sample is transferred to the gas chromatograph, and purging of the sampling system is done with nitrogen. The vials of the headspace apparatus are then filled with the liquid mixture and mounted in the cell holder, where they are thermostated to the experimental temperature for about 12 h. The temperature of the valve holder is kept at 15−20 K above the temperature of the cell holder. The line to the gas chromatograph is also kept at a higher temperature to prevent condensation in the sampling system.

The primary data collected in the headspace chromatographic measurements are the peak areas of CO_2, proportional to the mass of the gas in the sample loop, which is proportional to the partial pressure of the gas in the cell. Calibration measurements with pure carbon dioxide and a high-precision pressure transducer (SchaferDatametrics, Langen, Germany, type 590A-1000T-2Q1-V1X-4D) are performed to get the relationship between the peak area and the partial pressure in the cell. During calibration, the pressure ranged from 7 to 70 kPa, where the peak area is proportional to the partial pressure. The maximum systematic uncertainty in the pressure measurement ranges from about 0.05 kPa at a pressure of about 10 kPa to about 0.15 kPa at a pressure of about 70 kPa. The maximum relative deviation between the measured pressures and the calibration line is equal to 2%.

The stoichiometric molalities of the solutes are corrected in order to consider the transfer of CO_2 and water to the vapor phase, both in the second storage tank and in the vials. The saturation pressures of MDEA and PZ are low and are assumed to be negligible in the considered temperature range. The vapor phase volumes in all the containers are estimated using the densities of the liquids. As all the vapor phase volumes are small and the partial pressures of carbon dioxide and water, either calculated from a model or known from the experiments, are also small, the corrections to the stoichiometric molality of all solutes are small (between 0.05 and 1.5% for CO_2 and negligible for MDEA and PZ). The uncertainty in the stoichiometric molalities of MDEA and PZ from gravimetric preparation is lower than 0.04%. The total uncertainty in the amine molalities in the liquid phase in a vial is estimated to be less than 0.1%. The relative uncertainty of the stoichiometric molality of carbon dioxide in the liquid phase ranges from about 0.2% up to about 1%.

3.2.10. Najibi and Maleki. The authors considered the method by Park and Sandall[60] for determining the CO_2 loading, similarly to Jenab et al.[40] and to Vahidi et al.[41] The main difference, due to the different size of the cell considered by Najibi and Maleki,[44] is related to the amount of solvent fed to the unit, equal to 20 mL.

3.2.11. Dash and Bandyopadhyay. Carbon dioxide (purity higher than 99.9%), MDEA (purity higher than 95%), and PZ (purity higher than 99%) are used without further purification.[45] Double-distilled water degassed by prolonged boiling and cooled to ambient temperature under airtight conditions is employed for the mixture with MDEA and PZ. The equilibrium cell is filled with a known volume (25 mL) of the mixed solvent, and the solution is degassed (i.e., the liquid is only under its vapor pressure). Once the temperature is uniform, the pressures of the cell and of the buffer vessel are recorded. The pressure of the equilibrium cell is then set to the set value, with the pressure

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controller taken in line. The equilibrium is considered to be reached when the pressure of the equilibrium cell and the buffer vessel are constant for at least 1 h at constant temperature. The difference between the initial and the final pressures in the buffer and the equilibrium CO_2 partial pressure, estimated as the difference of the pressure of the buffer vessel and the one of the cell, is considered to calculate the CO_2 loading at the equilibrium. The Peng–Robinson equation of state is used for calculating the compressibility factor of CO_2 at the corresponding temperatures and pressures. The CO_2 loading is calculated as the ratio of the moles of CO_2 in the liquid phase to the moles of amine in the solvent.

3.2.12. Khan et al. MDEA (98 mol % pure) and PZ (99% pure) are used as received from the supplier without any further purification.[46] The carbon dioxide purity is higher than 99.99%, and the nitrogen purity is higher than 99.99%. The Millipore quality water is used. All of the samples are freshly prepared and retained for 24 h to ensure complete miscibility. The equilibrium cells are cleaned with acetone and water to remove any residues from the previous experiment. Nitrogen is then purged through both cells to prevent any contamination, and then CO_2 is fed to the mixing vessel. Vacuum is applied to the equilibrium cells; 5 mL of the solvent is introduced in one equilibrium cell and 7 mL into the other one using a metering pump. The temperature of the cell is adjusted to the required value, and the pressure is recorded to determine the vapor pressure of the solvent. The CO_2 gas is then transferred from the mixing vessel to the equilibrium cells while stirring is maintained. After almost 3–4 h, when no further pressure change in the equilibrium cell is observed, the system is considered to have reached thermodynamic equilibrium.

The pressure of CO_2 at equilibrium is calculated as the difference between the total pressure and the vapor pressure of the solvent. The moles of CO_2 transferred from the mixing vessel to the equilibrium cell are calculated using the pressure drop, the volume of the mixing vessel, and the temperature, with the compressibility factors determined employing the Peng–Robinson[61] equation of state. The moles of CO_2 remaining in the gas phase are calculated by the equilibrium pressure, the temperature, and the overhead gas volume. Then, the effective number of moles of CO_2 absorbed into the solvent can be calculated considering the difference of the moles transferred to the equilibrium cell and the moles remained in the gas phase, and the loading can be estimated by dividing the moles of CO_2 absorbed by the moles of amines.

3.2.13. Suleman et al. CO_2 is filled in the feed cell, up to 5000 kPa, and 2 h at 303.15 K are waited.[47] Then, 100 mL of freshly prepared and degassed amine solution (with purity of MDEA higher than 99% and of PZ higher than 99.5%) is filled in the solubility cell and flushed with nitrogen gas. The solubility cell is heated to the desired temperature, and CO_2 is slowly transferred. The moles of CO_2 transferred to the solubility cell are calculated with the Span and Wagner equation of state on the basis of the readings of the values of pressure and temperature in the feed cell before and after transferring CO_2. The pressure of carbon dioxide in the solubility cell decreases with time as the gas is dissolved in the aqueous amine blend; then, after waiting that the pressure in the solubility cell is stable for at least 1 h, the values of pressure and temperature are read.

The partial pressure of CO_2 at equilibrium is calculated as the difference of the total pressure and the sum of the partial pressures of nitrogen, water, and amine in the solubility cell at the equilibrium conditions, determined using a method based upon Dalton's law of partial pressure. The CO_2 loadings are determined as the ratio of the CO_2 absorbed to the amines.

3.2.14. Bishnoi and Rochelle, Chen et al., Li, and Du. The gravimetrically prepared solution is loaded into the system, and the total pressure and temperature of the experiment are set.[49−52] The inlet gaseous composition is fixed via the mass flow controllers, and the gas stream is routed to the IR analyzer through the bypass line. Once the CO_2 analyzer signal reaches a steady state, the reading is recorded (bypass mode value), and the simulated gas is redirected through the reaction chamber. When the CO_2 analyzer reading comes to a new steady state, the value is recorded (operating mode value), and the gas is again redirected through the bypass. While on bypass mode, gas concentrations are adjusted to test another CO_2 partial pressure. At each experimental condition, 12 CO_2 readings are collected: six CO_2 partial pressures operating in bypass mode and six in operation mode. The values obtained in bypass mode are used to build a calibration curve for the IR instrument, since CO_2 concentrations are known via the mass flow controllers. The experimental readings (operation mode) can then be fitted to the calibration curve. The bypass mode readings correspond to the inlet partial pressures, while the operation mode readings represent the outlet partial pressures. Three of the inlet partial pressures are greater than the equilibrium CO_2 partial pressure of the solution, leading to absorption of CO_2 and positive flux, while the other three correspond to desorption. The six partial pressures are not tested in increasing or decreasing order. A rotating absorption/desorption experimental design is implemented; this, together with the large solvent inventory, should guarantee a nearly constant loading during the six runs. The CO_2 flux for each of the six runs is calculated considering the inlet and outlet partial pressures. The obtained CO_2 fluxes can be plotted against the driving force. Since the gaseous CO_2 profile exhibits a somewhat curved or asymptotic shape along the WWC (assuming a plug flow for the gas phase), while the CO_2 concentration in the liquid phase, P_{CO2}*, remains essentially unchanged, the logarithmic mean driving force is expected to provide a more accurate weighted average of the driving forces present in the reaction chamber. This driving force can be calculated according to eq 2:

$$\left(P_{CO_2}{}^{b} - P_{CO_2}{}^{*}\right)_{LM} = \frac{\left(P_{CO_2}{}^{IN} - P_{CO_2}{}^{*}\right) - \left(P_{CO_2}{}^{OUT} - P_{CO_2}{}^{*}\right)}{\ln\left(\frac{P_{CO_2}{}^{IN} - P_{CO_2}{}^{*}}{P_{CO_2}{}^{OUT} - P_{CO_2}{}^{*}}\right)} \qquad (2)$$

The equilibrium partial pressure of the solution, P_{CO2}* in eq 2, is unknown, but the constraint of having 0 flux when the driving force is 0 has to be fulfilled. Therefore, the value for P_{CO2}* can be adjusted until the CO_2 flux-driving force relationship passes through the origin.

3.2.15. Xu. A 300–330 mL portion of CO_2-loaded aqueous amine is prepared and introduced into the equilibrium cell.[48] N_2 is used to purge air from the cell, which is then sealed. The initial pressure of N_2 and temperature are recorded. Then the cell is heated, and the recording of both temperatures and pressures begins once the temperature reaches 100 °C. After holding at a temperature for at least 30 min or until the pressure remains

Table 5. Main Characteristics of the Experimental Procedure for Each Source

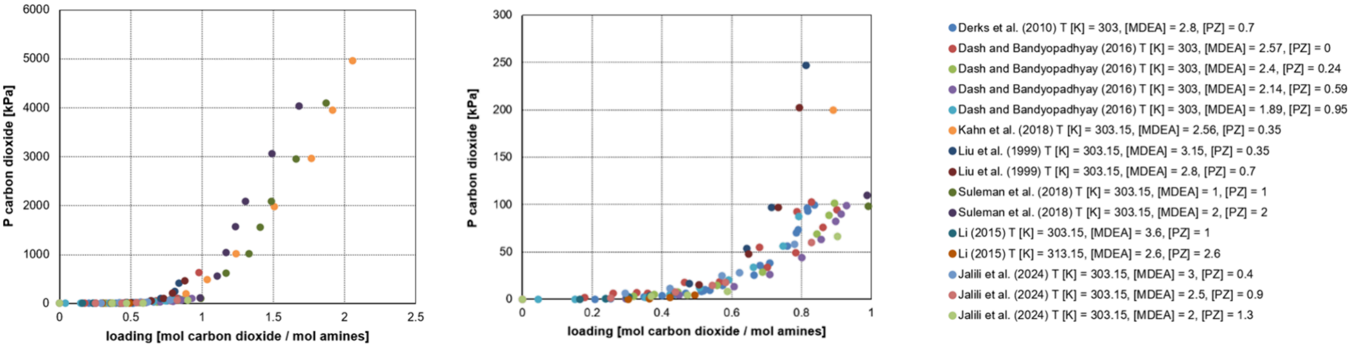
source	preadsorption	saturation	time before considering equilibrium	estimation of the loading
Xu et al.,[37] low pressure	yes	yes, at room temperature	4 h	addition of sulfuric acid
Xu et al., [37] high pressure		yes	6 h	addition of $BaCl_2$
Liu et al.[38]	yes	yes		volumetric analysis
Bishnoi and Rochelle[49]		yes		TIC analysis of a liquid sample of the solvent charged into the WWC
Kamps et al.[39]				based on a known amount of gas and of solvent fed to the cell
Ali and Aroua[35]			20 h	
Jenab et al.[40]			30 min	procedure by Park and Sandall
Bottger et al.[42]				based on a known amount of gas and of solvent fed to the cell
Vahidi et al.[41]			30 min	procedure by Park and Sandall
Derks et al.[34]		yes	30 min	volumetric analysis with the ideal gas law, with P_{CO2} determined in continuous mode or in batch-mode
Speyer et al.[43]				head space chromatography
Chen et al.[50]		yes		TIC analysis of a liquid sample of the solvent charged into the WWC
Xu[48]				TIC analysis + correction by volumetric analysis with the ideal gas law
Najibi and Maleki[44]				procedure by Park and Sandall
Nguyen[10]				head space FTIR analysis
Li[51]		yes		TIC analysis of a liquid sample of the solvent charged into the WWC
Du[52]		yes		TIC analysis of a liquid sample of the solvent charged into the WWC
Dash and Bandyopadhyay[45]				volumetric analysis, with the Peng–Robinson EoS
Khan et al.[46]			3–4 h	volumetric analysis, with the Peng–Robinson EoS
Suleman et al.[47]			1 h	volumetric analysis, with the Span and Wagner EoS
Jalili et al.[53]			2–4 h	procedure by Park and Sandall + online density measurement
			2–4 h	procedure by Park and Sandall

constant for 10 min, the system is considered to have reached the equilibrium. The solution is then heated to about 160 °C and then cooled down to 100 °C. Data are collected during both heating and cooling stages, typically at 10 °C intervals. After each run, the system is left to cool overnight. Liquid samples were collected before and after each experiment at room temperature and analyzed for total inorganic carbon (CO_2) and total alkalinity (amine). The measured total pressure represents the combined pressure of the amine-H_2O-CO_2 system and N_2. Thus, the total pressure, Pt, of amine-H_2O-CO_2 is the difference between the measured pressure and the partial pressure of N_2. N_2 is not absorbed in the liquid solution and is assumed to behave as an ideal gas; its partial pressure at the temperature of the experiment is therefore equal to the partial pressure of N_2 at the initial conditions times the ratio of temperatures. The partial pressure of CO_2 is then calculated by subtracting an estimate of the water partial pressure from Pt (the partial pressure of the amine is assumed to be negligible). Liquid analysis gives the total CO_2 loading at room temperature, which is corrected by the estimated amount of CO_2 in the vapor, evaluated through the ideal gas law. The experimental method has been validated by the comparison of the high-temperature CO_2 solubility obtained by Jou et al. in 30 wt % aqueous MEA[64] (temperature up to 150 °C and CO_2 partial pressure up to 20.0 kPa).

3.2.16. Nguyen. 500–525 g of solution was prepared by dissolving pure, analytical-grade amine in water to achieve the desired molality (m, moles of amine/kg water) and loaded in the reactor.[10] High concentrations of PZ were heated to dissolve the anhydrous solid PZ in water. CO_2 was sparged into the solutions in a glass cylinder placed on a balance to obtain the gravimetric CO_2 loading. The same technique has been used by all of the authors of the University of Texas. Amine solutions loaded with this technique produced CO_2 loadings within ±5.0% of the target loading based on an analysis of the loaded solution. At the start of each experiment, the bath temperature is set, and the headspace in the reactor is swept with excess N_2. Vapor from the reactor headspace is circulated at a rate of ∼5–10 L/min by a heated sample pump to the FTIR through a heated Teflon line. Both the line and analyzer are maintained at 180 °C to keep the material in the vapor phase. The FTIR measures the amine, CO_2 and water concentrations in the gas. The relative standard reproducibility in the vapor phase measurement was reported to be ±2% by Goff.[65] However, the margin of error in the readings increases at low analyte concentrations and can reach ±10% or higher. After passing through the FTIR, the gas is returned to the reactor through a heated line maintained at ∼55 °C above the reactor temperature. This temperature offset is necessary to maintain the water vapor balance and to ensure that the return gas does not upset the gas–liquid equilibrium within the reactor while also preventing potential heat loss at the bottom of the reactor. Upon completion of each experiment, approximately 25 mL of liquid sample is withdrawn to verify both the loading and amine concentration using TIC and amine titration, respectively. Vapor pressures of pure component (H_2O and MEA) and CO_2 solubility in MEA-CO_2-H_2O and PZ-CO_2-H_2O were measured and compared with literature data to validate the FTIR method.

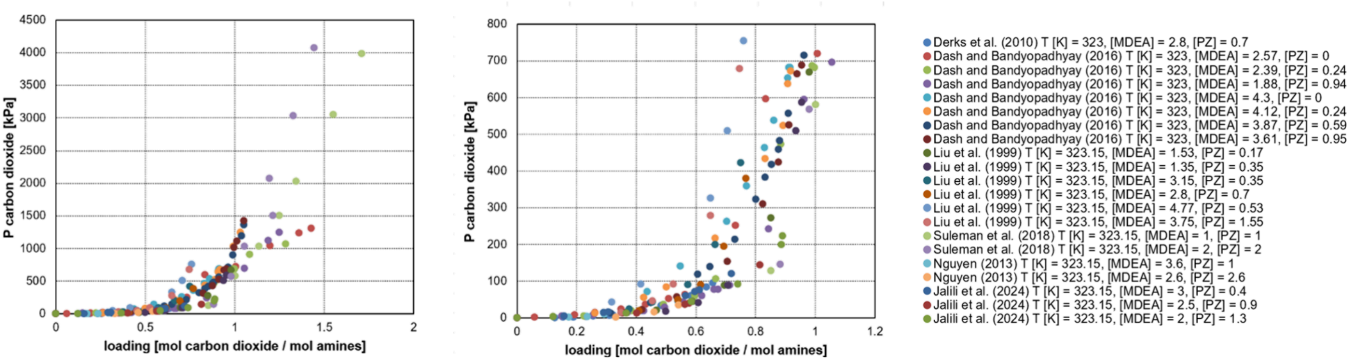
Details of the total inorganic carbon analysis and amine titration can be found in Hillard and Freeman PhD dissertations.[66,67]

3.2.17. Jalili et al. In each experiment, known amounts of gaseous solute and degassed solvent (∼150 cm^3) are contacted at a constant temperature inside the system (EC+VTD) of a known volume (VEC = 250 cm^3).[53] The equilibrium state, when the pressure and temperature inside the EC are constant, is attained after 2–4 h of liquid circulation through the closed loop



(a) (b)

Figure 1. CO_2 partial pressure as a function of the CO_2 loading for different sources at 303 K, considering (a) all the data and (b) a focus on the data for CO_2 partial pressures below 300 kPa.



(a) (b)

Figure 2. CO_2 partial pressure as a function of the CO_2 loading for different sources at 323 K, considering (a) all the data and (b) a focus on the data for CO_2 partial pressures below 800 kPa.

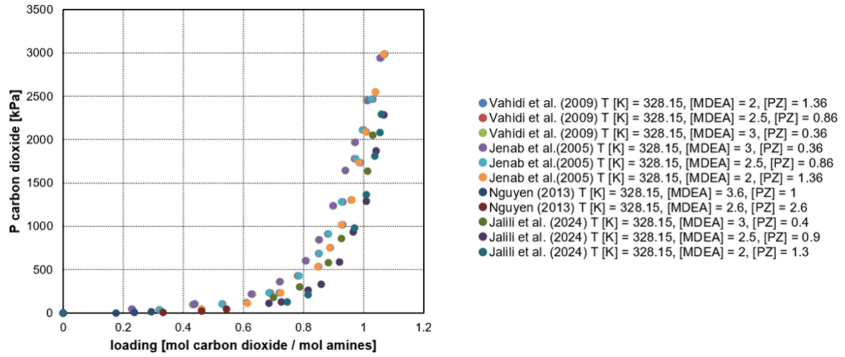
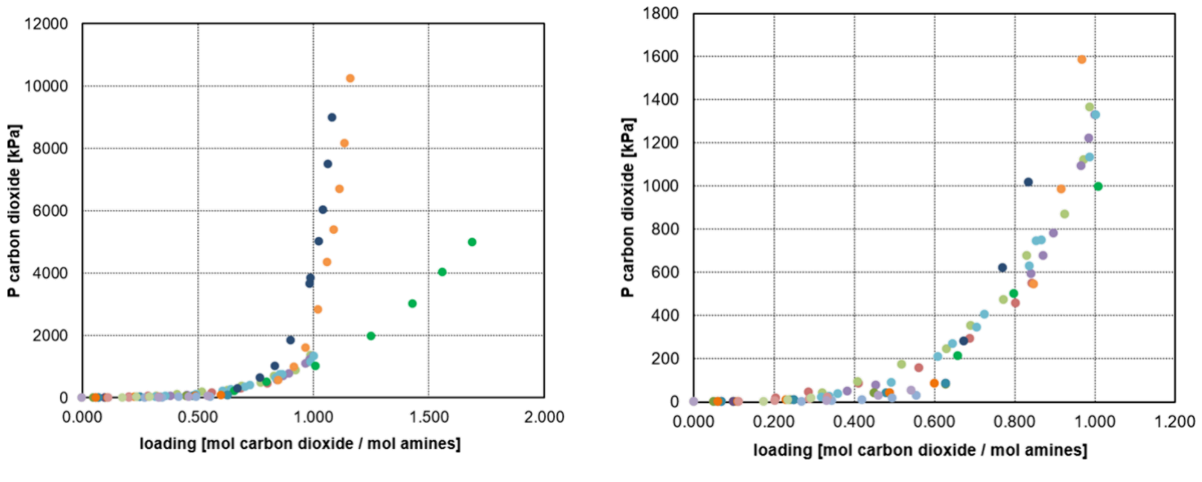


Figure 3. CO_2 partial pressure as a function of the CO_2 loading for different sources at 328 K, considering all of the data.

consisting of the VTD and the EC. In the next step, the liquid circulation pump is turned off, and the density of the solution is calculated considering the oscillation period measured by VTD. The procedures due to Park and Sandall[60] and Jenab et al.[40] are used to obtain the quantity of CO_2 gas introduced into the measurement system. Namely, the total quantity of acid gas introduced into the measurement system is calculated using the pressure drop, the volume of the gas container (GC), and the temperature, with the compressibility factors taken from the NIST scientific and technical databases. Then the partial pressure of CO_2 at equilibrium in the EC is calculated as the difference between the total pressure and the measured vapor pressure of the solution. The moles of CO_2 remaining in the gas phase are calculated by multiplying the CO_2 gas density (mol/cm^3) (evaluated at the partial pressure of the gas and at the temperature of the EC at equilibrium) and the overhead gas volume. This latter is calculated as the difference between the measuring system volume and the liquid volume, considering the actual density and CO_2 molality of the solution. An iterative approach is applied to obtain the CO_2 molality. Then the



(a) (b)

Figure 4. CO_2 partial pressure as a function of the CO_2 loading for different sources at temperatures from 331 to 333 K, considering (a) all the data and (b) a focus on the data for CO_2 partial pressures below 1800 kPa.

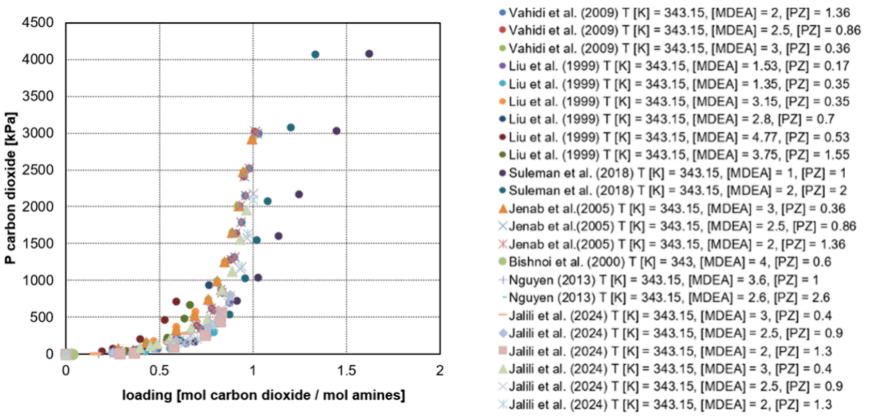


Figure 5. CO_2 partial pressure as a function of the CO_2 loading for different sources at 343 K, considering all of the data.

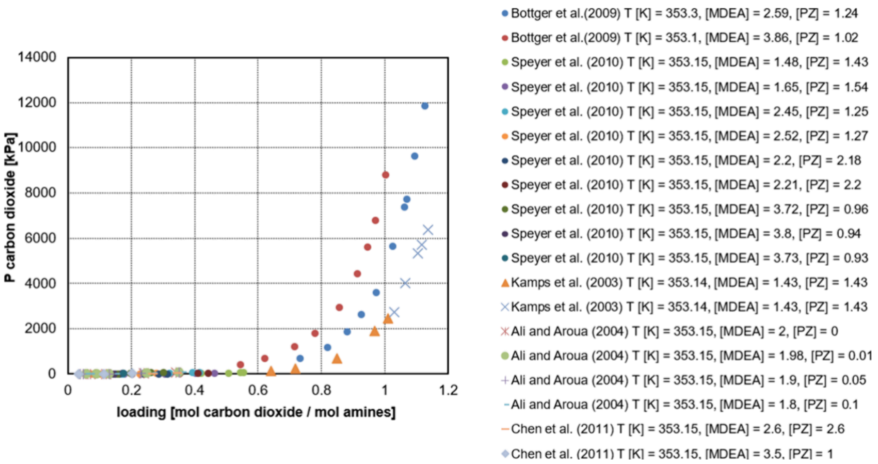


Figure 6. CO_2 partial pressure as a function of the CO_2 loading for different sources at 353 K, considering all of the data.

loading is estimated by dividing the moles of CO_2 in the liquid by the moles of amines in the unloaded solvent.

The operation of the second apparatus recalls that just described. The only difference lies in the amount of solvent charged in the equilibrium cell (w sol ≈ 30 g) and in the estimation of the number of moles remaining in the gas phase after the equilibration. In this case, the volume occupied by the liquid is calculated considering the density of the unloaded

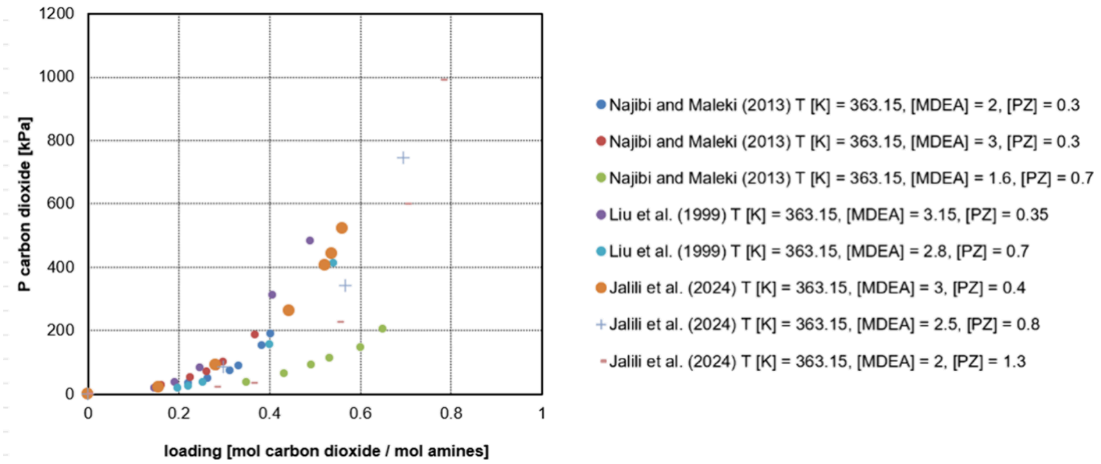


Figure 7. CO_2 partial pressure as a function of the CO_2 loading for different sources at 363 K, considering all of the data.

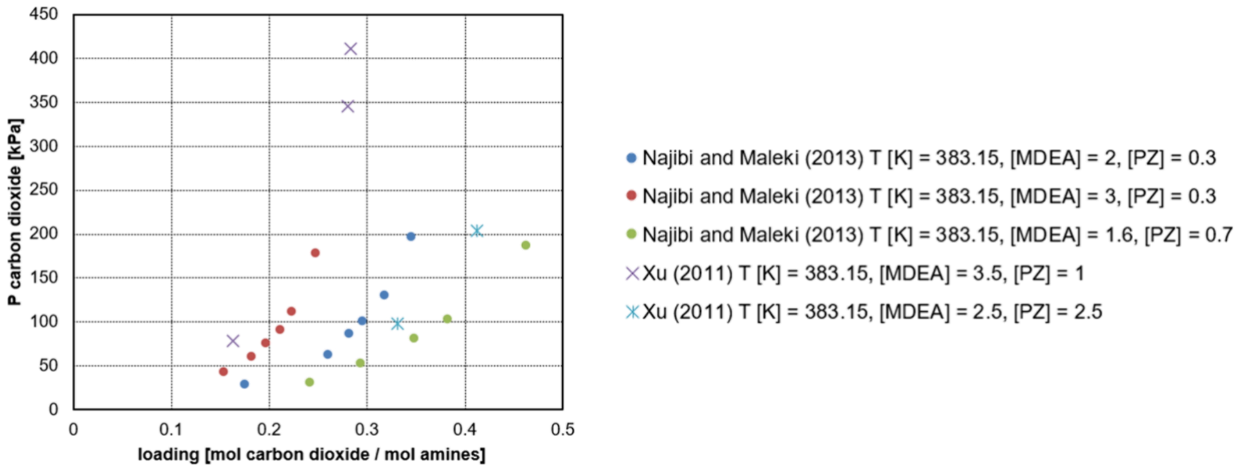
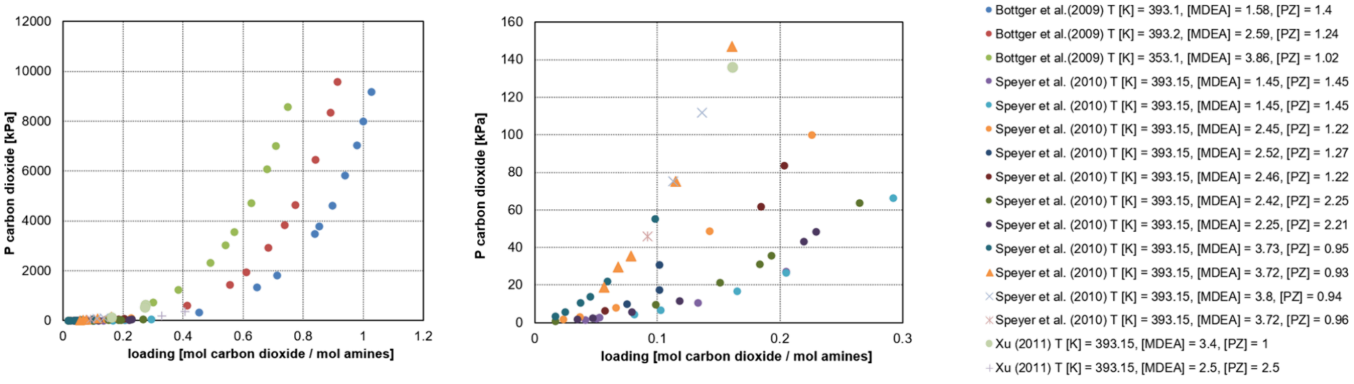


Figure 8. CO_2 partial pressure as a function of the CO_2 loading for different sources at 383 K, considering all of the data.

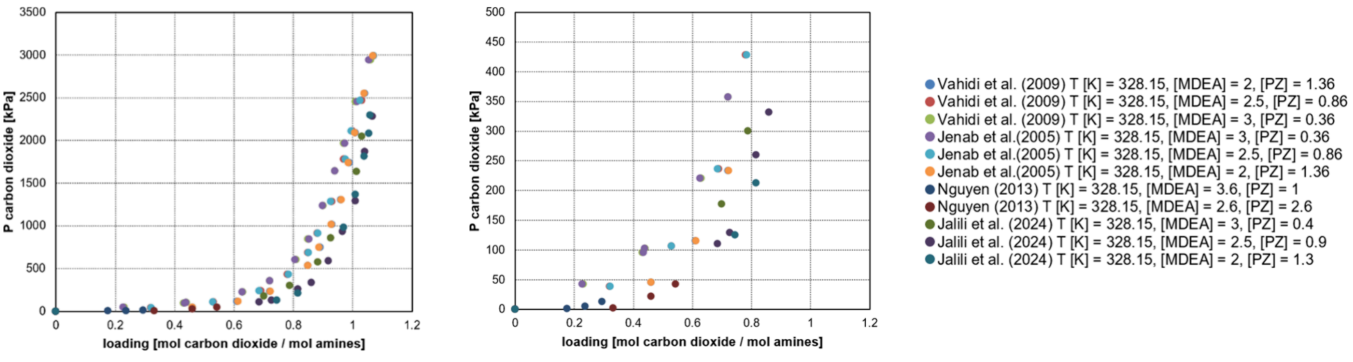


(a) (b)

Figure 9. CO_2 partial pressure as a function of the CO_2 loading for different sources at 393 K, considering (a) all the data and (b) a focus on the data for CO_2 partial pressures below 160 kPa.

solvent, measured by the Anton Paar model DMA HPM densimeter before the start of the test.

3.2.18. Comparison among the Different Procedures. Table 5 reports the main features of the experimental procedure for each source. The estimation of the values of loading of the solvent for a given partial pressure of CO_2 at equilibrium is carried out considering different methodologies. The one based on a volumetric analysis, which is also employed by Park and Sandall, is the most chosen by the different sources. The headspace chromatography is chosen only by Speyer et al.[43] It provides results that seem in line with the results obtained by the other sources with other methods, though the technique seems



(a) (b)

Figure 10. CO_2 partial pressure as a function of the CO_2 loading for different sources at 328 K, considering (a) all the data and (b) a focus on the data for CO_2 partial pressures below 500 kPa.

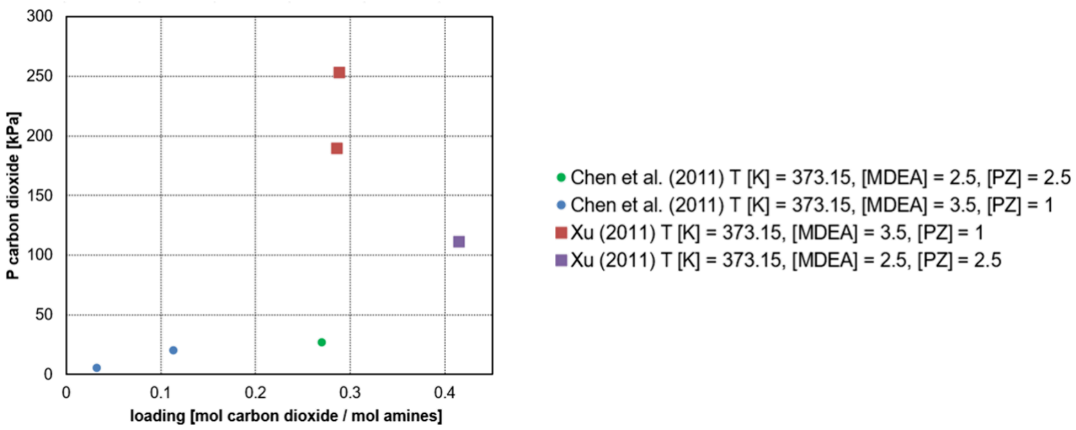


Figure 11. CO_2 partial pressure as a function of the CO_2 loading for different sources at 373 K, considering all of the data.

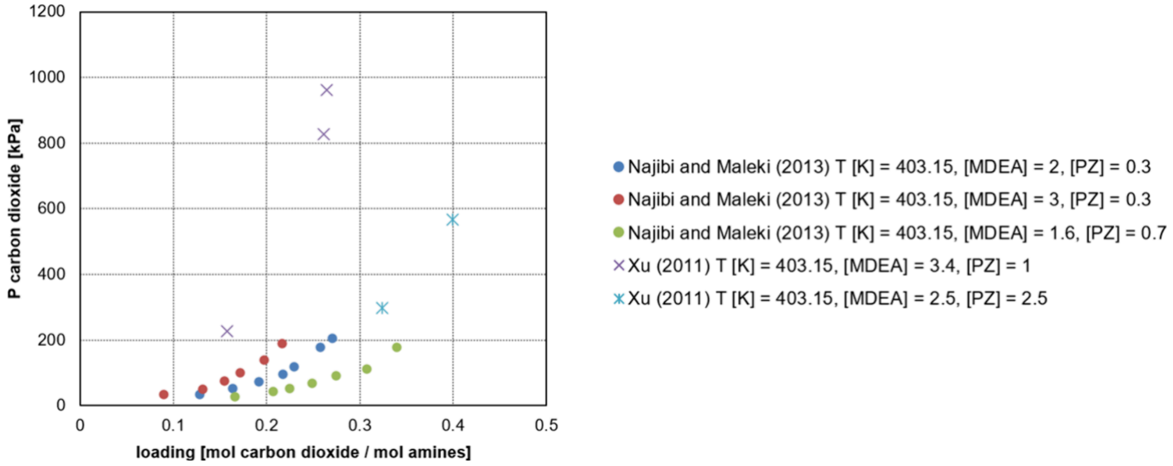


Figure 12. CO_2 partial pressure as a function of the CO_2 loading for different sources at 403 K, considering all of the data.

to be more complex. The addition of other chemicals has been performed only at the Research Institute of Chemical Technology, East China University of Science and Technology (Shanghai, People's Republic of China), and requires expertise for this type of chemical analysis.

4. ANALYSIS OF THE EXPERIMENTAL POINTS

From Figures 1−15, a comparison among all the sources listed in Tables 1−4 at different temperatures is reported. On the basis of the solubility data measured by Xu et al.,[37] it can be outsourced that in this work, the CO_2 loading increases with the concentration of PZ. In the paper, the temperature at which the experiment has been carried out is not reported together with the data in Table 5 of Xu et al.,[37] so these data could not be

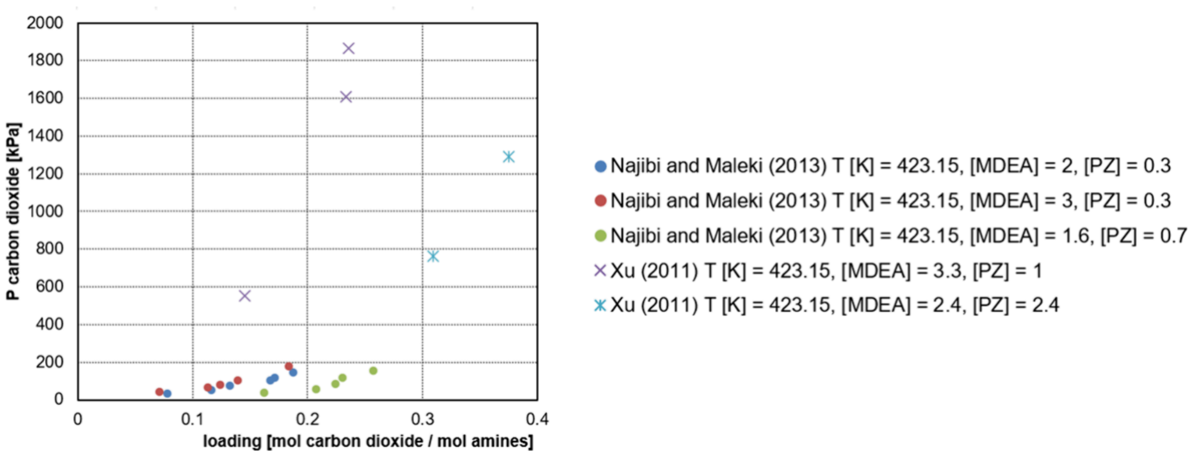


Figure 13. CO_2 partial pressure as a function of the CO_2 loading for different sources at 423 K, considering all of the data.

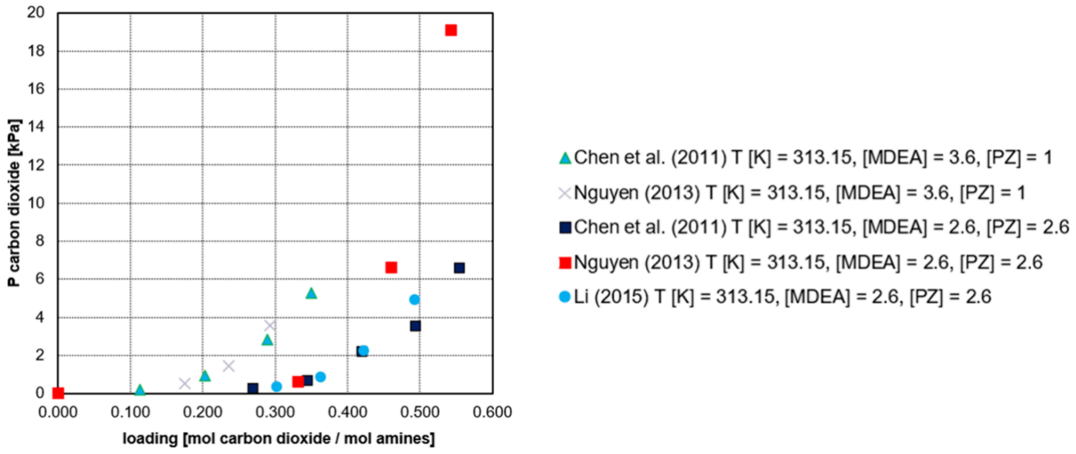


Figure 14. CO_2 partial pressure as a function of the CO_2 loading for different sources at 313 K.

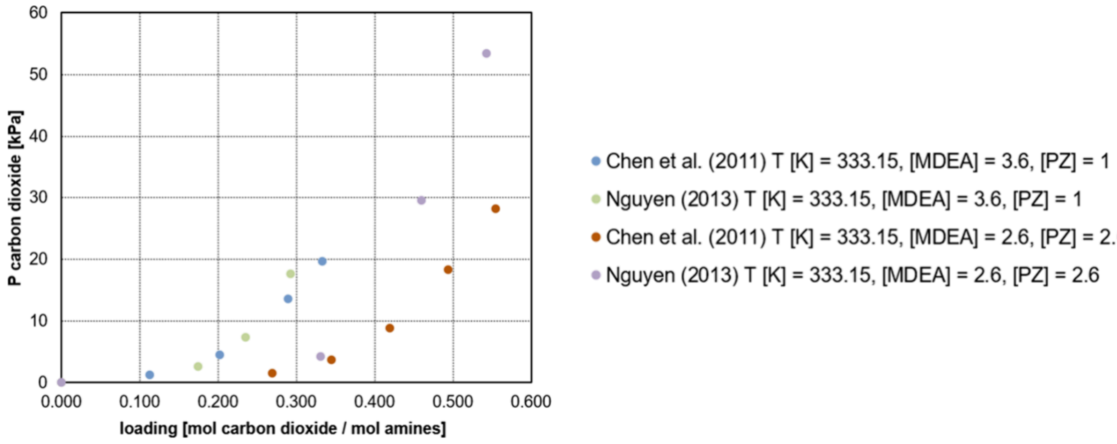


Figure 15. CO_2 partial pressure as a function of the CO_2 loading for different sources at 333 K.

considered for the comparison with the experimental data of other sources in this review.

The points by Bottger et al.[42] reported in Figure 4 are characterized by a different profile if compared to the other source of points at partial pressures of CO_2 higher than 1400 kPa, the one reported by Khan et al.,[46] which seems to continue the trend of almost all the experimental points at lower loadings. Bottger et al.[42] are the only authors who considered concentrations of PZ in the solvent higher than 1 M and do not report values of partial pressure of CO_2 in equilibrium for loadings lower than about 0.6, so a detailed comparison with the other sources cannot be carried out. One of the considered compositions is similar to the one of Khan et al.[46] only for the content of MDEA, though the content of PZ is significantly different.

The experimental data reported at 328 K have been collected only at two research institutes and are reported in Figure 10.

The experimental data reported at 373 K were collected for the same solvent compositions by different authors within a single research institute and are presented in Figure 11. However, the data are limited in number and were not collected at overlapping CO_2 loadings, making it difficult to assess the consistency or identify potential outliers.

For the temperatures of 383, 403, and 423 K, only two sources of experimental data have been found. The collection of additional experimental points, by different sources and in detail at these temperatures, could be of interest and is suggested to validate the points already measured.

The plots at 298, 413, and 433 K are not shown, as only one source reports data at each of these temperatures: Derks et al.[34] for 298 K and Najibi and Maleki[44] for 413 and 433 K. The experimental points at 313 K are a lot, and a plot with all of them together is difficult to read, so it has not been reported in this paper, though it has been analyzed.

The same MDEA/PZ mixtures—specifically 7 m MDEA + 2 m PZ and 5 m MDEA + 5 m PZ—have been investigated by different authors within the same research group at the University of Texas. A comparison of their experimental CO_2 solubility data at 313 and 333 K is presented in Figures 14 and 15. The measurements are generally in good agreement, demonstrating consistency in the data despite being collected by different researchers. However, for the 5/5 m mixture, the data reported by Nguyen show a noticeable deviation from the others. This divergence may be due to variations in experimental setups.

A comprehensive numerical comparison of each point of different sources cannot be done because the collected points are reported for different compositions of MDEA and PZ. Also, in the case of similar composition, a qualitative trend is usually considered for checking the validity of the CO_2 solubility points in chemical solvents. In general, the different sources of experimental data are in agreement with each other in a wide range of temperature and pressure conditions. Considering all the experimental points, it can be confirmed that the addition of PZ, as an activator for MDEA, increases the solubility of CO_2 in particular in the region of low CO_2 partial pressure, compared to pure MDEA. The CO_2 loading increases with decreasing the temperature, increasing the CO_2 partial pressure, and increasing the PZ concentration.

For evaluating the performance of the thermodynamic models and for choosing the best one, it is suggested to consider all the experimental points at different compositions, partial pressures of CO_2, and temperatures. Then, if a refinement of the model is needed by regressing some parameters, it can be performed, focusing on the solvent composition of interest, though considering that some variation may occur in the absorption and in the regeneration section mainly due to water volatility (that could modify the concentration of MDEA and of PZ) and to the MDEA volatility, which is higher than the PZ volatility, for which generally a makeup is needed.

5. CONCLUSIONS

This work is the first review focusing on extensive bibliographic research related to experimental data of CO_2 solubility in the MDEA+PZ aqueous solution, employed for chemical absorption to remove CO_2 from different gaseous sources.

All of the relevant literature on the subject has been examined with respect to the experimental conditions (temperature, pressure, and composition), the measurement setups, and the procedures adopted. The collected data were analyzed and compared where possible. The identification of outliers has been carried out to the extent feasible, as the comparison is often limited by the lack of overlap in the investigated concentrations among the different studies.

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Author Contributions

The manuscript was written through the contributions of all authors. The authors contributed equally. C.B.: literature review, writing, and editing of the original draft. S.M.: conceptualization, literature review, writing, review, and editing of the original draft.

Notes

The authors declare no competing financial interest.

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