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pH of CO₂ saturated water and CO₂ saturated brines:

Experimental measurements and modelling

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Abstract

In this work, both spectroscopic and electrometric methods were employed to measure the pH of water saturated with carbon dioxide at pressures up to 6 MPa, temperature ranges from 293.15 to 353.15 K and salinities up to 3 mol·kg⁻¹.

Furthermore, a model was developed to predict the changes in the pH due to the solubility of CO₂ in the aqueous phase at high pressure and high temperature conditions as well as the effect of NaCl. The pH model was developed by coupling the Cubic-Plus-Association Equation of State (CPA EoS) and the Pitzer equations. The former was used to determine the solubility of acid gases in aqueous solutions while the latter was employed to calculate activity coefficients for each ion species. The predictive capability of the pH model was evaluated against the data gathered from the literature and data measured in this work. The model allowed a prediction of the pH with an overall average absolute deviation (AAD) to measured data of 0.03 and 0.06 pH units in the CO₂-H₂O system using electrometric and spectroscopic techniques, respectively, and between 0.04 and 0.10 pH units in the CO₂-H₂O-NaCl systems by employing the spectroscopic technique.

KEYWORDS: pH; Carbon dioxide; Water; Sodium chloride

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1 **1. Introduction**

2 Atmospheric concentration of CO₂ has increased steadily from around the time of the industrial
3 era. This increase in concentration of CO₂ can cause serious global warming and climate
4 change issues. Hence, expanding the methods for removing CO₂ from atmosphere has become
5 an important topic. In the last decades, this issue has prompted researchers to identify methods
6 to combat global warming. Carbon Capture and Storage (CCS) is a set of technologies aimed
7 at alleviating the increase of CO₂ in the atmosphere. Currently, injecting CO₂ at high pressures
8 in deep geologic formations, such as oil and gas reservoirs and deep saline aquifers, is the main
9 alternative strategy for permanent or mid-term disposal of CO₂ instead of releasing it into the
10 atmosphere.

11 The concepts of pH and pH scales were introduced at the beginning of the last century, and
12 they have since been the most important parameters used to describe the acidity or basicity of
13 aqueous solutions. Since determining of pH is essential for different applications such as
14 marine, pharmaceutical and petroleum industries (Babić et al., 2007; Gray et al., 2011; Millero
15 et al., 2009). In the CCS contexts, the CO₂ injection will cause many chemical reactions as well
16 as hydrodynamic and mechanical changes (Gaus, 2010). As the formation water in deep
17 geological formations (i.e., deep saline aquifers) contains salts, measuring the pH in saline
18 water is a prerequisite to characterise the properties of solutions. For instance, the pH level
19 starts to drop in brine solutions due to CO₂ dissolution and formation of carbonic acid in the
20 reservoir as a result of the CO₂ injection. This variation in pH value in water might cause
21 corrosion of metallic materials in oil and gas wells and can also lead to mineral
22 dissolution/precipitation and scaling in pipelines transporting oil field waters (Crabtree et al.,
23 1999; Gray et al., 1989). Moreover, low values of pH can have a substantial impact on the
24 capture, storage and transportation of CO₂ due to the changes in the porosity and permeability
25 of the reservoir rock (Carroll et al., 2011). Hence, it is necessary to understand the interactions
26 between CO₂ and brine at downhole wellbore conditions (high pressure and temperature) to
27 prevent the formation of scale, corrosion and precipitation of minerals in pipelines as well as
28 for safety concerns in the downhole/wellbore region.

29 The electrometric technique is typically the most common method for pH measurement.
30 Different types of high pressure and high temperature glass electrodes are commercially
31 available to determine pH of aqueous samples under relevant conditions of temperature and
32 pressure. These glass and reference electrodes require careful handling, particularly during
33 depressurization. Significant amounts of CO₂ can dissolve into the electrode filling solution

1 when CO₂ is injected into the high pressure cell. Therefore it is necessary to depressurize the
2 system slowly to avoid electrode damage because of a sudden drop in pressure. Furthermore,
3 liquid junction potential is still one of the main drawbacks of this type of measurement,
4 particularly when the sample comprises a large amount of salt. When two different electrolyte
5 solutions come into contact with each other, liquid junction potential may occur between these
6 solutions resulting in an inaccurate pH measurement (Kakiuchi, 2011); several methods have
7 been suggested for decreasing the liquid junction potential (Shibata et al., 2010; Yamada et al.,
8 2015). Another disadvantage of this approach is that it is necessary to calibrate the glass
9 electrode frequently before each measurement using buffer solutions.

10 Spectroscopic techniques are the alternative technique for precise measurement of pH in CO₂-
11 brine-mineral systems. However, this technique requires the introduction of a specific quantity
12 of dye indicator into the aqueous phase for both calibration and testing samples. Furthermore,
13 each dye indicator covers a limited pH range; nonetheless mixtures of dye indicators at specific
14 concentrations can be prepared, in order to cover the required pH range. Unlike the
15 electrometric method, in the spectroscopic method, it is not necessary to calibrate the system
16 for pH measurement each time before the measurement using buffer solutions.

17 A number of researchers have shown that optical and electrometric techniques can be used to
18 measure the pH of CO₂ in water and brine at high pressures and temperatures with high
19 accuracy. Meyssami et al. (1992) measured the pH of CO₂ in various fluid systems using a pH
20 probe that was placed inside a high-pressure vessel. They performed all the measurements at
21 pressures up to 35 MPa and temperatures from 305 K to 315 K. An experimental investigation
22 was carried out by Rosenqvist et al. (2012) to measure the pH of water and mineral suspension
23 solution containing dissolved CO₂ using a pH probe at pressures up to 1 MPa and temperature
24 of 294 K. The measured pH values in deionised water were in good agreement with those
25 reported in the literature. Schaefer et al. (2003) reported the use of an electrometric technique to
26 determine the pH of both CO₂ saturated H₂O and NaCl systems at pressures up to 11 MPa and
27 temperatures up to 343 K. In this study, the molality of the NaCl solution varied from 1 to 4.49
28 mol·kg⁻¹ (m). Recently, the pH of the CO₂-H₂O system was measured at temperatures between
29 308 K and 423 K and pressures up to 15 MPa by Peng et al. (2013). They used a commercially-
30 available pH and Ag/AgCl electrodes mounted inside a high-pressure/high-temperature
31 equilibrium cell. All the measured values were compared with a chemical equilibrium model,
32 and a good agreement was obtained between the experimental and simulated data.

1 The applicability of ultraviolet-visible spectrometer to determine the pH of different fluid
2 systems was investigated by a few research groups. Toews et al. (1995) developed a
3 spectrometer analyser to determine the pH in the CO₂-H₂O system by observing the change in
4 the spectra of the dye indicator (Bromophenol Blue, BPB hereafter) at two specific
5 wavelengths (430 and 590 nm). Measurements were performed at pressures up to 20 MPa and
6 343K. In this study, the effect of a change in pressure on dissociation constant was neglected
7 for pH calculation. Parton et al. (2002) also employed UV-Vis spectroscopic technique to
8 determine pH in the CO₂-H₂O system at different pressure and temperature conditions. Several
9 spectroscopic studies have been carried out to measure the pH in seawater at atmospheric
10 pressure. Millero et al. (2009) reported the use of spectrometric techniques by dissolving m-
11 cresol purple indicator in NaCl solutions to measure dissociation constants as a function of
12 NaCl molality (0 to 5.5 m) and temperatures (278 to 318 K) at atmospheric pressure. They have
13 provided an equation to calculate the pH based on the dissociation constant of m-cresol purple
14 in brine. These results confirmed the applicability of the spectroscopic method to measure the
15 pH at high level salinities at high temperatures. Recently, Shao et al. (2013) employed the UV-
16 Visible spectrometer to measure the pH in the CO₂-H₂O and CO₂-H₂O-NaCl systems in the
17 presence of two chromophores, BPB and bromocresol green (BCG) which can cover the pH
18 range between 2.5 and 5.2. The experimental values were in good agreement with those
19 obtained through geochemical models. The maximum difference of the experimental data from
20 four different models was found to be 0.16 pH units (Shao et al., 2012). They led to the
21 conclusion that by selecting a suitable calibration procedure and appropriate dye indicators the
22 spectroscopic technique can provide an accurate and precise pH value for the rock-CO₂-brine
23 systems. Truche et al. (2016) reported the pH values in the CO₂-H₂O and CO₂-H₂O-NaCl in a
24 1.4 molal (m) NaCl solution systems by combining the Raman spectroscopy and the
25 electrometric techniques at temperatures up to 553.15K and pressures up to 15 MPa.
26 Furthermore, they introduced a new thermodynamic model by coupling a Pitzer specific-ion-
27 interaction aqueous model with the Phreeqc geochemical code (Parkhurst and Appelo, 1999).
28 Good agreement was obtained between the model and the experimental data for the CO₂-H₂O-
29 1.4m NaCl system at elevated pressures and temperatures.

30 To our knowledge, there are very limited experimental studies of pH in the CO₂-brine systems,
31 required to validate and improve the accuracy of model predictions. Hence, investigations of
32 pH in CO₂-brine solutions, particularly at high pressures and high salinities, can greatly
33 improve our knowledge about the change of pH after injecting CO₂ into deep ocean or saline

1 aquifers. The aim of the present research is to: (1) measure the pH of the CO₂-H₂O systems at
 2 pressures around 5.1 MPa and at temperatures up to 353.15 K using a commercially-available
 3 pH glass electrode; (2) spectroscopic measurement of pH in different fluid systems (i.e., CO₂-
 4 H₂O and CO₂-H₂O-NaCl) using BPB indicator which typically cover the appropriate pH range
 5 at pressures up to 6 MPa and temperatures up to 323.15 K ; (3) finally, compare all the
 6 experimental results from both methods and the literature data with the developed
 7 thermodynamic model.

8 **2. Theory of Spectroscopic Method for pH Measurements**

9 Changes in the colour of the dye indicator will result in a change in the absorbance spectra of
 10 protonated (HI⁻) and deprotonated (I²⁻) of the dye indicator. These indicators could exist in both
 11 the acid and base form, and the absorbance of light varies while the pH of the solution changes
 12 within a certain range of the pH value. The equilibrium between the protonated (acid) and
 13 deprotonated (base) of the dye indicator is utilised to measure the pH of the solution.



$$15 \quad pH = pK'_a + \log \frac{\gamma_B}{\gamma_A} + \log \frac{[B]}{[A]} = pK_a + \log \frac{[B]}{[A]} \quad (2)$$

16 Where A is the acid form of the dye indicator, B represents the indicator's base form and pK_a
 17 is equal to $-\log (K'_a \frac{\gamma_A}{\gamma_B})$ (K'_a is the dissociation constant of the BPB, γ_B and γ_A are the activity
 18 coefficients of base and acid form of the BPB) (Mathews et al., 2009; Raghuraman et al., 2006).
 19 BPB solutions exhibit clear changes in their absorbance while the pH value is changing from
 20 approximately 2.5 to 4.5. It was observed that BPB absorbs the visible part of spectrum
 21 maximally at a wavelength of 440 nm (λ_1) when it is in the acid form and the base form of BPB
 22 absorbs the visible light maximally at a wavelength of 590 nm (λ_2). Change in the pH of the
 23 solution that containing BPB results in a change in the relative heights of the absorption peaks
 24 at these two wavelengths that one corresponds to the concentration of the acid form and other
 25 corresponds to the concentration of the base form of the dye in the solution. Eq. (2) must be
 26 modified based on the spectral measurements. The absorbance spectrum of BPB in the acid
 27 form overlaps with the absorbance spectrum of BPB in the base form at a wavelength of 440
 28 nm (A (λ_1)). Thus, it is required to consider the small amount of the base form in the acid
 29 wavelength (See Fig. S1). The same modification requires being considered for the base
 30 wavelength (A (λ_2)). This can be performed by applying the Beer-lambert Law.

$$31 \quad c_{Total} = c_A + c_B \quad (3)$$

1 c_A and c_B are the concentration of the acid form and the base form of the dye indicator into the
 2 sample in $\text{mol} \cdot \text{kg}^{-1}$.

$$3 \quad A(\lambda_1) = \varepsilon_A^{\lambda_1} \cdot c_A \cdot l + \varepsilon_B^{\lambda_1} \cdot c_B \cdot l \quad (4)$$

$$4 \quad A(\lambda_2) = \varepsilon_A^{\lambda_2} \cdot c_A \cdot l + \varepsilon_B^{\lambda_2} \cdot c_B \cdot l \quad (5)$$

$$5 \quad R_{\lambda_1}^{\lambda_2} = \frac{A(\lambda_2)}{A(\lambda_1)} \quad (6)$$

$$6 \quad \frac{c_B}{c_A} = \frac{R_{\lambda_1}^{\lambda_2} \left(1 - \frac{\varepsilon_A^{\lambda_2}}{\varepsilon_A^{\lambda_1} \times R_{\lambda_1}^{\lambda_2}}\right)}{\frac{\varepsilon_B^{\lambda_2}}{\varepsilon_A^{\lambda_1}} \left(1 - \frac{\varepsilon_B^{\lambda_1}}{\varepsilon_B^{\lambda_2} \times R_{\lambda_1}^{\lambda_2}}\right)} \quad (7)$$

7 $\varepsilon_A^{\lambda_i}$ and $\varepsilon_B^{\lambda_i}$ are the molar absorptivity of the acid and base form at wavelengths of 440 nm and
 8 590 nm respectively, $R_{\lambda_1}^{\lambda_2}$ is the absorbance ratio and l is the path length, the distance that light
 9 travels through the sample. By modifying Eq. (2), one can calculate the pH of a buffer solution:

$$10 \quad pH = pK_a(t, p, \mu) + \log \frac{R_{\lambda_1}^{\lambda_2} - \frac{e_A^{\lambda_2}}{e_A^{\lambda_1}}}{\frac{e_B^{\lambda_2}}{e_A^{\lambda_1}} - R_{\lambda_1}^{\lambda_2} \cdot \frac{e_B^{\lambda_1}}{e_A^{\lambda_1}}} \quad (8)$$

$$11 \quad e_1 = \frac{e_A^{\lambda_2}}{e_A^{\lambda_1}} \quad e_2 = \frac{e_B^{\lambda_2}}{e_A^{\lambda_1}} \quad e_3 = \frac{e_B^{\lambda_1}}{e_A^{\lambda_1}} \quad (9)$$

12
 13 Where e_1 , e_2 and e_3 are the ratio of the molar absorptivity of the protonated (acid) and
 14 deprotonated (base) of BPB at two wavelengths (λ_1 & λ_2). A detailed description of the
 15 employed theory can be found in the literature (Clayton and Byrne, 1993; Raghuraman et al.,
 16 2006; Robert-Baldo et al., 1985; Zhang and Byrne, 1996). pK_a is defined as a function of
 17 temperature, pressure and ionic strength. The sensitivity of temperature and ionic strength on
 18 the pK_a can be examined experimentally. Furthermore, the effect of pressure on the dissociation
 19 constant ($K_a(t, p, \mu)$) can be derived using following equation.

$$20 \quad \frac{RT}{(P-1)} \ln \frac{K_a(t, p, \mu)}{K_a(t, 1, \mu)} = -\Delta V + \Delta k \frac{P-1}{2} \quad (10)$$

21 Where $K_a(t, 1, \mu)$ is the dissociation constant of BPB at atmospheric pressure (0.1 MPa). R is
 22 the gas constant ($8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$) and, P and T are the pressure and temperature of the fluid
 23 system inside the measurement cell. The value of volume changes (ΔV) and compressibility
 24 changes (Δk) for BPB were reported by Usha and Atkinson (1992). Using these values, one
 25 can solve Eq. (10) to get the dissociation constant of the BPB at various pressures. The

1 procedure that followed to determine the pK_a and e -values experimentally are discussed in
2 details in the section 5.1.

3 **2.1 Material**

4 The details of the materials used in this study are tabulated in Table 1. All the solutions were
5 prepared using deionised water. For solutions with zero salinity, the glass electrode was
6 calibrated using certified buffer solutions with pH of 4 (citric acid / sodium hydroxide / sodium
7 chloride solution) and 7 (potassium dihydrogen phosphate / disodium hydrogen phosphate).
8 For 1, 2 and 3 mol·kg⁻¹ NaCl solutions, Tris buffer (Trizma[®] base / Trizma[®] hydrochloride) and
9 HCl solutions with the same NaCl ionic strength were used for calibration of the glass
10 electrode.. Certified buffer solutions with pH of 4 and 7 were provided by Sigma-Aldrich and
11 Hanna instruments. Nitrogen and deionised water were also used for cleaning purposes.

12 **Table 1** Suppliers and specification as stated by the supplier of the materials used in this work.

Chemical name	Source	Purity
CO ₂	Air Liquide	>99.99%
NaCl	Sigma Aldrich	>99.95%
Trizma [®] base	Sigma Aldrich	>99%
Trizma [®] hydrochloride	Sigma Aldrich	>99%
BPB	Sigma Aldrich	-

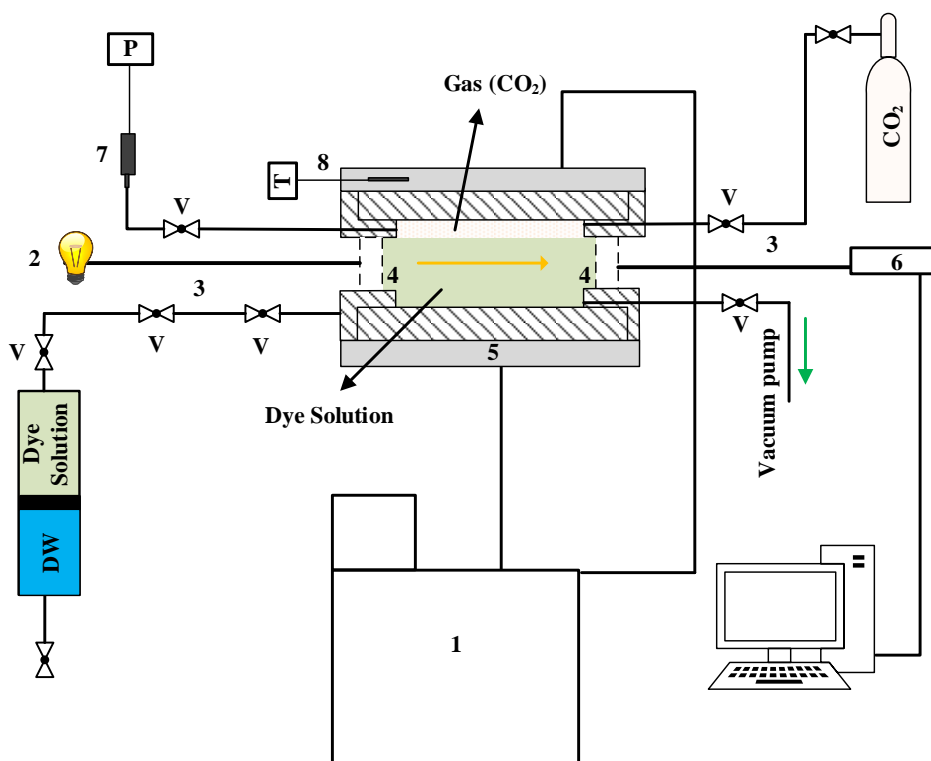
13

14 **2.2 Apparatus**

15 A UV-Vis-NIR spectrometer (C10082MD, Hamamatsu Ltd.) equipped with a UV/VIS/NIR
16 light source (L10290, Hamamatsu) was used for spectra acquisition between 200 to 1100 nm.
17 The light source was mounted to one end of a spectroscopic cell through a fibre optic cable.
18 Each end of the cell is fitted with windows to allow the light to pass through the sample. The
19 cell windows are designed to work at elevated pressures. All the samples were placed in the
20 high pressure titanium cell which can operate at pressures up to 30 MPa. The setup has been
21 designed to have a maximum working temperature of 353 K. The test cell has an effective
22 optical path length of approximately 1.4 cm and an internal diameter of 5.0 cm and internal
23 volume of about 27 cm³. The cell is housed in a metallic jacket with fluid circulating through
24 it from a cooling/heating bath. The pressure is measured using a Druck pressure transducer
25 with a pressure range up to 60 MPa and previously calibrated against a dead weight pressure
26 balance. This calibration procedure ensures a standard uncertainty of $U(P) = 0.05$ MPa
27 (Ahmadi et al., 2017). The temperature inside the cell is measured by a high precision PRT
28 probe inserted into the cell. The temperature is regularly calibrated against a Prema 3040

1 precision thermometer. This calibration procedure ensures standard uncertainties of $U(T) =$
 2 0.05 K for the temperature readings. A schematic of the apparatus is shown in Fig. 1.

3



4

5

6 **Fig. 1.** Schematic diagram of the spectroscopy setup for pH measurements, 1: Cooling /
 7 Heating bath, 2: Deuterium and tungsten light sources, 3: Fibre optic, 4: Sapphire windows, 5:
 8 High pressure cell, 6: Spectrometer, 7: Pressure transducer, 8: Temperature probe and V:
 9 Valve.

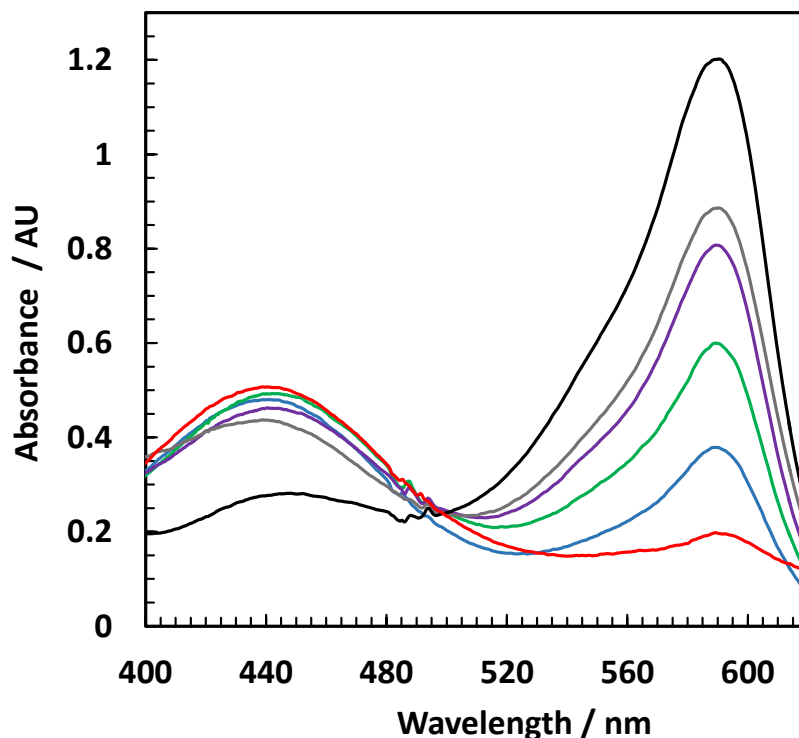
10 2.3 Calibration

11 Firstly, all the buffer solutions were prepared by combining a specific amount of $0.1\text{ mol}\cdot\text{kg}^{-1}$
 12 solution of citric acid and $0.1\text{ mol}\cdot\text{kg}^{-1}$ solution of trisodium citrate dihydrate. Various amounts
 13 of these stock solutions were combined together in order to reach target pH values. Sodium
 14 chloride was then used to set the ionic strength of the buffer solutions to molality of 1, 2 and 3
 15 $\text{mol}\cdot\text{kg}^{-1}$. The pH of all the prepared buffer solutions with various ionic strengths at
 16 atmospheric pressure and the test temperatures were measured using a pH meter a glass
 17 electrode with an Ag/AgCl probe as an internal reference, Hanna, HI-2002 Edge®).

18 For solutions without NaCl, the glass electrode was calibrated using pH 4 and 7 buffer solutions
 19 at 293.15 and 323.15 K. Since the addition of NaCl changes the pH of the prepared buffer
 20 solutions, it is required to calibrate the glass electrode using buffer solutions that have the same

1 ionic strength to determine the actual value of the pH (Marion et al., 2011). For this purpose,
2 $0.05 \text{ mol}\cdot\text{kg}^{-1}$ Tris buffer solutions (Tris/Tris HCl) and $0.01 \text{ mol}\cdot\text{kg}^{-1}$ HCl solutions were used
3 to calibrate the glass electrode for NaCl solutions ($1, 2$ and $3 \text{ mol}\cdot\text{kg}^{-1}$) at 293.15 and 323.15
4 K. The procedure for calibrating the glass electrode for the NaCl solutions is similar to the
5 procedure followed by Peng (2015). The pK_a of $0.05 \text{ mol}\cdot\text{kg}^{-1}$ Tris/Tris HCl solutions with
6 different NaCl concentrations ($0\text{-}5 \text{ mol}\cdot\text{kg}^{-1}$) at temperatures up to 393.15 K was reported by
7 Foti et al. (1999). Our developed model was used to calculate the pH of $0.01 \text{ mol}\cdot\text{kg}^{-1}$ HCl
8 solutions at various temperatures and ionic strengths (See Supplementary Information for
9 details). All the prepared buffer solutions were placed into a jacketed beaker connected to a
10 cooling/heating bath. The glass electrode was immersed into the solution at the target
11 temperature. Once the pH value remained constant, the value measured by the pH meter was
12 chosen as the true value for the calibration sample. No significant change was observed in the
13 measured pH value of different buffer solutions for 12 hours (The drift on the e.m.f values was
14 within $\pm 0.5 \text{ mV}$), showing the high stability of the pH measurement for calibration samples
15 using the glass electrode. All the standard solutions with different ionic strengths were prepared
16 in the pH range between 2.70 and 4.30 to cover the interested pH range within the range of the
17 P–T conditions studied (Fig. 2). After preparing the solutions with different pH and ionic
18 strength values, the high pressure cell was first vacuumed, and 25 ml of each solution was
19 placed into the cell. Then, the temperature of the cell was set at desired temperature, and the
20 spectrum was recorded as a blank spectrum when the desired equilibrium temperature was
21 reached. Afterwards, the BPB dye indicator was dissolved in the same solution at a
22 concentration of $2 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$, and the solution was then injected into the cell. A spectrum
23 of the sample was recorded at the same temperature.

24



1
 2 **Fig. 2.** Spectra of BPB solutions with different pH values at a pressure of 0.1 MPa, the
 3 temperature of 298.15 K and zero ionic strength. (2.95 (—), 3.45 (—), 3.65 (—), 3.85 (—), 3.98
 4 (—) and 4.25 (—)).

5 In order to measure the values of e_1 , e_2 , and e_3 (Eq. 10) experimentally in the absence of the
 6 NaCl, a buffer solution with pH of 7 was used as base solution and the pH of the acid solution
 7 set to approximately 1.5 by adding about $0.5 \text{ mol}\cdot\text{kg}^{-1}$ HCl solution to deionised water (Shao
 8 et al., 2012). For NaCl solutions, standard solutions with pH of 7 and 1.5 were prepared at each
 9 ionic strength (1, 2 and $3 \text{ mol}\cdot\text{kg}^{-1}$) to investigate the impact of NaCl concentrations in the BPB
 10 solutions on the e-values. The concentration of BPB in all the base and acid solutions (pH = 1.5
 11 and 7) was increased and adjusted to about $3 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$ to obtain the maximum absorbance
 12 for the BPB. All the prepared solutions were injected into the cell, and the spectra of the
 13 samples were recorded at two different temperatures and atmospheric pressure.

14 **2.4 Experimental procedures**

15 The experimental procedure consists of several steps. In order to record the spectra of different
 16 systems, first, the cell was filled with deionised water or brine solutions. When the system
 17 reached the desired equilibrium temperature, the spectrum was recorded as a blank. Then, the
 18 cell was vacuumed, and it filled with deionised water or brine with a BPB concentration of $2 \times$
 19 $10^{-5} \text{ mol}\cdot\text{kg}^{-1}$. A headspace was left at the top of the cell to allow the gas sample to enter into
 20 the cell and dissolve easily into the fluid. Pure CO_2 was then injected to achieve the desired
 21 equilibrium pressure. Equilibrium is assumed to have been reached when the total pressure

1 remains unchanged within 0.007 MPa during a period of 30 minutes. To accelerate the
2 thermodynamic equilibration process, the cell was placed on a pivotal axis, allowing the cell
3 to rock using a compressed air-driven mechanism for each equilibrium condition, the spectrum
4 was recorded three times in order to verify the measurements repeatability and to calculate the
5 standard deviations of the e_1 , e_2 , e_3 and pK_a .

6 **3. Electrometric Technique for pH Measurements**

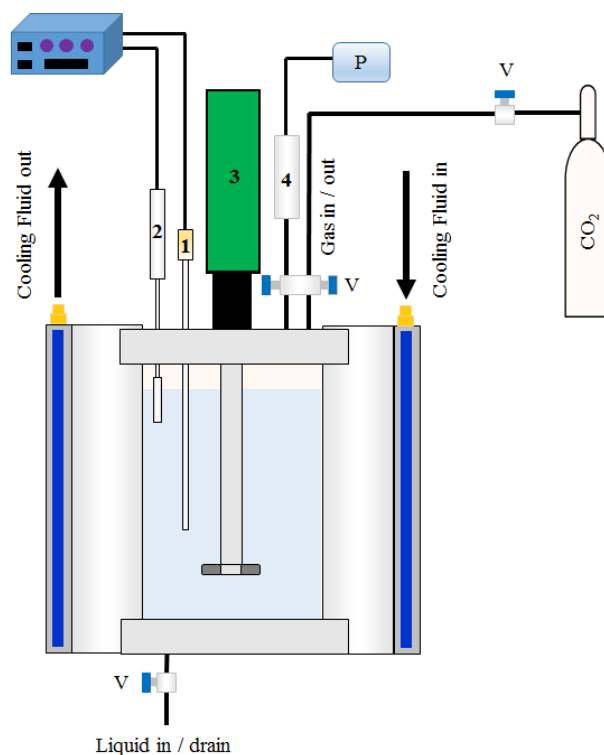
7 The electrometric technique is one of the most popular methods for pH measurement in
8 aqueous samples. The principal of electrometric technique is based on the Nernst equation
9 (Bates and Vijn, 1973).

$$10 \quad E = E^\circ - 2.3026 \left(\frac{RT}{F} \right) pH \quad (11)$$

11 Where R and F are the molar gas constant (8.3144 J mol⁻¹ K⁻¹) and the Faraday constant
12 (96.485 kC.mol⁻¹) respectively, T stands for the absolute temperature, E° is the standard
13 electrode potential and E is the measured e.m.f. in the presence of solution (Peng et al., 2013).
14 Different kinds of pH electrodes are available commercially that are suitable for pH
15 measurement over wide ranges of temperature and pressure (Shinwari et al., 2010). One
16 advantage of this method compared to the spectroscopic method is that the calibration
17 procedure is fast and simple but the glass electrode need to be calibrated frequently.

18 **3.1 Apparatus**

19 A high pressure vessel was purchased from Büchi Glas Uster. The cell volume is about 500
20 cm³, it is constructed from Hastelloy and wetted parts are corrosive-resistance. The pH
21 measurements were carried out using a glass combination pH probe with an internal standard
22 Ag/AgCl electrode as a reference electrode (Provided by Büchi Glas Uster). The pH probe
23 was mounted through the closure of the vessel as shown in Fig. 3. The glass combination pH
24 probe was designed to operate at pressures up to 6 MPa, and it is capable of being used at
25 temperatures up to 383 K. A pressure transducer was mounted directly on the top of the cell.
26 The system allows real-time readings and storage of pressures during pH measurement. A high
27 pressure magnetic stirrer was used to agitate the test fluids in order to accelerate the process of
28 achieving thermodynamic equilibrium. The cell was surrounded by a cooling jacket connected
29 to a cooling/heating bath for temperature control purposes. A temperature probe was used to
30 monitor the cell temperature. The pH and temperature probes were connected to a controller
31 box that records and displays both pH and temperature.



1

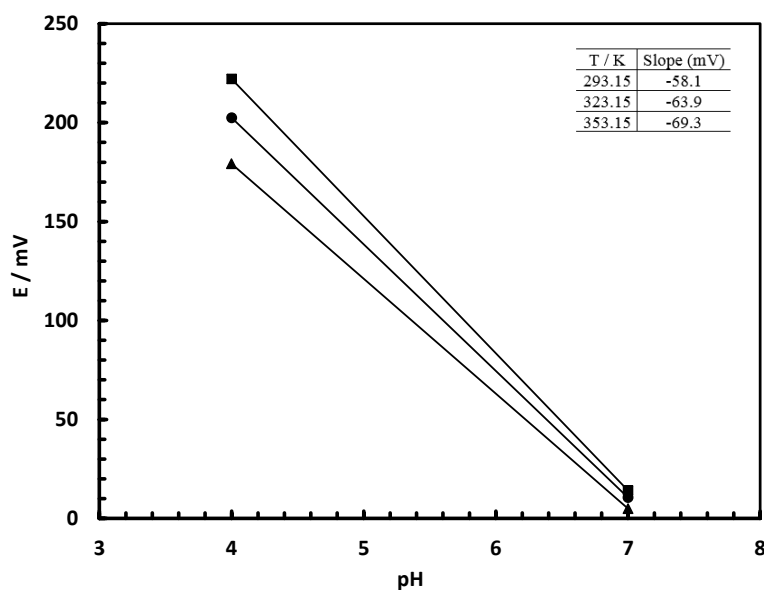
2 **Fig. 3.** Schematic diagram of the high pressure setup for pH measurements using the glass
 3 electrode, 1: pH probe 2: Temperature probe, 3: Magnetic stirrer, 4: Pressure transducer and
 4 V: Valve.

5

6 3.2 Calibration

7 The pressure transducer (ESI technology Ltd) was calibrated against a dead weight pressure
 8 balance .The pressure transducer was designed for pressure up to 6 MPa with the uncertainty
 9 of $U(P) = 0.05$ MPa. The cell temperature was measured by a PT100 temperature probe which
 10 is located on the upper level of the high pressure cell. The uncertainty of the measured
 11 temperature was $U(T) = 0.05$ K. For solutions with low ionic strengths (less than $0.1 \text{ mol} \cdot \text{kg}^{-1}$),
 12 certified buffer solutions (pH 7 & pH 4) were used to calibrate the glass electrode on the
 13 pH_{NBS} scale (Dickson, 1984; Waters and Millero, 2013). The calibration was performed at
 14 atmospheric pressure and three different temperatures ($T = 293.15, 323.15$ and 353.15 K). The
 15 calibration curve for the glass electrode is depicted in Fig. 4. The theoretical slope calculated
 16 using the Nernst equation is close to the slope of the calibration curve for the three isotherms.
 17 A stable reading on the measured e.m.f. was observed after 12 hours for all the calibration
 18 samples (± 0.5 mV).The pH probe was calibrated at every isotherm before starting the pH
 19 measurement. To investigate the influence of pressure on the accuracy of calibration, a buffer
 20 solution with known pH was placed into the high pressure vessel, and nitrogen was injected to

1 reach the maximum operating pressure. No significant change was noticed on the pH value of
 2 the buffer solution (The drift on the measured e.m.f values was less than 1 mv which is equal
 3 to approximately 0.02 pH unit) , showing that pressure does not affect the accuracy of pH
 4 measurements. The expanded relative uncertainty for the pH measurement using the
 5 electrometric technique in the CO₂-H₂O system was found to be $U(\text{pH}, k = 2) = 0.07$ at 95%
 6 confidence level (See appendix for details).



7
 8 **Fig. 4.** The e.m.f values measured by the glass electrode for calibration samples at three
 9 different temperatures. T = 293.15 K (▲), T = 323.15 K (●) and T = 353.15 K (■).

10

11 3.3 Experimental Procedure

12 Prior to starting the experiments, the entire system was cleaned with deionised water and
 13 nitrogen passed through the system to dry the cell, line and valves. Then, the cell was
 14 vacuumed, and deionised water was then injected. The cell was initially filled with about 450
 15 cm³ deionised water. In the next step, CO₂ was introduced to the system. CO₂ was injected
 16 slowly at a low rate into in order to avoid electrode damage. The stirrer was set at a low rate
 17 (rpm < 50). The pressure, temperature values were monitored and recorded every 5 seconds.
 18 Once the pH and pressure remained constant; the value of the pH was recorded. (When
 19 pressure, temperature and pH remained constant for a period of 30 minutes).

1 **4. Modelling Approach**

2 In general, most of the recent models have focused on describing the non-ideal behaviour of
3 the systems that arise at HPHT conditions, including both gaseous solubility and description
4 of chemical equilibria of ionic species in solution. In this work the Cubic-Plus-Association
5 Equation of State (CPA EoS) (Kontogeorgis et al., 2006a, b) was selected for determining the
6 solubility of acid gases (CO₂) in pure water and brines at HPHT conditions and the well-known
7 Pitzer's equations (Pitzer, 1973; Pitzer et al., 1984) were coupled for calculating the deviations
8 to the ideality of each ionic species in the liquid phase.

9 The CPA parameters used for H₂O were taken from Kontogeorgis et al. (1996). Water was
10 modelled using the 4C association scheme (Huang and Radosz, 1990). Critical properties of
11 carbon dioxide were taken from Poling et al. (2001). Binary interaction coefficients (k_{ij} s) within
12 the framework of this EoS were estimated from temperature-dependents functions established
13 in previous works ($k_{\text{CO}_2\text{-H}_2\text{O}}$ (Chapoy et al., 2014; Chapoy et al., 2012)). Carbon dioxide
14 assumed to be able to cross-associate with water (solvation). The effect of salts on the solubility
15 of CO₂ and H₂O are taken into account using the approach proposed by Aasberg-Petersen et
16 al. (1991) and extended to the CPA EoS (Haghighi et al., 2008; Haghighi et al., 2009).

17 The basic equation used to calculate the pH is defined by:

18

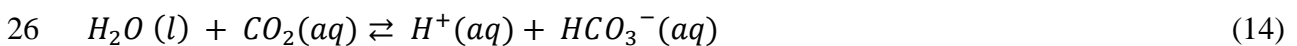
$$19 \text{pH} = -\log_{10}(a_{\text{H}^+}) = -\log_{10}(m_{\text{H}^+}) - \log_{10}(\gamma_{\text{H}^+}) \quad (12)$$

20

21 Where a_{H^+} is the activity (in mol·kg⁻¹), m_{H^+} is the molal concentration (in mol·kg⁻¹), and γ_{H^+}
22 is the activity coefficient (dimensionless) of hydrogen ions.

23 The equilibrium reactions considered for the systems of interest are as follows:

24 Pure water and carbon dioxide phase equilibria,



28 Salts equilibria,



1 The thermodynamic equilibrium constants for these reactions are:

$$2 \quad K_{H_2O} = m_{H^+(aq)} m_{OH^-(aq)} \frac{\gamma_{H^+(aq)} \gamma_{OH^-(aq)}}{a_{H_2O(aq)}} \quad (17)$$

$$3 \quad K_{CO_2,1} = \frac{m_{H^+(aq)} m_{HCO_3^-(aq)}}{m_{CO_2(aq)}} \frac{\gamma_{H^+(aq)} \gamma_{HCO_3^-(aq)}}{\gamma_{CO_2(aq)} a_{H_2O(aq)}} \quad (18)$$

$$4 \quad K_{CO_2,2} = \frac{m_{H^+(aq)} m_{CO_3^{2-}(aq)}}{m_{HCO_3^-(aq)}} \frac{\gamma_{H^+(aq)} \gamma_{CO_3^{2-}(aq)}}{\gamma_{HCO_3^-(aq)}} \quad (19)$$

$$5 \quad K_{NaCl} = m_{Na^+(aq)} m_{Cl^-(aq)} \gamma_{Na^+(aq)} \gamma_{Cl^-(aq)} \quad (20)$$

6 In order to calculate the pH with Eq. (12), the molality (m_{H^+}) and activity coefficient of the
7 hydrogen (γ_{H^+}) ions need to be determined. Whereas the molality of the ionic species is
8 uniquely given by equilibrium constants of pertinent reactions, the activity coefficients are
9 influenced by all the remaining factors.

10 In this work, we have followed the Pitzer's formalism (Pitzer, 1973; Pitzer et al., 1984) to
11 determine the activity coefficients present in Eqs. (17 to 20). The Pitzer's model for electrolytes
12 was derived from the Debye-Hückel's method in which the ionic strength and molality of all
13 ionic species in solution are combined to take into account electrostatic interactions between
14 ionic species. The expressions corresponding to this approach will not be addressed here. A
15 detailed description of this methodology can be referred to Pedersen et al. (2014).

16 The amount of each component in solution is determined by the equilibrium stoichiometric
17 constants and Eqs. (17 to 20). An accurate estimation of these quantities depends on the values
18 considered for the stoichiometric constants. These constants were here determined at each
19 temperature of interest using adjusted mathematical expressions. These adjusted mathematical
20 expressions for water were the recommended expression from the International Association
21 for the Properties of Water and Steam (IAPWS, 2007) and for others from Pedersen et al.
22 (2014). Furthermore, the effect of pressure on these values, excluding water, was neglected.
23 The amount of CO_2 (aq) and the effect of salts on these quantities were calculated with our
24 PVT model based on the CPA EoS.

25 The molality and activity coefficients for each ionic species are calculated together with the
26 resolution of the equation for electro neutrality, considering no mineral precipitation has
27 occurred, defined as follows:

1

$$\begin{aligned}
& m_{\text{H}^+(\text{aq})} - \frac{K_{\text{H}_2\text{O}} a_{\text{H}_2\text{O}(\text{aq})}}{m_{\text{H}^+(\text{aq})} \gamma_{\text{H}^+(\text{aq})} \gamma_{\text{OH}^-(\text{aq})}} - \frac{K_{\text{CO}_2,1} m_{\text{CO}_2(\text{aq})} \gamma_{\text{CO}_2(\text{aq})} a_{\text{H}_2\text{O}(\text{aq})}}{m_{\text{H}^+(\text{aq})} \gamma_{\text{H}^+(\text{aq})} \gamma_{\text{HCO}_3^-(\text{aq})}} - \\
& 2 \frac{K_{\text{CO}_2,2} m_{\text{HCO}_3^-(\text{aq})} \gamma_{\text{HCO}_3^-(\text{aq})}}{m_{\text{H}^+(\text{aq})} \gamma_{\text{H}^+(\text{aq})} \gamma_{\text{CO}_3^{2-}(\text{aq})}} = 0 \tag{21}
\end{aligned}$$

4 The amount of hydrogen ion (m_{H^+}) is calculated by solving Eq. (21) with a Newton-Raphson
5 iteration method and pH determined with Eq. (12).

6 5. Results and Discussion

7 5.1 Spectroscopic Technique – (pK_a and molar absorptivity coefficients of the BPB)

8 **As mentioned before, in the spectroscopic method, the measurements were performed at**
9 **pressures up to 6 MPa and temperatures of 293.15 K and 323.15 K. Some experiments**
10 **were carried out to investigate the e_1 , e_2 , and e_3 rates dependence on pressure,**
11 **temperature and ionic strength. In order to find the influence of pressure on the molar**
12 **absorptivity ratios, firstly, the spectra of the acid ($\text{pH} = 1.5$) and base solutions ($\text{pH} = 7$)**
13 **in the presence of BPB were measured. Then, nitrogen was introduced to the system to**
14 **measure the spectra of the acid and base samples at various pressures (up to 6 MPa). A**
15 **very small dependence of the molar absorptivity ratios to pressure was noticed and not**
16 **accounted for the pH calculations. It should be noted that the molar absorptivity**
17 **coefficients were measured at the calibrated temperatures (293.15 & 323.15 K) as**
18 **indicated in**

19

20 Table 2. To examine the influence of a change in salinity on the molar absorptivity ratios
21 values, the spectra of acid and base solutions with different ionic strengths (1, 2 and 3
22 $\text{mol}\cdot\text{kg}^{-1}$) at fixed temperature and atmospheric pressure were measured. Results revealed that
23 the changes in the e_1 , e_2 , and e_3 values are negligible at different ionic strengths. In terms of
24 the pK_a , various buffer solutions with different ionic strengths were prepared within the range
25 of study. Spectra of all these solutions in the presence of BPB were measured at the
26 atmospheric pressure and two different temperatures. After extracting the λ_1 and λ_2 from the
27 recorded spectra, the pK_a at each ionic strength and isotherm is determined from the intercept
28 of the line with the x-axis using the Eq. (8). It should be noted that all the spectra were
29 baseline corrected between the ranges from 340 to 655 nm before any calculation to
30 overcome baseline shift during measurement. The results for e_1 , e_2 , and e_3 and pK_a values at
31 different temperatures and ionic strengths at atmospheric pressure are listed in

32

33 Table 2.

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Table 2 Measured pK_a , e_1 , e_2 and e_3 of BPB at atmospheric pressure and different temperatures and ionic strengths.

T/K	$m_{NaCl} / mol \cdot kg^{-1}$	pK_a	$U^*(pK_a)$	e_1	$U(e_1)$	e_2	$U(e_2)$	e_3	$U(e_3)$
293.15	0	4.115	± 0.016						
	1	3.772	± 0.017	0.014	± 0.005	2.682	± 0.009	0.022	± 0.005
	2	3.791	± 0.017						
	3	3.882	± 0.019						
0	4.145	± 0.015							
323.15	1	3.751	± 0.015	0.018	± 0.006	2.712	± 0.009	0.0381	± 0.008
	2	3.762	± 0.014						
	3	3.853	± 0.018						

5

* U denotes the uncertainty. Uncertainties calculations are described in details in the appendix section.

6 The pK_a values obtained at 293.15 K and 323.15 for different fluid systems were close to those
7 reported by Shao et al. (2012) (See Supplementary Information). Calculated values for pK_a , e_1 ,
8 e_2 and e_3 were then used to determine the value of pH using the spectra collected for the CO₂-
9 H₂O and CO₂-H₂O-NaCl systems at 298.15 K and 323.15K and pressures up to 6 MPa. The
10 expanded uncertainty for the pH measurement using the spectroscopy technique was found to
11 be 0.09 at 95% confidence level (See the appendix section for details).

12 5.2 Equilibrium pH of CO₂ in Contact with Water and Brines

13 In this section, the results obtained experimentally by both the UV-Vis spectroscopic and
14 electrometric techniques with the available data in the open literature within the range of our
15 study are evaluated and compared. Three isotherms for the CO₂-H₂O system were studied in
16 the temperature range of 293.15 to 353.15 K and pressures up to 5.1 MPa using the
17 electrometric technique. For the spectroscopic technique, the pH was measured in the CO₂-
18 H₂O, and CO₂-H₂O-NaCl systems at pressures up to 6 MPa and temperatures up to 323.15 K.
19 The pH results obtained for both the spectroscopic and electrometric techniques in the CO₂-
20 H₂O system are tabulated in

21 **Table 3 and**

22 Table 4 and depicted in Fig. 5 and Fig. 6 respectively. Moreover, all the results were compared
23 with selected data from the literature. As can be seen in Fig. 5, the results that were measured
24 using the pH probe are in quite good agreement with those obtained by Peng et al. (2013),
25 indicating the consistency of this method for pH measurements in CO₂ saturated water. It is

1 apparent that, for all studied isotherms, the pH value decreases sharply with increasing
 2 pressures while the operating pressure is less than 3 MPa. This reduction in pH values is less
 3 for pressure higher than 3 MPa. For instance, in this study, pH decreased from 3.88 to 3.41
 4 when the pressure was increased from 0.23 to 2.15 MPa at 323.15 K. However the pH value at
 5 the same temperature reduced by 0.15 units from 3.44 MPa to 5.07 MPa. This reduction in the
 6 pH value is expected to be less at higher pressures, which can be described by the lower
 7 solubility of CO₂ in the liquid phase. A similar trend was observed by Peng et al. (2013) at T
 8 = 323.0 K, pH decreased by 0.40 units from 0.38 to 2.43 MPa due to the high solubility of CO₂
 9 in this range of pressure, whereas the pH value fell by 0.22 units while the pressure was
 10 increased from 2.43 to 6.23 MPa. Moreover, the results obtained in this study for the
 11 spectroscopic technique were compared with the available literature data for the same method
 12 within the range of the P–T conditions studied. As illustrated in Fig. 6, the general trend in this
 13 method is in good agreement with the data that reported by Shao et al. (2012) and Parton et al.
 14 (2002). The measured pH values in this work were close to values obtained by Shao et al.
 15 (2012), however, pH results reported at a pressure higher than 2 MPa and T = 308.15 K by
 16 Parton et al. (2002) are about 0.2 units lower than values measured in this study at T= 293.15
 17 K. This difference is even higher as they measured the pH at slightly higher temperature (pH
 18 values at T = 293.15 K in this study was compared to pH values at T = 308.15 K) which results
 19 in an increase in pH value due to the lower solubility of CO₂ at higher temperature. This
 20 difference in pH value may be attributed either to the procedure that was followed to calculate
 21 the pH or error of measurement. Overall, results obtained in this study by either the
 22 spectroscopic and electrometric methods for the CO₂-H₂O system follow a similar trend, fast
 23 drop in pH value while pressure is less than 3 MPa and lower changes in pH values at a pressure
 24 higher than 3 MPa.

25 **Table 3** Measured and predicted pH values (electrometric technique) in the CO₂-H₂O system.

<i>T/K</i>	<i>P/MPa</i>	<i>pH</i> <i>(Experimental)</i>	<i>pH</i> <i>(Model)</i>
293.15	0.23	3.78	3.77
	0.74	3.53	3.52
	1.45	3.39	3.37
	2.15	3.32	3.29
	3.44	3.23	3.20
	5.07	3.18	3.13
323.15	0.23	3.88	3.86
	0.74	3.61	3.60
	1.45	3.48	3.46
	2.15	3.41	3.38
	3.44	3.32	3.28
	5.07	3.17	3.20

353.15	0.23	4.00	4.02
	0.74	3.70	3.73
	1.45	3.54	3.57
	2.15	3.46	3.49
	3.44	3.36	3.39
	5.07	3.28	3.31

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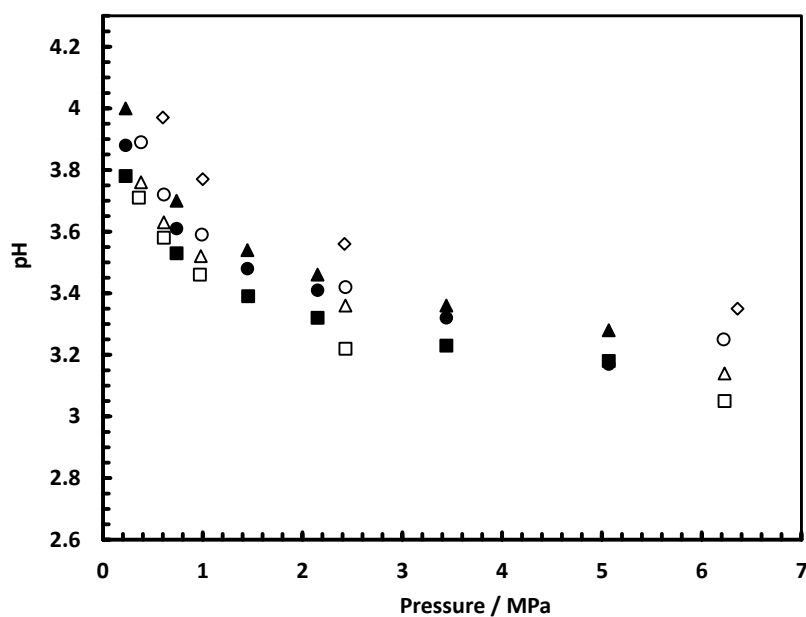
3 **Table 4** Measured and predicted pH values (spectroscopic technique) in the CO₂-H₂O system.

<i>T/K</i>	<i>P/MPa</i>	<i>pH</i> (<i>Experimental</i>)	<i>pH</i> (<i>Model</i>)
<i>T = 293.15</i>	0.60	3.58	3.65
	1.51	3.44	3.45
	2.25	3.36	3.27
	2.94	3.28	3.31
	4.41	3.19	3.23
	5.24	3.17	3.20
<i>T = 323.15</i>	1.14	3.59	3.51
	2.16	3.46	3.38
	3.25	3.40	3.29
	4.02	3.31	3.25
	5.51	3.27	3.19

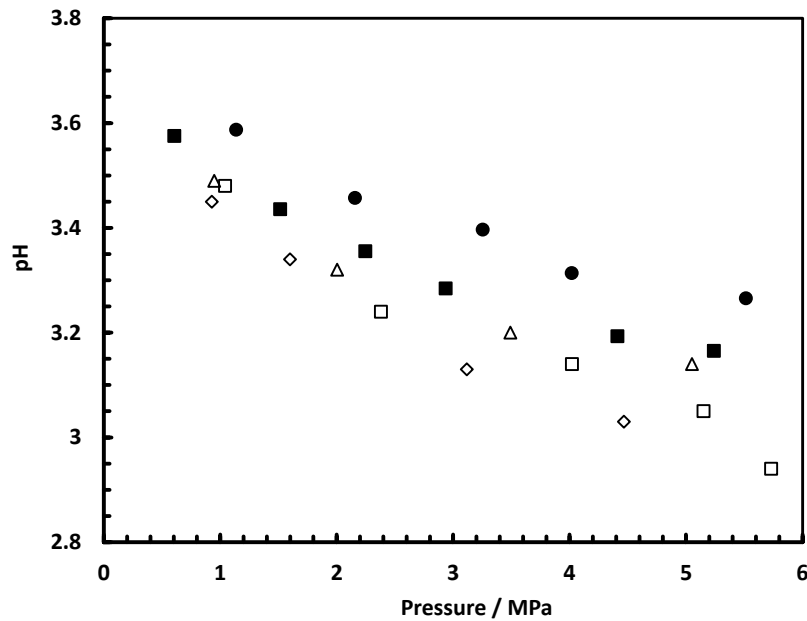
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5 Moreover, all the results were compared with selected data from the literature. As can be seen
6 in Fig. 5, the results that were measured using the pH probe are in quite good agreement with
7 those obtained by Peng et al. (2013), indicating the consistency of this method for pH
8 measurements in CO₂ saturated water. It is apparent that, for all studied isotherms, the pH value
9 decreases sharply with increasing pressures while the operating pressure is less than 3 MPa.
10 This reduction in pH values is less for pressure higher than 3 MPa. For instance, in this study,
11 pH decreased from 3.88 to 3.41 when the pressure was increased from 0.23 to 2.15 MPa at
12 323.15 K. However the pH value at the same temperature reduced by 0.15 units from 3.44 MPa
13 to 5.07 MPa. This reduction in the pH value is expected to be less at higher pressures, as the
14 changes in the solubility of carbon dioxide is greater relatively at low pressure (at 323.15 K a
15 tenfold increase in the CO₂ solubility is observed from 0.23 to 2.15 MPa, whereas from 3.44
16 to 5.07 MPa a 40% increase in solubility is observed). A similar trend was observed by Peng
17 et al. (2013) at T = 323.0 K, pH decreased by 0.40 units from 0.38 to 2.43 MPa due to the high
18 solubility of CO₂ in this range of pressure, whereas the pH value fell by 0.22 units while the
19 pressure was increased from 2.43 to 6.23 MPa. Moreover, the results obtained in this study for
20 the spectroscopic technique were compared with the available literature data for the same
21 method within the range of the P–T conditions studied. As illustrated in Fig. 6, the general

1 trend in this method is in good agreement with the data that reported by Shao et al. (2012) and
 2 Parton et al. (2002). The measured pH values in this work were close to values obtained by
 3 Shao et al. (2012), however, pH results reported at a pressure higher than 2 MPa and T = 308.15
 4 K by Parton et al. (2002) are about 0.2 units lower than values measured in this study at T=
 5 293.15 K. This difference is even higher as they measured the pH at slightly higher temperature
 6 (pH values at T = 293.15 K in this study was compared to pH values at T = 308.15 K) which
 7 results in an increase in pH value due to the lower solubility of CO₂ at higher temperature. This
 8 difference in pH value may be attributed either to the procedure that was followed to calculate
 9 the pH or error of measurement. Overall, results obtained in this study by either the
 10 spectroscopic and electrometric methods for the CO₂-H₂O system follow a similar trend, fast
 11 drop in pH value while pressure is less than 3 MPa and lower changes in pH values at a pressure
 12 higher than 3 MPa.



13
 14 **Fig. 5.** pH of CO₂ saturated solutions as a function of pressure in the CO₂-H₂O system (Electrometric technique). Filled symbols represent experimental data measured in this work :
 15 T = 293.15 K (■), T = 323.15 K (●) and T = 353.15 K (▲). Empty symbols represent the data
 16 measured by Peng et al. (2013): T = 308.3 K (□), T = 323.0 K (△), T = 343.0 K (○) and T =
 17 368.1 K (◇).
 18

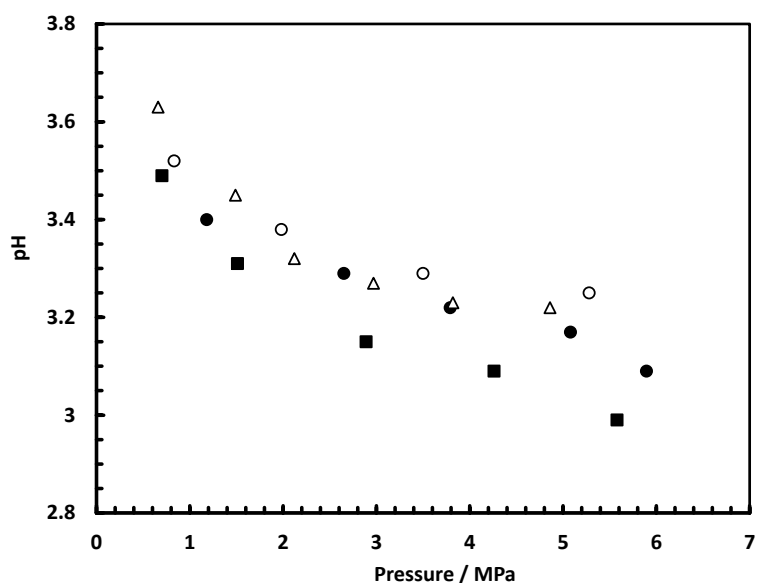


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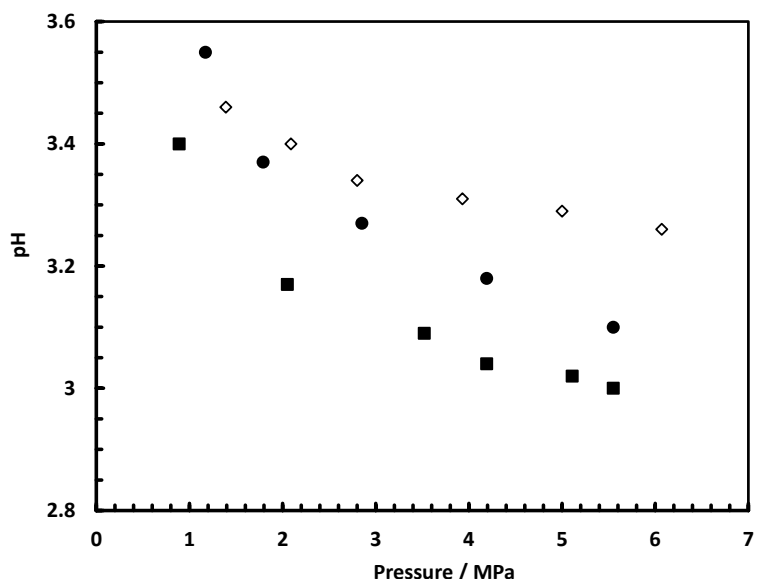
2 **Fig. 6.** pH of CO₂ saturated solutions as a function of pressure in the CO₂-H₂O system
3 (Spectroscopic technique). Filled symbols represent experimental data measured in this work:
4 T = 293.15K (■) and T = 323.15 K (●). Empty symbols represent the data measured by Schaefer
5 et al. (2003), T = 295.15 (□) ; Parton et al. (2002), T = 308.15 K (◇) and Shao et al. (2012),
6 T = 313.0 K (△).

7 Some limited data are available for pH in CO₂-brine systems at high pressures. Crolet and
8 Bonis (1983) reported the pH measurements for the CO₂-H₂O-0.5m NaCl system at
9 temperatures from 289.15 to 347.15 K and pressures up to 6 MPa. Shao et al. (2012) and Schaefer
10 et al. (2003) measured the pH in CO₂-brine systems at temperatures up to 366.15 K and
11 pressures up to 20 MPa using spectroscopic and electrometric methods respectively. In the
12 current study, pH was measured for aqueous solutions with different ionic strengths (1, 2 and
13 3 mol·kg⁻¹) at temperatures up to 323.15 K and pressures up to 6 MPa. Measured pH values
14 from this study and from those reported in the literature for solutions with different ionic
15 strengths are illustrated in Fig. 7 through Fig. 9. As can be seen from Fig. 7 and Fig. 8, for CO₂-
16 H₂O-1m NaCl and CO₂-H₂O-2m NaCl systems, the measured pH values are lower by about
17 0.2 to 0.3 unit than those measured by Schaefer et al. (2003). Furthermore, it is clear from the
18 aforementioned figures that the pH values reported by Schaefer et al. (2003) are increased with
19 an increase in salinity. This opposite trend and also the large difference between the measured
20 pH values from this study and those measured by Schaefer et al. (2003) could be due to the
21 occurrence of liquid junction potential between the liquid inside and outside glass electrode
22 which produces some errors in pH measurement. Due to the presence of a high concentration
23 of NaCl in the studied solutions, Na⁺ ions can diffuse into the liquid junction and produce an

- 1 undesirable potential difference between the filled solution inside the glass electrode and the
- 2 liquid outside of the glass electrode, causing offset in the pH value.

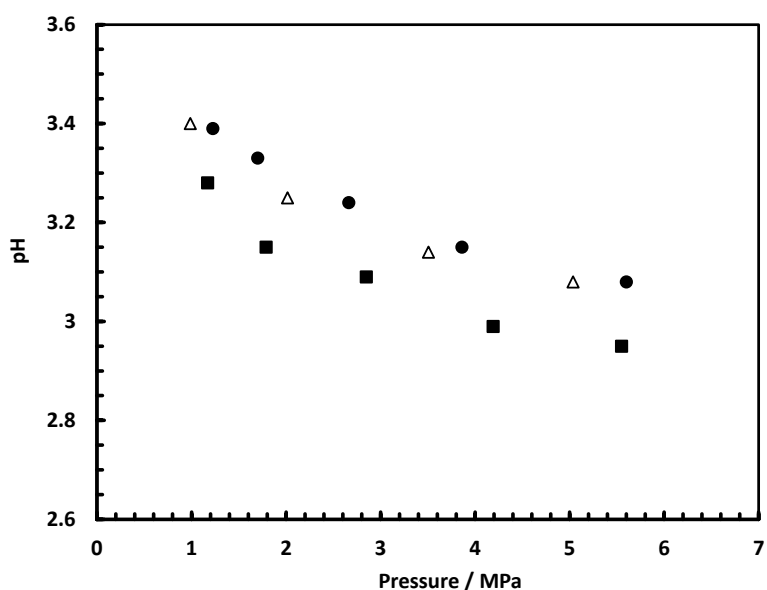


3
 4 **Fig. 7.** pH of CO₂ saturated solutions as a function of pressure in the CO₂-H₂O-NaCl system.
 5 Filled symbols represent experimental data measured in this work using spectroscopic
 6 technique ($m = 1 \text{ mol}\cdot\text{kg}^{-1}$): $T = 293.15\text{K}$ (\square) and $T = 323.15\text{K}$ (\bullet). Empty symbols represent
 7 the data measured using the electrometric technique by Schaef et al. (2003), ($m = 1.03 \text{ mol}\cdot\text{kg}^{-1}$):
 8 $T = 295.15\text{K}$ (\triangle) $T = 313.15\text{K}$ (\circ).



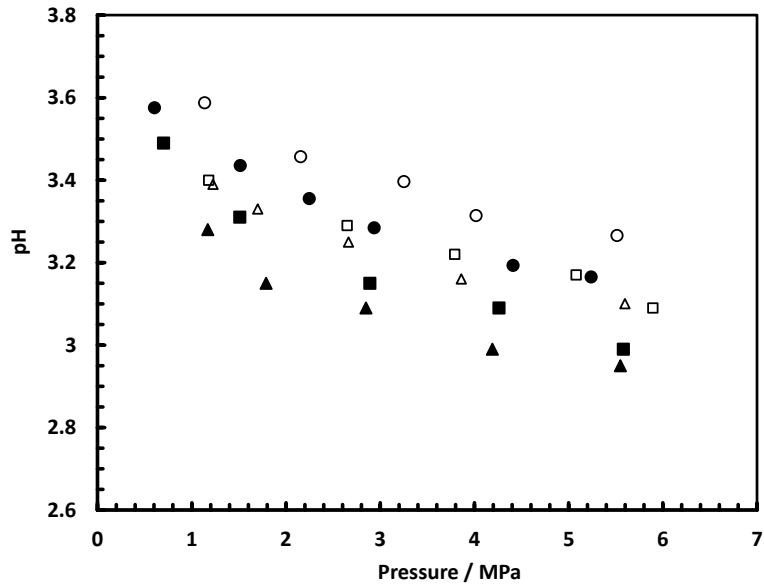
9
 10 **Fig. 8.** pH of CO₂ saturated solutions as a function of pressure in the CO₂-H₂O-NaCl system.
 11 Filled symbols represent experimental data measured in this work using spectroscopic
 12 technique ($m = 2 \text{ mol}\cdot\text{kg}^{-1}$): $T = 293.15\text{K}$ (\blacksquare) and $T = 323.15\text{K}$ (\bullet). Empty symbols represent
 13 the data measured using the electrometric technique by Schaef et al. (2003), ($m = 2.11 \text{ mol}\cdot\text{kg}^{-1}$):
 14 $T = 295.15\text{K}$ (\diamond).

1 As depicted in Fig. 9, our measured pH values at $T = 323.15$ K in the $\text{CO}_2\text{-H}_2\text{O-3m NaCl}$
2 system is close with data of Shao et al. (2012) at temperature of 313.15 K.



3
4 **Fig. 9.** pH of CO_2 saturated solutions as a function of pressure in the $\text{CO}_2\text{-H}_2\text{O-NaCl}$ system.
5 Filled symbols represent experimental data measured in this work using spectroscopic
6 technique ($m = 3 \text{ mol}\cdot\text{kg}^{-1}$): $T = 293.15\text{K}$ (■) and $T = 323.15 \text{ K}$ (●). Empty symbols represent
7 the data measured using the spectroscopic technique by Shao et al. (2012) ($m = 3 \text{ mol}\cdot\text{kg}^{-1}$): T
8 $= 313.15 \text{ K}$ (Δ).

9 It is clear from Fig. 10 that the salinity increase leads to a reduction of pH in acidified brine
10 solutions over the entire pressure range at a constant temperature. This behaviour was more
11 pronounced while the concentration of NaCl changed from 1 to $3 \text{ mol}\cdot\text{kg}^{-1}$. For instance, as
12 shown in Fig. 10 and Table 5, the pH drops by about 0.1 units at a pressure of about 5.5 MPa
13 and temperature of 293.15 K. A similar trend was observed by Crolet and Bonis (1983), they
14 measured the pH in CO_2 -brine systems (0 to $3.87 \text{ mol}\cdot\text{kg}^{-1}$) at 0.1 MPa and $T = 298.15 \text{ K}$, it
15 was observed that the pH decreases from 3.76 to 3.57 when the ionic strength increases from
16 1.03 to $3.87 \text{ mol}\cdot\text{kg}^{-1}$. It is known that CO_2 solubility decreases with the increase of NaCl
17 concentration in the solution but the activity coefficient (γ_{H^+}) increases significantly with the
18 increase of NaCl concentration in the solution, causing a drop in the pH value (See
19 Supplementary Information for details). However, an opposite trend was noticed by Shao et al.
20 (2012). They showed that the pH value increases in the CO_2 -brine systems from 2.94 to 2.98
21 as the salt concentration increases from 1 to $3 \text{ mol}\cdot\text{kg}^{-1}$ at a pressure of 10 MPa and $T = 313.15$
22 K.



1

2 **Fig. 10.** Effect of variation in ionic strength on the pH value of the CO₂ saturated solutions as
 3 a function of pressure (spectroscopic technique). T = 293.15 K; 0m NaCl (●), 1m NaCl (■)
 4 and 3m NaCl (▲). T =323.15 K; 0m NaCl (○), 1m NaCl (□) and 3m NaCl (△).

5 **Table 5** Measured and predicted pH value (spectroscopic technique) for different CO₂
 6 saturated brine systems.

T/K	P/MPa	$m_{NaCl} (mol \cdot kg^{-1})$	pH (Experimental)	pH (Model)
$T = 293.15$	0.70	1	3.49	3.42
	1.51	1	3.31	3.25
	2.89	1	3.15	3.12
	4.26	1	3.09	3.05
	5.58	1	3.04	3.00
$T = 323.15$	1.18	1	3.40	3.42
	2.65	1	3.29	3.25
	3.79	1	3.22	3.18
	5.08	1	3.17	3.13
	5.90	1	3.12	3.10
$T = 293.15$	0.89	2	3.40	3.28
	2.05	2	3.17	3.10
	3.52	2	3.09	3.00
	4.19	2	3.04	2.97
	5.55	2	3.00	2.90
$T = 323.15$	0.85	2	3.55	3.43
	1.57	2	3.37	3.30
	2.99	2	3.27	3.17
	4.45	2	3.18	3.10
	5.63	2	3.12	3.06
$T = 293.15$	1.17	3	3.28	3.14
	1.79	3	3.15	3.05
	2.85	3	3.09	2.96
	4.19	3	2.99	2.89
	5.55	3	2.95	2.84
$T = 323.15$	1.23	3	3.39	3.30
	1.70	3	3.33	3.23
	2.66	3	3.24	3.14
	3.86	3	3.15	3.07
	5.60	3	3.08	3.00

1

2 **5.3 Modelling Results**

3 The pH predictions calculated with our model were evaluated against literature data and these
 4 new measurements. Summary of the calculated AAD value (Average of all absolute deviations)
 5 between the predicted pH values by the model and the available experimental data in the open
 6 literature as well as the experimental data obtained in this study are listed in Table 6.

7

8 **Table 6** Summary of the calculated AAD value between the pH measured and predicted values
 9 in various fluid systems.

System	Data Source	T/K	P/MPa	NP ^a	AAD ^b
CO ₂ -H ₂ O	Peng et al. (2013)	308.3 to 423.2	0 to 15	37	0.04
	Shao et al. (2012)	298.15 to 366.15	0 to 20	18	0.03
	Truche et al. (2016)	423.15 to 553.15	0 to 15	14	0.06
	Schaef et al. (2003)	295.15 to 343.15	0 to 11	12	0.19
	Meysami et al. (1992)	305.15 to 315.15	0 to 35	26	0.06
	Toews et al. (1995)	298.15 to 343.15	7 to 20	20	0.24
	Parton et al. (2002)	308.15	0 to 9	6	0.09
	Rosenqvist et al. (2012)	294	0 to 1	3	0.07
	This work, ET ^c	293.15 to 353.15	0 to 6	18	0.03
	This work, ST ^d	293.15 to 323.15	0 to 5.5	11	0.06
CO ₂ -H ₂ O-1.02 m NaCl	Schaef et al. (2003)	295.15 to 343.15	0 to 10	25	0.14
CO ₂ -H ₂ O-1m NaCl	This work, ST	293.15 to 323.15	0 to 6	10	0.04
CO ₂ -H ₂ O-2.11m NaCl	Schaef et al. (2003)	295.15 to 343.15	0 to 11	9	0.32
CO ₂ -H ₂ O-2m NaCl	This work, ST	293.15 to 323.15	0 to 6	11	0.09
CO ₂ -H ₂ O-3m NaCl	Shao et al. (2012)	298.15 to 366.15	0 to 20	18	0.05
	This work, ST	293.15 to 323.15	0 to 6	10	0.10

10 ^a Number of points

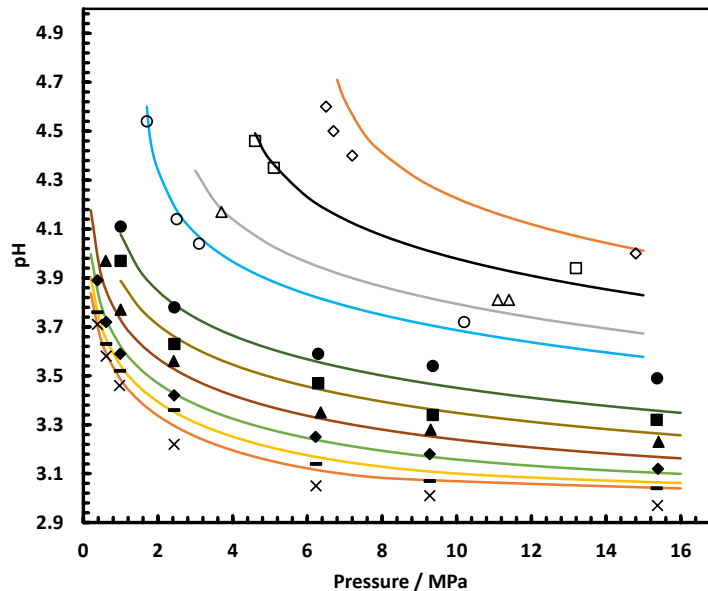
11 ^b $AAD = \frac{1}{NP} * \sum_1^{NP} |(pH_{Model} - pH_{Exp})|$

12 ^c Electrometric Technique13 ^d Spectroscopic Technique

14

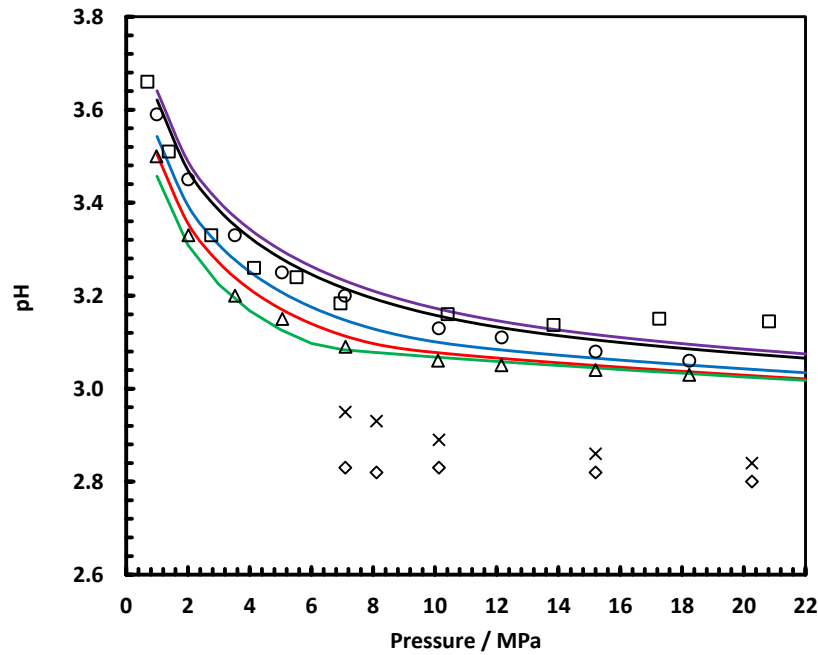
15 It can be seen from Table 6 the predicted pH values by the model provide a good representation
 16 of the measured data at pressures up to 6 MPa with an average absolute deviations (AAD) of
 17 0.03 pH units for the electrometric method in the temperature ranges from 293.15 to 353.15 K
 18 and AAD of 0.06 pH units for the spectroscopic method in temperatures up to 323.15 K.

1 Moreover, the accuracy of the model was investigated against values reported in the literature
 2 for pH in the CO₂-H₂O system at elevated temperatures and pressures. As can be seen from
 3 Fig. 11 and Fig. 12, the pH appears to abruptly decrease with pressure increase while this
 4 reduction in pH value at pressures higher than 10 MPa is very small. The model is able to
 5 predict the pH value in CO₂ saturated water system with an AAD of 0.04, 0.03 and 0.06 pH
 6 units to experimental points that were reported by Peng et al. (2013), Truche et al. (2016) and
 7 Shao et al. (2012) respectively at pressures up to 20 MPa and temperatures up to 553 K.
 8 Furthermore, the measured pH values by Toews et al. (1995) are about 0.2-0.3 units lower than
 9 pH values predicted by the model at same P-T conditions (see Fig. 12, AAD = 0.24 pH units).
 10 A possible reason behind this large difference between the model and measured pH values is
 11 because the impact of pressure and ionic strength were not considered in their calibration
 12 procedure. They reported the pH values for pressures between 7 MPa and 20 MPa in the CO₂-
 13 H₂O system. As can be seen in Fig. 12, the changes in pH are very small at pressures higher
 14 than 7 MPa (about 0.03 units). Similar behaviour was observed in the model, the pH decreased
 15 by about 0.06 units while the pressure increases from 7 MPa to 20 MPa at a temperature of
 16 298.15 K. This behaviour is closely linked to the amount of molecular CO₂ in the liquid phase
 17 (x_{CO₂}).



18

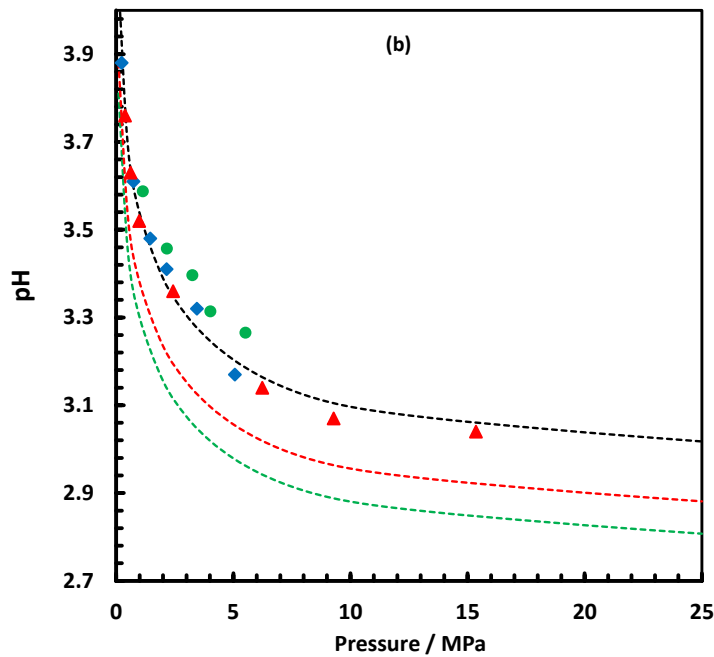
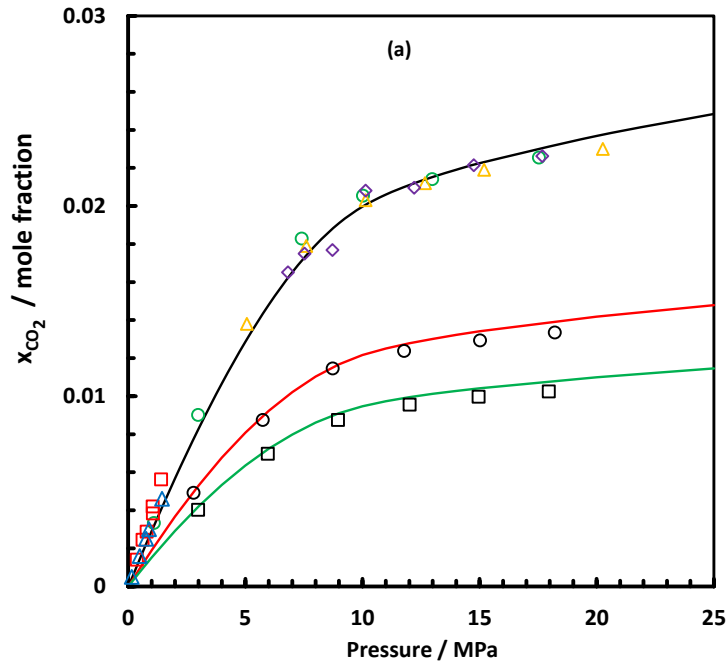
19 **Fig. 11.** pH of CO₂ saturated solutions as a function of pressure in the CO₂-H₂O system.
 20 Symbols represent experimental data from the literature: Peng et al. (2013) : T = 308.3 K (✕),
 21 T = 323 K (→), T = 343 (◆) T = 368.1 (▲) T = 398.3 (■) T = 423.2 (●). Empty symbols
 22 represent results that obtained by Truche et al. (2016) : T = 473.15 K (○), T = 493.15 K (△),
 23 523.15 K (□) and 553.15 K (◇). Solid lines represent the prediction from the model: T = 308.30
 24 K (→), T = 323 K (→), T = 343 (→) T = 368.1 (→) T = 398.3 (→) T = 423.2 (→) T = 473.15 K
 25 (→), T = 493.15 K (→), 523.15 K (→) and 553.15 K (→).



1

2 **Fig. 12.** pH of CO₂ saturated solutions as a function of pressure in the CO₂-H₂O system. Empty
 3 symbols represent experimental data from the literature: Meyssami et al. (1992), T = 315.15 K
 4 (□); Shao et al. (2012), T = 348.15 K (○); Shao et al. (2012), T = 313.15 K (△); Toews et al.
 5 (1995), T = 343.15 (×) and Toews et al. (1995), T = 298.15 (◇). Solid lines represent the
 6 prediction from the model: T = 298.15 (—), T = 313.15 K (—), T = 323.15 K (—), T = 343.15
 7 (—) and T = 348.15 (—).

8 In Fig. 13, one can see a steep increase in the composition of CO₂ for pressures up to 10 MPa
 9 and a moderate rise in this quantity for higher pressures. Such singularity produces small
 10 changes in the concentration of the CO₂ in the aqueous phase. As depicted in Fig. 13, the pH
 11 values seem to level off for higher pressures. We also plot the pH of the CO₂-H₂O system as
 12 a function of $-\log_{10}(x_{\text{CO}_2})$ (Fig. 14). A linear relationship was observed between pH and $-\log(x_{\text{CO}_2})$
 13 for the CO₂ saturated water system.



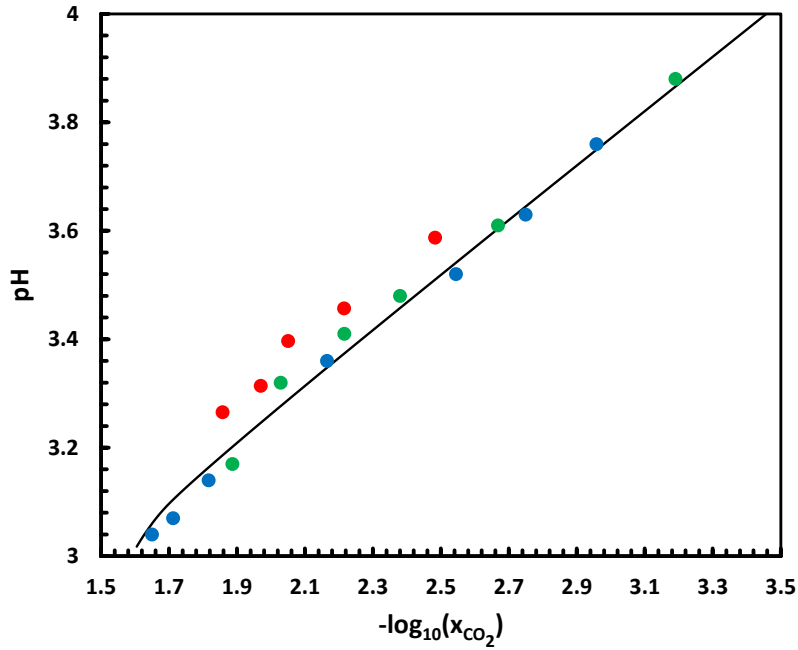
1

2

3 **Fig. 13.** x_{CO_2} -pressure (a) and pH-pressure (b) diagrams of the CO_2 - H_2O and CO_2 - H_2O - NaCl
 4 systems at temperature of 323.15 K. Empty symbols represent experimental mole fraction data
 5 of CO_2 in aqueous phase: 0 m NaCl (\square), Zaalishvili (1940); 0 m NaCl (\triangle) Zawisza and
 6 Malesinska (1981); 0 m NaCl (\circ), Hou et al. (2013a); 0 m NaCl (\triangle), Wiebe (1941); 0 m NaCl
 7 (\diamond), Briones et al. (1987); 2.5 and 4 m NaCl (\circ and \square), Hou et al. (2013b). Filled symbols
 8 represent experimental pH data : 0 m NaCl (\blacktriangle), Peng et al. (2013); 0 m NaCl (\bullet), this work
 9 (Spectroscopic technique) and 0 m NaCl (\blacklozenge), this work (Electrometric technique). Dashed and
 10 solid lines represent the pH and x_{CO_2} predictions at various temperatures from the model
 11 respectively (0 m NaCl (black), 2.5 m NaCl (red) and 4 m NaCl (green)).

12

13



1

2 **Fig. 14.** pH of the CO₂-H₂O system as a function of $-\log_{10}(x_{\text{CO}_2})$ at a temperature of 323.15 K.
 3 ●, Peng et al. (2013); ●, this work (Spectroscopic technique) and ●, this work (Electrometric
 4 technique).

5 The capability of the model to predict the effect of salts was also investigated. The deviation
 6 between the model and experimental data for various CO₂-brine systems are listed in Table 5.
 7 The measured pH values in this work for saline systems yield a good agreement with those
 8 obtained by the model. The model can reproduce the pH values in the CO₂-H₂O-1m NaCl,
 9 CO₂-H₂O-2m NaCl and CO₂-H₂O-3m NaCl systems with AAD of about 0.04-0.10 pH units.
 10 Similar to the CO₂-H₂O system, there is a linear dependence among pH and $-\log_{10}(x_{\text{CO}_2})$ in the
 11 CO₂ saturated brine systems (Fig. 15). Furthermore, low deviations were observed between the
 12 model and measured pH points by Shao et al. (2012) in the CO₂-H₂O-3m NaCl system with an
 13 AAD of 0.05 pH units., also indicating the adequacy of the model to predict the pH values at
 14 a variety of pressure and temperature conditions in highly concentrated NaCl brines. Overall,
 15 the model is performing well at various temperature and pressure ranges and various NaCl
 16 concentrations.

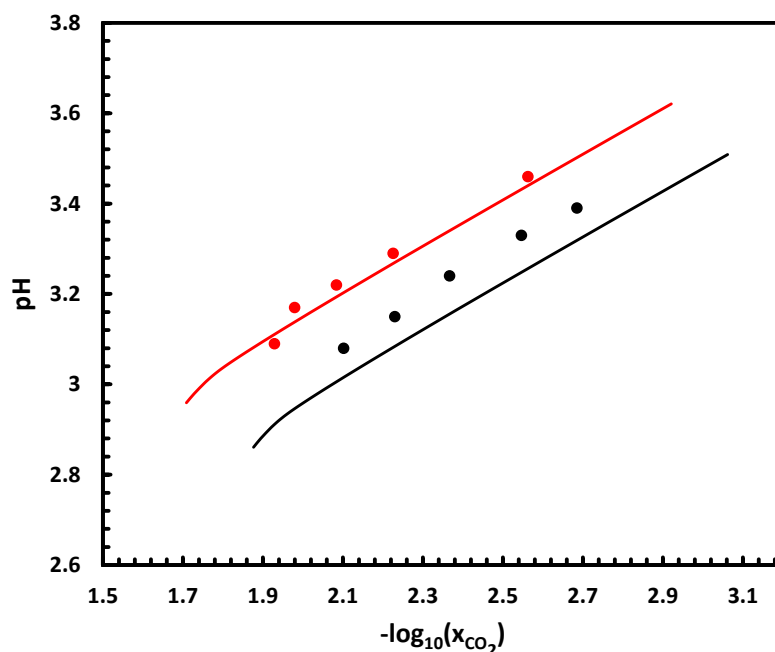
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18

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20

21 2



1
2

3 **Fig. 15.** pH of the CO₂-H₂O-NaCl systems as a function of $-\log_{10}(x_{\text{CO}_2})$ at a temperature of
4 323.15 K (This work, spectroscopic technique). ●, 1m NaCl and ●, 3m NaCl.

5 **6. Conclusions**

6 Two experimental setups based on either electrical or spectroscopic methods were employed
7 to measure the pH at various pressures and temperatures. The pH values were measured for the
8 CO₂-H₂O, CO₂-H₂O-NaCl (NaCl: 1 to 3m) systems at pressures up to 6 MPa and temperatures
9 up to 353.15K. Good agreement was obtained between literature data and measured values. It
10 was shown that the pH of all the studied systems starts to decrease with increasing pressure at
11 each isotherm. According to the spectroscopic, electrometric and modelling results this
12 reduction is sharp while the pressure is less than 3 MPa. This drop in pH value starts to reduce
13 gradually at pressures higher than 3 MPa. Such trends can be explained by the change in
14 solubility of CO₂ in the aqueous phase at different pressure conditions. Moreover, the effect of
15 variation in salinity on pH value was also investigated. It was observed that the pH of CO₂-
16 saturated solutions decreases with an increase in the concentration of NaCl in the solution while
17 the pressure and temperature kept constant.

18 Furthermore, we described and evaluated a model that uses a robust thermodynamic basis for
19 describing the solubility of gases in the liquid phase and Pitzer's theory for determining the
20 activity coefficients of the ionic species involved. This approach proved to be capable of
21 describing the chemical equilibria of the ionic species in the liquid phase under HPHT

1 conditions and in systems of interest. The model was tested in concentrated NaCl solutions
 2 under CO₂ pressure at realistic industrial operating temperatures. The algorithm presented in
 3 this work is prepared to account for the effect of carbon dioxide and the following ionic species:
 4 H⁺, Na⁺, OH⁻, Cl⁻, HCO₃⁻ and CO₃²⁻. All the experimental results for different fluid systems
 5 were compared with results that were reproduced by the model to investigate the capability of
 6 developed model for different fluid systems. A good agreement between predictions and
 7 experimental data is observed. It is noteworthy to mention very small deviations were found at
 8 different NaCl concentration, demonstrating the ability of the model to predict the pH in CO₂-
 9 brine solutions.

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 12 Engineering, Heriot-Watt University and the CTP laboratory of MINES ParisTech. The JIP
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 14 which is gratefully acknowledged. The author would also like to thank Jim Allison for his
 15 assistance.

16 **Appendix**

17 This section defines the calculations undertaken for uncertainty analysis for both the
 18 spectroscopy and electrometric techniques.

19 **1. Uncertainties calculation for the spectroscopy technique:**

20 As mentioned in the manuscript, for the spectroscopy technique, Eq. 8 was used to calculate
 21 the pH at various pressure and temperature conditions. Details of calculations used to determine
 22 the uncertainties are explained in the following sections for the spectroscopy technique.

23 **a) The e₁, e₂, e₃ and R uncertainties**

24 To calculate the uncertainty of the pH, it is required to first determine the uncertainty of the e₁,
 25 e₂, e₃, $R_{\lambda_1}^{\lambda_2}$ and pK_a. Eqs. (23, 25 and 27) were used to calculate the uncertainty of e₁, e₂, e₃
 26 respectively.

$$27 \quad \frac{U_{e_1}}{e_1} = \sqrt{\left(\frac{\Delta e_A^{\lambda_2}}{e_A^{\lambda_2}}\right)^2 + \left(\frac{\Delta e_A^{\lambda_1}}{e_A^{\lambda_1}}\right)^2} \quad (22)$$

$$28 \quad U_{e_1} = e_1 \cdot \sqrt{\left(\frac{\Delta e_A^{\lambda_2}}{e_A^{\lambda_2}}\right)^2 + \left(\frac{\Delta e_A^{\lambda_1}}{e_A^{\lambda_1}}\right)^2} \quad (23)$$

$$1 \quad \frac{U_{e_2}}{e_2} = \sqrt{\left(\frac{\Delta e_B^{\lambda_2}}{e_B^{\lambda_2}}\right)^2 + \left(\frac{\Delta e_A^{\lambda_1}}{e_A^{\lambda_1}}\right)^2} \quad (24)$$

$$2 \quad U_{e_2} = e_2 \cdot \sqrt{\left(\frac{\Delta e_B^{\lambda_2}}{e_B^{\lambda_2}}\right)^2 + \left(\frac{\Delta e_A^{\lambda_1}}{e_A^{\lambda_1}}\right)^2} \quad (25)$$

$$3 \quad \frac{U_{e_3}}{e_3} = \sqrt{\left(\frac{\Delta e_B^{\lambda_1}}{e_B^{\lambda_1}}\right)^2 + \left(\frac{\Delta e_A^{\lambda_1}}{e_A^{\lambda_1}}\right)^2} \quad (26)$$

$$4 \quad U_{e_3} = e_3 \cdot \sqrt{\left(\frac{\Delta e_B^{\lambda_1}}{e_B^{\lambda_1}}\right)^2 + \left(\frac{\Delta e_A^{\lambda_1}}{e_A^{\lambda_1}}\right)^2} \quad (27)$$

5

6 Where,

$$7 \quad \Delta e_A^{\lambda_2} = \Delta e_A^{\lambda_1} = \Delta e_B^{\lambda_2} = \Delta e_B^{\lambda_1} = \sqrt{(u_{system})^2 + (u_{repeatability})^2} \quad (28)$$

8 Therefore, U_{e_1} , U_{e_2} , U_{e_3} were calculated at different temperatures and ionic strengths using
 9 equations described in above. The $u_{repeatability}$ for each parameter is equivalent to the standard
 10 deviation of five measurements. Moreover, the response of the e_1 , e_2 and e_3 to pressure were
 11 less than the uncertainty of the measurement.

12 Eq. (30) used to calculate the uncertainty of the $R_{\lambda_1}^{\lambda_2}$.

$$13 \quad \frac{U_{R_{\lambda_1}^{\lambda_2}}}{R_{\lambda_1}^{\lambda_2}} = \sqrt{\left(\frac{\Delta A(\lambda_2)}{A(\lambda_2)}\right)^2 + \left(\frac{\Delta A(\lambda_1)}{A(\lambda_1)}\right)^2} \quad (29)$$

$$14 \quad U_{R_{\lambda_1}^{\lambda_2}} = R_{\lambda_1}^{\lambda_2} \cdot \sqrt{\left(\frac{\Delta A(\lambda_2)}{A(\lambda_2)}\right)^2 + \left(\frac{\Delta A(\lambda_1)}{A(\lambda_1)}\right)^2} \quad (30)$$

15 Where,

$$16 \quad \Delta A(\lambda_2) = \Delta A(\lambda_1) = \sqrt{(u_{system})^2 + (u_{repeatability})^2} \quad (31)$$

17 **b) pK_a uncertainty**

18 This section describes in detail the calculations undertaken to determine the uncertainty of the
 19 pK_a. Eq. (32) used to calculate the pK_a using different standard buffer solutions.

$$20 \quad pK_a = pH - \log \frac{R_{\lambda_1}^{\lambda_2} - e_1}{e_2 - R_{e_3}} \quad (32)$$

1 Eq. (32) was split into two parts ($pH, \log \frac{R_{\lambda_1}^{\lambda_2} - e_1}{e_2 - Re_3}$) for ease of calculation. To simplify the
 2 second part of the Eq. (32), C_1, C_2, C_3 and C_4 were defined as follows:

$$3 \quad C_1 = R_{\lambda_1}^{\lambda_2} - e_1 \quad (33)$$

$$4 \quad C_2 = e_2 - Re_3 \quad (34)$$

$$5 \quad C_3 = \frac{C_2}{C_1} \quad (35)$$

$$6 \quad C_4 = \log C_3 \quad (36)$$

7 The uncertainty of C_1, C_2, C_3 and C_4 were then calculated using the following equations:

$$8 \quad U_{C_1} = \sqrt{(\Delta R_{\lambda_1}^{\lambda_2})^2 + (\Delta e_1)^2} \quad (37)$$

$$9 \quad U_{C_2} = \sqrt{(\Delta e_2)^2 + (\Delta Re_3)^2} \quad (38)$$

$$10 \quad \frac{U_{C_3}}{C_3} = \sqrt{\left(\frac{\Delta C_2}{C_2}\right)^2 + \left(\frac{\Delta C_1}{C_1}\right)^2} \quad (39)$$

$$11 \quad U_{C_3} = C_3 \cdot \sqrt{\left(\frac{\Delta C_2}{C_2}\right)^2 + \left(\frac{\Delta C_1}{C_1}\right)^2} \quad (40)$$

$$12 \quad U_{C_4} = \frac{\Delta C_4}{C_4} \quad (41)$$

13 Eq.(42) used to calculate the uncertainty of the pH measured using the glass electrode (Hanna,
 14 HI-2002 Edge®).

$$15 \quad U_{pH} = \sqrt{(u_{system})^2 + (u_{calibration})^2 + (u_{repeatability})^2} \quad (42)$$

16 $u_{repeatability}$ and u_{system} were calculated to be 0.007 and 0.01 respectively. Moreover, the pH
 17 value was changed 0.01 unit, once the change in the e.m.f value was within ± 0.05 mV.
 18 Therefore the uncertainty of the calibration is considered to be 0.01. The uncertainty of the pK_a
 19 for each temperature and ionic strength was then calculated using Eq. (43).

$$20 \quad U_{pK_a, C} = \sqrt{(U_{pH})^2 + (U_{C_4})^2} \quad (43)$$

1 **c) pH uncertainty (spectroscopy technique)**

2 In this section equations used to calculate the uncertainty of the pH measured for the CO₂-H₂O
3 and CO₂-H₂O-NaCl systems using the spectroscopy technique are described in details. Eq. (44)
4 used to calculate the pH of the CO₂- water/brine systems at various pressures.

$$5 \quad pH = pK_a(t, p, \mu) + \log \frac{R_{K_1}^{\lambda_2} - e_1}{e_2 - Re_3} \quad (44)$$

6 As mentioned in the manuscript, pK_a is a function of pressure, temperature and ionic strength.
7 Since the pK_a was determined experimentally at the calibrated temperatures and ionic strengths
8 and the uncertainty of the pK_a was calculated separately at each isotherm and ionic strength, it
9 is also essential to calculate the uncertainty of the pK_a with respect to the pressure. As
10 mentioned in the manuscript Eq. (45) used to correct the pK_a values at various pressures.

$$11 \quad \frac{RT}{(P-1)} \ln \frac{K_a(t, p, \mu)}{K_a(t, 1, \mu)} = -\Delta V + \Delta k \frac{P-1}{2} \quad (45)$$

$$12 \quad K_a(t, p, \mu) = K_a(t, 1, \mu) \cdot e^{\frac{-\Delta V(P-1) + \Delta k (P-1)^2}{2RT}} \quad (46)$$

13

14 Where,

$$15 \quad pK_a = -\log \left(K_a(t, 1, \mu) \cdot e^{\left(\frac{-\Delta V(P-1) + \Delta k (P-1)^2}{2RT} \right)} \right) = -\frac{\ln \left(K_a(t, 1, \mu) \cdot e^{\left(\frac{-\Delta V(P-1) + \Delta k (P-1)^2}{2RT} \right)} \right)}{\ln(10)} \quad (47)$$

$$16 \quad pK_a = \frac{(-\ln K_a(t, 1, \mu)) - \left(\frac{-\Delta V(P-1) + \Delta k (P-1)^2}{2RT} \right)}{\ln(10)} \quad (48)$$

17 Eq. (49) shows the derivative of the pK_a equation with respect to pressure.

$$18 \quad \frac{dpK_a}{dp} = \frac{\Delta V - 2 \cdot \Delta k (P-1)}{2RT \cdot \ln(10)} \quad (49)$$

19 Thus, the uncertainty of the pK_{a,P} was found according to:

$$20 \quad U_{pK_{a,P}} = \left| \frac{dpK_a}{dP} \right| \cdot \Delta P \quad (50)$$

21 Where ΔP was found to be approximately 0.05 MPa. The total uncertainty of the pK_a was then
22 calculated by using Eq. (51).

$$23 \quad U_{pK_{a,Total}} = \sqrt{(U_{pK_{a,C}})^2 + (U_{pK_{a,P}})^2} \quad (51)$$

1 Finally, a final combined uncertainty can be calculated using Eq. (52) to estimate the
2 uncertainty of the pH using the spectroscopy technique.

$$3 \quad U_{pH} = \sqrt{(U_{pK_a, Total})^2 + (U_{C_4})^2} \quad (52)$$

4 **2. Uncertainties calculation for the electrometric technique**

5 Eq. (53) used to calculate the uncertainty of the pH for the CO₂-H₂O system.

$$6 \quad U_{pH} = \sqrt{(u_T)^2 + (u_P)^2 + (u_V)^2} = \sqrt{\left(\left|\frac{dpH}{dT}\right| \cdot \Delta T\right)^2 + \left(\left|\frac{dpH}{dP}\right| \cdot \Delta P\right)^2 + \left(\left|\frac{dpH}{dmV}\right| \cdot \Delta mV\right)^2}$$

7 (53)

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