

The *pH* of CO₂-saturated aqueous NaCl and NaHCO₃ solutions at temperatures between 308 K and 373 K at pressures up to 15 MPa

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Abstract

The *pH* is a critical variable for carbon storage in saline aquifers because it affects the reaction rate and equilibrium state of the reservoir rocks, thus influencing the rates of mineral dissolution or precipitation and the integrity of caprocks. In this work, high-pressure *pH* and Ag/AgCl-reference electrodes were used to measure the *pH* of CO₂-saturated aqueous solutions of NaCl and NaHCO₃. The expanded uncertainty of the *pH* measurements is 0.20 at 95 % probability. For CO₂-saturated NaCl(aq), measurements were carried out at total pressures from (0.37 to 15.3) MPa and temperatures from (308 to 373) K with NaCl molalities of (1, 3 and 5) mol·kg⁻¹. For CO₂-saturated NaHCO₃(aq), the *pH* was measured at total pressures from (0.2 to 15.3) MPa and temperatures from (308 to 353) K with NaHCO₃ molalities of (0.01, 0.1 and 1) mol·kg⁻¹. The *pH* was found to decrease with increase in pressure and with decrease in temperature for both CO₂-saturated NaCl and NaHCO₃ solutions. For CO₂-saturated NaCl(aq), the *pH* was observed to decrease with increase of salt molality, while for CO₂-saturated NaHCO₃, the opposite behaviour was observed. The results have been compared with predictions obtained from the PHREEQC geochemical simulator (version 3.3.9) incorporating the Pitzer activity-coefficient model with parameters taken from the literature. For CO₂-saturated NaCl(aq), agreement to within ±0.2 *pH* units was observed in most cases, although deviations of up to 0.3 were found at the highest molality. In the case of CO₂-saturated NaHCO₃(aq), the experimental data were found to deviate increasingly from the model with increasing salt molality and, at 1 mol·kg⁻¹, the model underestimated the *pH* by between 0.3 and 0.7 units.

Keywords: carbon dioxide; high pressure; high temperatures; *pH*; sodium chloride; sodium bicarbonate.

Nomenclature

E	Electromotive force, e.m.f.
$E^{\ominus}$	Reference e.m.f.
F	Faraday's constant
I	Ionic strength
K_A	Dissociation constant of species A
$K^{\ominus}$	Standard equilibrium constant
m	Molality
$m^{\ominus}$	Standard molality ($1 \text{ mol} \cdot \text{kg}^{-1}$)
p	Pressure
R	Gas constant
T	Temperature
u	Standard uncertainty
U	Expanded uncertainty
x	Mole fraction of dissolved CO_2

Greek letters

α	Activity
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1. Introduction

The link between anthropological greenhouse-gas emissions and a continuing process of global warming is clearly established and it is recognised that emissions of carbon dioxide, the most important greenhouse gas, must be dramatically reduced in the near future so as to slow and eventually arrest global warming. Carbon Capture and Storage (CCS) is the most promising large-scale option that will allow continued use of fossil fuels as a primary energy source while attaining an acceptable level of CO₂ emission [1]. In outline, CCS involves capture of CO₂ from large point sources, transportation and finally storage in a suitable sink. The most promising technique to permanently sequester CO₂ is through geological storage. Potential CO₂ geological storage sites include hydrocarbon reservoirs, coal seams and deep saline aquifers [2], amongst which deep saline aquifers have the greatest potential for CO₂ sequestration [3].

Many physical and chemical processes are known to occur both during and after CO₂ injection into a saline aquifer, including diagenetic chemical reactions and associated permeability changes [4]. The coupling of physical and chemical process occurs in various situations, ranging from the near-well-bore region to far in the reservoir, and has consequences for the long-term viability of CO₂ storage [5]. Therefore, it is essential to have a fundamental understanding of the physical and chemical properties of the fluids and minerals, and of the rock-fluid interactions, before implementing CO₂ storage in saline aquifers. One of the key parameters is the pH of the reservoir solution after CO₂ injection. The pH affects the reaction rate and equilibrium state of reservoir rocks and acts as a switch between reservoir mineral dissolution and precipitations [6]. Mineralisation trapping processes, mineral stability and cap-rock integrity are all controlled by solution pH, affecting total CO₂ storage capacity and integrity for a given site. In addition, reservoir mineral dissolution reactions at low pH conditions are of interest in a wide range of sub-surface processes, such as acid gas injection, acidization, CO₂ enhanced oil recovery (EOR) [7] and steam injection EOR [8]. A lack of understanding of dissolution processes can result in poor etched-fracture lengths and high corrosion rates, leading to unsuccessful well stimulation and an increase in operational risks [9].

According to the International Union of Pure and Applied Chemistry (IUPAC) [10], pH is defined as $-\log_{10}(\alpha_{\text{H}^+}/m^\ominus)$, where α_{H^+} is the hydrogen ion activity on a molality scale and $m^\ominus = 1 \text{ mol}\cdot\text{kg}^{-1}$. Unfortunately, direct measurement of single-ion activities may be impossible and practical realisations of pH involve additional assumptions. In the case of CO₂-saturated water, the total ionic strength is very low and the pH may be calculated by combining theoretical results, based on the Debye-Hückel equation, with experimental measurements of the dissociation constant(s) of CO₂ in aqueous solution, knowledge of the solubility of CO₂ in the aqueous phase and experimental or calculated values of the fugacity of CO₂ in the coexisting gas phase. The results of such detailed calculations are in good agreement with measured pH values CO₂ in aqueous solution, even at elevated temperatures and pressure [11]. Geochemical simulators, such as PHREEQC [12] or EQ3NR [13], can be employed in a similar way to predict the pH of a CO₂-acidified water or brine. However, in more concentrated electrolyte solutions, such as reservoir brines, the calculation of the hydrogen-ion activity coefficient, and hence the pH, requires assumptions

more drastic than invoking the Debye-Hückel equation and the Bates-Guggenheim convention [10]. Therefore both the measurement and calculation of pH generally depend upon an operational definition that may differ somewhat from $-\log_{10}(\alpha_{H^+}/m^\ominus)$. Nevertheless, experimental and calculated pH data based on the same operational definition may be compared in a meaningful way. Furthermore, the change in pH upon dissolution of CO_2 in a concentrated brine occurs at essentially constant ionic strength so that this change is nearly independent of the operational definition of pH employed. In this work we use an operational pH scale based on the MacInnes assumption, whereby the activity coefficients of K^+ and Cl^- are assumed to be equal and are identified with the well-known mean ionic activity coefficient of aqueous KCl . Thus the experiments were designed to test the change in pH that accompanies saturation of the brine with CO_2 under controlled conditions of temperature and pressure.

The most abundant salt present in seawater and many saline-aquifer brines is sodium chloride, which typically constitutes about 90% of the dissolved salts [14]. Seawaters typically have salinity (mass fraction of $NaCl$) of around 3.5 % [14], corresponding to a $NaCl$ molality of around $0.5 \text{ mol}\cdot\text{kg}^{-1}$. Deep saline aquifers, on the other hand, can have much higher salinity. For example, $NaCl$ molalities of aquifers in the North Sea average around $1 \text{ mol}\cdot\text{kg}^{-1}$ [15], while some of the brine reservoirs in the Middle East have $NaCl$ molalities as high as $5 \text{ mol}\cdot\text{kg}^{-1}$ [16, 17]. Therefore, a quantitative investigation of the pH of the CO_2 -saturated $NaCl$ solutions, particularly at high-temperature, high-pressure and high-molality conditions, is needed to validate our understanding of the change of pH after injecting CO_2 into either the deep ocean or a saline aquifer.

The two most widely used methods for pH measurements are electrometric and optical techniques. In the electrometric method, one measures the potential difference of an electrochemical cell, which is related to the pH of the solution it contains. In the optical method, pH is obtained from measurements of the absorption spectrum of an indicator dye. An examination of the literature shows that previous experimental studies of pH in the CO_2 acidified $NaCl$ system are very limited with few data published at high pressure conditions. Most of the pH measurements for seawater were focused on low temperature conditions ($\leq 298 \text{ K}$) at atmosphere pressure and with CO_2 partial pressure $\leq 0.1 \text{ MPa}$. Hinds et al. [18] reported pH measurements conducted on concentrated $NaCl$ solutions (up to $4.3 \text{ mol}\cdot\text{kg}^{-1}$) at a temperature of 298 K and CO_2 pressure of 0.1 MPa . They used two different glass combination pH electrodes with either single- or double-junction reference electrodes. They compared their results with unpublished data from two other laboratories. All measured data were in good agreement at zero salt molality, with pH values of between 3.90 to 3.96, and all showed a significant decrease of pH with increasing $NaCl$ molality at constant CO_2 partial pressure. However, at a $NaCl$ molality of $4.3 \text{ mol}\cdot\text{kg}^{-1}$, the four data sets were found to span a pH range from 3.2 to 3.6. This illustrates the difficulty in obtaining reliable measurements at high ionic strength, even when restricted to near ambient conditions of temperature and pressure. Kimuro et al. [19] also used an electrometric method and reported pH values as a function of the mole fraction x of dissolved CO_2 at temperatures between (276 and 293) K and at pressures between (10 and 32) MPa . They observed an approximately linear relation between pH and px , irrespective of temperature in the narrow range of their study. Truche et al. [20] have recently reported electrometric measurements of the pH of CO_2 -saturated water

and NaCl brine with a molality of $1.4 \text{ mol}\cdot\text{kg}^{-1}$. In contrast to other studies, these measurements were carried out in a high-temperature region ($473 \leq T/\text{K} \leq 553$) with pressures up to 13 MPa. A linear relation between $p\text{H}$ and p_x was assumed but the slope and intercept were clearly dependent upon temperature. Crolet and Bonis [21], also using an electrometric technique, measured the $p\text{H}$ of NaCl brines at concentrations of up to $3.5 \text{ mol}\cdot\text{L}^{-1}$ along three isotherms at temperature from (289 to 347) K with CO_2 pressure ranging from (0.1 to 3) MPa. A study performed by Schaef and co-workers [22, 23] also used the electrometric technique and measured the $p\text{H}$ of the CO_2 -saturated NaCl(aq) system at temperature between (295 and 343) K, pressure up to 11 MPa, and NaCl molality of $1 \text{ mol}\cdot\text{kg}^{-1}$. Most recently, Haghi et al. [24] measured the $p\text{H}$ of CO_2 -saturated NaCl brines at temperatures of (293 and 323) K, pressures up to about 6 MPa and molalities of (1, 2 and 3) $\text{mol}\cdot\text{kg}^{-1}$. They used an optical method with bromophenol blue as the indicator and the results were shown to be in generally good agreement with a model based on the Pitzer approach with CO_2 solubility determined from the CPA equation of state. Overall, it is found that experimental $p\text{H}$ data for CO_2 -saturated NaCl solutions are scarce for conditions of simultaneously high temperature, pressure and molality.

Bicarbonate (HCO_3^-) anions also exist in deep saline aquifers and can be the primary anion in aquifers with low NaCl concentration [25]. The bicarbonate concentration is mainly controlled by the geochemical composition of the formation rocks with which the brine is in contact. Carbonate minerals including limestone, dolomite and chalk can give rise to significant bicarbonate concentrations in the aquifer [17], although the majority of saline aquifers have a bicarbonate concentration of less than $0.1 \text{ mol}\cdot\text{kg}^{-1}$ [26]. Bicarbonate tends to make the aquifer brine slightly alkaline and its presence may serve to buffer the effect of injected CO_2 through the acid-base equilibria. For this reason, bicarbonate brines are of special interest.

Several researchers have reported experimental results on $p\text{H}$ and relevant thermodynamic properties of CO_2 -saturated aqueous solution containing NaHCO_3 . Stefánsson et al [27] measured $p\text{H}$ of the system ($\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + \text{NaOH} + \text{HCl} + \text{NaCl} + \text{H}_2\text{O}$) using spectrophotometry and optical $p\text{H}$ indicators at temperatures from (298 to 473) K, pressures of (1 to 2) MPa and ionic strengths between (0.001 and 0.43) $\text{mol}\cdot\text{kg}^{-1}$. Wang et al. [28] measured bicarbonate alkalinity of two produced water samples at total pressures ≤ 0.103 MPa and temperatures between (298 and 343) K. Wong et al. [29] reported the solubility of CO_2 in aqueous NaHCO_3 solution determined by the coulometric technique at ambient pressure and at temperatures of (278, 283, 287, and 298) K with NaHCO_3 molalities up to $0.5 \text{ mol}\cdot\text{kg}^{-1}$. Tang et al. [30] measured the solubility of CO_2 in aqueous solutions containing bicarbonate at temperatures of (308.15, 328.15, 368.15, and 408.15) K and pressures of (8 to 40) MPa. Recently, Hoballah [31] reported measurements of the solubility of CO_2 in NaHCO_3 brines of molality $0.8 \text{ mol}\cdot\text{kg}^{-1}$ at temperatures of (348 and 398) K with pressures up to 60 MPa. However, to the best of our knowledge, no direct $p\text{H}$ measurements of CO_2 -saturated NaHCO_3 aqueous solutions have been reported for conditions of simultaneous high temperature, high pressure and high salt molality.

The Pitzer model is an approach for estimating activity coefficients of both ionic and neutral solutes in aqueous solution over a broad range of ionic strengths up to $20 \text{ mol}\cdot\text{kg}^{-1}$ [32]. The

solutes of relevance to the present study are NaCl, HCl, NaHCO₃, Na₂CO₃ and CO₂. Pitzer interaction parameters have been reported in the literature for HCl and NaCl aqueous solutions over wide ranges of temperature [33-35]. For aqueous NaCl, Pitzer et al. [34] performed an extensive analysis of experimental data for the osmotic and activity coefficients, enthalpies of solution and solubility in water over the temperature range from (273 to 573) K, leading to a well-founded parameter set for this aqueous system. Ruaya and Seward [35] determined the Pitzer-model parameters of aqueous HCl by regressing the osmotic and activity coefficients of HCl at various temperatures up to 473 K and molalities up to 1 mol·kg⁻¹. The Pitzer parameters associated with NaHCO₃ and Na₂CO₃ at temperatures up to 523 K have recently been updated by Truche et al. [20] on the basis of experimental data reported by Polya et al. [36] and Li and Duan [37]. Many other electrolyte systems, some with dissolved gases, have also been studied and databases of Pitzer parameters are available for use with geochemical simulator [12, 13, 38, 39].

In summary, it can be concluded that additional *pH* measurements for CO₂-saturated NaCl and NaHCO₃ aqueous solutions, especially at elevated temperatures and pressures, would provide valuable experimental data to validate geochemical models and underpin studies of the chemical interactions between CO₂-saturated brines and reservoir minerals. Accordingly, in this work, a high-pressure *pH* measurement system was used to study CO₂-saturated NaCl and NaHCO₃ aqueous solutions. For CO₂-saturated NaCl(aq), measurements were carried out at temperatures of (308, 323, 343, 363 and 373) K and at pressures up to 15.3 MPa with NaCl molalities of (1, 3, 5) mol·kg⁻¹. For CO₂-saturated NaHCO₃(aq), the *pH* was measured at temperatures of (308, 323, 338 and 353) K at pressures up to 15.3 MPa with NaHCO₃ molalities of (0.01, 0.1 and 1) mol·kg⁻¹. Experimental results were compared with the predictions from the PHREEQC simulator using the Pitzer ion-interaction model with parameters from the literature.

2. Experiment

2.1 Materials

Table 1 details the materials used in this study. CP grade CO₂ was supplied by BOC with a minimum mole-fraction of 0.99995. Deionised water with an electrical resistivity > 18 MΩ·cm at *T* = 298 K was produced by a reverse-osmosis apparatus (Millipore). Oxygen-free N₂ was supplied by BOC. NaCl and NaHCO₃ were purchased from Sigma-Aldrich, with mass fraction purities ≥ 0.995. Na₂CO₃, Trizma base (2-Amino-2-(hydroxymethyl)-1,3-propanediol, abbreviated Tris) and Trizma hydrochloride (Tris(hydroxymethyl)aminomethane hydrochloride, abbreviated TrisH) with mass fraction ≥ 0.99 were purchased from Sigma Aldrich for *pH* electrodes calibration. Additionally, 0.01 M HCl(aq) solution (Sigma Aldrich) was used for *pH* electrodes calibration. Prior to solution preparation, salts were oven dried and aqueous solutions were vacuum degassed immediately before use. No other purification was undertaken.

Table 1. Description of chemical samples, where x is mole fraction, w is mass fraction and ρ_e is electrical resistivity at $T = 298.15$ K.

Chemical Name	CAS Number	Source	Purity as Supplied ^a	Analysis Method	Additional Purification
Carbon dioxide	124-38-9	BOC	$x \geq 0.99995$	-	None
Nitrogen	7727-37-9	BOC	$x \geq 0.99998$ ^b	-	None
Water	7732-18-5	Millipore	$\rho_e > 18 \text{ M}\Omega\cdot\text{cm}$	-	Vacuum degassed
NaCl	7440-23-5	Sigma Aldrich	$w \geq 0.995$	-	Oven dried
NaHCO ₃	144-55-8	Sigma Aldrich	$w \geq 0.995$	-	Oven dried
Na ₂ CO ₃	497-19-8	Sigma Aldrich	$w \geq 0.99$	-	Oven dried
HCl (aq)	7647-01-0	Sigma Aldrich		-	None
Trizma base	77-86-1	Sigma Aldrich	$w \geq 0.99$	-	None
Trizma HCl	1185-53-1	Sigma Aldrich	$w \geq 0.99$	-	None

^a Purities are as stated by the supplier

^b Includes argon

2.2 Experiment system

The apparatus used in this work was the same high-pressure electrometric system described in detail by Peng et al. [11] and used to measure the pH of CO₂-saturated water. Therefore, only a brief description is given here. A glass pH electrode, a zirconia pH electrode and a Ag/AgCl reference electrode (Corr Instruments LLC) were used in this work. The ZrO₂-based electrode used a Ag/Ag₂O solid electrode, while the reference electrode was of the external type with the Ag/AgCl located in the ambient-temperature part of the probe. The glass electrode was used for low temperature measurements (up to 353 K), while the zirconia electrode was used for temperatures of 363 K and higher. The electrical potential difference E developed between the reference electrode and the pH electrode was measured by a digital multimeter with an input impedance $> 10^{12} \Omega$. The electrodes were hermetically sealed through the wall of a titanium pressure vessel with a capacity of 91 mL. The vessel was fitted with an external heating shell and could be operated at pressures up to 24 MPa at $T \leq 473$ K. A PID process controller was used to regulate the shell temperature with a stability of better than ± 0.05 K. A PTFE-coated magnetic stirrer bar was placed at the bottom of the vessel and was rotated by an external magnetic drive to mix the solution *in situ*. The temperature was measured with a PT100 thermometer inserted into a vertical hole drilled in the wall of the vessel. The pressure was measured in the external tubing by means of a pressure transducer (OmegaDyne Model MMA) with a full range of 24.5 MPa. The fluid system included a high-pressure syringe pump for CO₂ injection, N₂ purge line, vacuum line, discharge line and appropriate valving. A key operational issue was that the Ag/AgCl reference probe can be damaged during rapid depressurisation. To counter this problem, a programmable back pressure regulator (Jasco BP-2080) was used to control the rate of depressurisation through the discharge line to $< 0.4 \text{ MPa}\cdot\text{hr}^{-1}$.

2.3 Operating procedure

To cover the temperature ranges investigated, both the glass and the zirconia pH electrodes were used for the CO₂-saturated NaCl(aq) system, while only the glass electrode was

required for CO₂-saturated NaHCO₃(aq). CO₂-free aqueous solutions were prepared gravimetrically, using water that had been degassed in an ultrasonic bath for 30 min. Prior to measurements on a particular brine solution, the pressure vessel was opened, and both the vessel and the electrodes were rinsed with DI water and the brine solution, before part filling the vessel with 80 mL of the brine. After sealing the system, the brine was degassed by stirring under vacuum for 1 h before commencing the measurements. The pH measurement for a particular brine solution were conducted along isobars, with the pressure being regulated automatically by the syringe pump, starting at the lowest temperature and proceeding to the highest. The temperature was then returned to the initial value for a check measurement before increasing the pressure to the next isobar. During the experiment, temperature, pressure, and e.m.f. were continuously monitored and logged. The dissolution of CO₂ into the solution could be monitored by the change of the syringe pump volume and the e.m.f. across the electrodes. The equilibrium saturated state was considered to be achieved after the pump volume reading and the e.m.f. across the electrodes were constant within ± 0.01 mL and ± 1 mV, respectively, over a period of one hour. Each equilibrium state was achieved by stirring the solution for at least 5 h, while at relatively high pressures (more than 10 MPa), stirring for 24 h was needed. The stirring speed was controlled to as low as 0.8 s⁻¹ to prevent entrainment of bubbles.

2.4 Calibration and uncertainty

The thermometer and pressure transducer were calibrated in the previous study [11] and the expanded uncertainties of temperature and pressure are estimated to be 0.05 K and 0.07 MPa, respectively at 95% confidence.

The pH probes required calibration at every temperature and ionic strength studied. Since the effect of pressure was determined to be negligible [11], all calibrations were carried out with the solution under a nitrogen atmosphere at pressure ≤ 1.5 MPa. For measurements on CO₂-saturated NaCl(aq), the calibration procedure was an extension of the system used previously and involved two points at pH values of approximately 8 and 2, with NaCl molality of (1, 3 or 5) mol·kg⁻¹. In this case, the higher pH calibration solution was Tris-TrisH buffer with a molality of 0.05 mol·kg⁻¹, while the lower pH calibration solution was aqueous HCl of molality 0.01 mol·kg⁻¹.

The Tris-TrisH buffer is favoured by the marine chemists and geochemist since it has a pH value similar to seawater. The pH of the Tris-TrisH buffer can be traced back to primary pH buffers by comparison measurements and its pH values at high ionic strength conditions have been studied and modelled on various pH scales. The reported pH values of Tris-TrisH buffers at high ionic strength conditions have been widely accepted and used. As a result, it is recommended that, for pH measurements in seawater or brines, Tris-TrisH solution should be used as a calibration buffer solution [40-43]. The dissociation constant K_{TrisH} in the Tris-TrisH buffer solution with NaCl was determined by Foti et al. [44] at temperatures from (273 to 373) K and ionic strengths of (0 to 5) mol·kg⁻¹. Millero et al. [41] determined that the values in dilute solution were in close agreement with experimental measurements by Bates and Hester [45]. Here K_{TrisH} is defined as

$$K_{\text{TrisH}} = \frac{m(\text{H}^+)m(\text{Tris})}{m(\text{TrisH})m^{\ominus}}. \quad (1)$$

The $p\text{H}$ was then obtained from the relation

$$p\text{H} = pK_{\text{TrisH}} - \log_{10} [m(\text{TrisH})/m(\text{Tris})] - \log_{10} [\gamma(\text{H}^+)], \quad (2)$$

using numerical values of pK_{TrisH} calculated from the correlation of Millero et al. [41] and proton activity coefficients $\gamma(\text{H}^+)$ calculated according to the Pitzer model, as implemented in PHREEQC version 3.3.9, assuming an NaCl medium of ionic strength equal to that of the buffer solution. Aqueous solution of (HCl + NaCl) are of course not buffers but the presence of only fully-dissociated 1:1 electrolytes makes the $p\text{H}$ relatively easy to predict by modelling, at least at low ionic strength. The $p\text{H}$ values of these solutions were also calculated from the Pitzer model as implemented in PHREEQC version 3.3.9 with the ion-interaction parameters reported by Truche et al. [20]. As mentioned in the introduction, the calculations are based on the MacInnes assumption. The Pitzer-model parameters for KCl, required to implement this assumption, were taken from Appelo et al. [46]. The calibration data are given in Table 2.

Table 2. Calibration data for the probes used in the study of CO_2 -saturated NaCl(aq), measured at NaCl molality m and temperatures T , where E denotes the e.m.f. in the calibration solutions at the specified $p\text{H}$.^a

m ($\text{kg}\cdot\text{mol}^{-1}$)	$p\text{H}$ (-)	E (mV)	$p\text{H}$ (-)	E (mV)	$p\text{H}$ (-)	E (mV)	$p\text{H}$ (-)	E (mV)	$p\text{H}$ (-)	E (mV)
	$T = 308.15 \text{ K}$		$T = 323.15 \text{ K}$		$T = 343.15 \text{ K}$		$T = 363.15 \text{ K}$		$T = 373.15 \text{ K}$	
1.00	2.031	367.0	2.044	387.2	2.065	399.5	2.088	794.2	2.100	801.1
	8.007	21.5	7.639	35.9	7.209	53.5	6.834	461.0	6.664	470.3
3.00	1.714	413.0	1.740	430.5	1.778	443.8	1.812	810.4	1.840	818.0
	8.035	48.2	7.669	61.8	7.242	81.0	6.871	463.2	6.704	470.3
5.00	1.355	448.5	1.393	465.7	1.446	479.8	1.501	839.0	1.529	845.2
	8.002	68.3	7.631	83.1	7.197	100.6	6.819	464.5	6.649	472.7

^a expanded uncertainties at 95% confidence are $U(T) = 0.05 \text{ K}$ and $U(E) = 1 \text{ mV}$.

The measurements on CO_2 -saturated NaHCO_3 solutions were made some two years after those on CO_2 -saturated NaCl(aq) and, considering both this elapsed time and the different ionic strengths to be studied, it was decided to re-calibrate the electrode system. In this case, only the glass electrode was used but a three-point calibration procedure was followed using $0.01 \text{ mol}\cdot\text{kg}^{-1}$ HCl solutions, $0.01 \text{ mol}\cdot\text{kg}^{-1}$ Tris-TrisH buffer, and $0.0025 \text{ mol}\cdot\text{kg}^{-1}$ ($\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$) buffer. In each case, the ionic strength was adjusted to (0.01, 0.1 or 1) $\text{mol}\cdot\text{kg}^{-1}$ with NaCl. The $p\text{H}$ of the HCl solutions and the Tris-TrisH solutions was calculated as before, and the $p\text{H}$ of the bicarbonate-carbonate buffer solutions was also obtained from the Pitzer model in PHREEQC using the ion-interaction parameters for NaHCO_3 and $\text{Na}_2\text{CO}_3^{2-}$ reported by Truche et al. [20]. The calibration data are given in Table 3.

Table 3. Calibration data for the probes used in the study of CO₂-saturated NaHCO₃(aq), measured at ionic strength I and temperatures T , where E denotes the e.m.f. in the calibration solutions at the specified pH.^a Also listed are values of K_{12} determined by fitting the data with equation (3).

I (kg·mol ⁻¹)	pH (-)	E (mV)	pH (-)	E (mV)	pH (-)	E (mV)	pH (-)	E (mV)
	$T = 308.15 \text{ K}$ $K_{12} = 0.4 \times 10^{-9}$		$T = 323.15 \text{ K}$ $K_{12} = 0.8 \times 10^{-9}$		$T = 338.15 \text{ K}$ $K_{12} = 1.3 \times 10^{-9}$		$T = 353.15 \text{ K}$ $K_{12} = 2.8 \times 10^{-9}$	
0.01	2.043	390.5	2.045	412.2	2.046	426.8	2.048	439.8
	6.771	121.6	6.406	140.7	6.079	156.6	5.785	172.3
	10.019	-62.7	9.868	-63.9	9.720	-64.6	9.573	-65.5
0.10	2.093	404.6	2.098	420.8	2.103	433.3	2.108	445.0
	6.835	127.5	6.470	151.1	6.142	170.6	5.847	187.8
	9.767	-47.5	9.634	-46.8	9.508	-46.0	9.381	-39.7
1.00	2.031	419.7	2.045	434.8	2.061	446.4	2.077	456.9
	6.931	132.8	6.564	153.4	6.235	172.5	5.939	193.8
	9.366	-9.1	9.254	-4.1	9.147	-2.4	9.043	6.0

^a expanded uncertainties at 95% confidence are $U(T) = 0.05 \text{ K}$ and $U(E) = 1 \text{ mV}$

For both the glass and the zirconia electrodes, the e.m.f. measured during calibration exhibited high stability over long periods of time, with drift of less than 1 mV (equivalent to approximately 0.02 pH units) over 24 hours. With the glass electrode, the measured e.m.f. was observed to increase with increase of the NaCl molality at constant pH. Such behaviour is attributed to ion interference effects associated specifically with Na⁺ in the solution. This can be described semi-quantitatively by a simplification of the Nikolsky-Eisenman equation [47-49]:

$$E = E^{\ominus} + E_1 \ln(\alpha_{\text{H}^+} + K_{12} \alpha_{\text{Na}^+}). \quad (3)$$

Here, $E^{\ominus}$ is a reference e.m.f., E_1 is a constant theoretically equal to RT/F , where F is Faraday's constant, R is the gas constant and T is the thermodynamic temperature. Also in equation (3), α_X denotes the activity of chemical species X, and K_{12} is an ion interference coefficient. Experimental data measured with glass electrodes may conform to equation (3) when E_1 is treated as an empirical parameter and when α_{Na^+} falls within a restricted range [49]. However, except at high pH, a linear calibration equation is expected as follows:

$$E = a + b \cdot \text{pH}, \quad (4)$$

where a and b depend upon both temperature and ionic strength. Accordingly, the system was calibrated at every temperature and ionic strength in terms of equation (4). Fig. 1 shows the calibration data gathered with the glass electrode at $T = 323.15 \text{ K}$ and ionic strengths I up to $1 \text{ mol} \cdot \text{kg}^{-1}$. These data are essentially linear over the calibration range ($2.05 \leq \text{pH} \leq 9.87$) and conform to equation (4) at each ionic strength to within $\pm 4 \text{ mV}$, equivalent to 0.07

pH units. The deviations from equation (4) tend to increase with increasing temperature with an overall standard deviation of 0.09 pH units.

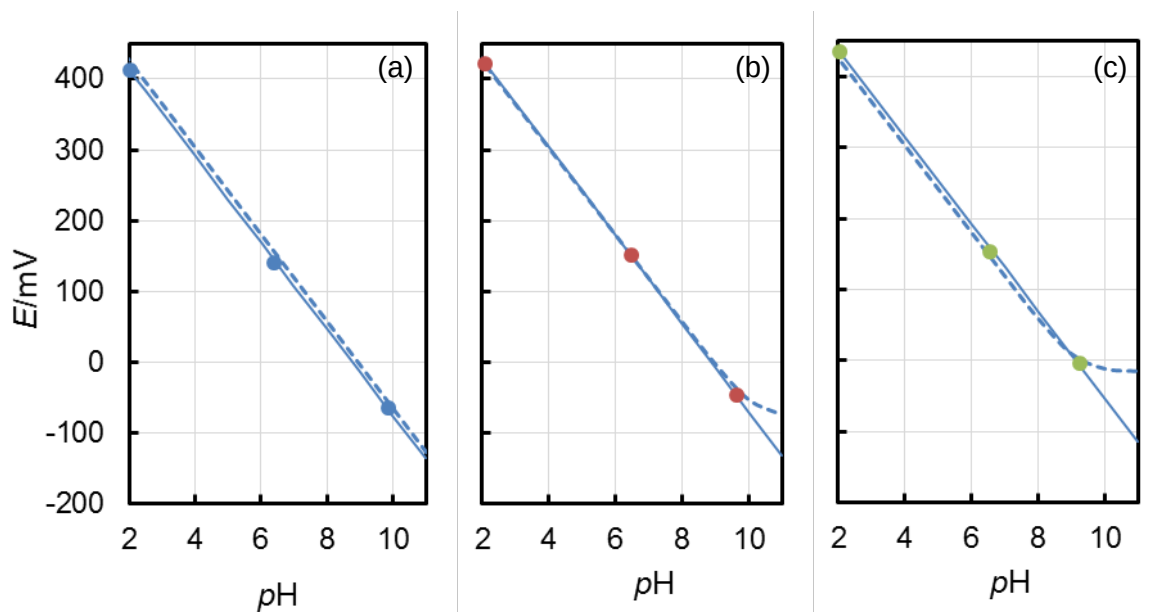


Fig. 1. Calibration data for the glass electrode at $T = 323.15$ K and (a) $I = 0.01$ mol·kg⁻¹, (b) $I = 0.10$ mol·kg⁻¹, and (c) $I = 1.00$ mol·kg⁻¹. Symbols represent the measured data, continuous lines are linear calibration functions, and dashed curves represent equation (3) with $K_1 = 8 \times 10^{-10}$.

Figure (1) also compares the calibration data at $T = 323.15$ K with the best fit using equation (3) with $E^\ominus$, E_1 and K_{12} as adjustable parameters, independent of ionic strength. One can see that the data do not in fact conform closely to equation (3), with small systematic deviations depending upon ionic strength. However, the analysis does provide an estimate of the sodium ion interference coefficient at this temperature: $K_{12} = 8 \times 10^{-10}$. The plots then shows that ion interference effects are only important, in the sense of deviations from a linear calibration relation, at $pH > 9$. The estimated values of K_{12} at each temperature are included in Table 3.

In the study of the NaCl brines, the calibration was restricted to $pH \leq 8.0$ and the measurements to $pH < 4$, under which conditions sodium ion interference effects are expected to be negligible. This justifies the linear calibration procedure using equation (4) with a and b determined at every temperature and salt molality. Ion interference effects are not expected with a zirconia electrode; nevertheless, calibrations were also carried out at every temperature and salt molality.

After the completion of the measurements on NaHCO₃ brines, one calibration point using (Na₂CO₃ + NaHCO₃) buffer at $T = 308$ K was repeated. The deviation between the measured e.m.f. at the initial calibration and at this repetition was found to be within 1 mV (corresponding to 0.02 pH units) which indicated a stable performance of the electrodes over the measurement period.

The overall combined standard uncertainty u_c of the measured pH was calculated from the relation

$$u_c^2 = u_{pH}^2 + \left[\frac{\partial pH}{\partial T} u_T \right]^2 + \left[\frac{\partial pH}{\partial p} u_p \right]^2 + \left[\frac{\partial pH}{\partial E} u_E \right]^2 + \left[\frac{\partial pH}{\partial m} u_m \right]^2, \quad (5)$$

where u_T , u_p , u_E and u_m are the standard uncertainties of temperature, pressure, e.m.f. and salt molality, respectively, and u_{pH} is the standard uncertainty of the calibration. The latter should include the uncertainty of the pH of the buffer solutions, evaluated under the MacInnes assumption. The standard uncertainty of the pH of the HCl(aq) and Tris-TrisH buffer solutions without added salts is less than 0.02 [44]. The pH of the (NaHCO₃ + Na₂CO₃) as calculated in this is about 0.05 below the measurements of Staples and Bates [50]. The additional uncertainty arising at high ionic strength from errors in the Pitzer model is difficult to evaluate. Based on the linearity of the three-point calibration relations and the standard uncertainty of the buffer solutions at low ionic strength, u_{pH} is estimated to be 0.09. The derivatives appearing in equation (5) were estimated numerically from the measured data. The resulting combined standard uncertainty of the pH was found to be 0.10, leading to a combined expanded uncertainty at 95% confidence of 0.20.

3. Results and discussion

3.1 CO₂-saturated NaCl solution

Five isotherms for the CO₂-saturated NaCl solution were studied spanning the range (308 to 373) K at pressures up to 15 MPa. The NaCl molalities investigated in this study were (1, 3, and 5) mol·kg⁻¹; the experimental pH data are listed in Table 4. We have included the measured e.m.f. data both during calibration (Table 2) and measurement (Table 4), so as to permit recalculation of the pH under alternative assumptions concerning the pH of the calibration solutions. The experimental data are plotted as functions of CO₂ partial pressure along each isotherm and at each salt molality in Fig. 2. As expected, the pH of (CO₂ + NaCl) system was observed to decrease with increase of CO₂ partial pressure and decrease of temperature when the salinity was kept constant. At constant temperature and salinity the pH is observed to vary as an approximately linear function of $\ln p_{CO_2}$.

As observed in the literature [18, 21], the pH of (CO₂ + NaCl) solutions decreases with increasing salt molality when temperature and pressure are kept constant. This trend clearly cannot be explained by the change of CO₂ solubility since the amount of dissolved CO₂ decreases sharply with increasing of salt molality at given pressure and temperature, as a consequence of the salting-out effect. Therefore the decrease of pH is attributed to ion interaction effects that increase the activity coefficients of CO₂ and H⁺ so as to exceed the reduction in the CO₂ solubility. It is instructive to plot the pH against $px = -\log_{10}(x)$, where x is the mole fraction of CO₂ in the solution. For this purpose, we calculated x from the solubility model of Spycher and Pruess [51] and, as an example, Fig. 3 shows the results at $T = 323$ K and $m = (0, 1 \text{ and } 5) \text{ mol}\cdot\text{kg}^{-1}$, where the data at $m = 0 \text{ mol}\cdot\text{kg}^{-1}$ are taken from our earlier study [11]. This shows that the pH is a linear function of px in the range investigated and that the pH declines with increasing NaCl molality under conditions of constant T and x .

Table 4. Experimental pH of CO₂-saturated NaCl(aq) at total pressure p , temperature T and salt molality m , where E is the measured e.m.f.^a

p (MPa)	T (K)	E (mV)	pH (-)	p (MPa)	T (K)	E (mV)	pH (-)	p (MPa)	T (K)	E (mV)	pH (-)
$m = 1 \text{ mol}\cdot\text{kg}^{-1}$				$m = 3 \text{ mol}\cdot\text{kg}^{-1}$				$m = 5 \text{ mol}\cdot\text{kg}^{-1}$			
0.37	308.20	281.5	3.51	0.39	308.20	305.4	3.58	0.35	308.10	335.6	3.33
0.37	323.15	286.6	3.65	0.39	323.00	314.1	3.61	0.34	323.00	343.5	3.39
0.38	343.30	287.2	3.73	0.39	343.20	315.4	3.71	0.35	343.00	344.4	3.50
0.60	308.20	286.0	3.43	0.61	308.15	318.7	3.35	0.60	308.30	342.5	3.21
0.62	323.20	293.8	3.53	0.61	323.00	323.4	3.46	0.60	323.15	351.3	3.26
0.61	343.20	295.8	3.61	0.61	343.00	325.8	3.56	0.61	343.15	355.3	3.33
0.60	363.00	676.8	3.76	0.61	363.20	685.9	3.63	0.61	363.00	709.0	3.35
0.60	373.00	678.0	3.80	0.61	373.20	687.2	3.67	0.61	373.00	711.1	3.37
1.00	308.20	294.1	3.29	1.01	308.20	327.8	3.19	1.01	308.30	352.2	3.04
1.00	323.20	302.1	3.40	1.00	323.00	332.8	3.31	1.00	323.00	362.7	3.07
1.00	343.00	304.7	3.47	1.01	343.10	334.9	3.42	1.00	343.00	365.0	3.19
1.00	363.00	686.2	3.63	1.01	363.10	693.5	3.52	1.01	363.20	717.6	3.22
1.00	373.00	689.0	3.65	1.01	373.20	694.5	3.57	1.01	373.00	718.6	3.27
2.43	308.30	309.3	3.03	2.44	308.00	346.7	2.86	2.44	308.30	367.0	2.78
2.43	323.20	317.5	3.15	2.44	323.20	351.1	3.02	2.44	323.30	374.7	2.88
2.43	343.00	321.1	3.23	2.44	343.20	353.6	3.14	2.45	343.20	378.9	2.98
2.44	363.00	703.5	3.38	2.44	363.20	706.5	3.33	2.44	363.00	735.0	2.98
2.44	372.90	706.6	3.40	2.44	373.20	709.4	3.36	2.44	373.00	736.0	3.03
6.22	308.20	324.5	2.77	6.22	308.10	355.5	2.71	6.24	308.20	380.4	2.55
6.24	323.20	329.8	2.96	6.20	323.00	360.0	2.87	6.25	322.90	387.0	2.68
6.24	342.90	332.5	3.06	6.24	343.00	362.8	3.00	6.24	342.90	389.6	2.81
6.24	363.00	716.2	3.20	6.24	363.00	722.1	3.10	6.24	362.90	749.0	2.78
6.25	373.00	718.3	3.24	6.24	373.00	725.0	3.14	6.24	373.20	751.2	2.82
9.25	308.15	326.2	2.74	9.27	308.30	357.8	2.67	9.26	308.30	385.0	2.47
9.26	323.20	331.6	2.93	9.25	322.90	361.9	2.84	9.27	323.00	389.6	2.63
9.25	342.90	334.6	3.03	9.27	343.00	365.8	2.95	9.27	343.00	395.0	2.73
9.28	363.30	719.8	3.15	9.28	363.00	729.4	2.99	9.27	363.00	750.3	2.76
9.28	373.00	722.6	3.18	9.28	373.30	732.5	3.04	9.27	373.20	753.0	2.80
15.38	308.30	329.1	2.69	15.25	308.30	360.1	2.63	15.36	308.15	386.3	2.44
15.36	323.20	335.1	2.87	15.25	323.30	365.6	2.78	15.36	322.90	392.6	2.58
15.39	343.00	339.7	2.95	15.27	343.20	369.3	2.90	15.36	343.00	397.5	2.69
15.30	363.00	723.0	3.10	15.30	363.00	731.1	2.97	15.31	362.90	754.4	2.70
15.36	373.20	728.0	3.11	15.29	373.00	733.4	3.02	15.31	373.00	755.0	2.77

^a Expanded uncertainties at 95% confidence are $U(p) = 0.07 \text{ MPa}$, $U(T) = 0.05 \text{ K}$ and $U(\text{pH}) = 0.2$.

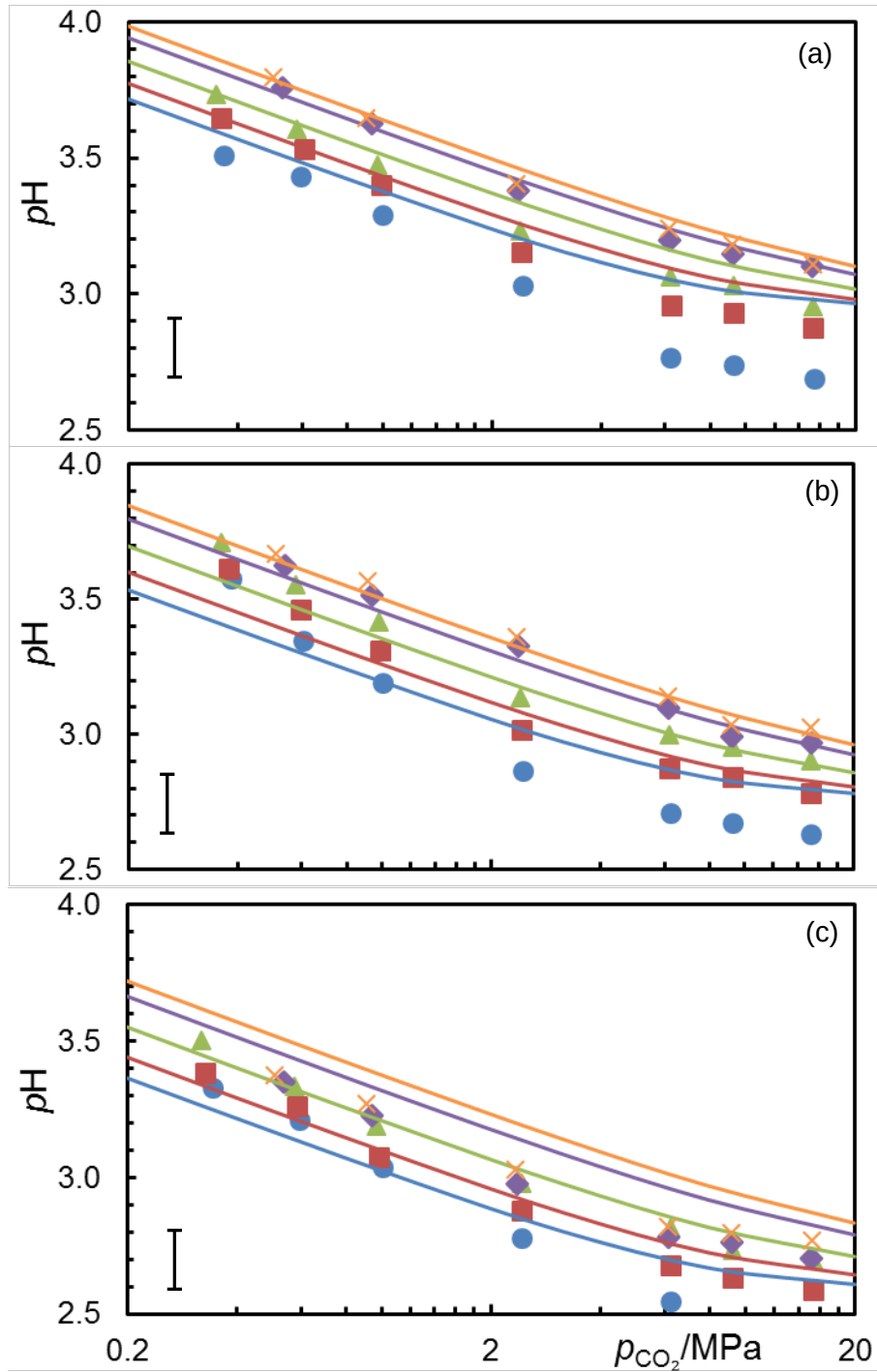


Fig. 2. pH of CO₂-saturated NaCl(aq) as a function of CO₂ partial pressure at molalities of: (a) 1 mol·kg⁻¹; (b) 3 mol·kg⁻¹; (c) 5 mol·kg⁻¹. Symbols: ●, $T = 308$ K; ■, $T = 323$ K; ▲, $T = 343$ K; ◆, $T = 363$ K; ×, $T = 373$ K. Lines show the pH calculated along each isotherm using PHREEQC. Error bar shows the standard uncertainty of the experimental data.

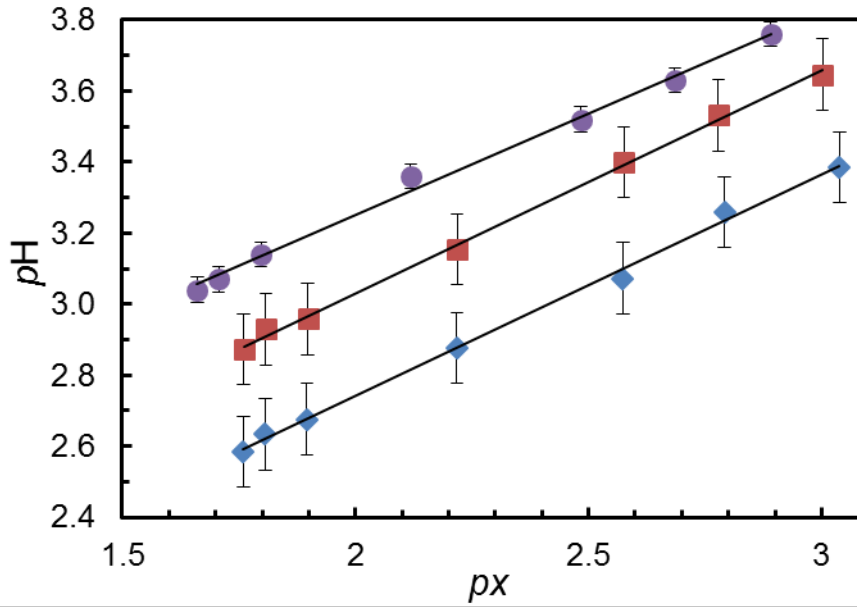
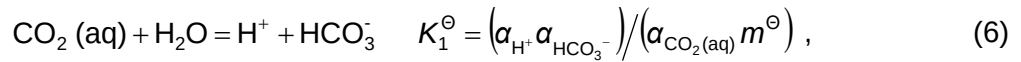


Fig. 3. pH of CO_2 -saturated $NaCl(aq)$ at $T = 323.15$ K as a function of $px = -\log_{10}(x)$, where x is the calculated mole fraction of $CO_2(aq)$ based on the model of Spycher and Pruess [51] for different brine molalities: ●, $m = 0$ mol·kg⁻¹ [11]; ■, $m = 1$ mol·kg⁻¹; ◆, $m = 5$ mol·kg⁻¹. Lines show linear regressions at $m = (0, 1$ and $5)$ mol·kg⁻¹. Error bar shows the standard uncertainty of the experimental data.

The experimental results have been compared with the predictions of the Pitzer model as implemented in PHREEQC version 3.3.9 using updated interaction parameters from the literature [20, 46], based on experimental data spanning the entire temperature range investigated in this work. As was the case for the HCl calibration solutions, these calculations of pH implement the MacInnes assumption. The primary dissociation reaction of CO_2 and the corresponding standard equilibrium constant $K_1^\ominus$ in aqueous solution can be expressed as follows



where $K_1^\ominus$ is correlated as a function of temperature. Full detailed of the chemical-equilibrium and activity-coefficient models, and values of the necessary parameters, as implemented in PHREEQC are given in the Supplementary Information. The input variables were the salt molalities in the original solution, the experimental temperature, and the partial pressure of CO_2 in the gas phase; the latter was obtained from the experimental total pressure by deducting the vapour pressure of pure water calculated from the equation of state of Wagner and Pruss [52].

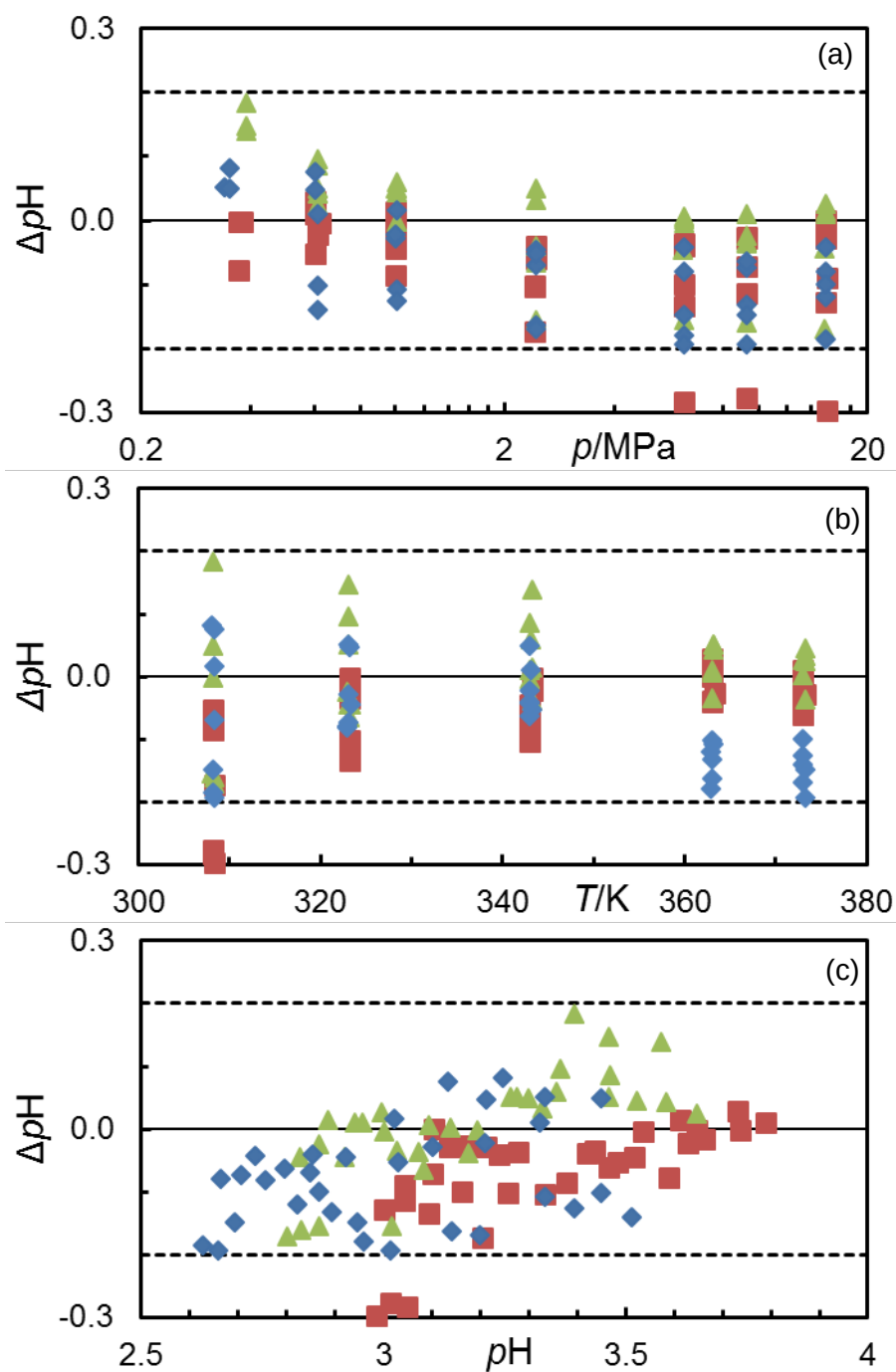


Fig. 4. Deviation $\Delta pH = pH(\text{experimental}) - pH(\text{calculated})$ of the measured pH from values calculated with PHREEQC for CO_2 -saturated $NaCl(aq)$ as functions of (a) pressure, (b) temperature and (c) pH for different brine molalities: $\blacksquare$, $m = 1 \text{ mol}\cdot\text{kg}^{-1}$; $\blacktriangle$, $m = 3 \text{ mol}\cdot\text{kg}^{-1}$; $\blacklozenge$, $m = 5 \text{ mol}\cdot\text{kg}^{-1}$. Dashed lines represent the expanded uncertainty of the experimental data at 95 % probability.

The model predictions are compared with the experimental data in Fig. 2 where one can see generally fair agreement. Fig. 4 shows deviations of the experimental pH data from the predictions of the model across all states investigated. Agreement is within about ± 0.2 pH units, and the root-mean-squared deviation over all points is 0.11. The deviations are slightly smaller at the higher temperatures studied and generally greater in magnitude at the lowest temperature studied. The calculated pH is influenced by numerous factors: the solubility of CO_2 in the aqueous phase and the associated salting-out effect, the ion-ion and ion-neutral interaction terms in the Pitzer model, and the standard equilibrium constant of reaction (6). The simulations shows a negligible molality of $CO_3^{2-}(aq)$ so that the H^+ molality is controlled by reaction (6). The low molalities of $CO_2(aq)$, $H^+(aq)$ and $HCO_3^-(aq)$ imply that the dominant interaction terms influencing K_1^O and α_{H^+} should be between those species, on the one hand, and Na^+ and Cl^- on the other. Evidence from the literature suggest that the CO_2 solubility [46, 53], chemical equilibrium constant [54] and ion interaction models [20, 46] used in the calculations are each in accord with independent experimental data. It is therefore difficult to attribute the observed differences between experiment and the model to specific failings of the latter. We also found that use of the CO_2 -ion interaction parameters determined by Truche et al. [20], in place of the default values in PHREEQC version 3.3.9, did not improve the agreement with experiment.

In Fig. 5, we compare the available experimental data for the pH of NaCl brines [18, 21, 22, 24] with the predictions of the Pitzer model in PHREEQC version 3.3.9. These data cover temperatures between (289 and 348) K, with pressures up to 11 MPa and molalities up to $4.3 \text{ mol}\cdot\text{kg}^{-1}$. Overall, one can observe a similar level of agreement as found with our new data. The bulk of the data at pressures between about (1 and 10) MPa are 0.0 to 0.2 higher than the predictions of the model. Comparing with our data in Fig. 4, where, in the same range, the most of the results are 0.0 to 0.2 below the model predictions, we can conclude that the present results are in fair agreement with the literature with average differences of about 0.2. These differences may include disparities in the operational definitions of pH adopted by different workers. Although not plotted in Fig. 5, the data of Truche et al. [20] at $473 \leq T/K \leq 553$ were reported to be in agreement with the model to within about ± 0.1 .

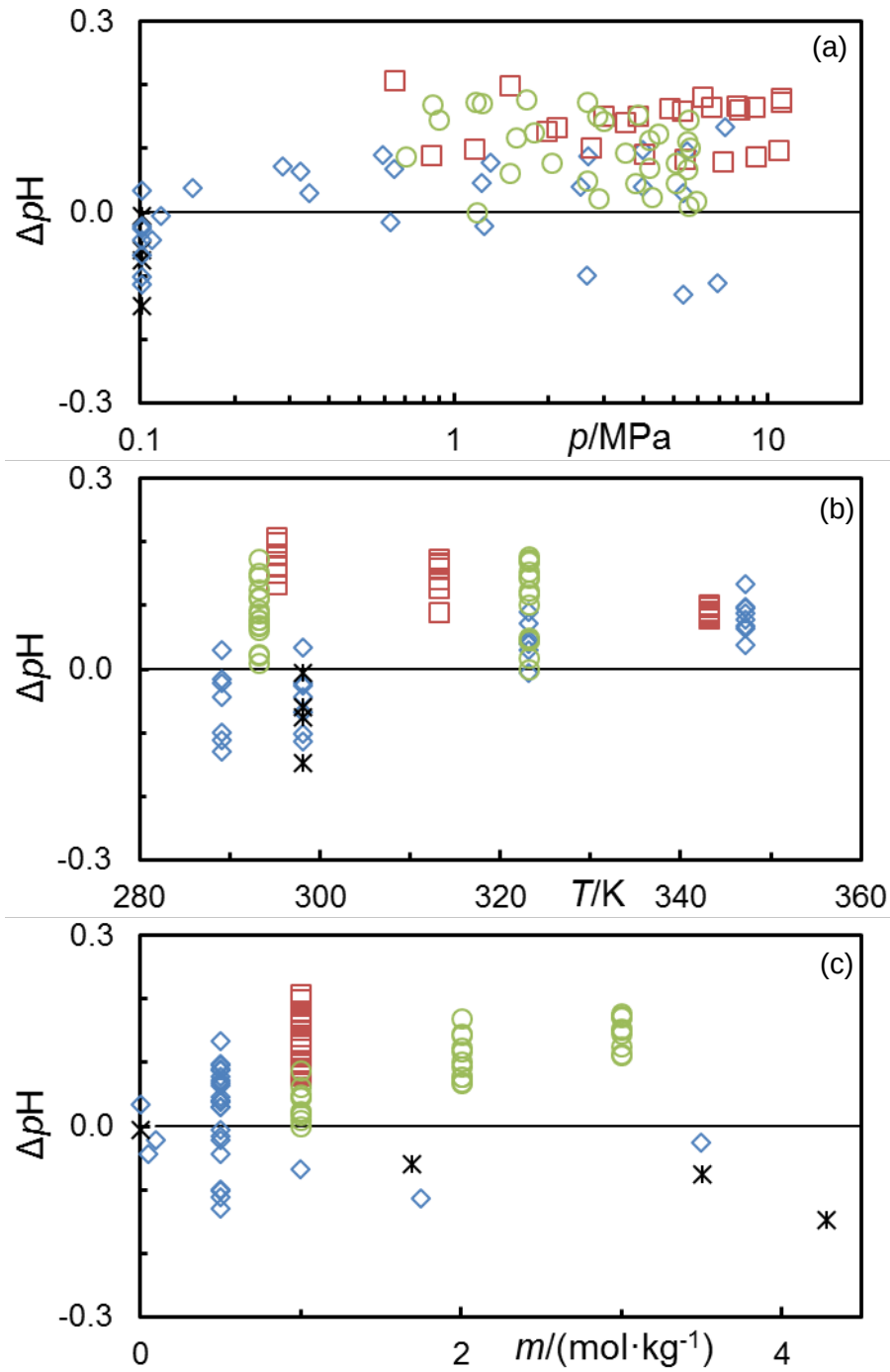


Fig. 5. Deviation $\Delta pH = pH(\text{experimental}) - pH(\text{calculated})$ of the literature pH data from values calculated with PHREEQC for CO_2 -saturated $NaCl(aq)$ as functions of (a) pressure, (b) temperature and (c) $NaCl$ molality: *, Hinds et al. [18]; $\diamond$; Crolet and Bonis [21]; $\square$, Schaef and McGrail [22]; $\circ$, Haghi et al. [24].

3.2 CO₂-saturated NaHCO₃ solution

Four isotherms for the CO₂-saturated NaHCO₃ solution were studied at temperatures of (308, 323, 338 and 353) K, pressures up to 15.3 MPa and NaHCO₃ molalities of (0.01, 0.10 and 1.00) mol·kg⁻¹; the results are presented in Table 5 and plotted as function of pressure in Fig. 6.

Table 5. Experimental pH of CO₂-saturated NaHCO₃(aq) at total pressure p , temperature T and salt molality m , where E is the measured e.m.f.^a

p (MPa)	T (K)	E (mV)	pH (-)	p (MPa)	T (K)	E (mV)	pH (-)	p (MPa)	T (K)	E (mV)	pH (-)
$m = 0.01 \text{ mol}\cdot\text{kg}^{-1}$				$m = 0.10 \text{ mol}\cdot\text{kg}^{-1}$				$m = 1.00 \text{ mol}\cdot\text{kg}^{-1}$			
0.20	308.17	196.4	5.46	0.20	308.14	146.9	6.48	0.22	308.13	84.9	7.75
0.20	323.16	195.5	5.57	0.20	323.17	141.3	6.61	0.21	323.15	72.5	7.96
0.20	338.15	186.4	5.74	0.21	338.19	131.3	6.76	0.21	338.14	59.9	8.11
0.20	353.15	172.9	5.94	0.21	353.13	114.5	7.03	0.21	353.07	43.4	8.39
0.43	308.12	221.7	5.01	0.43	308.13	169.5	6.10	0.44	308.17	102.6	7.45
0.43	323.15	217.8	5.21	0.41	323.19	161.2	6.29	0.43	323.11	90.9	7.65
0.42	338.10	211.3	5.35	0.43	338.19	150.9	6.46	0.43	338.10	80.1	7.79
0.43	353.15	201.4	5.52	0.43	353.08	139.4	6.65	0.44	353.11	71.6	7.96
0.92	308.10	243.3	4.63	0.90	308.13	188.6	5.77	0.92	308.18	129.4	6.99
0.94	323.17	239.6	4.85	0.93	323.15	185.2	5.90	0.94	323.12	120.5	7.17
0.91	338.08	232.9	5.01	0.92	338.16	175.5	6.08	0.92	338.14	108.5	7.34
0.91	353.11	225.6	5.16	0.92	353.16	163.7	6.29	0.93	353.15	97.4	7.56
2.00	308.18	261.4	4.31	2.00	308.09	208.3	5.44	2.00	308.13	146.0	6.71
1.95	323.15	258.7	4.53	2.01	323.12	204.0	5.60	2.00	323.16	139.1	6.86
2.03	338.20	254.2	4.68	2.00	338.17	195.9	5.76	2.00	338.18	129.5	7.01
1.97	353.10	249.0	4.81	2.02	353.18	187.7	5.93	2.00	353.17	122.7	7.17
4.32	308.21	279.1	4.00	4.32	308.20	212.9	5.36	4.31	308.22	162.7	6.42
4.31	323.15	278.8	4.20	4.33	323.00	210.6	5.49	4.31	323.18	159.2	6.54
4.31	338.12	277.4	4.32	4.29	338.15	205.3	5.62	4.31	338.18	147.8	6.72
4.31	353.18	273.3	4.44	4.30	353.09	202.5	5.71	4.32	353.08	138.3	6.93
9.28	308.16	285.0	3.90	9.27	308.20	218.2	5.27	9.28	308.14	168.4	6.33
9.28	323.15	287.9	4.06	9.28	323.12	216.3	5.40	9.28	323.11	162.8	6.48
9.29	338.14	288.4	4.15	9.28	338.16	212.1	5.51	9.30	338.17	158.5	6.55
9.31	353.06	289.5	4.20	9.28	353.21	207.6	5.63	9.28	353.18	152.3	6.71
15.35	308.17	289.3	3.82	15.33	308.15	220.5	5.23	15.36	308.16	170.3	6.29
15.35	323.00	291.7	3.99	15.35	323.15	219.5	5.35	15.35	323.16	165.6	6.43
15.36	338.15	292.9	4.08	15.36	338.15	216.0	5.45	15.35	338.16	161.0	6.52
15.32	353.15	293.1	4.15	15.35	353.15	209.9	5.59	15.36	353.16	154.7	6.68

^a Expanded uncertainties at 95% confidence are $U(p) = 0.07 \text{ MPa}$, $U(T) = 0.05 \text{ K}$ and $U(\text{pH}) = 0.2$.

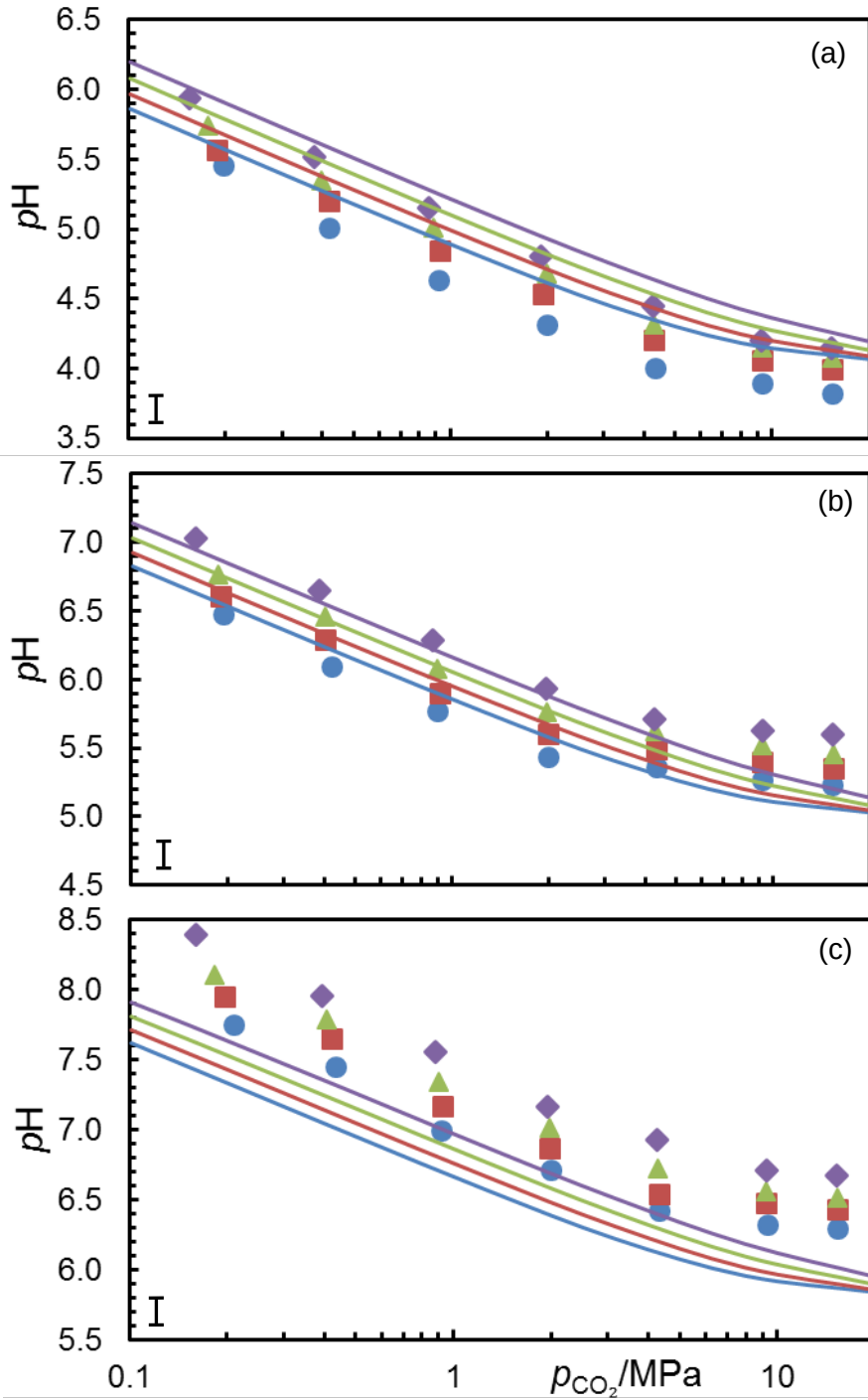


Fig. 6. pH of CO_2 -saturated $NaHCO_3(aq)$ as a function of CO_2 partial pressure at molalities of: (a) $0.01 \text{ mol}\cdot\text{kg}^{-1}$; (b) $0.10 \text{ mol}\cdot\text{kg}^{-1}$; (c) $1.00 \text{ mol}\cdot\text{kg}^{-1}$. Symbols: $\bullet$, $T = 308 \text{ K}$; $\blacksquare$, $T = 323 \text{ K}$; $\blacktriangle$, $T = 338 \text{ K}$; $\blacklozenge$, $T = 353 \text{ K}$. Lines show the pH calculated along each isotherm using PHREEQC. Error bar shows the standard uncertainty of the experimental data.

As expected, the pH falls with increasing CO_2 partial pressure and decreasing temperature. In contrast to the unreactive $NaCl$ brine, bicarbonate brines exhibit acid-base equilibria according to the following reactions



Fig. 7 shows the pH data as a function of px , calculated according to the model of Spycher and Pruess [51] as recently modified for NaHCO_3 brines by Hoballah [31]. One obvious feature is that pH rises rapidly with increasing bicarbonate molality in the original solution. A noticeable difference from the case of CO_2 -saturated NaCl(aq) is that relation between pH and px is not linear and this reflects the buffering capacity of the solution arising from reactions (7) and (8).

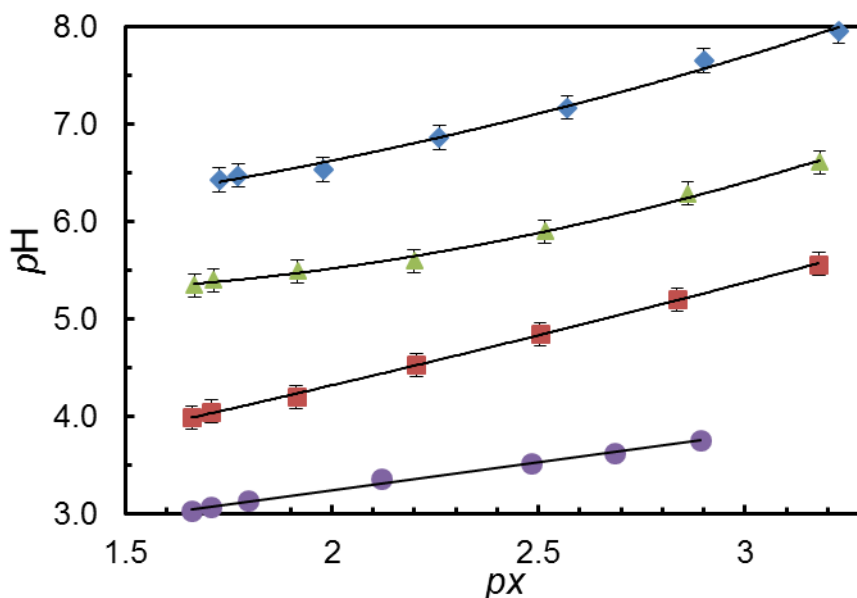


Fig. 7. pH of CO_2 -saturated $\text{NaHCO}_3(\text{aq})$ as a function of $px = -\log_{10}(x)$, where x is the calculated mole fraction of $\text{CO}_2(\text{aq})$ based on the model of Spycher and Pruess,[51] as modified by Hoballah [31], for different brine molalities: ●, $m = 0 \text{ mol}\cdot\text{kg}^{-1}$ [11]; ■, $m = 0.01 \text{ mol}\cdot\text{kg}^{-1}$ [11] ▲, $m = 0.10 \text{ mol}\cdot\text{kg}^{-1}$; ◆, $m = 1.00 \text{ mol}\cdot\text{kg}^{-1}$. Lines show quadratic regression functions. Error bar shows the standard uncertainty of the experimental data.

Also shown in Fig. 6 are the predictions of PHREEQC, again calculated at specified temperatures, CO_2 partial pressure and original salt molalities (in this case specified as the molality of Na^+ and total inorganic C). The deviations of the experimental data from the predictions of PHREEQC are plotted as functions of pressure and temperature in Fig. 8. One can observe that agreement with the model is similar to that observed for CO_2 -saturated NaCl(aq) at the two lower bicarbonate molalities but that quite-large positive deviations, averaging about 0.45 pH units, are observed at the highest salt molality. Generally, the deviations develop a slight positive bias with increasing temperature and are not strongly dependent upon pressure. Again, it is difficult to attribute the observed differences to specific failings in the modelling.

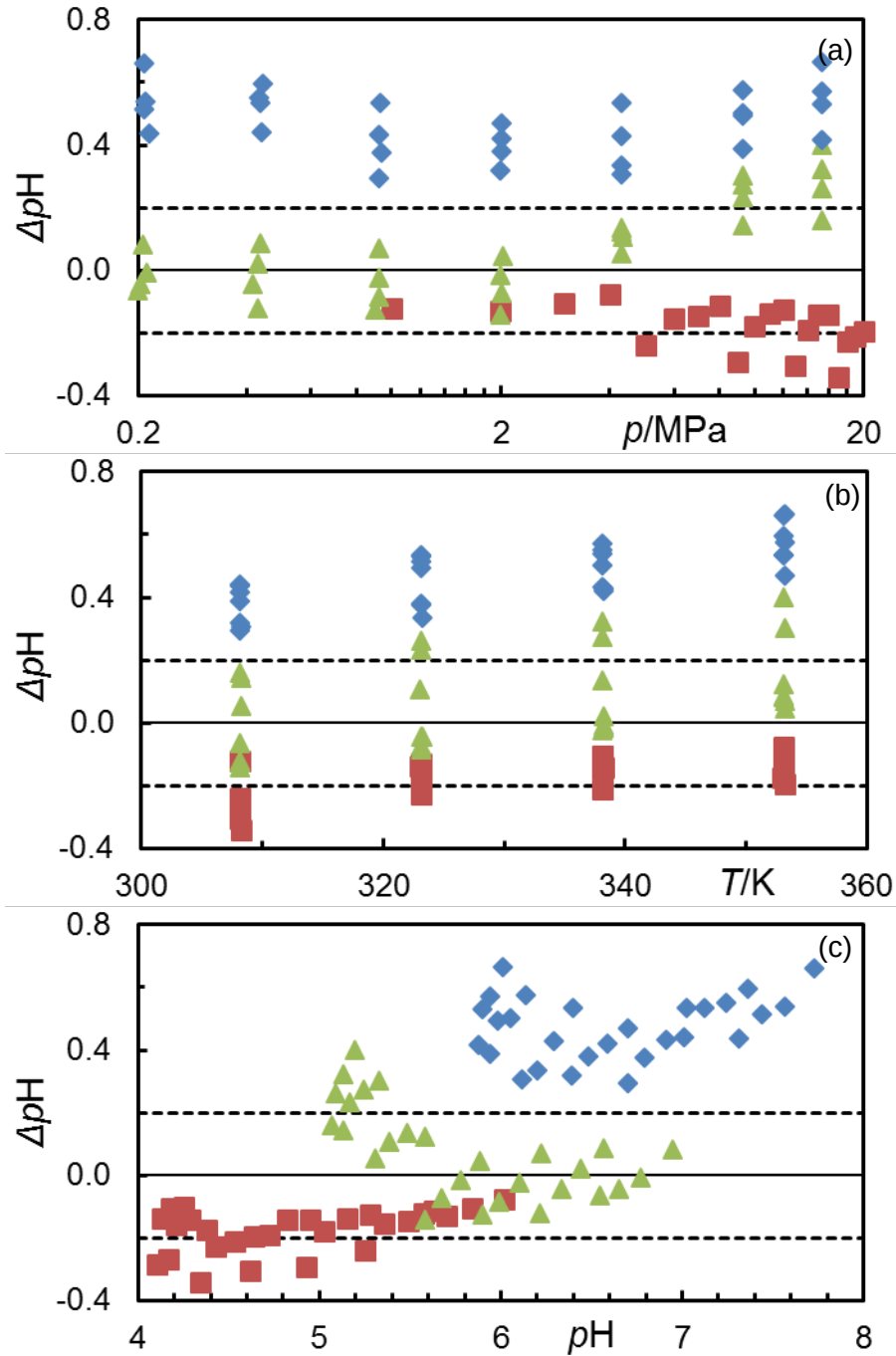


Fig. 8. Deviation $\Delta pH = pH(\text{experimental}) - pH(\text{calculated})$ of the measured pH from values calculated with PHREEQC for CO_2 -saturated $NaHCO_3(aq)$ as functions of (a) pressure, (b) temperature and (c) pH for different brine molalities: $\blacksquare$, $m = 0.01$ mol·kg⁻¹; $\blacktriangle$, $m = 0.10$ mol·kg⁻¹; $\blacklozenge$, $m = 1.00$ mol·kg⁻¹. Dashed lines represent the expanded uncertainty of the experimental data at 95 % probability.

4. Conclusions

The objectives of the present study were (a) to provide new experimental data for the pH of CO_2 -saturated brines at intermediate temperature and high pressures; and (b) to test the predictions of the PHREEQC geochemical simulator with the Pitzer model against these data when using the recent parameters from the literature. $NaCl$ and $NaHCO_3$ brines were

both studied over wide ranges of salt molality, temperature and pressure and results obtained with an expanded uncertainty of 0.20 at 95 % probability. The data extend to regions of simultaneously higher temperature, pressure and molality than previously studied in the literature. In the case of NaCl brines, we observe agreement with about ± 0.2 pH units between the model and both our experimental results and data from the literature. Similarly good agreement was observed for NaHCO₃ brines at the two lower molalities studied but, at $m = 1 \text{ mol}\cdot\text{kg}^{-1}$, the model systematically under-estimates the experimental results by about 0.5 pH units. We are unable to attribute this difference to failings of any specific aspect of the model.

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The pH of CO₂-saturated aqueous NaCl and NaHCO₃ solutions at temperatures between 308 K and 373 K at pressures up to 15 MPa

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Supplementary Information

1. Equations and parameters used in PHREEQC

The models used in PHREEQC in this work have been detailed by Plummer et al. [1] and, more recently, by Parkhurst and Appelo [2]; they are outlined briefly here together with the values of all relevant parameters used in the present study. Thermodynamic activities and mass-action equations are described for aqueous species in PHREEQC. For CO₂ gas, the fugacity coefficient is calculated with the Peng-Robinson equation of state to account for the real gas properties. Activity coefficients are calculated using the Pitzer model [3-5]. A set of functions are solved simultaneously using a modified Newton-Raphson method to determine equilibrium for a given initial condition. Many of these functions are derived from mole-balance equations for each element or from mass-action equations for pure phases. Additional functions are derived for the activity of water, aqueous charge balance, gas-phase equilibria and ionic strength.

Mass-Action Equations

PHREEQC rewrites all chemical equations in terms of master species. Equilibrium among aqueous species in an ion-association model requires that all mass-action equations for aqueous species are satisfied. In general, mass-action equations can be written as

$$K_i = \alpha_i \prod_j^{\alpha_j} \alpha_j^{-c_{ji}} \quad (\text{A.1})$$

where K_i is a temperature-dependent equilibrium constant, α_i is the activity of species i , c_{ji} is the stoichiometric coefficient of master species j in species i and N_{aq} is the total number of aqueous master species. In PHREEQC, terms on the right-hand side of an association reaction are assigned negative coefficients and terms on the left-hand side are assigned positive coefficients.

The total amount n_i of an aqueous species i can be derived from the mass-action expression:

$$n_i = m_i w_w = (K_i w_w / \gamma_i) \prod_j^{N_{aq}} a_j^{c_{j,i}} \quad (A.2)$$

where m_i is molality for species i , w_w is the mass of solvent (water) in the solution and γ_i is the activity coefficient of species i . The Newton-Raphson method uses the total derivative of the amounts of substance with respect to the master unknowns:

$$dn_i = n_i \left[d \ln(w_w) + \sum_j^{N_{aq}} c_{j,i} d \ln(a_j) - \frac{\partial}{\partial I} \ln(\gamma_i) dI \right] \quad (A.3)$$

where I is the ionic strength of the solution. The ionic strength of the aqueous solution is a master unknown and is defined as

$$I = \frac{1}{2w_w} \sum_i^{N_{aq}} z_i^2 n_i \quad (A.4)$$

where z_i is ionic charge of aqueous species i . The equilibrium constant for each chemical reaction is represented as functions of temperature by the following general form:

$$\log_{10} K = A_1 + A_2(T / K) + A_3(K / T) + A_4 \log_{10}(T / K) + A_5(K / T)^2 + A_6(T / K)^2 \quad (A.5)$$

Relevant parameters are given in Table A.1

Table A.1

The temperature-dependent constant used in PHREEQC

Chemical equation	A_1	A_2	A_3	A_4	A_5	$10^5 A_6$
$\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$	107.8975	0.03252849	-5151.79	-38.92561	563713.9	
$\text{CO}_3^{2-} + 2\text{H}^+ = \text{CO}_2 + \text{H}_2\text{O}$	464.1965	0.09344813	-26986.16	-165.75951	2248628.9	
$\text{NaCl} = \text{Cl}^- + \text{Na}^+$	159.605	0.084294	-3975.6	-66.857	0	-4.9364
$\text{NaHCO}_3 = \text{CO}_3^{2-} + \text{H}^+ + \text{Na}^+$	-10.742					
$\text{CO}_{2(g)} = \text{CO}_{2(aq)}$	10.5624	-0.023547	-3972.8		0	587460
						1.9194

CO₂ Solubility Model

The molality m_{CO_2} of dissolved CO₂ is given by an extended form of Henry's law as follows

$$m_{\text{CO}_2} = K_H \frac{\phi_{\text{CO}_2} p_{\text{CO}_2}}{\gamma_{\text{CO}_2}} \quad (A.6)$$

where γ_{CO_2} is the activity coefficient of CO₂ in solution, K_H is the equilibrium constant, p_{CO_2} is the partial pressure of CO₂, and ϕ_{CO_2} is the fugacity coefficient of CO₂. In PHREEQC, the constant K_H is correlated as a function of temperature according to equation (A.5) and the relevant parameters are given in Table A.1. PHREEQC calculates the fugacity coefficient from the Peng-Robinson equation of state with classical van der Waals one-fluid mixing rules [6]. For CO₂, the critical temperature, critical pressure and acentric factor used are 304.2 K, 7.373 MPa and 0.225 respectively; for H₂O, the corresponding values were 647.3 K, 22.05 MPa and 0.344. The CO₂-H₂O binary interaction parameter was 0.19 [7].

Pitzer Model for Activity Coefficients

The Pitzer model is used to calculate the activity coefficients of aqueous species in the solution. The Pitzer equation combines the Debye–Hückel equation with additional terms in the form of a virial expansion and this has proved to be a great success in predicting the behavior of single- and mixed-salt solutions up to a high concentration [3, 8]. As implemented in PHREEQC, the activity coefficients of cations (M), anions (X) and neutral species (N) are given as follows:

$$\ln \gamma_M = z_M^2 F + \sum_{a=1}^{N_a} m_a (2B_{Ma} + ZC_{Ma}) + \sum_{c=1}^{N_c} m_c (2\Phi_{Mc} + \sum_{a=1}^{N_a} m_a \Psi_{Mca}) + \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \Psi_{Maa'} \\ + |z_M| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + 2 \sum_{n=1}^{N_n} (m_n \lambda_{nM}) + 6 \sum_{n=1}^{N_n} \sum_{a=1}^{N_a} m_n m_a \xi_{Mna} \quad (\text{A.7})$$

$$\ln \gamma_X = z_X^2 F + \sum_{c=1}^{N_c} m_c (2B_{cX} + ZC_{cX}) + \sum_{a=1}^{N_a} m_a (2\Phi_{Xa} + \sum_{c=1}^{N_c} m_c \Psi_{Xac}) + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} \Psi_{cc'X} \\ + |z_X| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + 2 \sum_{n=1}^{N_n} (m_n \lambda_{nX}) + 6 \sum_{n=1}^{N_n} \sum_{a=1}^{N_a} m_n m_a \xi_{ncX} \quad (\text{A.8})$$

$$\ln \gamma_N = 2 \sum_{n=1}^{N_n} m_n \lambda_{Nn} + 2 \sum_{a=1}^{N_a} m_a \lambda_{Na} + 2 \sum_{c=1}^{N_c} m_c \lambda_{Nc} \quad (\text{A.9})$$

Here, N_a is the number of anions, N_c is the number of cations, N_n is the number of neutral solutes, m denotes molality, z denotes charge number and Z is given by

$$Z = \sum_i m_i |z_i|. \quad (\text{A.10})$$

The function F is based on the extended Debye–Hückel equation and is given by

$$F = -A^\phi \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right] + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a B'_{ca} + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} \Phi'_{cc'} + \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \Phi'_{aa'} \quad (\text{A.11})$$

with $b = 1.2$. The term A^ϕ is a function of temperature, closely related to the Debye–Hückel ‘constant’, and is given numerically by

$$A^\phi = \left(1400684 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \left(\frac{\rho_w / (1000 \text{ kg} \cdot \text{m}^{-3})}{\epsilon_w (T / \text{K})} \right)^{3/2} \right), \quad (\text{A.12})$$

where ϵ_w is the relative permittivity (dielectric constant) and ρ_w is the density of saturated liquid water. The parameters B_{MX} and B'_{MX} depend on the ionic strength and are given as follows:

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 I^{0.5}) + \beta_{MX}^{(2)} g(\alpha_2 I^{0.5}) \quad (\text{A.13})$$

$$B'_{MX} = [\beta_{MX}^{(1)} g'(\alpha_1 I^{0.5}) + \beta_{MX}^{(2)} g'(\alpha_2 I^{0.5})] / I. \quad (\text{A.14})$$

Here, α_1 and α_2 are constants depending on the charge of the ions in solution. In the present case, where we have solutions containing at least one univalent ion, α_1 and α_2 are (2.0 and 0) $\text{kg}^{1/2} \cdot \text{mol}^{-1/2}$, respectively. The functions $g(x)$ and $g'(x)$ are defined as follows:

$$g(x) = 2x^{-2} [1 - (1+x)e^{-x}] \quad (\text{A.15})$$

$$g'(x) = -2x^{-2}[1 - (1 + x + \frac{1}{2}x^2)e^{-x}] \quad (\text{A.16})$$

The remaining terms are given by

$$C_{MX} = C_{MX}^{\phi} / (2\sqrt{|z_M z_X|}) \quad (\text{A.17})$$

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad (\text{A.18})$$

$$\Phi'_{ij} = {}^E\theta'_{ij}(I) \quad (\text{A.19})$$

where ${}^E\theta_{ij}(I)$ and ${}^E\theta'_{ij}(I)$ are functions of ionic strength defined by Pitzer [4]. The parameters appearing in these equations are $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, C_{MX}^{ϕ} , θ_{ij} , λ_{Nj} and ψ_{ijk} , each of which is generally temperature dependent. In PHREEQC, Pitzer coefficients, P , are correlated as functions of temperature in the following general form:

$$P(T) = B_0 + B_1(K/T - K/T_R) + B_2 \log(T/T_R) + B_3[(T - T_R)/K] + B_4[(T^2 - T_R^2)/K^2] + B_5[(K/T)^2 - (K/T_R)^2] \quad (\text{A.17})$$

where $T_R = 298.15$ K. The relevant parameters used in this work are given in Table A.2. Example PHREEQ input files are given in Table A.3.

Table A.2. Parameters used in the Pitzer database with PHREEQC (unlisted parameters are zero)

Ions	B_0	B_1	B_2	B_3	B_4	B_5	Ref
$\beta_{MX}^{(0)}$							
Na ⁺ Cl ⁻	0.07534	9598.4	35.48	$-5.8731 \cdot 10^{-2}$	$1.798 \cdot 10^{-5}$	0	[9]
K ⁺ Cl ⁻	0.04808	-758.48	-4.7062	0.010072	$-3.7599 \cdot 10^{-6}$	0	[9]
H ⁺ Cl ⁻	0.1775	0	0	$-3.081 \cdot 10^{-4}$	0	0	[1]
Na ⁺ OH ⁻	0.0864	0	0	$7.00 \cdot 10^{-4}$	0	0	[1]
Na ⁺ HCO ₃ ⁻	0.0290	$1.16 \cdot 10^3$	6.96	$-1.00 \cdot 10^{-2}$	0	0	[10]
Na ⁺ CO ₃ ²⁻	0.0370	$-1.32 \cdot 10^3$	-5.0990	$4.55 \cdot 10^{-3}$	0	0	[10]
$\beta_{MX}^{(1)}$							
Na ⁺ Cl ⁻	0.2769	$1.377 \cdot 10^4$	46.8	$-6.9512 \cdot 10^{-2}$	$2 \cdot 10^{-5}$	$-7.4823 \cdot 10^5$	[9]
K ⁺ Cl ⁻	0.2168	0	-6.895	$2.262 \cdot 10^{-2}$	$-9.293 \cdot 10^{-6}$	$-1 \cdot 10^5$	[9]
H ⁺ Cl ⁻	0.2945	0	0	$1.419 \cdot 10^{-4}$	0	0	[1]
Na ⁺ OH ⁻	0.2530	0	0	$1.34 \cdot 10^{-4}$	0	0	[1]
Na ⁺ HCO ₃ ⁻	0.0410	$-1.91 \cdot 10^2$	-0.1323	$-3.91 \cdot 10^{-4}$	0	0	[10]
Na ⁺ CO ₃ ²⁻	1.4940	$-1.70 \cdot 10^4$	-95.909	$1.36 \cdot 10^{-1}$	0	0	[10]
$\beta_{MX}^{(2)}$							
Na ⁺ OH ⁻	8.22	0	0	-0.049	0	0	[9]
$C_{MX}^{(\phi)}$							
Na ⁺ Cl ⁻	$1.48 \cdot 10^{-3}$	-120.5	-0.2081	0	$1.166 \cdot 10^{-7}$	11121	[9]
K ⁺ Cl ⁻	$-7.88 \cdot 10^{-4}$	91.27	0.58643	$-1.298 \cdot 10^{-3}$	$4.9567 \cdot 10^{-7}$	0	[9]
H ⁺ Cl ⁻	0.0008	0	0	$6.21 \cdot 10^{-5}$	0	0	[1]
Na ⁺ OH ⁻	0.0044	0	0	$-1.894 \cdot 10^{-4}$	0	0	[1]
Na ⁺ HCO ₃ ⁻	0	0	0	0	0	0	[10]
Na ⁺ CO ₃ ²⁻	0.0052	$1.08 \cdot 10^2$	-0.0835	$8.47 \cdot 10^{-4}$	0	0	[10]
θ_{ij}							
Cl ⁻ CO ₃ ²⁻	-0.02	0	0	0	0	0	[1]
Cl ⁻ HCO ₃ ⁻	0.03	0	0	0	0	0	[1]
Cl ⁻ OH ⁻	-0.05	0	0	0	0	0	[1]
CO ₃ ²⁻ OH ⁻	0.1	0	0	0	0	0	[1]
H ⁺ Na ⁺	0.036	0	0	0	0	0	[1]
K ⁺ Na ⁺	-0.012	0	0	0	0	0	[1]
HCO ₃ ⁻ CO ₃ ²⁻	-0.04	0	0	0	0	0	[1]
λ_{Nj}							
CO ₂ Cl ⁻	-0.005	0	0	0	0	0	[1]
CO ₂ Na ⁺	0.085	0	0	0	0	0	[1]
CO ₂ HCO ₃ ⁻	-0.0418	0	0	0	0	0	[11]
CO ₂ CO ₂	$-1.34 \cdot 10^{-2}$	348	0.803	0	0	0	
ψ_{ijk}							
Cl ⁻ CO ₃ ²⁻ Na ⁺	0.0085	0	0	0	0	0	[1]
Cl ⁻ H ⁺ Na ⁺	-0.004	0	0	0	0	0	[1]
Cl ⁻ HCO ₃ ⁻ Na ⁺	0	0	0	0	0	0	[9]
Cl ⁻ Na ⁺ OH ⁻	-0.006	0	0	0	0	0	[1]
CO ₃ ²⁻ HCO ₃ ⁻ Na ⁺	0.002	0	0	0	0	0	[1]
CO ₃ ²⁻ Na ⁺ OH ⁻	-0.017	0	0	0	0	0	[1]

Table A.3. Example PHREEQ input files to compute the pH of calibration solutions and of CO_2 -saturated brines.

Calibration solution comprising 5 mol·kg ⁻¹ NaCl + 0.01 mol·kg ⁻¹ HCl at $t/^\circ C = 35, 50, 70, 90$ and 100	Calibration solution comprising 0.0125 mol·kg ⁻¹ NaCl + 0.0025 mol·kg ⁻¹ NaHCO ₃ + 0.0025 mol·kg ⁻¹ Na ₂ CO ₃ at $t/^\circ C = 35, 50, 65$ and 80	5 mol·kg ⁻¹ NaCl(aq) saturated with CO ₂ at $\Omega_{CO_2} = 2.295$ * and $t = 35.09$ °C.
SOLUTION 1 temp 20 pH 7 pe 4 redox pe units mol/kgw density 1 Na 5 Cl 5 -water 1 # kg REACTION 1 HCl 1 0.01 moles in 1 steps save solution 1 end PITZER -MacInnes true -use_etheta true -redox false use solution 1 REACTION_TEMPERATURE 1 35 50 70 90 100	SOLUTION 1 temp 20 pH 7 charge pe 4 redox pe units mol/kgw density 1 C 0.005 Cl 0.00125 Na 0.00875 -water 1 # kg save solution 1 end PITZER -MacInnes true -use_etheta true -redox false use solution 1 REACTION_TEMPERATURE 1 35 50 65 80	PITZER -MacInnes true -use_etheta true -redox false EQUILIBRIUM_PHASES 1 CO2(g) 2.295 100 SOLUTION 1 temp 35.09 pH 7 charge pe 4 redox pe units mol/kgw density 1 Cl 5 Na 5

* $\Omega_{CO_2} = -\log_{10}(p_{CO_2}/p_0)$ where p_{CO_2} is the partial pressure of CO₂ and $p_0 = 0.010325$ MPa.

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