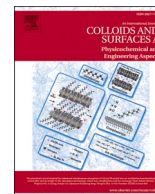




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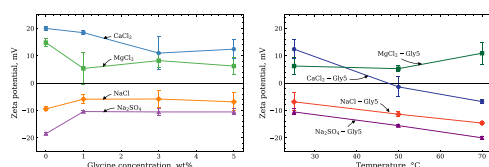
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The impact of glycine on the zeta potential of calcite at different temperatures and brine compositions

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GRAPHICAL ABSTRACT



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ABSTRACT

This study presents zeta potential (ZP) measurements of synthetic calcite in glycine solutions using the electrophoretic method. We tested samples with glycine concentrations of 1, 3, and 5 wt% at 25°C, while the ZP of 5 wt% glycine solutions was also measured at 50 and 75°C. The first set of measurements consisted of single-component brines prepared with CaCl₂, MgCl₂, Na₂SO₄, and NaCl salts with an ionic strength of 0.05 M. The second set of measurements consisted of formation brine (FB) with an ionic strength of 6.37 M and FB diluted 2-, 10-, and 100-times (2dFB, 10dFB, 100dFB, respectively). Results show that the effect of glycine on calcite's ZP depended on its initial ZP value. Moreover, the increase in temperature significantly decreased calcite's ZP in most samples. The ZP values in CaCl₂ and MgCl₂ brines were initially positive and decreased with the addition of glycine. Conversely, the ZP values of calcite in NaCl and Na₂SO₄ brines were initially negative and increased with the addition of glycine. The trends of ZP versus glycine concentration for 2dFB and 10dFB were analogous to the ones with CaCl₂ and MgCl₂ brines. Similar trends were observed between 100dFB, NaCl, and Na₂SO₄ brines. Finally, the increase of temperature from 25°C to 50°C and 70°C significantly reduced the ZP of calcite's particles in CaCl₂, Na₂SO₄, and NaCl brines, while the ZP of FB and its dilutions slightly decreased at 50°C. This is the first time the ZP measurements of calcite in glycine solutions were reported, to the best of our knowledge. Results are mainly explained by (1) the adsorption of glycine anion onto the calcite's surface, (2) the decrease of the brine's pH from the addition of glycine, and (3) the complex formation of glycine with divalent ions. Given the ubiquity and abundance of calcite in nature, we expect this study to increase the understanding of the electrostatic interactions between amino acids and calcite in phenomena such as wettability alteration and biomineralization.

1. Introduction

The addition of glycine (Fig. 1) to waterflooding operations has been

investigated as an enhanced oil recovery method for carbonate reservoirs by shifting the originally oil-wet rock surface towards a water-wetting state [1]. The working hypothesis is that wettability alteration

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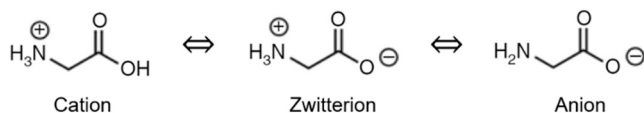


Fig. 1. Chemical structure of the cationic, zwitterion (neutral), and anionic forms of glycine.

by glycine occurs when the solution pH is larger than glycine's isoelectric point (pI). Under this condition, the glycine anion can favorably interact with the positively-charged calcite surface, removing the adsorbed carboxylic acids that have rendered the calcite surface oil-wet. This change of the calcite surface wetting-state has been linked to the change in calcite's electrostatic properties in many studies [2,3]. The objective of this research is to determine the impact of glycine on the zeta potential (ZP) of calcite as a function of brine composition and temperature. The results are expected to help understand the mechanisms and conditions that affect the performance of glycine as a wettability modifier for carbonate rocks.

The ZP of calcite is a function of the adsorption of the ions in solution – called 'potential determining ions' (PDIs) – that can form complexes with the calcite surface sites, $>\text{CaOH}$ and $>\text{CO}_3\text{H}$, where $>$ denotes a crystal lattice [4]. Most studies have focused on the divalent ions Ca^{2+} , Mg^{2+} , CO_3^{2-} , and SO_4^{2-} that are abundant in seawater, while Na^+ and Cl^- ions have been considered indifferent ions [5–10]. In general, the adsorption of the cations Ca^{2+} and Mg^{2+} will increase the ZP of calcite, while the adsorption of the SO_4^{2-} and CO_3^{2-} anions will decrease the ZP.

The ZP of carbonate rocks has been observed to decrease as the solution pH increases [11–13]. These results had been previously explained by the protonation/deprotonation of $>\text{CaOH}$ and $>\text{CO}_3\text{H}$ surface sites [4]. However, it has been shown that, within experimental error, ZP does not change as a function of pH when the calcium concentration is kept constant [6]. The explanation is that the change in pH shifts the speciation of carbonate species in solution and influences the dissolution and precipitation of calcite [6,14–16]. Hence, the ZP of carbonate rocks is indirectly affected by the solution pH that controls the concentration of Ca^{2+} and CO_3^{2-} ions in solution.

In this research, we present zeta potential measurements of calcite particles using the electrophoretic method. The impact of brine composition was investigated by measuring the ZP of calcite in 1, 3, and 5-wt% glycine solutions with the single-component brines, NaCl, CaCl_2 , MgCl_2 , and Na_2SO_4 , at 25, 50, and 70°C. The impact of glycine on the ZP

of calcite was also investigated in a non-ideal synthetic brine with a composition based on the formation brine of a carbonate reservoir [1], also at temperatures of 25, 50, and 70°C.

2. Materials and methods

We prepared samples using deionized water with a resistivity of 18 MΩ-cm and pH of 5.6 at room conditions. High purity salts were purchased from Sigma-Aldrich: NaCl (>99.5%), Na_2SO_4 (>99%), NaHCO_3 (>99.7%), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (>99%), and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (>96%). Tables 1–3 give the brine compositions used in this research. Glycine was obtained from Sigma-Aldrich as a powder with a purity of 99%. Synthetic calcite powder with a purity of > 99.5% and a particle diameter of 5 μm was purchased from Alfa Aesar.

For each sample, a 50-ml plastic vial was filled with the solution to be tested and its pH was recorded. To prepare the calcite suspension, we added 1 g of synthetic calcite powder to the solution and ultrasonicated for 30 min to disperse the calcite particles (Fig. 2a). These solutions were then stored in capped vials for 10 days to achieve chemical equilibrium. After equilibration, the final samples were obtained by transferring 15 ml of supernatant from the equilibrated solutions to a new plastic vial, which was then ultrasonicated for 30 min before performing the ZP measurements (Fig. 2b). After the ZP measurements, the equilibrium pH was measured using the remaining samples. The equilibrium condition was confirmed by comparing the initial and equilibrium pH values with the ones calculated by thermodynamic modeling using PHREEQC v3.6.2 (Appendix).

We used a Zetasizer Nano ZS from Malvern Instruments for the ZP measurements. This instrument, based on the phase-analysis light-scattering (ζ-PALS) technique, measures the electrophoretic mobility of calcite particles and calculates the ZP according to the Helmholtz-Smoluchowski equation [17]. This instrument requires a disposable folded capillary cell (DTS1070 from Malvern Instruments) for the measurements, which has a minimum sample volume of 0.75 ml and is compatible up to 70°C.

The experimental procedure was based on Ding and Rahman [18], who used the same instrument. The capillary cells were carefully filled with 1 ml of sample avoiding the introduction of air bubbles and inserted into the equipment. Then, the temperature was set to 25°C allowing for 5 min of equilibration before starting the measurements. Next, the ZP is measured five times using the monomodal analysis that

Table 1

Ionic compositions of brines with various mixing ratios of NaCl with CaCl_2 , MgCl_2 , and Na_2SO_4 with an ionic strength of 0.05 M.

Brine	Composition (mg/L)						Ionic strength (mol/kgw)
	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	
25%- CaCl_2	671.77	36.87	0	1101.18	0	0	0.05
50%- CaCl_2	163.44	239.01	0	674.9	0	0	0.05
75%- CaCl_2	12.55	479.11	0	866.96	0	12.55	0.05
25%- MgCl_2	623.89	0	27.98	1043.75	0	0	0.05
50%- MgCl_2	131.34	0	156.28	658.39	0	0	0.05
75%- MgCl_2	9.6	0	293.71	871.51	0	0	0.05
25%- Na_2SO_4	764.15	0	0	1135.26	58.47	0	0.05
50%- Na_2SO_4	459.17	0	0	351.66	482.89	0	0.05
75%- Na_2SO_4	554.75	0	0	0	1117.23	0	0.05

Table 2

Ionic compositions of brines using NaCl, CaCl_2 , MgCl_2 , and Na_2SO_4 with an ionic strength of 0.05 M.

Brine	Composition (mg/L)						Ionic strength (mol/kgw)
	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	
NaCl	1149.49	0	0	1772.65	0	0	0.05
CaCl_2	0	668	0	1181.76	0	0	0.05
MgCl_2	0	0	405.16	1181.76	0	0	0.05
Na_2SO_4	766.32	0	0	0	1601	0	0.05

Table 3
Ionic compositions of formation brine (FB) and its dilutions.

Brine	Composition (mg/L)						Ionic strength (mol/kgw)
	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	
FB	70,991	19,080	2561	150,165	588	186	6.37
2dFB	35495.5	9540	1280.5	75082.5	294	93	3.32
10dFB	7099.1	1908	256.1	15016.5	58.8	18	0.49
100dFB	709.91	190.81	25.61	1501.65	5.88	1.86	0.05

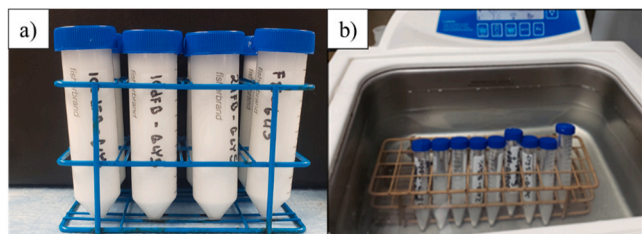


Fig. 2. a) Initial 50 ml samples equilibrated with synthetic calcite for 10 days at room conditions and b) ultrasonication of final 15 ml samples obtained from the supernatant of the initial 50 ml samples.

reports the mean ZP of the sample. Each ZP measurement consisted of a minimum of 50 runs. The average and standard deviation of the 5 measured ZP were reported.

For the high-temperature ZP measurements, the single-component brine samples were equilibrated for 10 days at room temperature. The samples prepared with formation brine and its dilutions were equilibrated for 10 days at the corresponding temperature of the measurement, 50°C and 70°C, instead of at room temperature. At the time of the measurement, the instrument was set to the temperatures of interest, 50°C and then 70°C, allowing for 5 min for thermal equilibrium. If significant corrosion was observed on the cell's electrodes, it was discarded, and a new cell was used for subsequent measurements. Otherwise, the cell was reused by first thoroughly cleaning it with deionized water and then rinsing the cell with the next sample to be tested.

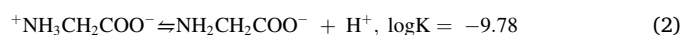
3. Results and discussions

3.1. Single component brines

This section presents the ZP results of calcite particles in glycine solutions prepared with the single-component brines, NaCl, CaCl₂, MgCl₂, and Na₂SO₄, at a fixed ionic strength of 0.05 M. First, a comparison is presented between the measured ZP values and the data reported in the literature for brines without glycine. Then, the ZP values for 1, 3, and 5 wt% glycine solutions prepared with single-component brines at 25°C are reported and discussed. Finally, the effect of temperature is discussed based on the ZP values obtained for glycine solutions at 50°C and 70°C.

3.1.1. Effect of glycine concentration on solution pH

Fig. 3 shows the initial and equilibrium solution pH of single-component brine with respect to glycine concentration. The addition of glycine significantly reduced the solution pH of all brines. The pH values also converge to glycine's isoelectric point of 6.06 [19]. The chemical reactions controlling glycine's speciation are given by



The solution pH decreased because of the deprotonation of glycine zwitterion to form glycine anion as given by Eq. (2).

We measured the solution pH again after adding calcite powder and the samples were then equilibrated for 10 days at room conditions (Fig. 3b). The equilibrium pH for all brines increased after equilibration because of calcite dissolution, as given by

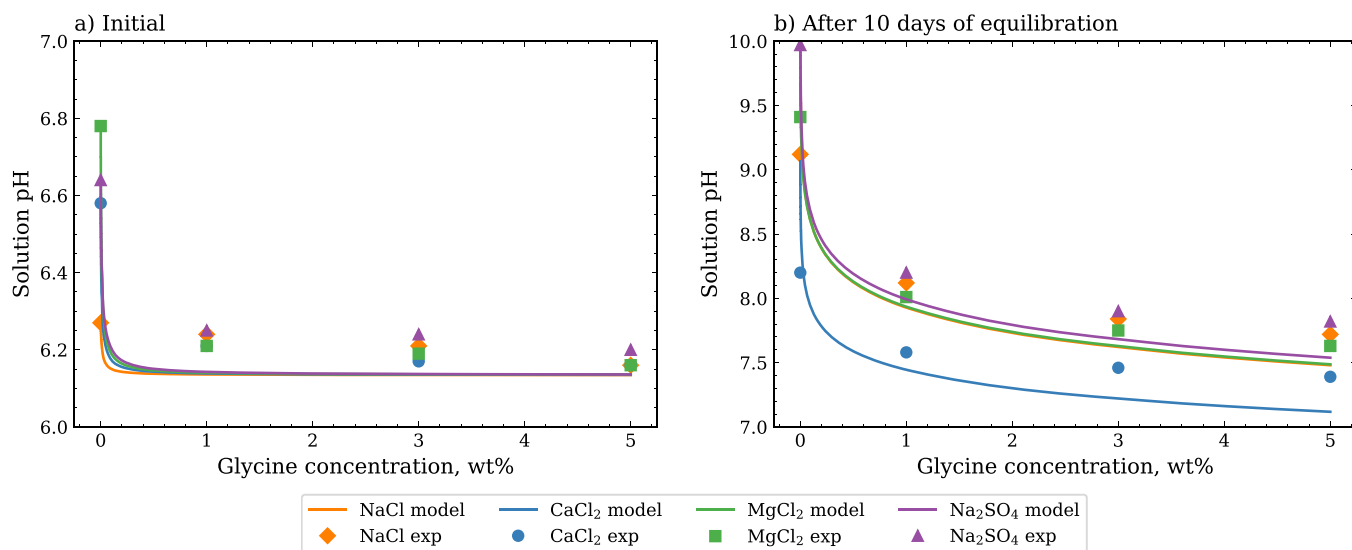


Fig. 3. Solution pH versus glycine concentration for a) initial values and b) after 10 days of equilibration at room conditions. The glycine solutions were prepared with the 0.05 M single-component brines NaCl, CaCl₂, MgCl₂, and Na₂SO₄. The solid lines represent the pH values predicted by PHREEQC (Appendix).

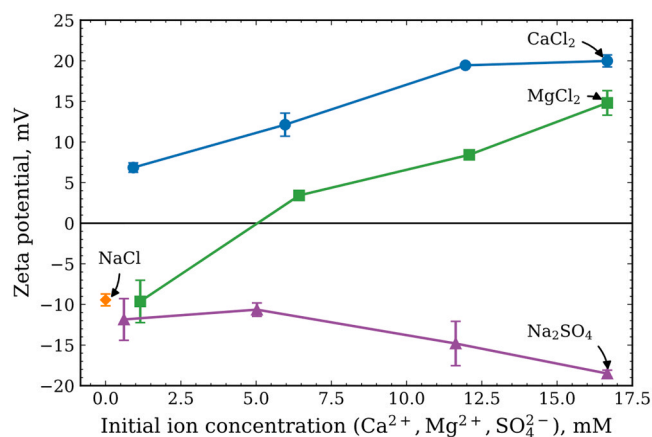


Fig. 4. Zeta potential versus initial concentration of Ca^{2+} , Mg^{2+} and SO_4^{2-} for single component brines prepared with CaCl_2 , MgCl_2 , and Na_2SO_4 , respectively. The initial ionic concentrations refer to the brine composition before the addition of calcite.

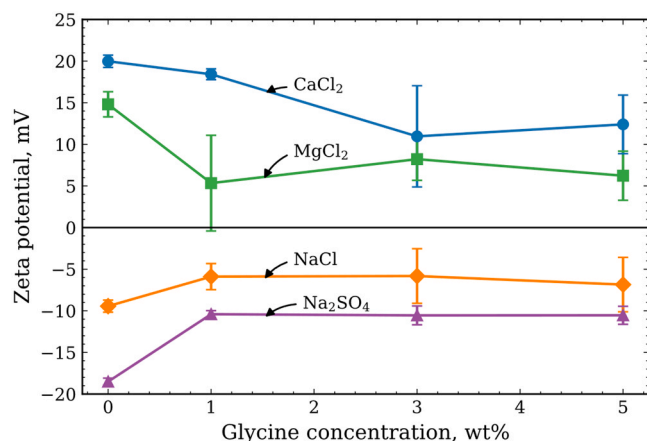


Fig. 5. Zeta potential measured at different glycine concentrations for glycine solutions in the 0.05 M single-component brines NaCl , CaCl_2 , MgCl_2 , and Na_2SO_4 . The measurements were at 25°C and 1 atm.

The initial pH value of NaCl , CaCl_2 , MgCl_2 , and Na_2SO_4 brines were used as an input to calculate the change in pH as a function of glycine concentration and the equilibrium pH after equilibration with calcite (Appendix). The comparison shown in Fig. 3 shows a good agreement between the experimental values and the chemical model; hence, the samples can be assumed close to be in equilibrium with calcite.

3.1.2. Validation of experimental procedure

To validate the sample preparation and experimental procedure, we conducted ZP measurements with increasing amounts of PDIs, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , with a fixed ionic strength of 0.05 M, and compared the results with previous studies. The brines were prepared by mixing NaCl with CaCl_2 , MgCl_2 , Na_2SO_4 at different mass ratios (1:4, 1:1, and 4:1), with a constant ionic strength of 0.05 M (Table 1). The measured ZPs of the brines prepared with CaCl_2 , MgCl_2 , and Na_2SO_4 salts are plotted in Fig. 4 as a function of the PDIs concentration, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , respectively. The reference point is the ZP of calcite particles measured in 0.05 M NaCl brine.

Fig. 4 shows an increasing trend of ZP with increasing calcium concentrations. This is consistent with the results reported by previous studies, in which increasing concentrations of Ca^{2+} ions led to higher ZP values for synthetic calcite [7] and carbonate rocks [5,8]. The impact of calcium concentration on the ZP of calcite has been explained by the

adsorption of Ca^{2+} ions onto the surface of the calcite particles [20]. Similarly, the ZP of MgCl_2 brines in Fig. 4 shows an increasing trend with increasing magnesium concentrations. Although the impact of Mg^{2+} ions on the ZP of calcite surface has not been studied as extensively as the impact of Ca^{2+} ions, both divalent ions are expected to influence ZP to a similar extent [7,9]. The ZP of Na_2SO_4 brines in Fig. 4 shows a decreasing trend with increasing sulfate concentration. Several studies reported that ZP became smaller by increasing the SO_4^{2-} concentration in Na_2SO_4 brines [5,7] or enriching seawater with sulfate ions [9,18]. This has been explained by the direct adsorption of SO_4^{2-} ions onto the calcite surface [8].

The ZP trends for the single-component brines, CaCl_2 , MgCl_2 , Na_2SO_4 , satisfactorily agreed with the trends reported in the literature [5,7,18]. The ZP values for single-component brines were similar in magnitude and sign to the values reported in Alotaibi and Yousef [9]. Therefore, the ZP results presented for single-component brines in this section serve as base cases for the following ZP measurements with glycine solutions.

3.1.3. Effect of glycine concentration on zeta potential

Fig. 5 presents the calculate ZP values measured for CaCl_2 , MgCl_2 , Na_2SO_4 , and NaCl at 1, 3, and 5 wt% glycine at 25°C. The impact of glycine on the calcite ZP depended on the sign of the ZP values of the brines without glycine. For initially positive ZP, the addition of glycine resulted in a reduction of the ZP as was the case for CaCl_2 and MgCl_2 brines. For initially negative ZP, like NaCl and Na_2SO_4 brines, the ZP increased with the addition of glycine. In both cases, the impact of glycine reached a plateau at a concentration of 3 wt%.

The impact of glycine on the ZP of CaCl_2 and MgCl_2 brines can be explained by two mechanisms. Glycine can directly reduce calcite's ZP by adsorption of glycine anion on the positively charged surface. This occurs because the solution pH is larger than glycine's pI. Also, glycine can indirectly reduce the ZP by chelating Ca^{2+} and Mg^{2+} present in the solution [21]. The reduction of the activity of calcium and magnesium ions results in decreasing the adsorption from the calcite particle's surface. The combined effect on calcite's ZP of glycine adsorption and the reduction of calcium and magnesium activities must be greater than the impact of decreasing the solution pH when the calcite ZP reduces with increasing concentration of glycine.

For Na_2SO_4 and NaCl brines, the initial ZP was negative, and the addition of glycine resulted in an increase of ZP for 1 wt% glycine solutions, with no significant changes of the ZP for larger glycine concentrations. As described before, the addition of glycine results in a significant decrease of the solution pH, which in turn increases the ZP. At larger glycine concentrations, however, the ZP does not significantly change because the solution pH remains almost constant (Fig. 3). Moreover, the adsorption of glycine anion is not significant because the surface is initially negatively charged. The overall result is that ZP does not significantly change after adding 1 wt% glycine for Na_2SO_4 and NaCl brines.

3.1.4. Effect of temperature on zeta potential with glycine solutions

Previous studies reported equilibrium constant values for the reactions controlling glycine speciation, Eqs. (1) and (2), for temperatures up to 275°C [22–25]. The isoelectric point of glycine decreases with increasing temperature. This means that at a given solution pH, the concentration of the glycine anion will increase with temperature, promoting its adsorption onto the calcite surface and, as consequence, decreasing the ZP of calcite.

Fig. 6 presents the ZP measurements for glycine solutions with single-component brines at different temperatures. For the glycine solutions with CaCl_2 , Na_2SO_4 and NaCl brines, increasing the temperature resulted in a significant decrease of the ZP. This can be explained by the increasing adsorption of the glycine anion at higher temperatures, as explained above. The glycine solutions prepared with MgCl_2 brine followed an opposite trend compared to the glycine solutions with CaCl_2 ,

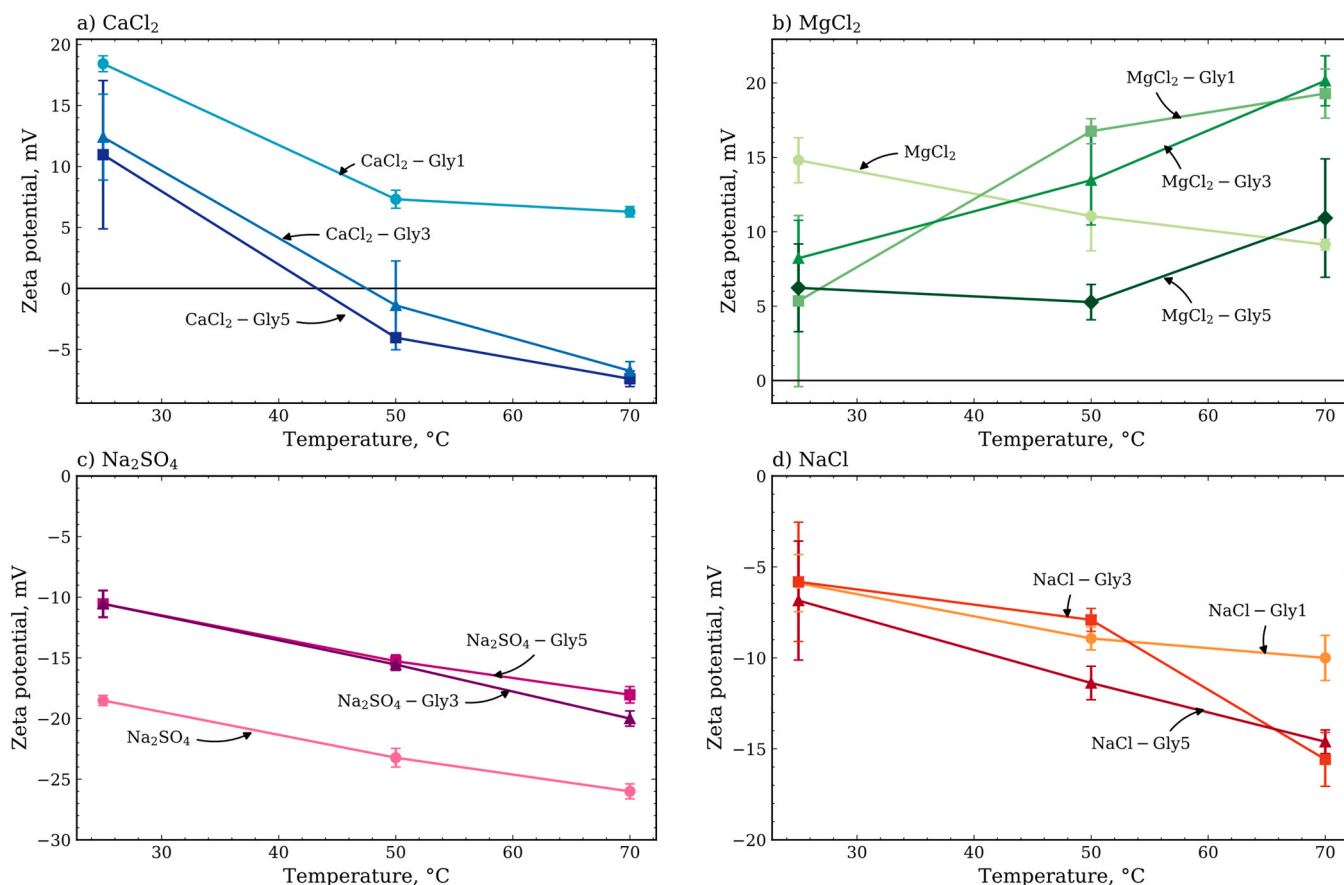


Fig. 6. Zeta potential as a function of temperature of glycine solutions in the single-component brines: a) CaCl₂, b) MgCl₂, c) Na₂SO₄, and d) NaCl at 1 atm.

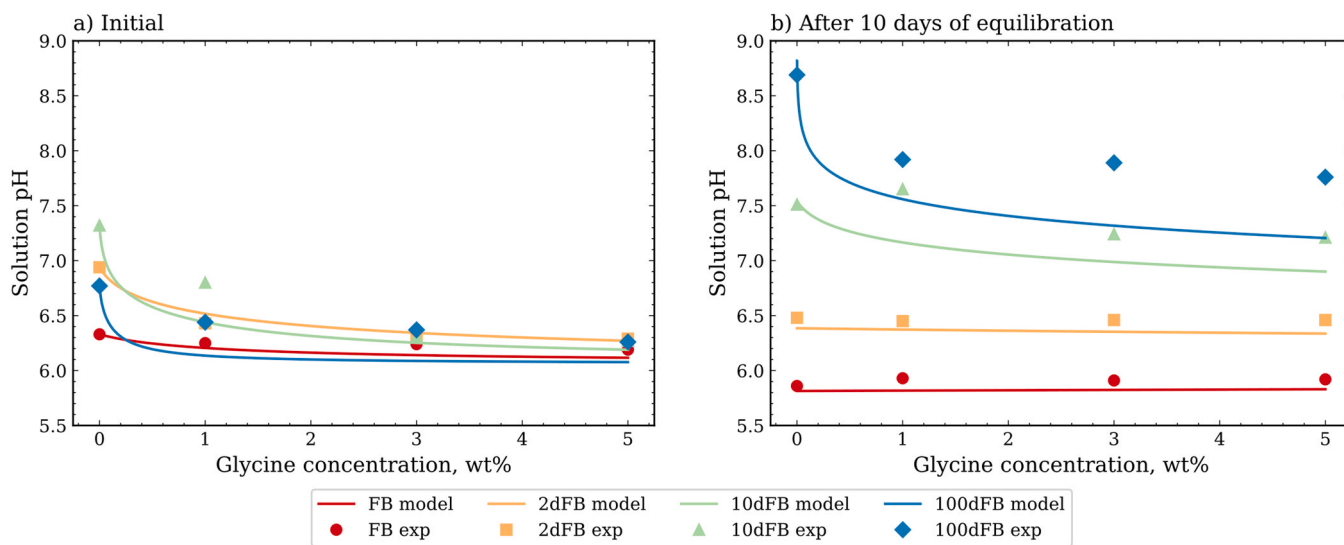


Fig. 7. Solution pH of formation brine and its dilution after 10 days of equilibration with calcite at room conditions. FB, 2dFB, 10dFB, and 100dFB indicate formation brine, 2-, 10-, and 100-times diluted versions of formation brine, respectively. The measurements were at 25°C and 1 atm. The solid lines represent the pH values predicted by PHREEQC (Appendix).

Na₂SO₄ and NaCl brines; that is, the ZP increased for higher temperatures. A possible explanation would be the incorporation of magnesium ions into the calcite lattice [26], which might be promoted by the decrease of the activity of calcium ions because of the formation of aqueous complexes with glycine. The modification of the calcite particle's mineralogy caused by MgCO₃ could reduce the affinity of glycine

anion for the surface and, consequently, its impact on the measured ZP.

3.2. Formation brine and its dilutions

3.2.1. Effect of glycine on solution pH

Fig. 7 presents the initial and equilibrium pH values for FB and its

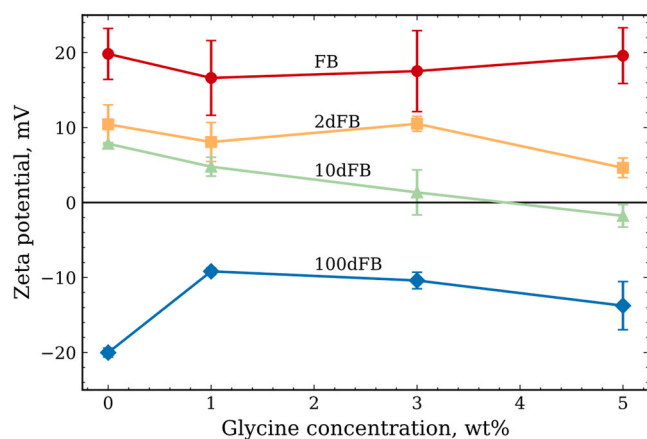


Fig. 8. Zeta potential values at different glycine concentrations for formation brine and its dilutions 25°C and 1 atm. FB, 2dFB, 10dFB, and 100dFB indicate formation brine, 2-, 10-, and 100-times diluted versions of formation brine, respectively.

dilutions at glycine concentrations of 1, 3, and 5 wt%. As with the single-component brines, the initial pH of FB and its dilutions decreased as a function of glycine concentration because of the deprotonation of glycine zwitterion (Eq. 2). Whether the pH increased or decreased after aging depended on the saturation of calcite for the given brine. The pH of FB and 2dFB decreased after equilibration likely because of precipitation of calcite. While the pH of 10dFB and 100dFB increased after equilibration because of calcite dissolution. The measured pH values are in good agreement with the ones calculated by PHREEQC. Only for 100dFB, the model underpredicted both the initial and the equilibrium pH as a function of glycine concentration.

3.2.2. Effect of glycine concentration on zeta potential

The activity of glycine in solution is affected by the presence of high concentrations of divalent ions, such as Ca^{2+} , Mg^{2+} , and SO_4^{2-} [27]. One approach to including the change of glycine's activity given by the formation of complexes between glycine and the ions in solution is to modify equilibrium constants that describe the glycine speciation. In this fashion, De Stefano and co-workers [19,28] proposed Debye-Hückel type correlations that relate the change of the equilibrium constants for the reactions in Eqs. (1) and (2) as a function of the solution's ionic strength. In general, an increase of the ionic strength will increase glycine's isoelectric point, leading to a smaller population of glycine anion. This consequently reduces the adsorption of glycine onto the calcite surface and increases the calcite ZP.

Fig. 8 gives the ZP values measured for FB and its dilutions at 1, 3, and 5 wt% glycine concentrations. For FB, ZP slightly decreased and then increased with increasing glycine concentration. However, the change of the average ZP was small compared to the standard deviation of the measurements. For 2dFB and 10dFB, there was a clear decreasing trend of ZP with increasing glycine concentration. This trend is analogous to the one observed with the single-component brines CaCl_2 and MgCl_2 (Fig. 5). For 100dFB, ZP significantly increased for the 1 wt% glycine solution and then decreased for larger glycine concentrations, which was also analogous to the trend observed with the single-component brines, Na_2SO_4 , and NaCl (Fig. 5).

The ZP results for FB and its dilutions can be explained by their pH and the speciation of glycine. For 100dFB, the increase of the ZP at 1 wt% glycine (Fig. 8) correlates with the drop of its pH (Fig. 7). The following decrease of the ZP for larger glycine concentrations can be attributed to both the adsorption of the glycine anion on the calcite surface and the reduction of the activity of calcium ions because of the complexation of glycine via chelation to divalent cations. For 10dFB and 2dFB, there was an evident decrease of ZP as a function of glycine

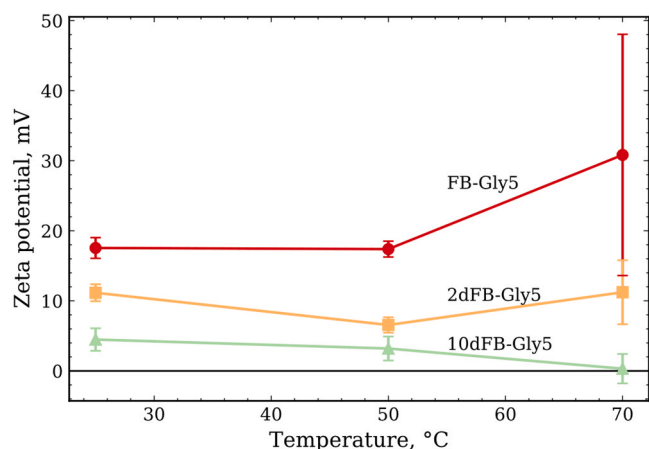


Fig. 9. Zeta potential versus temperature for 5 wt% glycine solutions in formation brine and its dilutions equilibrated for 10 days at the measurement temperature. FB-Gly5, 2dFB-Gly5, and 10dFB-Gly5 indicate formation brine, 2-, and 10-times diluted versions of formation brine, respectively, with a glycine concentration of 5 wt%.

concentration. In this case, the change of the solution pH was not significant and, since the calcite surface was initially positively charged, increasing the concentration resulted in the adsorption of glycine anion and the consequent reduction of ZP. Interestingly, the ZP for FB seemed to be insensitive to glycine concentration because the solution pH was smaller than the isoelectric point of glycine. Moreover, as explained before, the brine's large ionic strength might have also increased the isoelectric point of glycine, reducing the effective concentration of glycine anion.

3.2.3. Effect of temperature on zeta potential with glycine solutions

We investigated the effect of temperature on calcite's ZP for 5 wt% glycine solutions prepared with FB, 2dFB, and 10dFB (Fig. 9). The ZP is expected to decrease for higher temperatures as the increase in glycine anion concentration would promote its adsorption. However, this expected trend was only observed for 10dFB-Gly5. For 2dFB-Gly5, ZP decreased when the temperature increased from 25 to 50°C, but it increased again at 70°C. The ZP for FB-Gly5 did not significantly change when temperature was increased from 25 to 50°C. The measured ZP for FB-Gly5 at 70°C is only included for completeness since it has a very large standard deviation. The color of the sample after the measurement at 70°C changed to purple, indicating a chemical reaction that could have occurred at high temperatures.

The distinct ZP trends observed for FB and its dilutions as a function of temperature could be explained by their difference in PDIs concentrations and the impact of temperature on the adsorption of PDIs on carbonate rocks. Zhang and co-workers concluded that the adsorption of Mg^{2+} and SO_4^{2-} was enhanced at high temperatures as observed from the injection of seawater in a chalk core at 130°C [8,29]. In this case, the concentration of Mg^{2+} was more than four times higher than SO_4^{2-} for the composition of FB and its dilutions (Table 3). It is possible then that the ZP for FB-Gly5 at 70°C increased because of the enhanced adsorption of Mg^{2+} at high temperatures. For 10dFB-Gly5, the decreasing trend of ZP as a function of temperature could be mainly attributed to the adsorption of glycine given the low concentration of PDIs.

4. Conclusions

We investigated the impact of glycine on the zeta potential of the synthetic calcite using glycine solutions at concentrations of 1, 3, and 5 wt%. The glycine samples were prepared with single-component brines consisting of NaCl , CaCl_2 , MgCl_2 , and Na_2SO_4 with a fixed ionic strength of 0.05 M. Glycine solutions were also prepared with synthetic

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SOLUTION_SPECIES
  GlyH = GlyH;          log_k      0

  GlyH + H+ = GlyH2+;   log_k      2.34
  GlyH = Gly- + H+;     log_k     -9.78

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  Temp 25
  units mg/L

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  Mg    {Mg}
  Na    {Na}
  Cl    {Cl}
  S(6)  {S}
  C(4)  {C}

END

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  -reset false
  -temperature true
  -ionic_strength true
  -pH
  -saturation_indices Calcite

END

USE SOLUTION 1;
REACTION 1
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  {Gly} moles in 1 steps
EQUILIBRIUM_PHASES
  Calcite 0.0

END

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Fig. A1. PHREEQC input file to calculate the solution pH in equilibrium with calcite at a given glycine concentration. To calculate the initial pH, the EQUILIBRIUM_PHASES keyword was removed.

brine, with the composition of formation brine from a carbonate reservoir, and its dilutions: 2-times, 10-times, and 100-times diluted. The impact of temperature on the zeta potential of calcite in the glycine solutions was also investigated for 25, 50, and 75°C.

Most of the results were satisfactorily explained by considering the impact of the solution pH on the zeta potential of the calcite particles and the electrostatic interactions between glycine anion and the calcite surface, where glycine speciation depended on the brine composition, salinity, and temperature. For single-component brines, the impact of glycine depended more on the initial sign of the zeta potential than the brine composition. Glycine reduced the initial positive zeta potential (CaCl₂ and MgCl₂ brines) and increased the initial negative zeta potential (NaCl and Na₂SO₄ brines). For formation brine, glycine had no

significant impact on the zeta potential; however, the zeta potential of 2-times, 10-times, and 100-times diluted formation brine decreased because of the adsorption of glycine anion on the calcite surface.

Defining the specific mechanisms affecting the zeta potential of calcite as a function of temperature is a challenge. Both the activity of the chemical species and the equilibrium constants of the reactions are affected to different degrees by the increase of temperature. The zeta potential of the single-component brines, CaCl₂, NaCl, Na₂SO₄, decreased with higher temperatures. This was explained by the reduction of glycine's isoelectric point with increasing temperature that resulted in the increased adsorption of glycine anion. The glycine solutions with MgCl₂ brine, however, showed the opposite trend of zeta potential with temperature. The hypothesis, in this case, is that the

substitution of magnesium ions into the calcite lattice reduced the affinity of glycine for the surface. Finally, the second set of zeta potential measurements for glycine solutions with formation brine and its dilutions decreased the zeta potential when the temperature was increased from 25°C to 50°C. However, the ZP results at 70°C were inconclusive because of the larger standard deviation values for FB-Gly5 and 2dFB-Gly5 as a result of the solutions' non-ideality.

CRedit authorship contribution statement

Ricardo A. Lara Orozco: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. **Gayana A. Abeykoon:** Methodology, Validation, Formal analysis, Investigation, Resources, Writing - review & editing. **Ryosuke Okuno:** Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Larry W. Lake:** Conceptualization, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix

The solution pH at different glycine concentrations at equilibrium with calcite was calculated using the open-source geochemical solver PHREEQC v3.6.2 [30] developed by the United States Geological Survey (USGS). Fig. A1 shows the PHREEQC input file that was run using the phreeqc.dat database, where glycine's cation, zwitterion, an anion species (Fig. 1) were included as GlyH₂⁺, GlyH, and Gly⁻, respectively.

The script was run for each brine and glycine concentration using the brines composition in Tables 2 and 3 along with the initial solution pH measured without glycine in Fig. 3(a). To calculate the initial pH as a function of glycine concentration, the script was run without the EQUILIBRIUM_PHASES keyword since the brines were assumed to not be in equilibrium with calcite or atmospheric CO₂. To calculate the equilibrium pH, we considered the brines to be in equilibrium with calcite but not with atmospheric CO₂ since the brines were equilibrated in closed vials.

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