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Influence of mineralogy and surfactant concentration on zeta potential in intact sandstone at high pressure

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GRAPHICAL ABSTRACT
The clay-poor sandstone has thinner hydration layer than SDBS treated clay-poor sandstone.

Hypothesis:: Zeta-potential in the presence of brine has been studied for its application within hydrocarbon reservoirs. These studies have shown that sandstone's zeta-potential remains negatively charged, non-zero, and levels-off at salinities > 0.4 mol.dm$^{-3}$, thus becoming independent of salinity when ionic strength is increased further. However, research conducted to date has not yet considered clay-rich (i.e. clay ≥ 5 wt%) sandstones.

Experiments:: Firstly, streaming potential measurements were conducted on Bandera Gray sandstones (clay-rich and clay-poor) with 0.6 and 2 mol.dm$^{-3}$ NaCl brine-saturated in pressurised environments (6.895 MPa overburden and 3.447 MPa back-pressure). Secondly, the streaming potential was determined at identical conditions for the effect of two surfactants, SDBS and CTAB, at concentrations of 0.01 and 0.1 wt% on the clay-poor sample in 0.6 mol.dm$^{-3}$ NaCl. Thirdly, a comparison of zeta potentials...
Electrophoretic potential

CTAB: Cetyl Trimethyl Ammonium Bromide
CSC: Critical Salt Concentration
CTAB: Cetyl Trimethyl Ammonium Bromide
CSP: Streaming Potential Coupling coefficient, mV.Pa$^{-1}$
EOR: Enhanced Oil Recovery
EDL: Electric Double Layer
F: Formation factor, dimensionless (F = $\sigma_w/\sigma_{rw}$) used when surface electrical conductivity was negligible for salinities <$0.1$ mol.dm$^{-3}$)
FTIR: Fourier Transform Infrared
IEP: Iso-Electric Point
I: Ionic Strength, mol.dm$^{-3}$
IS: Ionic Strength, mol.dm$^{-3}$
L: Length
m NMR: Nuclear Magnetic Resonance
R: Resistance, ohm
$R_m$: Resistance at minimum X, ohm
r: Radius of the cylindrical core sample, m

One important parameter that is required for interpreting SP data is zeta potential ($\zeta$), a measure of the electrical potential (neutral, positive, or negative charge) on rock, mineral or colloidal surface in the presence of an electrolyte (usually water-based brines in our research area). Accordingly, $\zeta$ (in terms of its magnitude and polarity) is directly proportional to SP [21–22], as $\zeta$ dictates electrostatic interactions between rock (or mineral/colloid) surfaces and polar species in brine [4,23–25]. Consequently, $\zeta$ is a vital regulator of:

- (a) rock wettability [26–27],
- (b) adsorption and exchange capacity of polar species on subsurface rock surfaces [28–29],
- (c) subsurface geophysical monitoring [30], and
- (d) engineering process optimisation (e.g., controlling the physico-chemistry of injected brine during hydraulic fracturing or water flooding in hydrocarbon reservoirs) [31–32].

Previously, several critical parameters associated with SP measurements in sandstone have been examined, including sandstone micro-structure, pressure, temperature, pH value, salinity, as well as the impact on oil recovery [19–20,22,33–35]. However, little attention has been paid to the mineralogical composition of exposed rock surfaces, as evident in Table 1, as well as the impact of additives (for instance, those used in enhanced oil recovery operations [36–40]) on $\zeta$ has received little attention.

Thus, in this study, we measured SPs in intact sandstone samples and interpret the impact of clay and additive content. The results can be widely applied, for example, to optimise hydrocarbon recovery, CO$_2$ geo-sequestration, hydrogen storage or water production.

2. Experimental methods and materials

2.1. Electrolyte formulation

Two brine salinities (0.6 and 2 mol.dm$^{-3}$ NaCl in deionised water) above critical salt concentration (CSC) were used in this study. CSC (with regards to $\zeta$) is reported at 0.4 mol.dm$^{-3}$ NaCl [3–4,22]. Further, these salinities are consistent with sandstone formation water salinities [4,22,41–42].
Additive-influence tests were conducted only with the 0.6 mol. dm\(^{-3}\) NaCl brine on clay-poor sandstone, as this salinity, value is considered standard salinity and is above the CSC. The EOR additives\(^{[43–45]}\) used in this study were anionic (Sodium Dodecyl Benzenz Sulfonate; SDBS; Molecular formula: C\(_{18}\)H\(_{29}\)NaO\(_3\)S, Molecular weight: 348.48 g.mol\(^{-1}\)) and cationic (Cetyl Trimethyl Ammonium Bromide; CTAB; Molecular formula: C\(_{19}\)H\(_{42}\)BrN, Molecular weight: 364.45 g.mol\(^{-1}\)). SDBS has been stabilised via heat treatment (973 K for 2 h), resulting in a clay-poor sample. XRD analyses indicated that the clay-poor sample’s quartz content was 76.24 wt% after thermal treatment as compared to 67.93 wt% quartz for the clay-rich sandstone. The clay-poor sample was obtained after all swelling clay (kaolinite and chlorite) had been stabilised via heat treatment (973 K for 2 h), resulting in more quartz content (which is actually meta-kaolinite as explained below), but no clays, as shown in Table 1. Note that no permeability alteration occurred post-heating, consistent with data in the literature\(^{[48–49]}\).

Thermal treatment of sandstone between 723 and 973 K causes kaolinite (Al\(_2\)O\(_3\).2SiO\(_2\).2H\(_2\)O) to change to meta-kaolinite (Al\(_2\)O\(_3\).2SiO\(_2\)) by de-hydroxylation\(^{[50]}\). The meta-kaolinite is an amorphous aluminosilicate (that is no longer detectable by XRD)\(^{[50]}\). The reaction scheme is given as follows:

\[
\text{Al}_2\text{O}_3.2\text{SiO}_2.2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3.2\text{SiO}_2 + 2\text{H}_2\text{O}
\]

The kaolinite and chlorite XRD peaks (see supplementary S-1 and S-2) disappeared after thermal treatment at 973 K for 120 min, as consistent with the literature.\(^{[33,34]}\)

The thermodynamic stability of ordered ankerite (CaFe(CO\(_3\))\(_2\) - carbonate component) is compromised at temperature < 723 K\(^{[51]}\), resulting in carbonates reduction. The increase in feldspar concentration can be noticed in Table 1, owing to a reduction in clay components and thus an increase in relative proportion\(^{[52]}\).

The cylindrical sandstone samples were 63.8 mm in length and 38.4 mm in diameter. NMR porosity (GeoSpec + 2/53 Magnet Assembly, operating frequency: 2 MHz, Oxford Instrument) and Helium porosity (measured via UltraPoroPerm-910; Core Laboratories) were 18 and 20%, respectively; while Klinkenberg (measured in addition, an identical clay-rich sample was heated at 973 K for 2 h to burn off the clay minerals\(^{[48]}\), resulting in a clay-poor sample. XRD analyses indicated that the clay-poor sample’s quartz content was 76.24 wt% after thermal treatment as compared to 67.93 wt% quartz for the clay-rich sandstone. The clay-poor sample was obtained after all swelling clay (kaolinite and chlorite) had been stabilised via heat treatment (973 K for 2 h), resulting in more quartz content (which is actually meta-kaolinite as explained below), but no clays, as shown in Table 1. Note that no permeability alteration occurred post-heating, consistent with data in the literature\(^{[48–49]}\).
via Nano-Perm, Core Laboratories) and brine permeability (measured via the core flood apparatus, Fig. 1) were 18 ± 1 and 8.8 ± 0.2 mD, respectively. Note that the permeability was measured at 15 MPa effective stress. Errors reported were estimated based on three test replicates.

Fourier Transform Infrared Spectroscopy (FTIR) was performed with a PerkinElmer Spectrum UATR Two instrument (see supplementary information for details).

2.3. Streaming potential measurements

The sample systems were thermodynamically and geochemically equilibrated prior to the SP experiments [20,22]; thus, paired stabilisation SP experiments were conducted. Paired Stabilisation: The samples were equilibrated with brine in a pressurised PEEK core holder. Brine was then repeatedly injected through the sample (at 16.667 mm³.s⁻¹) from one high-precision syringe pump tank to another high precision syringe pump tank (Teledyne ISCO, Model 500D Hastelloy, flow accuracy ~ 0.5% of setpoint, pressure accuracy within 0.1% full scale; same model) until paired stabilisation was reached. Paired stabilisation occurs when both tanks are at the same geochemical conditions (such as pH, conductivity and aliquots concentration) after the brine permeates through the core sample and equilibrates with the rock. Previously, paired stabilisation was reached when the brine’s conductivity (53.45 ± 1.35 mS.cm⁻¹ for all 0.6 mol.dm⁻³ NaCl brines and 179.12 ± 0.95 mS.cm⁻¹ for 2 mol.dm⁻³ NaCl brine) and pH value (6.4 ± 0.1) in each pump tank remained constant within 2% tolerance [20]. A Starter 3100 pH meter (Ohaus Corporation) was used to measure and monitor the pH of the prepared formulations, where the instrument was calibrated on a daily basis using three-point calibration (95–98% accuracy). The brine’s pH and conductivity in each pump tank were continuously measured during the experiments to ensure repeatability and accuracy of the measurements. Accordingly, brine samples were bled for sampling from both tanks after each side run to determine their pH and conductivity for equilibration.

Streaming potential experiments: Following paired stabilisation, overburden stress of 6.895 MPa were applied, and the formulations were injected from one side (at various flow rates of 8.33 to 50 mm².s⁻¹ for at least 30 mins). This resulted in a pressure differential and voltage (recorded at a frequency of 1 Hz) across the pressurised core holder. Accordingly, the dynamic pressure and voltage evolution could be measured by forward and reverse flooding in both directions. A schematic of the core flood system is illustrated in Fig. 1.

Flow in one direction was terminated when a stable voltage and stable pressure drop was obtained (injection of 1.127, 2.254, 4.508, 6.762 pore volumes at flow rates of 8.334, 16.667, 33.334 and 50 mm³.s⁻¹ for at least 30 mins), followed by a system relax (i.e. a static voltage, zero pressure differential – no flow). After the system relaxed, a reverse direction flow was conducted, and the flow was terminated again when a stable voltage and a stable pressure drop was obtained for 30 mins.

Note that the voltage and pressure differential were measured within the experimental error of < 0.01 mV and < 0.7 kPa, respectively. The average Streaming potential coupling coefficient (Csp) standard deviation remained at 0.327 mV/MPa, while the average standard deviation of Streaming zeta potential (ζsp) remained at 3.61 mV.

2.4. Interpretation of zeta potential

ζ was calculated via the Helmholtz-Smoluchowski (H–S) equation [54], equation (1):

\[ \zeta = \mu_w \sigma_{rw} F C_{sp} / e_w \] (1)

Where, ζ is zeta potential, mV; \( \mu_w \) is dynamic viscosity, Pa.s; \( \sigma_{rw} \) is conductivity of saturated core, S.m⁻¹; \( F \) is Formation factor, dimensionless; \( C_{sp} \) is Streaming potential Coupling coefficient, mV.Pa⁻¹ and \( e_w \) is Dielectric permittivity, F.m⁻¹.

Determination of the Streaming Potential Coupling Coefficient: The SP coupling coefficient “Csp” was determined by plotting AP versus ΔV (measured at chemical equilibrium and zero electrical current “j”). The coupling coefficient is the slope of ΔV / ΔP (at constant ionic strength, additive concentration, pH value, back-
pressure, over-burden pressure, and temperature but varying flow rates), as depicted in Equation (2).

\[
C_{sp} = \frac{L}{R_m \pi r^2} \quad \text{and} \quad \text{3. Results and discussion}
\]

The impact of mineralogy, additives, brine salinity and measurement techniques on the observed streaming \( \zeta \) are reported and discussed in detail in this section.

3.1. Relationship between flow rate, pressure drop and voltage

In order to examine the flow rate-pressure relationship, a series of experiments at various flow rates (8.334, 16.667, 33.334 and 50 nm²s⁻¹ and reverse values) were conducted, compare Figure S3 in the supplementary file. A linear relationship was observed, implying flow to be governed by Darcy’s law, as expected. Permeability was consequently calculated using Darcy’s equation.

3.2. Effect of mineralogy on zeta potential

Natural groundwater (i.e. freshwater) systems are typically less saline than 0.01 mol.dm⁻³, whilst aquifers in hydrocarbon reservoir systems possess a higher ionic strength (IS) than freshwater [57]. As has been well-established, \( \zeta \) depends on salinity, where to the best of our knowledge, only a few studies have investigated \( \zeta \) for high ionic strength brines [4–5,19–20,22], while most studies have focused on deionised water or dilute NaCl / KCl solutions. \( \zeta \) data for salinities IS > 0.01 mol.dm⁻³ in sandstone cores have been compiled in Table 1 [4–5,19–20,22]; thus at high salinity (typically > 0.4 mol.dm⁻³), \( \zeta \) levels off (also known as \( \zeta \) offset) [5,22]. At salinities > 0.4 mol.dm⁻³ (which is considered to be critical salt concentration, CSC, with reference to \( \zeta_{sp} \) values), \( \zeta \) reaches a small, constant, non-zero and limiting value (i.e. typically between \(-50 \leq \zeta \leq 50 \) mV), which is known as zeta offset value. At zeta offset, \( \zeta \) becomes independent of electrolyte salinity, pH, temperature, and additive composition (\( \zeta \) measured on sandstone remained between \(-12 \) to \(-29 \) mV) [3–4,19–20,22], while mineralogy and rock texture were reported to have no significant influence [3–4,19–20,22].

The studies reported in Table 1 were only performed on relatively clay-poor sandstones (<5 wt% clay). Further, the SP coefficient in these studies increased exponentially with salinity (up to approximately 1 mol.dm⁻³ NaCl brine) before plateauing out [22]. Equation (5) has been proposed by Vinogradov et al. (2010) as a correlation between brine salinity (\( C_i \)) and SP coefficient (\( C_{sp} \)) [22].

\[
C_{sp} = -1.36 C_{i}^{0.9123}
\]

\( C_{sp} \) and \( C_i \) correlations available in the literature are tabulated in Table 3.

The impact of mineralogy, additives, brine salinity and measurement techniques on the observed streaming \( \zeta \) are reported and discussed in detail in this section.

The Electric Double Layer (EDL) theory describes the charge generated at the interface of a solid surface when it is exposed to an electrolyte. Boltzmann equation-based models assume ions as point-charges, where the diffuse layer thickness collapses to zero at higher brine salinities whilst the counter-charge is totally contained within the Stern layer [5]. Further, the maximum charge density is limited by hydrated counter-ions size; consequently, there is always some mobile counter-ion left within the diffuse layer [5].

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required to balance the mineral surface charge is not totally accommodated within the Stern layer, preventing the diffuse layer from collapsing to zero. Additionally, within the diffuse layer, some of the counter-charge remains mobile, with maximum charge density limited by the size of the hydrated counter-ions.

Hence, in our study at 0.6 mol.dm\(^{-3}\) NaCl salinity (>0.4 mol.dm\(^{-3}\) zeta-level off salinity), the combined adsorption of Cl\(^-\) ions (from NaCl dissociation) and OH\(^-\) ions (from clay) induced greater negative \(\zeta\) values (~31.17 mV in case of clay-rich Bandera Grey sandstone) at 0.6 mol.dm\(^{-3}\) NaCl salinity. A comparative analysis with respect to clay content in the literature and our study is presented in Fig. 2 (c). Thus, we conclude that \(\zeta\) values at 0.6 mol.dm\(^{-3}\) NaCl salinity on clay-rich quartz surface yields Debye lengths (diffuse layer’s maximum charge density) equivalent to the diameter of the counter-ions [4,20].

### 3.3. Effect of additives on zeta potential

SDBS anions added to the brine drastically reduced \(\zeta\) from ~22.26 mV (0 wt% SDBS) to ~41.86 mV (0.1 wt% SDBS) in 0.6 mol.dm\(^{-3}\) NaCl brine, as evident in Fig. 3. This is consistent with \(\zeta\) alteration measured on coal surfaces in which \(\zeta\) reduced from ~15 to ~52 mV in the presence of 0 and 0.1 wt% SDBS respectively [29]. A significant reduction in \(\zeta\) to ~31.17 mV was observed for 0.01 wt% SDBS concentration. The results of SDBS supercharging the quartz surface charge is also consistent with Al-Anssari et al. (2017), who demonstrated that SDS (1000 mg/L) at salinities 1 to 5 wt% NaCl results in maximum stability of silica nanofluids [47]. However, the addition of CTAB had the opposite effect, i.e. CTAB increased \(\zeta\) (but reduced its magnitude). Specifically, the zeta potential increased from ~22.26 mV (zero CTAB concentration) to ~15.14 mV and ~10.69 mV when 0.01 wt% and 0.1 wt% CTAB were added, respectively. These results are consistent with independent study [63].

Mechanistically, the anionic SDBS head attaches to the silica surface, reducing surface charge and, thus, zeta potential. This was observed via FTIR measurements, as seen in Fig. 4. FTIR results identified a silica group stretching wavenumber (800–1200 cm\(^{-1}\)) region, and as expected, the clay-rich sample had smaller silica contents than the clay-poor sample.

Reduced transmittance was observed in the SDBS treated clay-poor sample (wavenumber range of 1000–1200 cm\(^{-1}\)) owing to dodecyl benzene sulfonate adsorbing on and supercharging the sandstone surface. The peak at 1195–1168 cm\(^{-1}\) relates to the
S=O stretching wavenumber, where sulfonate peaks appeared at 1350–1470 cm⁻¹ indicating medium O–H bending as rendered due to intramolecular bonding between silicate-based sandstones and alcohol groups (from SDBS). However, CTAB resulted in reduced transmission overall, specifically for negative charged stretching regions of S=O and O–H bonding.

**Fig. 3.** (a) Streaming potential coefficients, (b) zeta potentials as a function of surfactant concentration in 0.6 mol dm⁻³ NaCl brine; SDBS is Sodium dodecylbenzene sulfonate, and CTAB is Cetyl trimethyl ammonium bromide.

**Fig. 4.** FTIR Fingerprint region of various clay–poor Bandera grey sample powders; as received, treated with Sodium dodecylbenzene sulfonate (SDBS) and treated with Cetyl trimethyl ammonium bromide (CTAB).
SDBS adsorption was reversible as a result of the thickening of electric double-layer formation at the quartz surface [64]. As the sandstone surface was already negatively charged, following absorbance of weak sodium ions (positive head) and strong dodecyl benzene sulfonate molecules (negative tail), the overall negative charge density increased and stabilised the sandstone. SDBS consists of a hydrophilic sulfonate head-group and a hydrophobic dodecyl benzene tail-group, where the size of SDBS is 20 Å [65].

Brine chemistry (salinity and pH) has a significant impact on the rock wettability of a surface [66,67]; thus, brine chemistry plays a critical role in water film stability, which again is directly related to the surface charge at rock/brine and oil/brine interfaces. This water film is very stable at alkaline pH, with lesser salinities when the surface is negatively charged, thus resulting in more water-wet conditions [68].

When SDBS (0.1 wt%) was added to the brine, it decreased $\zeta_{\text{sp}}$ from –22.26 mV (at 0 wt% SDBS) to –41.86 mV at standard salinity (at pH of 6.4), resulting in more water-wet brine that would ultimately yield improved oil recovery. The implications of a greater absolute $\zeta$ would render the surface more water-wet, where near isoelectric point (IEP), the surfaces would be oil-wet. However, when planning for CO$_2$-geo sequestration, higher zeta potential in brine/rock would actually assist in greater CO$_2$ containment security.

### 3.4. Comparison between zeta potential measurement methods

$\zeta$ can be measured via electrophoretic measurements ($\zeta_{\text{ep}}$) or SP measurements ($\zeta_{\text{sp}}$) [69]. Whilst $\zeta_{\text{sp}}$ measurements are much more complicated; they are also more representative of geologic processes and applications. $\zeta$ was thus also measured via electrophoretic measurements, and the results were compared with $\zeta$ measured via SP measurements, as shown in Fig. 5. Electrophoretic mobilities were measured for each sample, with their associated $\zeta$ displayed in Table 3. The conductivity of the 0.6 mol.dm$^{-3}$ and 2 mol.dm$^{-3}$ NaCl brine remained constant at 53.45 ± 1.35 mS.cm$^{-1}$ and 179.12 ± 0.95 mS.cm$^{-1}$, respectively, showing that the surfactant additives (i.e. SDBS and CTAB) had an infinitesimal impact on electric conductivity.

The electrophoretic mobility of a particle suspension can be measured using the dynamic light scattering (DLS) method, where a light source, usually a visible-wavelength laser, illuminates the suspension. An optical system attached to a photodetector and signal processing system samples the scattered light from the suspension, allowing the Doppler effect to be used to determine particle mobility. The suspended entities’ random Brownian motion is then superimposed on a directed motion generated by introducing an electric field in DLS. The electric charges carried by the suspended particles, modified by the presence of the suspending liquid, are responsible for this motion.

The electrophoretic mobility was shown to be directly proportional to $\zeta$ in this study; thus, as mobility increased, $\zeta_{\text{ep}}$ increased, as evident in Equation (6). Two formulations (in 0.6 mol.dm$^{-3}$ NaCl brine), 0.01 wt% SDBS and 0.1 wt% CTAB had similar (but inverse) mobilities (-1.214 and 1.221 m$^2$.cm.V.s$^{-1}$) and $\zeta_{\text{ep}}$ values (-15.9 and +14.75 mV) respectively, as seen in Table 4. Note that the charge (negative or positive) denotes the surface charge of the suspended particles.

Electrophoretic zeta potential has a direct relationship with electrophoretic mobility, as can be seen in Table 4. Equation (6) is obtained and would be valid for salinities > 0.4 mol.dm$^{-3}$

\[
\zeta_{\text{ep}} = 12.692 \times \mu_e
\]

Where, $\zeta_{\text{ep}}$ is electrophoretic zeta potential mV, $\mu_e$ is electrophoretic mobility, m$^2$.cm.V.s$^{-1}$

![Fig. 5. Electrophoretic $\zeta$ versus streaming $\zeta$ for (a) the clay-rich sample, (b) the clay-poor sample, (c) SDBS treated clay-poor sample, and (d) CTAB treated clay-poor sample. ((c) and (d) were measured for 0.6 mol.dm$^{-3}$ NaCl brine).](image-url)
The constant 12.692 can be compared with the Smoluchowski equation’s \( \mu_{sw}/\varepsilon_r\varepsilon_0 \) \[70\]. Where, \( \mu_{sw} \) is dynamic viscosity, Pa.s; \( \varepsilon_r \) is dielectric constant of the dispersion medium, unitless and \( \varepsilon_0 \) is permittivity of free space, \( C^2 N^{-1} m^{-2} \).

Further, a \( \zeta \) difference between electrophoretic measurements and streaming measurements of 20.57 mV at high salinities \( \geq 0.6 \text{ mol.dm}^{-3} \text{ NaCl} \) was observed, as illustrated in Fig. 5. The reasons for this deviation could be as follows:

1. The rock surface was negatively charged in the presence of the dissociated ions (Na\(^+\) and Cl\(^-\)); hence, a dominance of the negative charge in electrophoretic and streaming determinations was observed.
2. The rock core sample was equilibrated at pressurised conditions via flow into the rock and brine vacuumed before the streaming potential measurement. In contrast, the particles were not well-equilibrated for the electrophoretic \( \zeta \) ep [71].
3. In the streaming potential measurements, the intact sandstone contained a more solid phase at 81 wt% (depending upon the porosity). In contrast, electrophoretic measurements with only 0.05 wt% of powdered rock particles were added to the brine to measure the \( \zeta \) ep. Accordingly, concentration (volume of solids to volume of liquid) plays an important role.
4. The electrophoretic \( \zeta \) measurements are accurate only for low-ionic strength liquids \( (\leq 0.1 \text{ mol.dm}^{-3} \text{ salt concentration}) \), at lower temperatures \( \leq 298 \text{ K} \) and ambient pressure \( (0.1 \text{ MPa}) \).
5. A constant difference of 20.57 was observed, where the dynamic light scattering method is accurate, i.e. at lower salinities \( < 0.1 \text{ mol.dm}^{-3} \), and if a suspension has enough counter-ions (via higher salinity brine) to enhance particle aggregation and result in measuring zeta potential near IEP.

In electrophoretic \( \zeta \), CTAB rendered charge shift effect from 0.428 to 14.75 mV (i.e. from near-neutral to positive \( \zeta \)) since CTAB engulfed all the sandstone particles; however, in streaming \( \zeta \), the CTAB only reduced the charge of the sandstone rock from \( -22.26 \text{ mV} \) to the incipiently stable zone (i.e., \( -10.69 \text{ and} -15.14 \text{ mV} \)) at 0.1 wt% and 0.01 wt% CTAB respectively.

Thus, SDBS was a useful additive for sandstone surfaces as sandstones are negatively charged in the presence of NaCl brines \[72–73\]. We conclude that SDBS can be an excellent wettability-alteration agent for hydraulic fracturing (as sandstone fines dispersing agent), water flooding, and EOR applications.

### 4. Limitations and recommendations

The presented work was limited by operating experimental conditions such as sandstone mineralogy, pH, temperature, pressure (overburden and pore pressure), ionic strength and type of salts, surfactants etc. Future work can be conducted on various experimental conditions to gain a fundamental and/or comprehensive deeper understanding of solution-phase adsorption on quartz surfaces. The feasibility of pre-conditioning the subsurface reservoir for CO2-sequestration (in the presence of organic acids) or Enhanced Oil Recovery projects can be implored \[74–75\]. Additionally, pore scale investigation of changes in the microstructure can be investigated via tomographic studies \[79,80\].

### 5. Conclusions

A systematic \( \zeta \) ep analysis on the clay mineralogy effect was conducted on sandstone rocks in this study. Accordingly, \( \zeta \) ep was shown to alter the surface chemistry of sandstone using anionic and cationic surfactants. We thus conclude that the \( \zeta \) level-off behaviour as a function of salinity exists; however, contradictory to previously reported cut-offs at \( < 0.4 \text{ mol.dm}^{-3} \) NaBr \[4,22\], \( \zeta \) in the presented study, was subject to the sandstone sample’s mineralogy at salinities of 0.6 and 2 mol.dm\(^{-3}\) NaCl brine. Additionally, this research notes contradictory results to previous studies for a clay-rich sample, where clay-content (mineralogy dependence) exists and can elucidate alteration in zeta potential. Thus, the findings reported in this research apply at salinities \( \geq 0.4 \text{ mol.dm}^{-3} \) to subsurface clay-rich sandstones, where we hypothesise that clay-rich sandstone is a better candidate than clay-poor sandstone owing to its higher EDL to the brine. The streaming potential (SP) method has more accuracy than the Dynamic Light Scattering (DLS) electrophoretic method of \( \zeta \) determination.

Based on the results of this study, it is likely that the clay-poor sandstone would be a more suitable candidate for CO2 storage than clay-rich sandstone owing to clay-poor’s higher zeta potential \[24,76\]. Consequently, sandstone formations treated with CTAB should turn sandstone formations into being more CO2-wet; thus, resulting in enhanced storage capacities and containment security. SDBS treatment has proven to result in Enhanced Oil Recovery (EOR) \[73\].

The \( \zeta \) was reduced from \(-23 \text{ mV} \) to \(-41 \text{ mV} \) when the sandstone rock was treated with 0.1 wt% SDBS, showing that the synergistic ion-exchange dominancy plays a vital role in \( \zeta \) alteration when ions of inorganic salt and surfactant interact amongst each other at the rock-fluid interface \[77–78\]. We hypothesise that this reduction is due to SDBS’s capability to supercharge an anionic surface via its sodium-ion adsorption; thus, thickening the EDL. Thus, we conclude that additives (anionic, cationic, or non-ionic) can influence \( \zeta \) level-off.

The streaming potential \( \zeta \) can be altered subject to mineralogical changes in sandstones. The zeta potential of intact sandstones can also be altered via surfactants, influencing their wettability and recovery factor. Future work should focus on a wide range of surfactants at salinities consistent with reservoir aquifers.

CRediT authorship contribution statement

Faisal Ur Rahman Awan: Data curation, Formal analysis, Software, Writing – original draft, Investigation, Methodology, Validat-
tion. Ahmed Al-Yaseri: Conceptualization, Methodology, Project administration. Hamed Akhondzadeh: Formal analysis, Visualization. Stefan Iglauer: Resources, Supervision, Writing – review & editing. Alireza Keshavarz: Project administration, Funding acquisition, Supervision, Writing – review & editing.

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 A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2021.08.015.

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