Central Lancashire Online Knowledge (CLoK)

Title	Maximising CO2 sequestration efficiency in deep saline aquifers through in-situ generation of CO2-in-brine foam incorporating novel CO2-soluble non-ionic surfactants
Type	Article
URL	https://clok.uclan.ac.uk/id/eprint/56386/
DOI	https://doi.org/10.1016/j.cej.2025.166102
Date	2025
Citation	Gandomkar, Asghar, Torabi, Farshid, Nasriani, Hamid Reza and Enick, Robert M. (2025) Maximising CO2 sequestration efficiency in deep saline aquifers through in-situ generation of CO2-in-brine foam incorporating novel CO2-soluble non-ionic surfactants. Chemical Engineering Journal, 521. p. 166102. ISSN 1385-8947
Creators	Gandomkar, Asghar, Torabi, Farshid, Nasriani, Hamid Reza and Enick, Robert M.

Chemical Engineering Journal 521 (2025) 166102

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Maximising CO_2 sequestration efficiency in deep saline aquifers through in-situ generation of CO_2-in-brine foam incorporating novel CO_2-soluble non-ionic surfactants

Asghar Gandomkar [a,b,*], Farshid Torabi [b], Hamid Reza Nasriani [c], Robert M. Enick [d]

[a] Department of Chemical and Petroleum Engineering, Shi.C., Islamic Azad University, Shiraz, Iran
[b] Faculty of Engineering and Applied Science, University of Regina, Regina, SK S4S 0A2, Canada
[c] School of Engineering, Faculty of Science and Technology, University of Central Lancashire, Preston PR1 2HE, United Kingdom
[d] Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA, 15261, United States

ARTICLE INFO

Keywords:
Aquifers
CO_2 storage
CO_2-in-brine foam
Cloud point pressure
CO_2-soluble non-ionic surfactants

ABSTRACT

The geological sequestration of carbon dioxide (CO_2) within deep saline aquifers remains a critical pathway for achieving long-term climate stabilisation and net-zero targets. This study presents a novel strategy to augment both the efficiency and security of CO_2 storage through the in-situ formation of CO_2-in-brine foams facilitated by non-ionic CO_2-soluble propoxylated-ethoxylated alcohols surfactants, specifically 2EH-PO_5-EO_9 and 2EH-PO_5-EO_{15}. A comprehensive suite of laboratory investigations was conducted under representative reservoir conditions (70 °C and 3200 psi), including cloud point pressure analysis, foam stability monitoring, interfacial tension (IFT) reduction, wettability alteration studies, CO_2 solubility measurements, and core flooding experiments. The results reveal that both surfactants exhibit strong solubility in supercritical CO_2 and brine, enabling stable foam generation without degradation. Among them, 2EH-PO_5-EO_{15} demonstrated superior performance, achieving a marked reduction in CO_2–brine IFT, from 32 to 6.7 dyne/cm, and enhancing CO_2 solubility in brine by over 100 % (from 1.25 to 2.51 mol%) compared to pure CO_2 scenario; thus strengthening solubility trapping. In parallel, wettability characterisation showed a transformation of the sandstone substrate from strongly water-wet ($\theta \approx 18°$) to an intermediate gas-wet condition ($\theta \approx 71°$), significantly amplifying the potential for residual trapping. Core flooding assessments corroborated these synergistic effects, demonstrating reduced CO_2 mobility and improved sweep efficiency through foam stabilisation and rock–fluid interfacial modification. Altogether, this work underscores the efficacy of CO_2-soluble non-ionic surfactants in enhancing storage security and injectivity, offering a technically and economically attractive approach to large-scale CO_2 sequestration in saline aquifers. Also, the current results establish a strong foundation for advancing toward field-scale implementation and represent a significant step forward in creating sustainable solutions for carbon management.

1. Introduction

Sustained industrial expansion contributes to increasing concentrations of atmospheric carbon dioxide, exerting significant pressure on the global climate system and damaging ecological balance [1]. Employing subsurface geological formations for carbon dioxide storage presents a technically sound and realistic strategy to confront the mounting difficulties posed by climate change. Indeed, diminishing the atmospheric burden of CO_2 and mitigating the wider environmental stresses linked to human-generated emissions relies heavily on such techniques, which achieve long-term removal of CO_2 from the atmosphere [2,3]. The geological settings primarily under consideration for CO_2 sequestration today include deep saline aquifers, alongside depleted oil and gas fields and coal seams deemed unmineable. Within this group, saline aquifers hold particular promise; their widespread occurrence and sheer storage volume offer significant advantages. Alternative options, in contrast, frequently suffer from lower overall capacity, depend on technological frameworks that are less mature or more intricate, and can demand extra processing stages like CO_2 separation and subsequent reinjection, thereby inflating both operational difficulty and costs [4,5]. Saline aquifers, commonly found within expansive sedimentary basins, emerge as leading candidates for sequestering CO_2 on a substantial scale. They

---

* Corresponding author at: Department of Chemical and Petroleum Engineering, Shi.C., Islamic Azad University, Shiraz, Iran.
E-mail address: agandomkar@shirazu.ac.ir (A. Gandomkar).

https://doi.org/10.1016/j.cej.2025.166102
Received 15 April 2025; Received in revised form 26 June 2025; Accepted 15 July 2025

possess a compelling set of inherent qualities: vast geographical availability, immense storage potential, favourable pore structures and flow characteristics (porosity and permeability), and proven geological stability over long timescales. These attributes underpin the widespread view that storing CO_2 deep within these brine-saturated formations constitutes the most feasible and readily scalable approach to carbon sequestration currently viable [6–8]. Inside saline aquifers, CO_2 is retained through four main processes: structural trapping, residual (or capillary) trapping, solubility trapping, and mineral trapping [9]. The first two, structural and residual, fall under the umbrella of physical containment, while solubility and mineral effects are considered chemical trapping mechanisms [10,11]. It's crucial to recognise that none of these four mechanisms are static; they are dynamic processes. The relative importance of structural, residual, solubility, and mineral trapping tend to shift and grow over time as conditions within the subsurface evolve [3,12]. While structural trapping can quickly accommodate large volumes of CO_2, it places high demands on the integrity of the overlying seal. Reliable containment hinges on an effective cap rock; any weaknesses – like poor sealing or fractures caused by injecting at too high a pressure – could allow CO_2 to escape. Residual trapping, on the other hand, doesn't rely so heavily on specific large-scale geological features. It's generally viewed as a more inherently safe and stable mechanism, offering durable containment across the entire project lifespan for CO_2 storage in saline aquifers [6,8]. Ensuring long-term safety and subsurface stability currently ranks among the primary research challenges in the field of CO_2 storage. Upon injection into porous formations such as saline aquifers, CO_2, due to its significantly lower viscosity relative to brine fails to displace the resident fluids uniformly. Instead, it preferentially migrates through high-permeability pathways, a phenomenon commonly referred to as viscous or capillary fingering [13]. Therefore, one method of improving the CO_2 storage and safety is through the generation of foam during the injection of CO_2 in saline aquifers in the presence of surfactants. Typically, the foam can be introduced into the saline aquifers either by an in-situ generation or by pregenerated ex-situ and then injected into the saline aquifers during the injection of CO_2 [14]. However, the in situ foam generation is more preferable than the ex-situ foam generation due to some technical challenges including foam generation and foam stability in the surface facility and tubing [15]. Several investigations of CO_2-in-brine foam have been performed to store the CO_2 in saline aquifers in both cases of CO_2-soluble and brine-soluble surfactants as follows. In the case of brine-soluble surfactants (surfactant alternating CO_2 injection), in a research work conducted by Wen et al., [16] CO_2 foams were formulated using biopolysaccharides in combination with an environmentally friendly surfactant, alkyl polyglycosides, with the objective of improving CO_2 sequestration efficiency in saline aquifers. The results demonstrated that CO_2 foam significantly decreases water saturation within macro pores, thereby increasing flow resistance and promoting the diversion of the foam into mesoporous and microporous regions of the reservoir. Work by Li et al. [17] detailed a novel technique involving the creation and application of a high-dryness CO_2 foam specifically formulated to improve sweep efficiency and bolster storage security in saline aquifer systems. The outcomes of their experiments revealed gas saturation reaching 83.86 % within the sand pack for an injected foam quality of 85 %. Critically, the foam also demonstrated effectiveness in curtailing CO_2 mobility and increasing its apparent viscosity, thus enhancing containment and the overall integrity of storage within the aquifer. In a different investigation, Al-Darweesh et al. [18] explored how the presence of various ionic species in formation water affected CO_2 foam stability under taxing reservoir conditions (specifically 100 °C and 1000 psi). For their study, they prepared a liquid phase incorporating 0.5 wt% Armovis surfactant within formation water adjusted to ionic concentrations of 0.1, 0.5, and 1 M. Analysis conducted with a high-pressure; high-temperature (HPHT) foam analyser suggested that increased salinity actually promoted better foam stability. Rezk et al., [19] turned their attention to how foam impacts capillary trapping in the context of gas storage within saline aquifers. Their method involved adding a non-ionic ethoxylated fluorocarbon surfactant to the brine, varying its concentration between 0.05 wt% and 2.5 wt%. They discovered that deploying foam during gas injection into saline aquifers yielded marked improvements in both sweep efficiency and capillary trapping levels. It must be acknowledged, however, that predicting foam flow behaviour in porous rock formations remains a complex challenge. A range of factors heavily dictates performance, encompassing the specific surfactant chemistry involved, the mineral make-up of the formation rock, prevailing reservoir conditions, the characteristics of the in-situ formation fluids, and the chosen operational methodologies [20,21]. Furthermore, the application of conventional water-soluble surfactants faces several key hurdles: the tendency for surfactants to adsorb onto reservoir rock, potential limitations on CO_2 injectivity during surfactant alternating CO_2 injection, the need for precise conditions to generate effective foam, and the inherent difficulty in maintaining foam stability once subjected to reservoir conditions [22–24].

Against this backdrop, surfactants specifically designed to be soluble in CO_2, intended for in-situ foam generation and controlling gas mobility, have lately attracted considerable research interest [25,26]. There are fewer publications for in-situ generation of CO_2-in-brine foam via CO_2-soluble surfactants compared to brine-soluble surfactants to store CO_2 in saline aquifers. However, recently, the application of CO_2-soluble surfactants to improve the CO_2 storage in saline aquifers via in-situ foam generation was introduced by Wu et al., [27] and Burrows et al., [28]. Wu et al., [27] examined how CO_2-soluble non-ionic surfactants (alkyl ethoxylates and propoxylates) can enhance carbon storage in carbonate saline aquifers through core flooding tests. It was observed that during continuous CO_2 injection, foam formation occurred at the displacement front when a surfactant concentration of 0.39 g/L was employed. This approach led to a CO_2 saturation level of approximately 60 % after the injection of one pore volume, representing an increase of nearly 50 % compared to conventional CO_2 injection without surfactant assistance. Furthermore, Burrows et al., [28] investigated CO_2-soluble non-ionic tridecyl ethoxylate surfactants that contain between 11 and 18 ethoxylate groups to improve CO_2 storage through in-situ foam generation in saline aquifers in the United States. These surfactants demonstrated adequate solubility in CO_2 and effectively reduced the IFT between CO_2 and brine, contributing to the formation and stabilisation of bulk CO_2-in-brine foams. During core flooding experiments using brine-saturated Berea sandstone, they were also found to suppress CO_2 mobility. Although the surfactants did not significantly alter the wettability of the Berea rock, modelling outcomes indicated that incorporating TDA-11 at a concentration of 0.1 wt% led to a 17 % increase in both the available CO_2 storage capacity and overall storage efficiency.

As a result, CO_2-soluble non-ionic surfactants may enhance CO_2 injectivity and boost CO_2 storage in saline aquifers compared to brine-soluble surfactants. This is accomplished through several key mechanisms: inducing a greater affinity of the rock surface for CO_2 (increasing CO_2-wettability), lowering the interfacial tension at the CO_2-brine boundary, augmenting the dissolution of CO_2 within the brine phase, and elevating the apparent viscosity of the CO_2 phase via the in-situ creation of foam. Furthermore, this innovative injection method, combined with effective non-ionic surfactants, offers a promising solution for carbon sequestration in saline aquifers. It effectively manages CO_2 mobility at the displacement front while ensuring acceptable injectivity in the field. Therefore, our current study proposes the use of non-ionic propoxylated-ethoxylated alcohols surfactants that can be dissolved in CO_2 to generate in-situ CO_2-in-brine foam for improving CO_2 storage in saline aquifers during CO_2 injection. To the best of our knowledge, there are no reports in the literature on application of this type of non-ionic surfactants for improving CO_2 storage in actual saline aquifers. Also, as we mentioned above, there are only two publications for in-situ generation of CO_2-in-brine foam via CO_2-soluble surfactants including Wu et al., [27] and Burrows et al., [28]. They used only ethoxylates and propoxylates surfactants not propoxylated-ethoxylated surfactants. Moreover, our current study is performed in sandstone aquifers while Wu et al., [27] was investigated in carbonate saline aquifers. In addition, based on the Burrows et al., [28] the ethoxylate surfactants did not significantly alter the wettability of the Berea rock; so it needs more investigation via new type of non-ionic surfactants including propoxylated-ethoxylated groups. However, in the current study, the propoxylated-ethoxylated alcohols, 2EH-PO$_5$-EO$_9$ and 2EH-PO$_5$-EO$_{15}$ (2EH is 2-ethyl hexyl) are considered as CO$_2$-soluble non-ionic surfactants during CO$_2$ injection in sandstone saline aquifers. These surfactants were chosen due to various criteria, particularly their low cost and environmental safety. Further, this type of surfactant has been previously shown to improve the gas mobility control via dissolution in CO$_2$ during enhanced oil recovery [29–31]. In addition, the non-ionic surfactants containing the POyEOx group are more hydrophilic than the POx group and these are a good candidate for CO$_2$-in-brine foams [32]. Moreover, Wu et al., [27] examined how CO$_2$-soluble non-ionic surfactants can enhance carbon storage in carbonate saline aquifers only through core flooding tests. But, in our current study, several experimental tests are performed to investigate the effect of CO$_2$-soluble non-ionic surfactants on CO$_2$ storage in sandstone aquifers. In our current study, the surfactants are dissolved in CO$_2$ at dilute concentrations of 500, 1000, 3000, and 5000 ppm via cloud point pressure (CPP) measurements. Furthermore, the cloud point temperature (surfactant solubility in brine) and foam stability tests are performed to illustrate the performance of non-ionic surfactant. Then, the high pressure-high temperature contact angle method, interfacial tension (IFT) measurement, and CO$_2$ solubility in brine is considered to investigate their effect on the CO$_2$ storage in saline aquifer in the presence of CO$_2$-soluble non-ionic surfactants. Additionally, the generation of CO$_2$-in-brine foam was investigated at aquifer conditions (70 °C and 3200 psi) during the core flooding tests to indicate the impact of CO$_2$-soluble non-ionic surfactants on CO$_2$ storage in saline aquifers. Furthermore, in comparison to Burrows et al. [28] investigation, based on their reports, they did not have access to the high pressure, windowed CO$_2$- surfactant mixing vessel that would have allowed them to generate the single phase CO$_2$/surfactant solution. Therefore, they added the surfactant to the brine, saturated the core with the aqueous surfactant solution, and injected CO$_2$. But, in our current study, all experiments were conducted under temperature and pressure conditions that exceeded the CPPs of the corresponding CO$_2$/surfactant solutions to ensure that the CO$_2$/surfactant solutions remained in single-phase conditions without any surfactants precipitating out of the solution. This technique would more accurately represent the proposed technology.

2. Materials and methods

2.1. Rock and fluids properties

To physically simulate the sandstone aquifers, all laboratory experiments were performed on the sandstone rock. The XRD (X-Ray Diffraction) technique was utilised to determine the chemical composition of sandstone rock. The findings indicate that the crushed material comprises approximately 91 % quartz (SiO$_2$), 5 % feldspar, and 4 % clay. Also, the brine was considered to saturate the sandstone rock during the CO$_2$ storage in deep saline aquifers by in-situ generation of CO$_2$-in-brine foams using CO$_2$-soluble non-ionic surfactants. Also, the chemical composition of brine with total dissolved solids of 211,846 ppm is reported in Table 1. The aquifer temperature and pressure are 70 °C and 3200 psi respectively. Moreover, CO$_2$ (Mw = 44 g/mol) was received from Hoek Loos with purity greater than 99.9 mol%.

Table 1
The chemical composition of aquifer water.

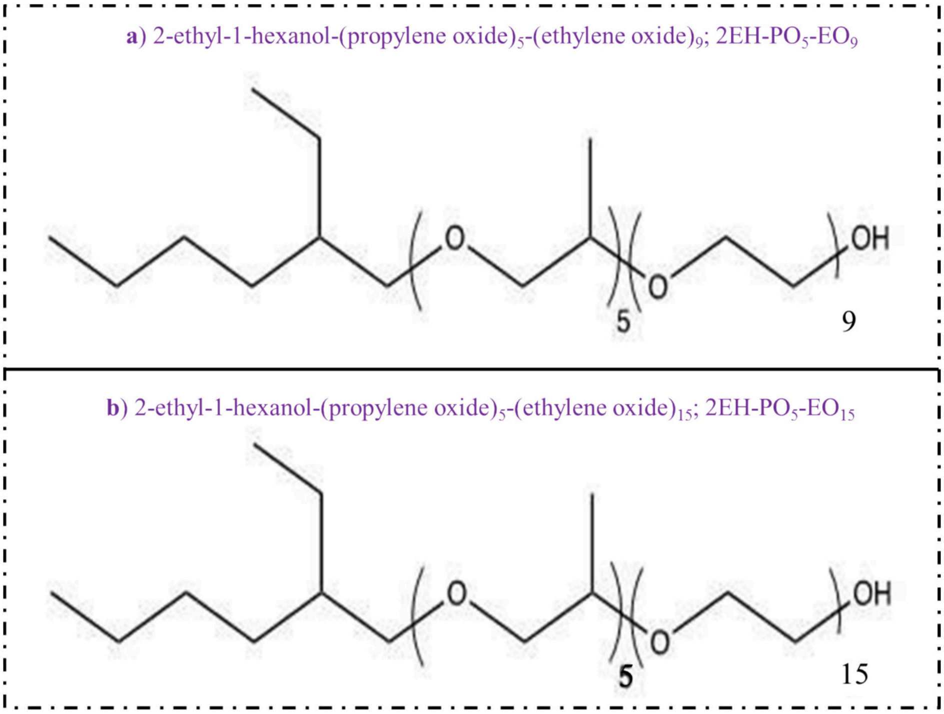
Ions	Concentration (ppm)
Na$^+$	69,370
Mg^{2+}	2375
Ca^{2+}	11,482
Cl$^-$	128,511
HCO$_3^-$	65
SO$_4^{2-}$	14
K$^+$	26
Br$^-$	3
TDS	211,846
pH	7.64
Density (gr/cc)	1.054

2.2. CO$_2$-soluble surfactants

Surfactants that dissolve in CO$_2$, characterised by varying functional head groups and hydrocarbon tail groups; and two non-ionic surfactants; a) 2EH-PO$_5$-EO$_9$, with the chemical formula of $C_{41}H_{83}O_{15}$ (Mw = 815 g/mol) and b) 2EH-PO$_5$-EO$_{15}$, with the chemical formula of $C_{53}H_{107}O_{21}$ (Mw = 1079 g/mol) we selected after surfactant screening. Both of low molecular weight non-ionic surfactants were supplied by Shanghai Aokeshiye Co. Ltd., (China) and were used as received [29,33–35]. These are pure liquids, fluorine-free, and containing no solvents or other additives. Fig. 1 shows the chemical structures of both non-ionic surfactants [31,36,37]. The surfactants contain the same base alcohol, 2-ethyl-1-hexanol, with a linker of five propylene oxides (POx) groups but differed in the length of the ethylene oxide (EOx) groups chain (9 and15). There are two electronegative-oxygen atoms and one electropositive-carbon atom in the chemical structure of non-ionic surfactants which leads to decrease the electrostatic interactions and increase the tendency to dissolve in CO$_2$ [28]. Also, another reason behind the selected both of these non-ionic surfactants are their dissolution in CO$_2$ at pressures and temperatures consistent with CO$_2$ injection scenarios without any co-solvent requirement. Moreover, the EOx unit or POyEOx group is much more hydrophilic than the POx unit. Therefore, the both 2EH-PO$_5$-EO$_9$ and 2EH-PO$_5$-EO$_{15}$ are good candidates for in-situ generation of CO$_2$-in-water foams during the injection of CO$_2$/non-ionic surfactant solution in saline aquifers [38].

2.3. Solubility of surfactants in brine

Furthermore, the solubility of $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ in brine was measured at different concentrations to calculate the cloud point temperature (CPT). Both non-ionic surfactants were mixed with brine at different concentrations (500, 1000, 3000, and 5000 ppm) in a windowed high-pressure cell at favourable pressure and different temperatures, Fig. 2. After that, the windowed cell containing the non-ionic surfactant solutions was put on a stir plate in an air bath at different temperatures to examine the impact of temperature on the solubility of $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ in brine. Also, this procedure continued until the non-ionic surfactant solutions became cloudy, which indicates the cloud point temperature. At the cloud point temperature and higher than that, the non-ionic surfactants degrade and cannot generate the in-situ foam [27,39]. In addition, by adding the HCl get the pH of the brine to ~3. During the injection of carbon dioxide into deep saline aquifers, contact between high-pressure CO$_2$ and brine leads to the formation of carbonic acid, resulting in a lowered pH environment. Although this represents the minimum pH attainable under such conditions, adjusting the brine's pH directly offers a method to simulate this low-pH state when evaluating the behaviour of non-ionic surfactants. Consequently, the cloud point temperature determination procedure was employed to examine pH's influence on brine's surfactant solubility. For effective in-situ foam generation, it is essential that the non-ionic surfactants remain soluble in the brine at the prevailing formation temperature. Expressed differently, the cloud point temperature of the surfactant solution must exceed the reservoir's operational temperature to ensure surfactant stability and prevent degradation [28].


a) 2-ethyl-1-hexanol-(propylene oxide)$_5$-(ethylene oxide)$_9$; 2EH-PO$_5$-EO$_9$

b) 2-ethyl-1-hexanol-(propylene oxide)$_5$-(ethylene oxide)$_{15}$; 2EH-PO$_5$-EO$_{15}$

Fig. 1. The chemical structure of non-ionic surfactants, a) 2EH-PO$_5$-EO$_9$ and b) 2EH-PO$_5$-EO$_{15}$.

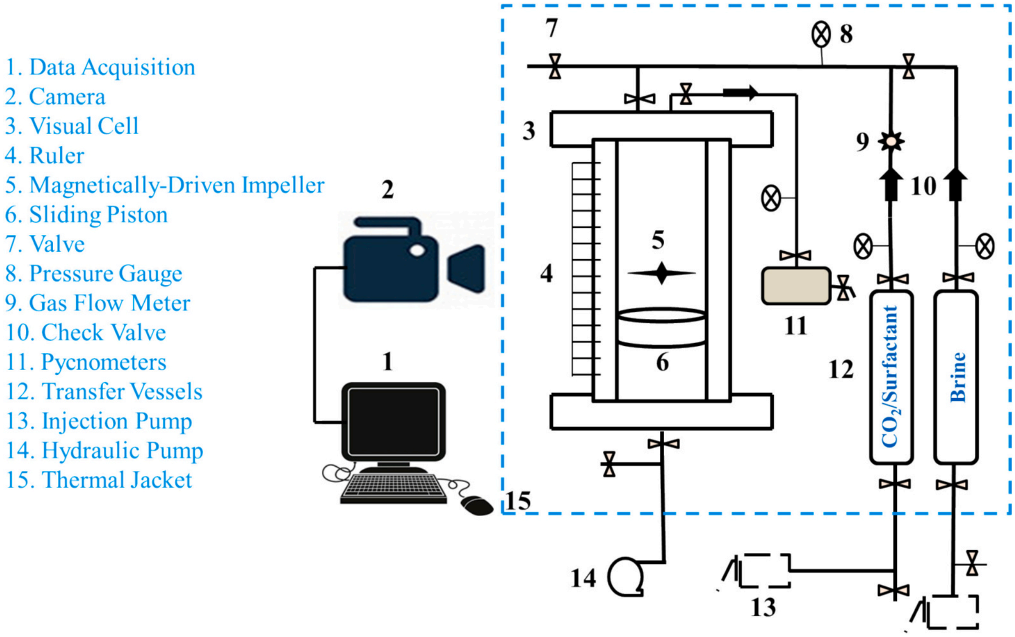


Fig. 2. The schematic of a high-pressure high-temperature windowed cell using for measurement of CPT, CPP, Foam stability, and CO$_2$/surfactant solubility in brine.

2.4. The measurements of dissolution of surfactant in CO$_2$

The solubility of the non-ionic surfactants, $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$; in supercritical CO$_2$ was determined experimentally using visual observation methods within a high-pressure, high-temperature (HPHT) windowed cell (Vinci technology), Fig. 2. A detailed description of this apparatus has been provided in prior research undertaken by our research group [40,41]. The experimental procedure involved first introducing a precisely weighed amount of the surfactant into the cell's sample chamber. Subsequently, a specific quantity of CO$_2$, calculated to yield the desired overall mixture composition, was charged into the cell volume. The cell was heated to the desired temperature. A magnetically driven stirrer operating at 2000 rpm was employed to ensure thorough mixing of the components. The process was carried out under sufficiently high pressure to facilitate the formation of a clear, single-phase solution that uniformly occupied the entire sample volume upon completion of mixing. Then, the intervals of 20 psi were considered to decrease the pressure in the sample through a constant-composition expansion (CCE) of the variable-volume window cell (i.e., the gradual descent of the sliding piston that divides the sample volume from the overburden fluid). The system was allowed to reach equilibrium over a two-hour period. The cloud point pressure was identified as the highest pressure (first pressure) at which the initially transparent single-phase solution began to exhibit a slight haze, characterised by the appearance of surfactant-rich droplets dispersed within the CO_2-rich phase. It was performed at least 3 times, with ±5 psi repeatability for two non-ionic CO_2-soluble surfactants. This process was performed for concentrations of 500, 1000, 3000, and 5000 ppm at commensurate pressures and temperatures with CO_2 injection scenarios without any co-solvent requirement. All subsequent experiments were conducted under temperature and pressure conditions that exceeded the CPPs of the corresponding CO_2/surfactant solutions to ensure that the CO_2/surfactant solutions remained in single-phase conditions without any surfactants precipitating out of the solution. The CO_2-rich phase that contains a dissolved non-ionic surfactant has a CO_2-like property at supercritical conditions.

2.5. Stability of CO_2-brine-surfactant foam

To evaluate the persistence of the CO_2-brine-surfactant foams, the previously mentioned windowed, variable-volume view cell was employed, Fig. 2. Initially, the view cell was charged with identical volumes of the CO_2/surfactant solution (volume determined by CO_2 density at 70 °C and 3200 psi) and brine containing 1000 ppm surfactant relative to its mass. Following sealing, the cell's internal conditions were adjusted to a temperature of 70 °C and a pressure of 3200 psi. A slotted fin impeller agitated the contents at 2000 rpm for 15 min. Immediately upon cessation of stirring, a white foam was observed to occupy the entire sample volume. The subsequent assessment of foam stability involved monitoring the interfaces between the foam and any separated excess brine below, as well as any excess CO_2 phase above, over a 24-h duration. It was anticipated that an excess brine layer would progressively form beneath the CO_2-in-brine foam, potentially followed by the appearance of an excess CO_2 phase supernatant to the foam [28,32].

2.6. IFT between CO_2/surfactant solutions and brine

The determination of interfacial tensions (IFTs) between brine and either pure CO_2 or CO_2/surfactant mixtures was carried out using an available HPHT IFT 700 apparatus, Fig. 3. Within this setup, the brine phase, situated at the tip of a capillary needle, is enveloped by the pure CO_2 or CO_2/surfactant phase. Equilibrium IFT values across a range of surfactant concentrations were subsequently derived through the application of the axisymmetric drop shape analysis method [42]. A prerequisite for accurate IFT calculation under the relevant experimental conditions is the precise knowledge of densities for both interacting phases – the brine, and the CO_2 phase (whether pure or containing surfactant). For pure CO_2, density figures were sourced from the PPDS software package, which utilises a comprehensive fluid property database from the UK's National Engineering Laboratory [43]. Densities for the CO_2/surfactant solutions, however, were directly measured utilising a high-pressure, high-temperature (HPHT) visual cell. Operating within the single-phase domain, the density at specific temperature and pressure points was ascertained by relating the known total mass of CO_2 and surfactant introduced into the sample chamber to the chamber's precisely measured volume, determined via the position of an internal sliding piston [40,44]. All these measurements and calculations were performed reflecting the target aquifer temperature of 70 °C and pressures spanning 2800 to 3200 psi.

2.7. Wettability alteration

Investigations into potential wettability shifts induced by the CO_2-soluble surfactants were conducted through contact angle observations under high-pressure, high-temperature conditions within a windowed cell, Fig. 3. The primary aim was to illustrate surfactant impact on the wettability of sandstone aquifer rock. To mimic the native reservoir state, sandstone substrates were first subjected to an ageing process designed to enforce a strongly water-wet condition. This involved immersing the substrates in formation brine held within a glass container, followed by incubation in an oven set to 70 °C for no less than one month. Such treatment allows for equilibration between the brine and substrate surfaces, effectively conditioning the sandstone to restore its original wetting preferences [40]. The effectiveness of this ageing in achieving the strongly water-wet state was confirmed by contact angle measurements (brine droplet in CO_2 environment), which yielded values

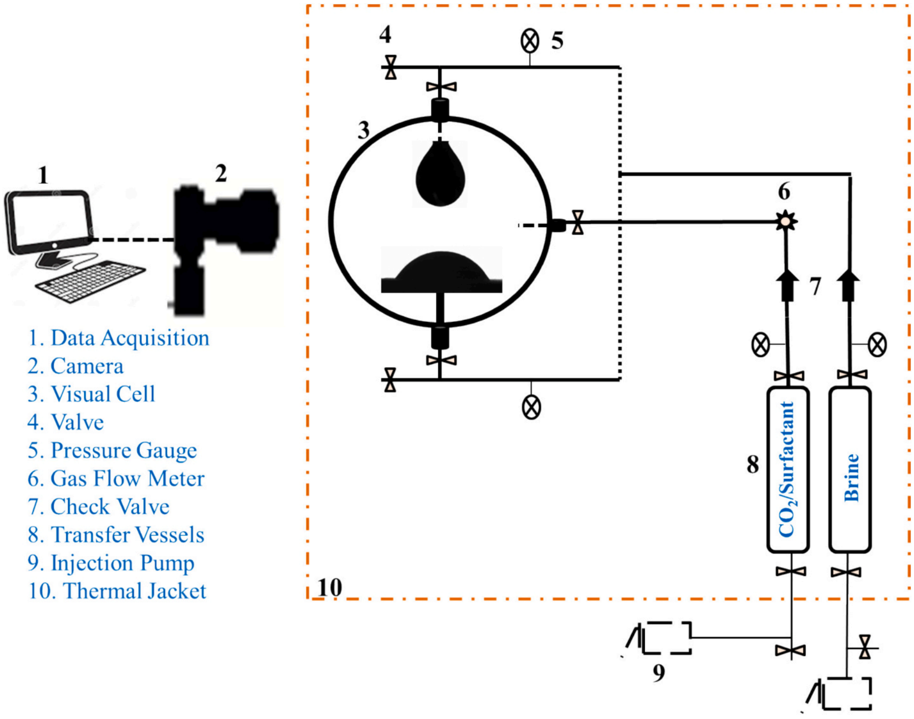


Fig. 3. The schematic of high-pressure high-temperature IFT 700 apparatus, using for measurement of IFT and wettability.

near 18° (ϴ ~ 18°). Following this preparation, the aged substrates were carefully mounted inside the top section of the windowed cell. Brine was then charged into the cell's lower portion, before the entire system was pressurised with either pure CO_2 or the relevant CO_2/surfactant solution. Subsequently, the cell's temperature was adjusted to the target aquifer condition ($T_{aquifer} = 70$ °C) Once thermal stability was achieved, the pressure was ramped up to the representative aquifer pressure of 3200 psi. The CO_2 phase (pure or with surfactant) and the brine phase, residing at the cell's base, were then allowed ample time to equilibrate under these set conditions before measurements began. For each contact angle test, a brine droplet of consistent volume, drawn from the equilibrated phase, was deposited onto the limestone substrates. Droplet behaviour was monitored visually using a camera system, with the contact angle determined by averaging the left and right angles measured over time, specifically after a four-day equilibration period [32]. Distinct experimental runs were performed using pure CO_2 and the different CO_2/surfactant solutions to specifically isolate and demonstrate the influence of these surfactant solutions on sandstone rock wettability under simulated aquifer conditions (P = 3200 psi, T = 70 °C).

2.8. The solubility of CO_2 in brine

The PVT cell, designed for high pressure and high temperature, primarily includes an air bath, a windowed equilibrium cell, an ISCO displacement pump, and high-pressure pycnometers (as sampling cylinders) used to investigate the CO_2 solubility in brine in presence of non-ionic surfactants [45], Fig. 2. In the beginning, high-pressure pure CO_2, CO_2/surfactant solutions, and brine, each stored in separate transfer cylinders, were introduced sequentially into the windowed equilibrium cell. The precise volumes of CO_2, CO_2/surfactant mixtures, and brine were not critical, provided that both CO_2 and brine phases were present at equilibrium. Typically, approximately 90 ml of brine was injected to ensure sufficient volume for collecting at least two representative samples. The air bath was adjusted to match the target aquifer temperature of 70 °C. Once thermal stability was achieved, the system pressure was elevated to the representative aquifer pressure of 3200 psi. The mixture was agitated for a period of 2 h and subsequently left to equilibrate overnight under constant pressure conditions, maintained throughout by the ISCO displacement pump. Prior to sampling, the connecting tubing was purged with a minimum of 10 ml of equilibrium brine to ensure the collection of a representative fluid sample. The sampling cylinder was first evacuated and weighed before being connected to the apparatus. The sampling process was conducted under constant pressure control via the ISCO pump. To ensure the accuracy of the measurements, care was taken to extract only the brine phase at equilibrium. Upon withdrawal, the high-pressure, single-phase brine was depressurised within the sampling cylinder, resulting in a two-phase mixture. Once the cylinder had returned to ambient temperature, it was reweighed. The quantity of dissolved CO_2 was determined by gradually venting the gas from the top of the cylinder until no further mass loss was observed, indicating complete release of the dissolved phase. The final mass, comprising the remaining brine and any residual gas at atmospheric pressure, was then recorded. Finally, the total volume of CO_2 dissolved in the brine was calculated using the analytical method described in Yan et al. (2011). This procedure is repeated for different non-ionic surfactant concentrations at the aquifer conditions.

2.9. In-situ foam generation during core flooding tests

There are two common approaches to measure the two phase relative permeability including steady state and un-steady state methods. The unsteady-state method involves injecting one fluid to displace the other, while steady-state technique considers simultaneously injecting both fluids at a constant flow rate under stable conditions. The main difference lies in whether saturation equilibrium is achieved during the measurement, with steady-state methods aiming for equilibrium, and un-steady state methods allowing for transient flow and changes in saturation over time. Therefore, the primary advantage of the unsteady-state method is that it is faster and easier to handle than the steady-state method. The displacement of CO_2 and single-phase CO_2/surfactant solutions in saline aquifer was investigated during the corefloodingtests by measuring the un-steady state two phase relative permeability through similar sandstone cores, Table 2. The CO_2-brine and CO_2/surfactant-brine relative permeabilities were evaluated to illustrate the effect of in-situ foam generation on CO_2 mobility and then CO_2 storage in deep saline aquifers, Fig. 4.

However, the two phase relative permeability data was measured using the un-steady state analytical approach proposed by Johnson, Bossler, and Neumann (JBN) and modified by Welge and Buckley and Leverett. The modified Johnson–Bossler–Neumann (JBN) method yields relative permeability data that are less sensitive to variations in injection rate and the capillary-to-viscous force ratio than those derived using the original JBN formulation. Furthermore, the immiscible core flooding experiments conducted through the injection of pure CO_2 and single-phase CO_2/surfactant solutions; has been previously described in detail in our earlier work [41]. The essence of core preparation involves returning the core to its initial wettability, specifically water-wet, and its saturation level of 100 % water. The core-flooding scenarios were performed at an injection rate of 0.1 cc/min for the injection of 3 pore volumes of pure CO_2 and single-phase CO_2/surfactant solutions at aquifer conditions, i.e., 3200 psi and 70 °C. Also, the pressure drops and produced rate of water and CO_2 or CO_2/surfactant are required data to calculate the two-phase relative permeability during immiscible CO_2 or CO_2/surfactant scenarios. Moreover, the end-point relative permeabilities of pure CO_2 or CO_2/surfactant were measured [46,47]. However, Fig. 5 presented the flowchart of our current experimental work.

3. Results and discussion

3.1. Dissolution of surfactants in brine by CPT measurements

Both non-ionic surfactants, $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$; were mixed with brine at 3000 ppm concentration in small glass vials (25 cc). Based on our observations both surfactants were dissolved in brine at ambient condition. After that, the windowed cells containing separately the $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ were put on a stir plate in an air bath at different temperatures; i.e. 50 and 70 °C at constant pressure (3200 psi). The observation illustrated that both $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ solutions were clear at temperatures of 50 and 70 °C, thus the cloud point temperatures for both non-ionic surfactants are higher than 70 °C. This procedure continued and both solutions heated up until it is cloudy. Therefore, the $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ solutions were cloudy at 92 and 106 °C respectively, and that's the cloud point temperature. Also, the cloud point temperature is a weak function of surfactant concentration and the same results were approximately obtained for different non-ionic surfactant concentrations, i.e. 500, 1000, and 5000 ppm. Therefore, the non-ionic surfactants containing the POyEOx group are more hydrophilic than the case of POx and EOx group alone and these are a good candidate for CO_2-in-brine foams [32]. Additionally, acidic conditions were incorporated to mimic the pH of brine with carbonic acid resulting from high-pressure CO_2 presence. In addition, by adding the HCl get the pH of the brine to ~3. That is the lowest value of pH for

Table 2
The physical properties of sandstone cores.

Core number	Length (cm)	Diameter (inch)	Porosity (%)	Permeability (mD)
S1	7.3	1.5	13.7	49.1
S2	7.4	1.5	14.0	52.7
S3	7.8	1.5	14.5	50.3

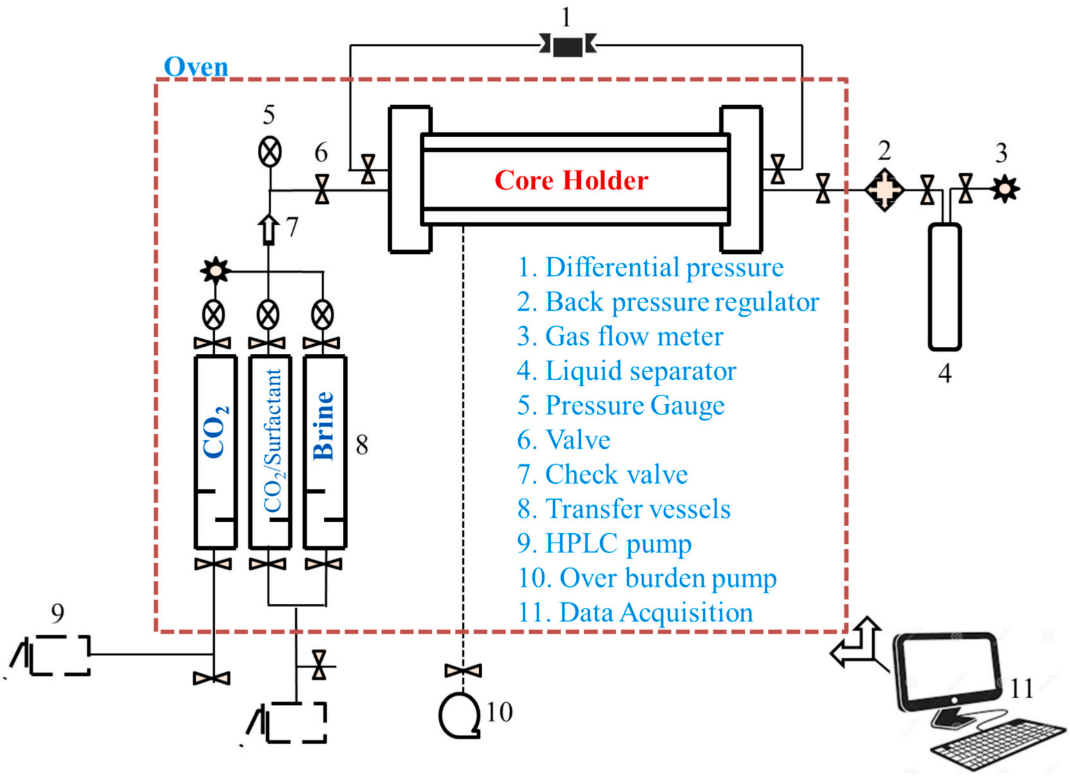


Fig. 4. Schematic of core flooding setup using for measurement of two phase relative permeability, un-steady state approach [41].

the carbonic acid that forms when high pressure CO_2 contacts brine during the injection of CO_2 in deep saline aquifers. However, the cloud point temperature procedure was considered to investigate the effect of pH on surfactant solubility in brine. Based on the our results, in the case of acidic conditions (pH ~3), the cloud point temperatures were increased to 97 and 112 °C for $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ solutions at 3000 ppm concentration respectively. The results showed that the cloud points for $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ are well above the aquifer temperatures (70 °C) in both case of $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ solutions. It should be noted that the boiling point of water exceeds the cloud point temperature at 3200 psi. Table 3 shows the cloud point temperature results in both cases of brine and acidified brine. During the CO_2 injection in deep saline aquifers, the non-ionic surfactants must be soluble in brine at a favourable temperature to make a good in-situ foam. In other words, the cloud point temperature of the surfactant in brine must be higher than the aquifer temperature to ensure that surfactant degradation does not occur and that the surfactant partitions into the aquifer brine [28,48]. However, both $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ non-ionic surfactants are a good candidate for CO_2-in-brine foams at maximum temperature of ~100 °C and at the case of higher than 100 °C it needs more investigation via current materials.

3.2. *Dissolution of surfactants in CO_2 by CPP measurements*

The solubility behaviour of $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ in CO_2 was investigated through the determination of cloud point pressures. The cloud point pressure was defined as the pressure at which a homogenous, single-phase solution formed under the specified temperature and pressure conditions. These single-phase mixtures were subsequently used in all further experimental procedures to ensure consistency. The measured cloud point pressures for the CO_2/surfactant systems—at surfactant concentrations of 500, 1000, 3000, and 5000 ppm—were recorded at two temperatures, 70 °C and 100 °C, as illustrated in Fig. 6. The measured cloud point pressures ranged from 1720 to 2360 psi. The results indicate a generally linear increase in cloud point pressure with rising temperature and surfactant concentration, highlighting the sensitivity of solubility behaviour to both parameters in the CO_2/surfactant systems. For example, these were 1830 and 2150 psi for CO_2/$C_{41}H_{83}O_{15}$ and 1930 and 2290 psi for CO_2/$C_{53}H_{107}O_{21}$ solutions at 70 and 100 °C, respectively at 3000 ppm non-ionic surfactant concentration. It is found that the determined CPPs of CO_2/$C_{53}H_{107}O_{21}$ are higher than the CPP values of CO_2/$C_{41}H_{83}O_{15}$; at the same temperature and concentration. Both surfactants contains the same base alcohol 2-ethyl-1-hexanol with a linker of 5 propylene oxide (POx) groups but differed in the length of the ethylene oxide (EOx) groups chain (9 and15). However, the surfactants have better solubility due to the side chain length in the free volume. The findings also revealed that lower temperatures favour greater surfactant solubility in CO_2. This behaviour can be attributed to the thermodynamic influence of mixing entropy, which plays a central role in governing solubility under varying conditions. While the density of the non-ionic surfactants remains relatively stable with temperature, the density of CO_2 increases as temperature decreases. This results in a greater density contrast between the components and a corresponding reduction in the entropy of mixing, thereby explaining the inverse relationship observed between temperature and solubility during the dissolution process [41,49]. As a result, our findings indicated that both CO_2-soluble non-ionic surfactants readily dissolved in CO_2 under temperatures and pressures typical of CO_2 injection conditions. In addition, during the remaining trials of our current study, we maintained the pressure above the cloud point pressure to ensure that the non-ionic surfactant remained dissolved and did not precipitate due to any phase changes.

3.3. *Foam generation and stability in the CO_2/surfactant/brine system*

In this study, visually monitors the surfactant stabilisation of bulk CO_2/surfactant/brine foam. The equal volumes of CO_2/surfactant solutions and brine were added to the visual cell at 70 °C and 3200 psi for both $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ at 1000, 3000, and 5000 ppm concentrations. The mixture was agitated at 2000 rpm for 15 min, after

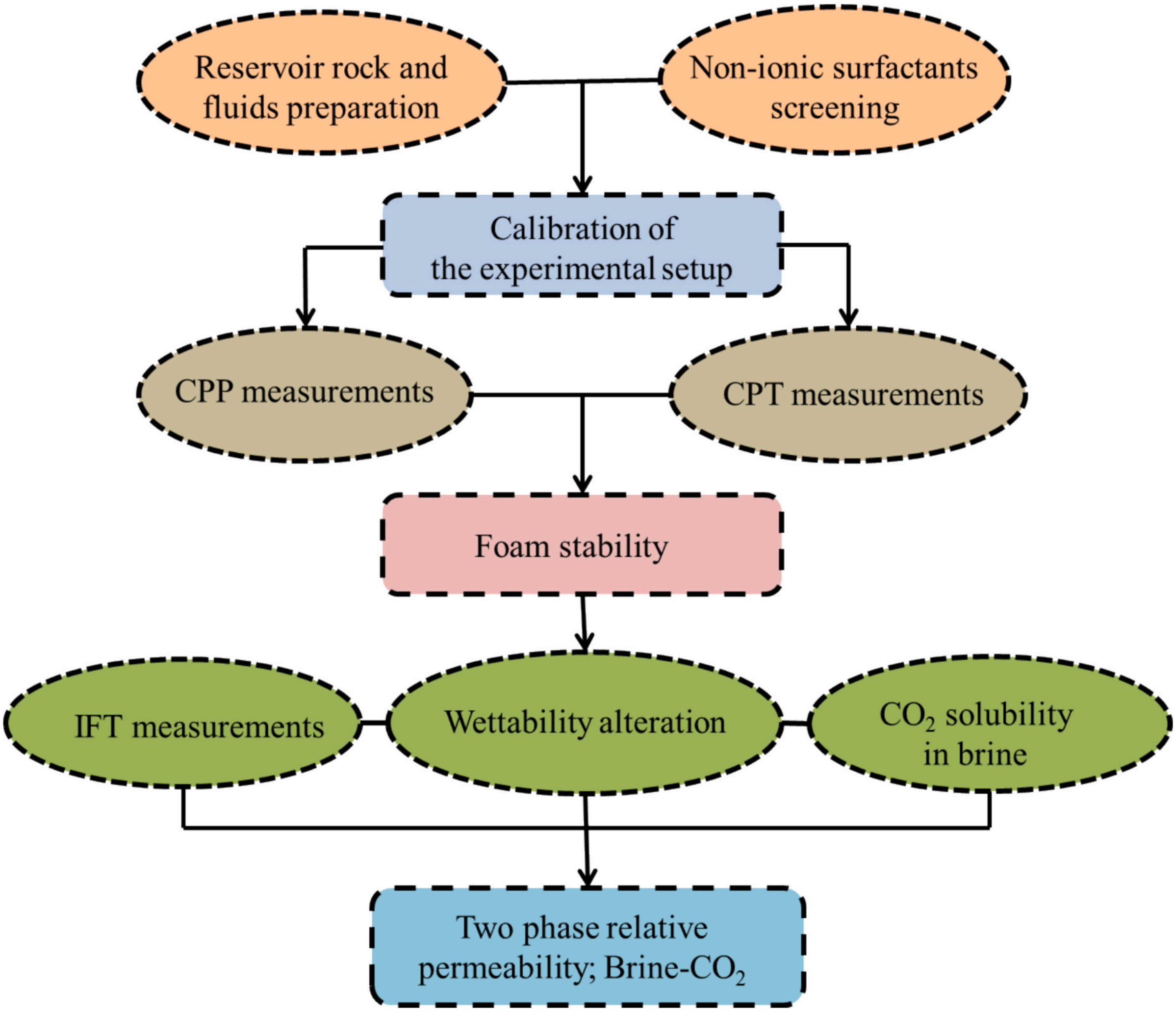


Fig. 5. The flowchart of our current experimental work.

Table 3
The cloud point temperatures of non-ionic surfactants in brine and acidified brine.

Non-ionic surfactants (3000 ppm)	Cloud point temperatures (°C)	
	Brine (pH ~ 7.12)	Brine (pH ~ 3)
$C_{41}H_{83}O_{15}$	92	97
$C_{53}H_{107}O_{21}$	106	112

which foam formation was observed to occur immediately, filling the entire volume of the sample cell. Subsequently, the persistence of the foam was quantified by monitoring the locations of the brine–foam and foam–CO_2 boundaries throughout a 24-h observation window. During this timeframe, a layer of excess brine gradually accumulated beneath the CO_2-in-brine foam, while, in some cases, an excess CO_2 phase began to appear above the foam column. Visual observations revealed that both $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ produced foams composed of micro-bubbles with diameters ranging from 10 to 100 μm, indicating good foam stability across the range of tested concentrations. In contrast, formulations that yielded larger bubbles, between 1 and 10 mm; were associated with immediate separation of brine and CO_2 phases and rapid foam collapse, typically within 1 h. Overall, both non-ionic surfactants exhibited promising performance in stabilising CO_2-in-brine foams under the evaluated conditions.

Visually, all foams produced with the surfactants presented as white and non-transparent, structurally characterised by discrete bubbles of CO_2 encapsulated within continuous lamellae of brine. Fig. 7 shows the proportions of brine to foam volumes over a 24 h period for both $C_{53}H_{107}O_{21}$ (Fig. 7A) and $C_{41}H_{83}O_{15}$ (Fig. 7B) at different concentrations. Initially, the foam occupied nearly 100 % of the cell volume, indicating the complete incorporation of both CO_2 and brine within the foam structure. Over the subsequent 1 to 24-h period, however, progressive foam collapse was observed, accompanied by a gradual reduction in the proportion of brine and CO_2 retained within the foam phase. Based on these results, stabilized CO_2-in-brine foams remained in the cell after 24 h. Also, during our visual monitoring the volume of excess brine phase remained constant approximately after 15 h for all scenarios. Moreover, no excess CO_2 phase was observed at the top of the sample volume for any of the surfactant systems, indicating effective gas retention within the foam structure. Both surfactants produced foams with substantial brine content distributed within the lamellae; however, after 24 h, $C_{53}H_{107}O_{21}$ consistently demonstrated superior foam stability compared to $C_{41}H_{83}O_{15}$. These findings suggest that increasing the surfactant concentration within the range of 1000 to 3000 ppm in CO_2 is likely to enhance foam performance under reservoir-relevant conditions. The best foam after 24 h was for case of $C_{53}H_{107}O_{21}$ at 5000 ppm concentration. The cell contained a minimal excess of CO_2 and brine phase. It is worth mentioning that, after 24 h, the volume of foams stabilized at 3000 ppm and 5000 ppm concentrations were about the same [50]. Therefore, the concentration of 3000 ppm is logistically reasonable for generation and stabilisation of in-situ foam during our

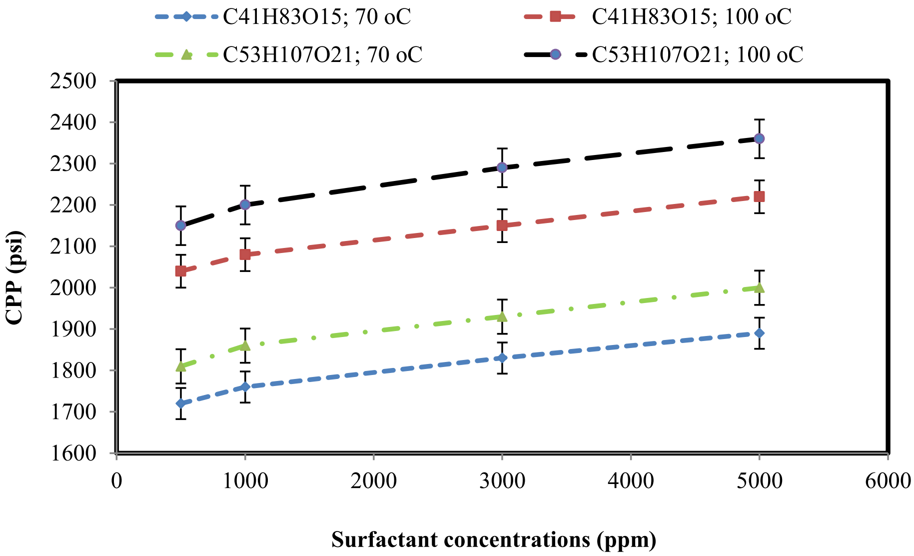


Fig. 6. The cloud point pressures of $CO_2/C_{41}H_{83}O_{15}$ and $CO_2/C_{53}H_{107}O_{21}$ at different surfactant concentrations, 500, 1000, 3000, and 5000 ppm at both 70 and 100 °C.

current study for CO_2 storage in saline aquifers. The additional costs associated with surfactant purchases and delivery, small surfactant pumps and static mixers will obviously impact the economics of CO_2 sequestration. Unlike CO_2-EOR, CO_2 injection into an aquifer does not produce an income stream from an oil product. Therefore, if a large-scale CO_2 storage project does occur (funded by either tax credits for CO_2 storage and/or income from the power plant or chemical plant that generates and captures the CO_2) the costs of surfactant introduction must be compensated by one or more of the following; an increased rate of CO_2 injection at lower pressures due to wettability changes, an increased swept storage volume of CO_2 at that location due to better mobility control, and/or increased solubility of CO_2 in brine. In general, it is clear that the economic penalties are reduced if dilute concentrations of these surfactants, which typically cost roughly \$2–3/lb. delivered, can be used effectively. For example, at a concentration of 3000 ppm, the chemical cost alone for the surfactant would be roughly \$12–18 surfactant/ton CO_2 [51]. Certainly, concentrations less than 1 wt% (10,000 ppm), and preferably less than 0.1 wt% (1000 ppm), would be preferable. More investigation is needed to optimize, and hopefully further reduce, the surfactant concentration. These surfactants were chosen due to various criteria, particularly their low cost, availability in large quantity, pumpability, and environmental and worker safety. Further, this type of surfactant has been previously shown to improve the gas mobility control via dissolution in CO_2 during enhanced oil recovery [29–31]. Therefore, these surfactants may prove to be an economically attractive approach to large-scale CO_2 sequestration in saline aquifers.

3.4. The effect of IFTs on CO_2 storage

This study determined the IFTs of the (CO_2/surfactant)-brine system under aquifer conditions, i.e., 3200 psi and 70 °C. Table 4 reported that the dissolution of both non-ionic surfactants in CO_2 has the ability to reduce the interfacial tension (IFT) between brine and the CO_2/surfactant mixture. In addition, the $C_{53}H_{107}O_{21}$ surfactant can perform better than $C_{41}H_{83}O_{15}$ in IFT reduction. For example, the interfacial tension between brine and pure CO_2 measured 32 dyne/cm under aquifer conditions. These were decreased to 9.5 and 6.7 dyne/cm for $CO_2/C_{41}H_{83}O_{15}$ and $CO_2/C_{53}H_{107}O_{21}$ cases respectively at 3000 ppm concentration. In addition, higher concentrations of non-ionic surfactants led to reduced IFT values, likely as a result of increased CO_2 density [40]. Consequently, IFT reduction leads to increase the CO_2 storage du to capillary trapping (residual sequestration) with a high degree of safety in saline aquifers [52]. Moreover, this decrease in IFT aligns with the capability of both non-ionic surfactants to produce the CO_2-in-brine foams discussed earlier.

3.5. The impact of wettability alteration on CO_2 storage

The ageing sandstone substrates (strongly water-wet, $\Theta \sim 18°$) were considered during the contact angle measurements of CO_2/surfactant and brine systems. The 1000 and 3000 ppm non-ionic surfactant concentrations were considered since these two concentrations seemed to be the most promising options according to the CPT, CPP, IFT, and foam stability results for low and high surfactant concentrations respectively. Fig. 8 shows the contact angles of brine and pure CO_2, $CO_2/C_{41}H_{83}O_{15}$, and $CO_2/C_{53}H_{107}O_{21}$ systems after 24 h soaking at aquifer conditions, i.e., 3200 psi and 70 °C. Based on these results, after 24 h soaking of sandstone substrates with pure CO_2, the contact angle did not change. Moreover, it altered from 18° to 32 and 41° for $CO_2/C_{41}H_{83}O_{15}$ scenarios and to 53 and 71^o for $CO_2/C_{53}H_{107}O_{21}$ solutions at 1000 and 3000 ppm respectively. It is worth mentioning that both $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ non-ionic surfactants can significantly change the sandstone rock wettability. Furthermore, increasing in the non-ionic surfactant concentration can significantly change the sandstone rock wettability. In addition, the $CO_2/C_{53}H_{107}O_{21}$ solution (3000 ppm) can alter the sandstone rock wettability from strongly water-wet ($\Theta \sim 18°$) to intermediate gas-wet ($\Theta \sim 71°$). As it seems the $CO_2/C_{53}H_{107}O_{21}$ solution can perform better than $CO_2/C_{41}H_{83}O_{15}$ solution in changing the sandstone rock wettability. In our current study, both non-ionic surfactants contains the same base alcohol 2-ethyl-1-hexanol with a linker of 5 propylene oxide (POx) groups but differed in the length of the ethylene oxide (EOx) groups chain (9 and15). Moreover, the EOx unit or POyEOx group is much more hydrophilic than the POx unit. Accordingly, the change in sandstone rock wettability from strongly water-wet to water-wet and intermediate gas-wet can increase the CO_2 storage in saline aquifers due to residual sequestration during gas injection. This wettability alteration may be attributed to the adsorption of the propoxylated-ethoxylated surfactant on the rock surface such that the surface becomes more CO_2-philic and less hydrophilic. Moreover, residual trapping happens when capillary effects and the rock's wetting properties combine to decrease the CO_2 mobility due to an intermediate gas-wet condition within the pore network. Consequently, the altering in sandstone rock wettability along with synergy of in-situ foam generation

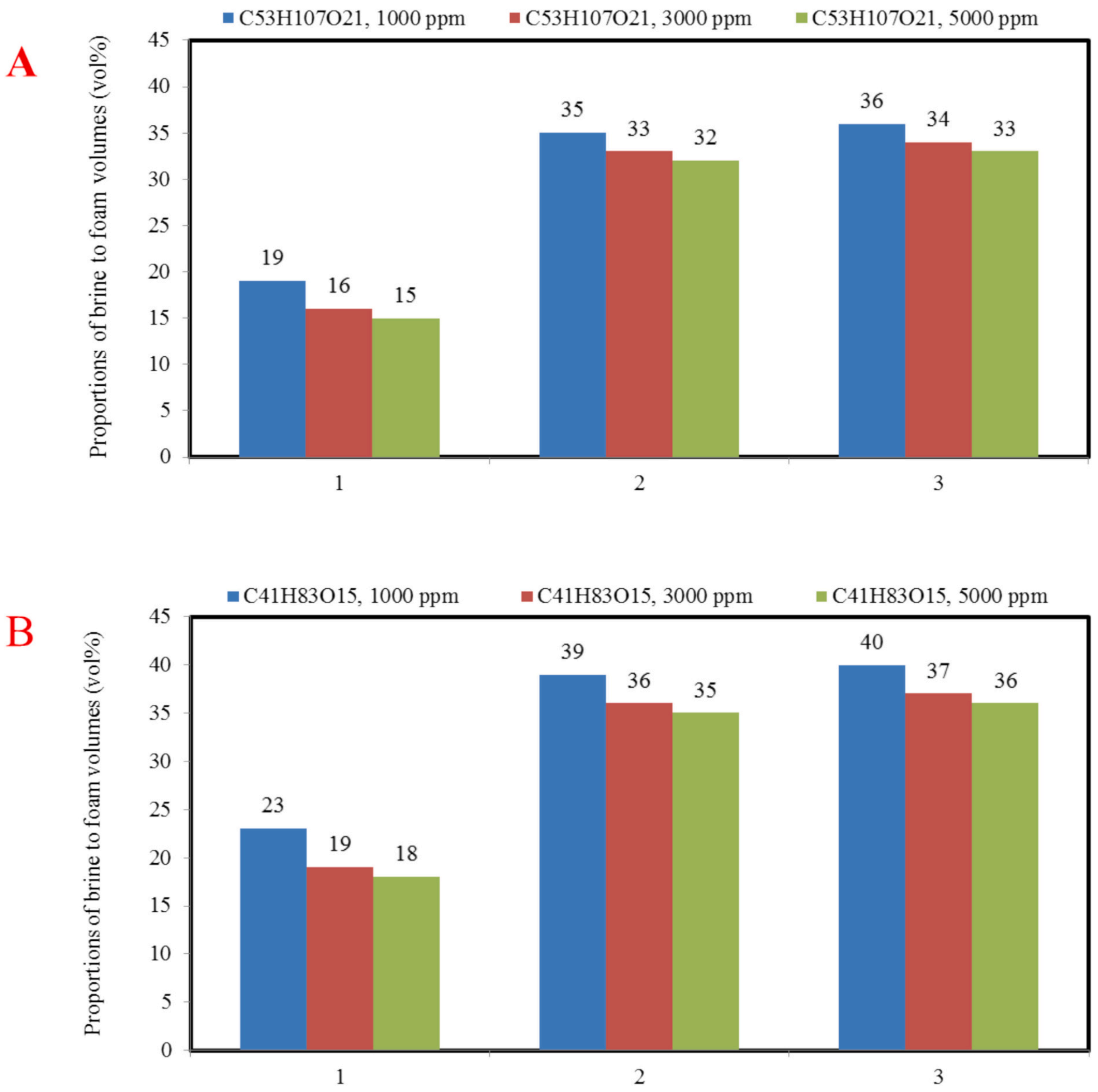


Fig. 7. The proportions of brine to foam volumes for both $C_{53}H_{107}O_{21}$ (Fig. 7A) and $C_{41}H_{83}O_{15}$ (Fig. 7B) at different concentrations at 1) 1 h; 2) 10 h; 3) 24 h.

during the CO_2/surfactant injection can control the gas mobility and increase the CO_2 trapping in saline aquifers [53]. Therefore, both $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ can be a promising candidate to improve the CO_2 storage in saline aquifers at dilute concentrations.

3.6. *The effect of CO_2 solubility in brine on CO_2 storage*

The solubility of CO_2 in water and NaC1 solution has been well studied by many investigators and reported by Yan et al., [54]. This work presents a laboratory study of CO_2 solubility in an actual sample of brine from saline aquifers. Fig. 9 indicated that the solubility of CO_2 in actual saline aquifer brine for different dilute concentrations of both $CO_2/C_{41}H_{83}O_{15}$ and $CO_2/C_{53}H_{107}O_{21}$ scenarios. Based on the results, the solubility of pure CO_2 in saline aquifer brine was 1.25 mol percent at aquifer conditions, i.e., 70 °C and 3200 psi. Moreover, it increased while CO_2/surfactant solutions have been considered instead of pure CO_2 case. Also, by increasing in surfactant concentrations, the solubility of CO_2 in brine increased for both $CO_2/C_{41}H_{83}O_{15}$ and $CO_2/C_{53}H_{107}O_{21}$ scenarios. Our current results indicated that the $CO_2/C_{53}H_{107}O_{21}$ can perform better than $CO_2/C_{41}H_{83}O_{15}$ and increased the CO_2 solubility by a factor of approximately two (1.25 to 2.51 mol%) compared to pure CO_2 scenario. This increase in CO_2 solubility may be attributable to the solubilization of CO_2 into cores of surfactant micelles in the brine. Therefore, increasing in the CO_2 solubility can improve the CO_2 storage in form of solubility sequestration mechanism. In addition, based on the literature reports, for high salinity brines the brine density decreases after CO_2 dissolution [42]. Thus, it causes more IFT reduction between CO_2/surfactant and brine system so increases the CO_2 trapping. Consequently, the solubility of CO_2 in saline aquifers can increase the CO_2 storage in both forms of solubility and residual sequestration mechanisms.

3.7. *In-situ foam generation during CO_2 soluble non-ionic surfactants injection*

Based on the previous sections, 3 core flooding scenarios were performed to investigate the role of in-situe foam generation on CO_2 mobillity and CO_2 storage in sandstone quifers. Based on our results, the CO_2/surfactant solutions can generate the stabilized CO_2-in-brine foams; decrease the CO_2-brine IFT, change the sandstone aquifer to intermediate gas-wet, and increase the CO_2 solubility in brine. However,

Table 4

The CO_2-brine interfacial tensions of both non-ionic surfactants at aquifer conditions, i.e., 3200 psi and 70 °C.

Two phase system	Surfactant concentration	IFT (dyn/cm)
Brine and Pure CO_2	0	32.4
Brine and CO_2/ $C_{53}H_{107}O_{21}$	500	16.8
Brine and CO_2/ $C_{53}H_{107}O_{21}$	1000	12.5
Brine and CO_2/ $C_{53}H_{107}O_{21}$	2000	9.3
Brine and CO_2/ $C_{53}H_{107}O_{21}$	3000	6.7
Brine and CO_2/ $C_{53}H_{107}O_{21}$	5000	2.3
Brine and CO_2/ $C_{41}H_{83}O_{15}$	500	19.6
Brine and CO_2/ $C_{41}H_{83}O_{15}$	1000	16.1
Brine and CO_2/ $C_{41}H_{83}O_{15}$	2000	13.9
Brine and CO_2/ $C_{41}H_{83}O_{15}$	3000	9.5
Brine and CO_2/ $C_{41}H_{83}O_{15}$	5000	4.7
		
IFT = 13.9 (dyn/cm) Brine and CO_2/ $C_{41}H_{83}O_{15}$ 2000 ppm	IFT = 2.3 (dyn/cm) Brine and CO_2/ $C_{53}H_{107}O_{21}$ 5000 ppm	IFT = 32.4 (dyn/cm) Brine and Pure CO_2

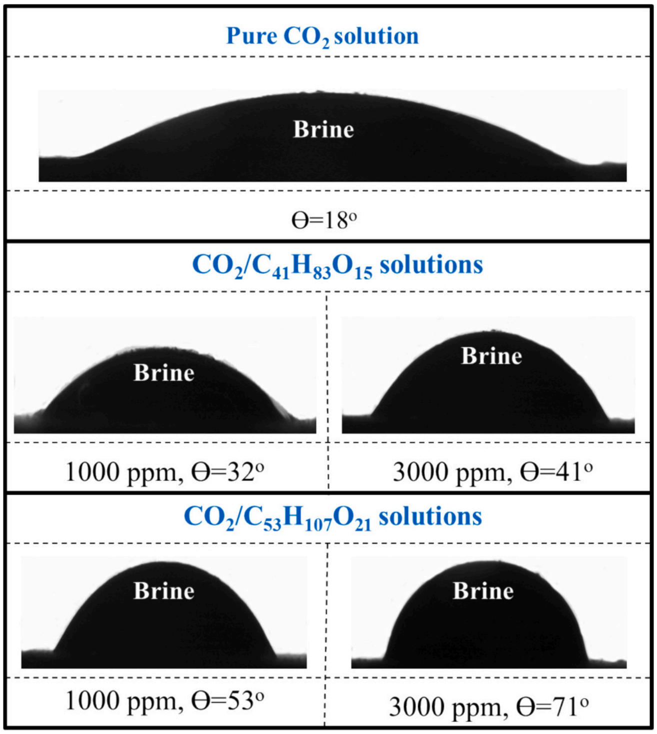


Fig. 8. The contact angles of brine and pure CO_2, $CO_2/C_{41}H_{83}O_{15}$, and $CO_2/C_{53}H_{107}O_{21}$ systems after 24 h soaking at aquifer conditions, i.e., 3200 psi and 70 °C.

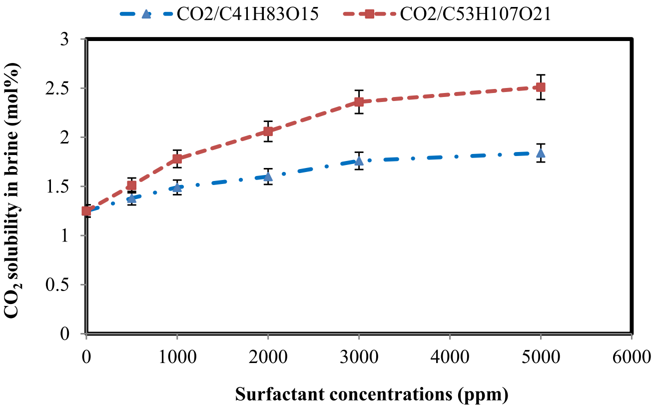


Fig. 9. The solubility of both $CO_2/C_{41}H_{83}O_{15}$ and $CO_2/C_{53}H_{107}O_{21}$ in actual saline aquifer brine for different dilute concentration of non-ionic surfactants at 70 °C and 3200 psi, the solubility of pure CO_2 in saline aquifer brine was 1.25 mol percent at these conditions.

the synergy of these mechanisms affects on the CO_2 flow and increases the CO_2 storage in saline aquifers. It has been investigated during the core flooding scenarios. Fig. 10 indicated the two phase relative permeability curves of brine and pure CO_2, $CO_2/C_{41}H_{83}O_{15}$, and $CO_2/C_{53}H_{107}O_{21}$ systems containing 3000 ppm surfactant at aquifer conditions. Results showed that the intersection points of pure CO_2, $CO_2/C_{41}H_{83}O_{15}$, and $CO_2/C_{53}H_{107}O_{21}$ scenarios were at $S_w = 0.85$, 0.74, and 0.68 respectively at reservoir conditions. It showed that the crossing of CO_2 and brine relative permeability curves moved to the left due to the wettability alteration toward intermediate CO_2-oil wet via CO_2/surfactant solutions. Also, it changed the end-point relative permeabilities and increased the CO_2 trapping compared to pure CO_2 injection. Furthermore, these findings showed that enhanced mobility control was achieved in both CO_2/surfactant scenarios due to the interplay of several mechanisms mentioned earlier. Moreover, based on the core flooding experiments during the two phase relative permeability measurement, the maximum pressure gradients were around 1.4, 1.55, and 1.7 psi/ft. for pure CO_2, $CO_2/C_{41}H_{83}O_{15}$, and $CO_2/C_{53}H_{107}O_{21}$ scenarios containing 3000 ppm surfactant at aquifer conditions. It is worth mentioning that, it occurs at an injection rate of 0.1 cc/min during injection in the sandstone rock with about 50 md permeability. These 10 % and 21 % increases in the pressure gradients for the CO_2/surfactant solutions are a confirmation of in-situ foam generation, but the CO_2/surfactant solution injectivity may not be unreasonable for field application. Moreover, the CO_2/surfactant solution injectivity is higher than that the injectivity of the co-injection of pure CO_2 and an aqueous surfactant solution (foam injection) that results in the presence of gas, water and surfactant solution phases in the injection stream simultaneously. Therefore, our current approach of injecting a CO_2/surfactant solution may provide an acceptable injectivity at the field scale. Consequently, both $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ can dissolve in CO_2 at pressure and temperature commensurate to CO_2 injection, generate the stabilized CO_2-in-brine foams, decrease the CO_2-brine IFT, change the sandstone aquifer to intermediate gas-wet, improve the CO_2 mobility control, and increase the CO_2 solubility in brine. Therefore, these non-ionic surfactants can be a promising candidate to improve the CO_2 storage in saline aquifers at dilute concentrations [28,55].

4. Conclusion

The present study investigated the potential of in-situ generation of CO_2-in-brine foams using CO_2-soluble non-ionic propoxylated-ethoxylated alcohols surfactants, to enhance CO_2 storage efficiency in deep saline aquifers. However the following results can be drawn:

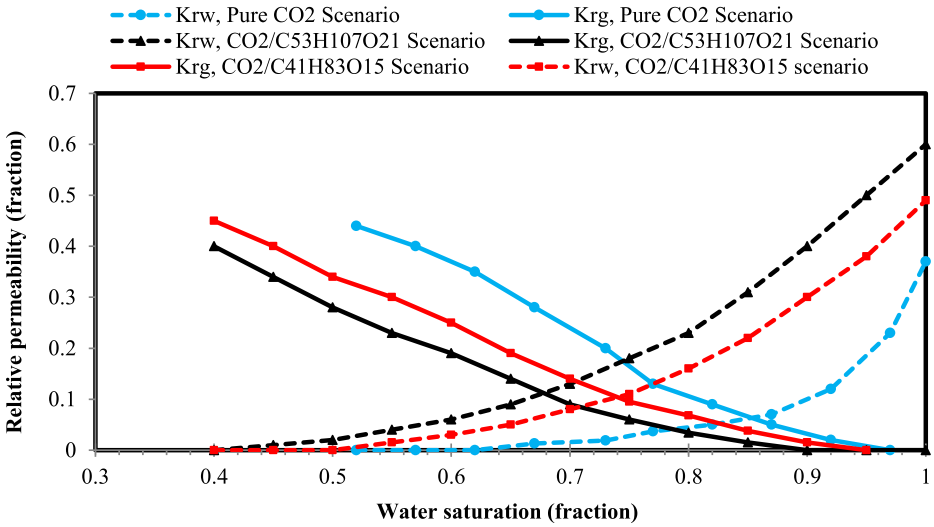


Fig. 10. The two phase relative permeability curves of brine and pure CO_2, $CO_2/C_{41}H_{83}O_{15}$, and $CO_2/C_{53}H_{107}O_{21}$ systems containing 3000 ppm surfactant at 70 °C and 3200 psi.

1. Based on the cloud point temperature results, both 2EH-PO_5-EO_9 ($C_{41}H_{83}O_{15}$) and 2EH-PO_5-EO_{15} ($C_{53}H_{107}O_{21}$) non-ionic surfactants are good candidates for CO_2-in-brine foams at a maximum temperature of ~100C. Therefore, surfactant degradation does not happen in aquifer conditions.
2. The cloud point pressure measurements indicated that both $C_{41}H_{83}O_{15}$ and $C_{53}H_{107}O_{21}$ non-ionic surfactants can dissolve in CO_2 under conditions of pressure and temperature typical of CO_2 injection scenarios, eliminating the need for any co-solvent.
3. The foam formed with good foam stability for both surfactants but $C_{53}H_{107}O_{21}$ exhibited better foam rather than $C_{41}H_{83}O_{15}$.
4. The dissolution of both non-ionic surfactants in CO_2 can decrease the interfacial tension between brine and CO_2/surfactant, leading to an increase in CO_2 storage due to capillary trapping, ensuring a high degree of safety in saline aquifers.
5. The transition of sandstone rock wettability from being strongly water-wet to water-wet and partially gas-wet can enhance CO_2 storage in saline aquifers by promoting residual sequestration during gas injection.
6. The alteration of sandstone rock wettability, combined with the synergy of in-situ foam generation during CO_2/surfactant injection, can control gas mobility and enhance CO_2 trapping in saline aquifers.
7. The dissolution of non-ionic surfactants in CO_2 can increase CO_2 solubility in brine, thereby improving CO_2 storage through the solubility sequestration mechanism.
8. The relative permeability data validated all mechanisms linked to the dissolution of non-ionic surfactants in CO_2, which includes the reduction of interfacial tension, changes in wettability, and control over CO_2 mobility. Thus, these non-ionic surfactants emerge as promising candidates for enhancing CO_2 storage in saline aquifers at low concentrations.

CRediT authorship contribution statement

Asghar Gandomkar: Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Farshid Torabi:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Hamid Reza Nasriani:** Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Conceptualization. **Robert M. Enick:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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.

Data availability

Data will be made available on request.

References

[1] E. Hanson, Ch. Nwakile, V.O. Hammed, Carbon capture, utilization, and storage (CCUS) technologies: evaluating the effectiveness of advanced CCUS solutions for reducing CO_2 emissions, Results Surf Interfaces 18 (2025) 100381.
[2] Y. Yin, L. Zhang, X. Cao, Y. Wang, Progress, challenges, and prospects of CO_2 mineral sequestration in basalt: a critical review, Appl. Energy 381 (2025) 125127.
[3] H. Yu, H. Tang, P. Song, Y. Wang, Enhanced oil recovery and CO_2 storage by enhanced carbonated water injection: a mini-review, Energy Fuels 38 (14) (2024) 12409–12432.
[4] D. Akindipe, S. Saraji, M. Piri, Salt precipitation during geological sequestration of supercritical CO_2 in saline aquifers: A pore-scale experimental investigation, Adv. Water Resour. 155 (2021) 104011.
[5] M. Mahmoudi, K. Kahzadvand, Sh. Shahin, New connectionist tools for prediction of CO_2 diffusion coefficient in brine at high pressure and temperature-implications for CO_2 sequestration in deep saline aquifers, Fuel 384 (2025), 134000.
[6] A. Lua, Y. Li, X. Chen, Zh. Xhu, Y. Peng, Review of CO_2 sequestration mechanism in saline aquifers, Natural Gas Industry B 9 (4) (2022) 383–393.
[7] R.T. Mim, B.M. Negash, Sh.R. Jufar, F. Ali, Minireview on CO_2 storage in deep saline aquifers: methods, opportunities, challenges, and perspectives, Energy Fuel 37 (23) (2023) 18467–18484.
[8] Y. Zhao, K. Itakura, A state-of-the-art review on technology for carbon utilization and storage, Energies 16 (2023) 3992.
[9] H. Oh, H. Yoon, Y. Kim, H. Jeong, Estimation of CO_2 storage capacities in saline aquifers using material balance, Fuel 374 (2024) 132411.
[10] M.F. Irfan, T.M. Bisson, T. Babadagli, CO_2 storage in saline aquifers by dissolution and residual trapping under supercritical conditions: an experimental investigation, Colloids Surf. A Physicochem. Eng. Asp. 548 (2018) 37–45.
[11] A. Izadpanahi, M.J. Blunt, N. Kumar, M.A. Sampaio, A review of carbon storage in saline aquifers: mechanisms, prerequisites, and key considerations, Fuel 369 (2024) 131744.
[12] P. Karvounis, M.J. Blunt, Assessment of CO_2 geological storage capacity of saline aquifers under the North Sea, International Journal of Greenhouse Gas Control 111 (2021) 103463.
[13] M.G. Rezk, A.F. Ibrahim, A.R. Adebayo, Influence of impurities on reactive transport of during geo-sequestration in saline aquifers, Fuel 344 (2023) 127994.

[14] L. Ding, A.M. AlSofi, P. Patil, CO2 Soluble Surfactants Assisted Carbon Storage under Achievable Pressure Gradients: Effect of Surfactant Partitioning Behavior during Continuous CO2 Injection, International Petroleum Technology Conference, Saudi Arabia, IPTC-23958-MS, 2024.

[15] A. Gandomkar, R. Kharrat, The tertiary FAWAG process on gas and water invaded zones: an experimental study, journal of, Energy Sources, Part A 34 (20) (2012) 1913–1922.

[16] Y. Wen, N. Zheng, L. Xu, P. Zeng, Application of biopolysaccharide green foam fluid to enhance CO_2 sequestration in high-temperature and high-salinity saline aquifer, Geoenergy Science and Engineering 236 (2024) 212749.

[17] S. Li, P. Wang, Z. Wang, H. Cheng, K. Zhang, Strategy to enhance geological CO_2 storage capacity in saline aquifer, Geophys. Res. Lett. 50 (3) (2023) e2022GL101431.

[18] J. Al-Darweesh, M.S. Aljawad, M. Mahmoud, D. Al-Shehri, Water chemistry role in the stability of CO_2 foam for carbon sequestration in water aquifers, Gas Sci. Eng. 118 (2023) 205090.

[19] M.G. Rezk, R.S. Babu, S.O. Badmus, A.R. Adebayo, Foam-assisted capillary trapping in saline aquifers-an initial-residual saturation analysis, Energies 15 (17) (2022) 6305.

[20] T. Føyen, B. Brattekas, M.A. Fernø, A. Barrabino, T. Holt, Increased CO_2 storage capacity using CO_2 foam, International Journal of Greenhouse Gas Control 96 (2020) 103016.

[21] G. Ren, Q.P. Nguyen, Development of New Surfactants for CO2 Foam Enhanced Oil Recovery, Materials for Energy, Efficiency and Sustainability: TechConnect Briefs, 2015.

[22] Y. Chen, A. Saeedi, Q. Xie, Interfacial interactions of CO_2-brine-rock system in saline aquifers for CO_2 geological storage: a critical review, The International Journal of Coal Geology 274 (2023) 104272.

[23] R. Farajzadeh, A.A. Eftekhari, G. Dafnomilis, L.W. Lake, J. Bruining, On the sustainability of CO_2 storage through CO_2-enhanced oil recovery, Appl. Energy 261 (2020) 114467.

[24] Y. Wen, T. Yu, L. Xu, P. Zeng, Q. Li, Molecular dynamics and experimental study of the effect of pressure on CO_2 foam stability and its effect on the sequestration capacity of CO_2 in saline aquifer, Chem. Eng. Sci. 284 (2024) 119518.

[25] G. Jian, L. Zhang, C. Da, M. Puerto, K.P. Johnston, G.J. Hirasaki, Evaluating the transport behavior of CO_2 foam in the presence of crude oil under high temperature and high-salinity conditions for carbonate reservoirs, Energy Fuel 33 (7) (2019) 6038–6047.

[26] R. Tripathi, Z.P. Alcorn, A. Graue, S.D. Graue, Combination of non-ionic and cationic surfactants in generating stable CO_2 foam for enhanced oil recovery and carbon storage, Adv. Geo-Energy Res. 13 (1) (2024) 42–55.

[27] Q. Wu, L. Ding, L. Zhao, P. Patil, Z. Fan, CO_2 soluble surfactants for carbon storage in carbonate saline aquifers with achievable injectivity: implications from the continuous CO_2 injection study, Energy 290 (2024) 130064.

[28] L.C. Burrows, F. Haeri, D. Tapriyal, P.G. Shah, R.M. Enick, A. Goodman, CO_2-soluble nonionic surfactants for enhanced CO_2 storage via in situ foam generation, Energy Fuel 37 (2023) 12089–12100.

[29] G. Adam, R.M. Campbell, C. Jacob, K. Amit, K. Troy, Nonionic surfactant compositions for enhanced oil recovery by carbon dioxide flooding, WO 2018/075237 A1, 2018.

[30] X. Chen, S.S. Adkins, Q.P. Nguyen, K.P. Johnston, Interfacial tension and the behavior of microemulsions and macroemulsions of water and carbon dioxide with a branched hydrocarbon nonionic surfactant, J. Supercrit. Fluids 55 (2010) 712–723.

[31] A. Sanders, E.G. Rightor, K.P. Johnston, S. Adkins, X. Chen, Compositions for oil recovery and methods of their use, US 8,857,527 B2, 2014.

[32] L.C. Burrows, F. Haeri, D. Tapriyal, M.E. Enick, A. Goodman, Dissolving nonionic surfactants in CO_2 to improve oil recovery in unconventional reservoirs via wettability alteration, Energy Fuel. 36 (2022) 11913–11929.

[33] G. Ren, Assess the potentials of CO_2 soluble surfactant when applying supercritical CO_2 foam, part I: effects of dual phase partition, Fuel 277 (2020) 118086.

[34] G. Ren, A.w. Sanders, Q.P. Nguyen, New method for the determination of surfactant solubility and partitioning between CO_2 and brine, J. Supercrit. Fluids 91 (2014) 77–83.

[35] C. Zhang, l. Xi, P. Wu, Zh. Li, A novel system for reducing CO_2-crude oil minimum miscibility pressure with CO_2-soluble surfactants, Fuel 281 (2020) 118690.

[36] S. Li, J. Zhu, Zh. Wang, K. Zhang, Chemical strategies for enhancing CO_2-hydrocarbon miscibility, Sep. Purif. Technol. 337 (2024) 126436.

[37] S. Wang, G. Zhang, L. Jiang, Y. Song, Accelerating CO_2 dissolution trapping in deep saline aquifers through a microbubble injection strategy, Energy Fuels 39 (6) (2025) 3217–3225.

[38] Y. Chen, A.S. Elhag, L. Cui, K.P. Johnston, CO_2-in-water foam at elevated temperature and salinity stabilized with a nonionic surfactant with a high degree of Ethoxylation, Ind. Eng. Chem. Res. 54 (2015) 4252–4263.

[39] P.G. Ranjith, M.S.A. Perera, E. Khan, A study of safe CO_2 storage capacity in saline aquifers: a numerical study, Int. J. Energy Res. 37 (2013) 189–199.

[40] A. Gandomkar, F. Torabi, R.M. Enick, Enhanced oil recovery via dissolution of low molecular weight PDMS in CO_2 during immiscible gas injection in matrix-fracture system, Chem. Eng. Res. Des. 203 (2024) 18–28.

[41] F. Torabi, A. Gandomkar, Experimental evaluation of CO_2-soluble non-ionic surfactants for wettability alteration to intermediate CO_2-oil wet during immiscible gas injection, SPE J. 29 (09) (2024) 5071–5086.

[42] J. Wang, Ch. Ehlig-Economides, Salinity effect on CO2 solubility in live formation water under reservoir conditions, The SPWLA 64th Annual Logging Symposium, Lake Conroe, Texas, USA, SPWLA-2023-0010, 2023.

[43] M. Cao, Ch. Han, Sh. Wang, Y. Chen, Investigation of density, viscosity and derived thermodynamic properties of CO_2-free and CO_2-loaded poly(ethylene imine) aqueous systems at different temperatures and 0.1 MPa, J. Mol. Liq. 377 (2023) 121523.

[44] M. Sequeira, T. Avelino, F. Caetano, J. Fareleira, Viscosity and density measurements of poly(ethyleneglycol) 200 and poly(ethyleneglycol) 600 at high pressures, The Journal of Chemical & Engineering Data 68 (1) (2023) 64–72.

[45] Zh. Wang, L. Lin, H. Guo, W. Lu, Diffusion coefficients of water in CO_2 under the condition of CO_2 sequestration in saline aquifers, J. Hydrol. 650 (2025) 132546.

[46] M. Motealleh, R. Kharrat, A. Gandomkar, M.H. Ghazanfari, An experimental study on the applicability of water-alternating-CO_2 injection in the secondary and tertiary recovery in one Iranian reservoir, Pet. Sci. Technol. 30 (24) (2012) 2571–2581.

[47] M. Nematzadeh, R. Kharrat, A. Gandomkar, An experimental study of secondary WAG injection in a low-temperature carbonate reservoir in different miscibility conditions, Pet. Sci. Technol. 30 (13) (2012) 1359–1368.

[48] H. Thanh, Q. Yasin, K. Lee, Knowledge-based machine learning techniques for accurate prediction of CO_2 storage performance in underground saline aquifers, Appl. Energy 314 (2025), 118985.

[49] A. Gandomkar, H.N. Nasriani, R.M. Enick, F. Torabi, The effect of CO_2-philic thickeners on gravity drainage mechanism in gas invaded zone, Fuel Journal 331 (Part 1) (2023) 125760.

[50] S. Dai, Zh. Chen, W. Li, Enhancing sCO_2 nano-emulsion stability with trisiloxane surfactants for CCUS, Appl. Surf. Sci. 680 (2025) 161273.

[51] I. Iranzi, H. Son, Evaluation of the physical and economic potential of surfactant-based CO_2 capture and storage in a saline aquifer, J. Ind. Eng. Chem. 147 (2025) 259–277.

[52] P. Moradi, M. Simjoo, M. Chahardowli, Experimental insights into the effect of aquifer salinity on interfacial properties of fluorinated surfactants: relevant for underground gas storage, J. Mol. Liq. 414 (Part B) (2024) 126203.

[53] A.A. Elryes, B.M. Negash, R.T. Mim, Enhancing CO_2 sequestration in saline aquifer through wettability alteration: a comprehensive review of in-situ factors and application of Nanofluid technology, Energy Fuel 38 (2024) 21.

[54] W. Yan, S. Huang, E.H. Stenby, Measurement and modeling of CO_2 solubility in NaCl brine and CO_2-saturated NaCl brine density, International Journal of Greenhouse Gas Control 5 (2011) 1460–1477.

[55] J. Liu, Y. Zhu, H. Pan, Multi-objective optimization for efficient CO_2 storage under pressure buildup constraint in saline aquifer, Appl. Energy 382 (2025) 125175.