The Hidden Forces: Interfacial Energies in the Advancement of Subsurface Energy Storage

BY WAYNE SNODGRASS AND RYAN CARBAJAL

MENTOR: PARISA BAZAZI, ASSISTANT PROFESSOR OF PETROLEUM ENGINEERING

Introduction

Subsurface energy storage, a critical component of the energy transition economy, provides a pathway to balancing supply and demand, ensuring energy security, and facilitating the integration of renewable resources. Utilizing abandoned underground spaces for compressed air and hydrogen storage presents a low-environmental-impact alternative, offering promising strategies to address the challenges of sustainable energy supply [1].

In this study, we aim to quantify the role of interfacial energies within subsurface energy storage systems to understand how these forces shape the entrapment and mobility of injected fluids. We measure the contact angle and surface tension for two types of rock types, silica-based and carbonate, and a series of synthetic geofluids.

Methods

Materials

Hexadecyl trimethylammonium bromide (CTAB, Sigma) is used as the cationic surfactant. The molecular weight and critical micelle concentration of CTAB are 364.45 g/mol and 0.92 mM, respectively. Sodium dodecyl sulfate (SDS, Sigma) is used as the anionic surfactant with a molecular weight of 288.372 and g/mol CMC of 8.3 mM. We use sodium chloride (NaCl, Sigma) as the source of salt solution. Glass slides (VWR) are used as the silica-based surface and carbonate rock samples are purchased from Boreal Science and used without further treatment.

Surface Tension and Contact Angle Measurement

The dynamic surface tension (ST) of solutions is measured using the pendant drop method (DSA30, Kruss). A pendant drop of the aqueous phase is formed at a stainless-steel needle (OD=1.8 mm). For contact angle measurement, we place a 15-microliter droplet over the solid surface. We record the data for 1000 seconds and each test is repeated three times.

Results and Discussion

We first discuss the surface tension of aqueous solutions (surfactant, salt, and salt-surfactants) in air. Figure 1 presents the data for salt and cationic surfactant. The surface tension of several liquids is measured over a 1000 second interval period from a pendant drop. The volume of DI-Water droplet is 3.0 µL while the volume of other tested fluids is set at 2.5 µL. The surface tension of DI-Water is 72 mN/m. Salt solutions have same value of surface tension as water at the beginning, however, the surface tension of Salt 1.0% is reduced to 64 mN/m after 600 seconds. The surface tension of CTAB 0.1 CMC starts at 54 mN/m and decreases continuously over time until it reach to 35 mN/m. Salt 1.0% + CTAB 1.0 CMC steadily decreases from 37 mN/m to 33 mN/m. Salt 0.01% + CTAB 1.0 CMC also decreases from 37 mN/m to 36 mN/m.

Figure 2 presents the data for salt and anionic surfactant. The surface tension of several liquids is measured over a 1000 second interval period from a pendant drop. Similar

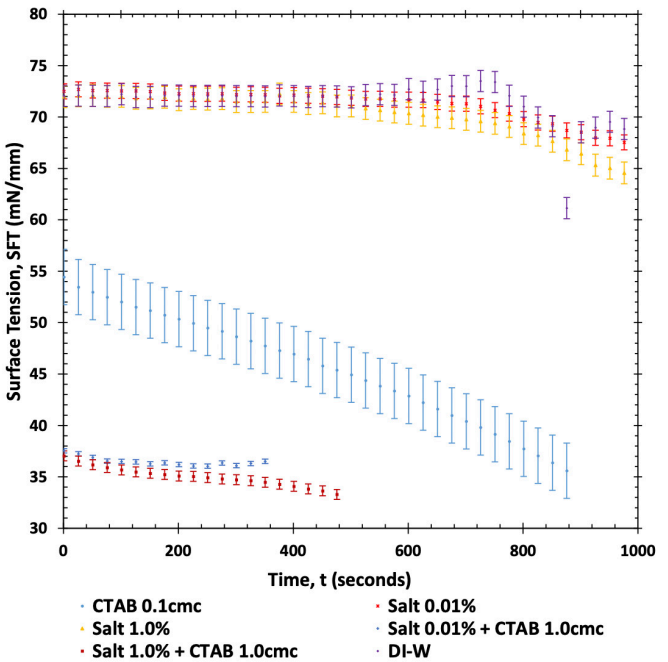

Figure 1 *Surface Tension Measurements from a Pendant Drop.* *CTAB 0.1 CMC (Blue Filled Circle Line), Salt 1.0% (Yellow Triangle Line), DI-Water (Purple Diamond Line), Salt 0.01% (Red Cross Line), Salt 1.0% + CTAB 1.0 CMC (Red Filled Square Line), and Salt 0.01% + CTAB 1.0 CMC (Blue Cross Line). All data represented comes from the average of 3 trials ran for each solution, and another average was taken from the averages for every 25 second intervals. For the data sets that ended before 1000 interval second period, the droplet detaches from the needle during the measurement.*

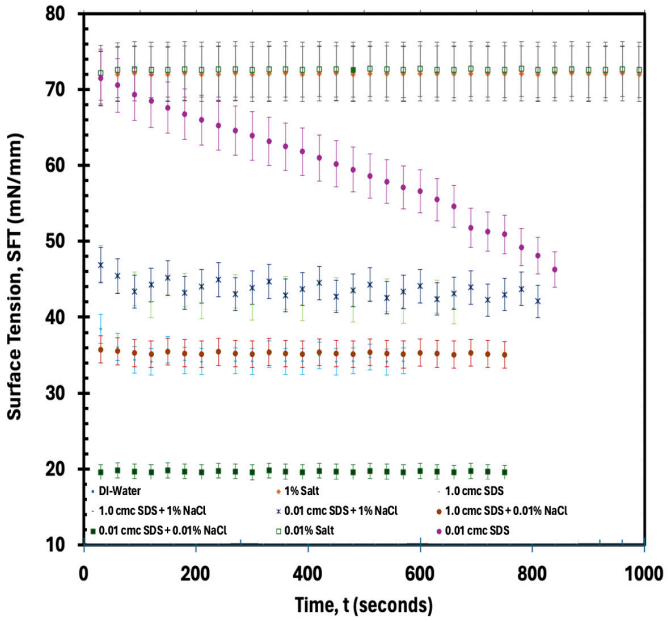

Figure 2 *Surface Tension Measurements from a Pendant Drop.* *SDS 1.0 CMC (Blue Filled Circle), Salt 1.0% (Orange Diamond), DI-Water (Blue Square), Salt 0.01% (Green Empty Square), Salt 1.0% + SDS 1.0 CMC (Brown Circle), and Salt 0.01% + SDS 0.01 CMC (Green Filled Square). All data represented comes from the average of 3 trials ran for each solution, and another average was taken from the averages for every 25 second intervals. For the data sets that ended before 1000 interval second period, the droplet detaches from the needle during the measurement.*

to the cationic surfactant, the addition of the anionic surfactant reduces the surface tension. The data also indicates the synergism effect between salt and anionic surfactant which further enhances the surface tension reduction.

Next, we discuss how addition of surfactant and salt influence the liquid-solid interactions. A drop with the volume of 15 µL is placed on the solid surface and the surrounding phase is air. Figure 3 shows the contact angle of different liquids (with surfactant and salt) on the glass surface. DI-Water (Purple Diamond Line) begins at 65° and declines to 62° over the interval period. The CTAB 0.1 CMC solution (Light Blue Round Line) shows that the CTAB showed a higher starting contact angle than the DI-W but unlike DI-W, the CTAB 0.1 CMC solution decreased from 88° to 68°. Salt 1.0% (Yellow Triangle Line) follows a linear decrease from 72° to 65°. Similarly, Salt 0.01% (Red X Line) starts from 72° to 66°. The difference between the 0.01% and the 1.0% Salt solutions indicates that the higher concentration of NaCl has more effect on the contact angle. More proof of this is shown through the Salt 0.01% + CTAB 1.0 CMC solution (Red Box Line) and

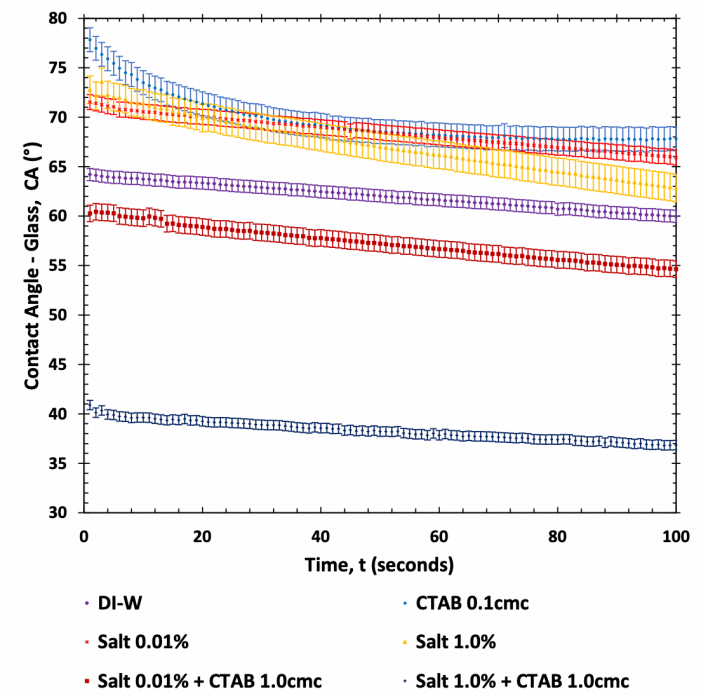

Figure 3 *Glass Surface Contact Angle Measurements.*

The contact angle values for DI-Water (Purple Diamond Line), The CTAB 0.1 CMC solution (Light Blue Round Line), Salt 0.01% (Red X Line), Salt 0.01% + CTAB 1.0 CMC solution (Red Box Line), and the 1.0% Salt + CTAB 1.0 CMC solution (Dark Blue Plus Line) droplets on the glass surface. The data points present the average of three measurements.

the 1.0% Salt + CTAB 1.0 CMC solution (Dark Blue Plus Line). The lower salt concentration CTAB solution decreased the contact angle from 61° to 55°, a change of 5°. Whereas the higher salt concentration CTAB solution starts from 42° to 36°, a change of 6°.

Figure 4 presents the contact angle values for the tested fluids on the carbonate surface. Similar to the glass surface, the addition of salt and surfactant significantly reduces the surface energy between fluid and solid surface.

Studies have shown that the surface tension and contact angle on carbonate surfaces can be significantly altered by the composition of the surrounding fluids. For instance, low density ionic mixtures have been found to reduce the surface tension, with a notable decrease observed when using a mixture of $MgCl_2$ and K_2SO_4, leading to a 72% reduction compared to the initial measurements with fresh water and oil [6]. This indicates that solutions with diluted binary salts can enhance the wetting properties on carbonate surfaces suggesting a potential for improved energy storage methods in subsurface environments. Additionally, pressure and salinity have been observed to influence the wetting behavior on carbonate surfaces, where increased pressure and salinity can alter the advancing and receding contact angles, pointing to the complexity of subsurface storage optimization.

On the other hand, research on quartz and glass surfaces has highlighted the impact of CO_2 saturation and surface contamination on contact angles, shedding light on the surface-specific interactions that influence fluid behavior in subsurface storage contexts. The role of surfactants in modifying fluid properties to increase wetting efficiency has also been explored, with findings suggesting that surfactant concentration can significantly impact the contact angle [7]. Furthermore, the wettability of carbonate rocks under varying conditions has been studied to better understand CO_2

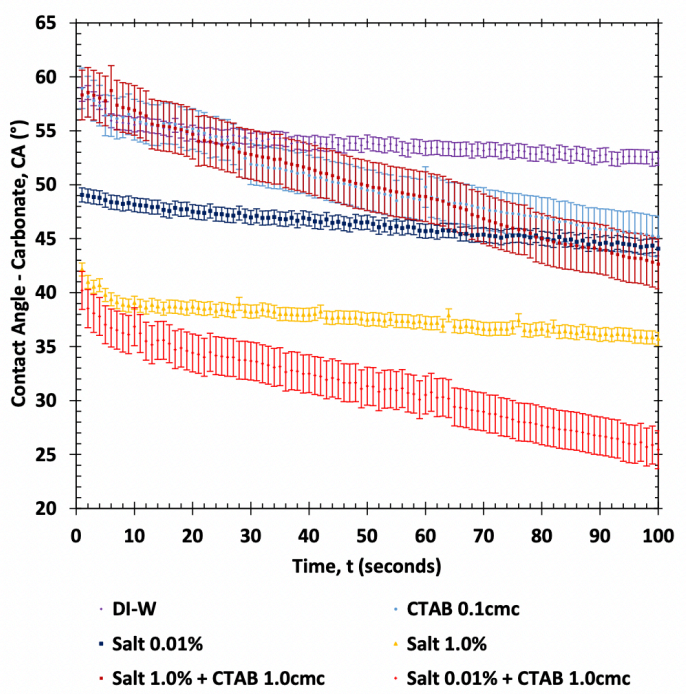

Figure 4 *Carbonate Surface Contact Angle Measurements.*

Several substances had their contact angle measured from a sessile drop over a 100 second interval period on a Carbonate surface. The drop size measured for each substance was 15 µL and surrounded by air. DI-Water (Purple Diamond Line) declines continuously from 58° to 52°. Similarly, Salt 1.0% + CTAB 1.0 CMC (Blue Filled Square Line) decreases from 58° to 42°, CTAB 0.1 CMC (Blue Filled Circle) decreases linearly from 58° to 45°, and Salt 0.01% (Red Empty Square Line) decreases linearly from 49° to 46°. Salt 1.0% (Yellow Triangle Line) begins at 42° and ends at 49° while Salt 0.01% + CTAB 1.0 CMC (Red Cross Line) begins at 40° and ends at 35°.

sequestration processes, indicating that temperature and pressure can affect rock wettability. These insights are crucial for advancing the development of efficient and effective subsurface energy storage and CO_2 sequestration technologies.

Summary

In our current investigations, we have conducted contact angle and surface tension experiments in an air phase at ambient pressure, revealing that CTAB, a cationic surfactant, effectively lowers both surface tension and contact angle, whereas the addition of salt impacts only the contact angle on Calcite surfaces without significantly altering surface tension measurements. Similarly, SDS, an anionic surfactant, diminishes surface tension, regardless of salt presence. Moving forward, our research continuous into the influence of pressure on these experiments, as well as introducing hydrogen into a high-pressure Dynamic Surface Analysis (DSA) cell to explore the interactions between brine, rock, and hydrogen, thereby expanding our understanding of subsurface storage dynamics and potential applications in energy storage and CO_2 sequestration technologies.

Ryan Carbajal (pictured) is a Master's student currently studying Quantitative Biosciences and Engineering (QBE) at Colorado School of Mines. He is a part of Dr. Bazazis' interdisciplinary research group, where they have studied fluid interactions in Underground Hydrogen Storage (UHS) systems. His work focuses on understanding the role of methanogens and sulfate-reducing bacteria in hydrogen storage, contributing to energy storage solutions. With a background in QBE and a minor in Chemistry, he is passionate about research to improve clean energy initiatives through his Masters in QBE.

Wayne Snodgrass is a Petroleum Engineering student.

Together, Wayne and Ryan received a travel grant to present at the American Chemical Society conference in 2024.

References

[1] C. R. Matos, J. F. Carneiro, and P. P. Silva, "Overview of Large-Scale Underground Energy Storage Technologies for Integration of Renewable Energies and Criteria for Reservoir Identification," Journal of Energy Storage, vol. 21, pp. 241–258, Feb. 2019, doi: https://doi.org/10.1016/j.est.2018.11.023.

[2] N. S. Muhammed et al., "Hydrogen Storage in Depleted Gas reservoirs: a Comprehensive Review," Fuel, vol. 337, p. 127032, Apr. 2023, doi: https://doi.org/10.1016/j.fuel.2022.127032.

[3] Hamid Esfandyari, M. Hosseini, M. Ali, S. Iglauer, M. Haghighi, and A. Keshavarz, "Assessment of the Interfacial Properties of Various Mineral/Hydrogen/Water Systems," Journal of Energy Storage, vol. 60, pp. 106637–106637, Apr. 2023, doi: https://doi.org/10.1016/j.est.2023.106637.

[4] J. M. Miocic, N. Heinemann, J. Alcalde, Katriona Edlmann, and R. A. Schultz, "Enabling Secure Subsurface Storage in Future Energy systems: an Introduction," Geological Society, London, Special Publications, vol. 528, no. 1, pp. 1–14, Jun. 2023, doi: https://doi.org/10.1144/sp528-2023-5.

[5] M. Delshad, M. M. Alhotan, B. Fernandes, Y. Umurzakov, and Kamy Sepehrnoori, "Modeling Flow and Transport in Saline Aquifers and Depleted Hydrocarbon Reservoirs for Hydrogen Energy Storage," SPE Journal, vol. 28, no. 05, pp. 2547–2565, May 2023, doi: https://doi.org/10.2118/210351-pa.

[6] I. Nowrouzi, A. K. Manshad, and A. H. Mohammadi, "Effects of Dissolved Binary Ionic Compounds and Different Densities of Brine on Interfacial Tension (IFT), Wettability alteration, and Contact Angle in Smart Water and Carbonated Smart Water Injection Processes in Carbonate Oil Reservoirs," Journal of Molecular Liquids, vol. 254, pp. 83–92, Mar. 2018, doi: https://doi.org/10.1016/j.molliq.2017.12.144.

[7] Jean Vicente Ferrari et al., "Influence of Carbonate Reservoir Mineral Heterogeneities on Contact Angle Measurements," Elsevier Journal of Petroleum Science and Engineering, vol. 199, pp. 108313–108313, Apr. 2021, doi: https://doi.org/10.1016/j.petrol.2020.108313.