Introduction

Current energy policies focus on maximising current hydrocarbon resources and minimising carbon emissions. Consequently, fresh importance is placed on understanding the behaviour and properties of CO₂ for the following reasons:

a) CO₂ is a natural constituent of hydrocarbon reservoirs. Concentrations vary from 2 - 80% and the presence of CO₂ can greatly influence the hydrocarbon behaviour.
b) CO₂ is widely used for Enhanced Oil Recovery (EOR), in both miscible (WAG) and immiscible (cyclic) programmes.
c) The geological storage of CO₂ is an effective means of curbing carbon emissions, Carbon Capture & Storage, CCS.

To date, the reservoir fluids of principle concern to rock physics community have been hydrocarbon fluids (oils and gasses) and brine. It is now apparent that a better understanding of CO₂ is of paramount importance.

CO₂ Properties

It is well known that CO₂ is not a simple fluid. Whilst gaseous (~2kg/m³) at surface temperatures and pressures, it exhibits supercritical (sc) behaviour beyond 7.4MPa and 31°C (464kg/m³) which correspond to approximately 840 m depth at a normal onshore geothermal gradient of 25°C/km. At that geothermal gradient a liquid phase of CO₂ (680-690 kg/m³) may precede the supercritical phase transition. In the reservoir column, CO₂ could vary in density by almost three orders of magnitude and be in all four fluid states (vapour, gas, liquid and super critical (scCO₂)).

In addition to this, CO₂ is a non-polar compound and thus has no intermolecular interactions when pure. However, when mixing with polar molecules such as water/brine a quadrupole is induced on the CO₂ molecule [1]. This will affect the behaviour (viscosity, supercritical point etc) of the CO₂ fluid according to the molecules with which it’s interacting.

CO₂ storage

The reservoirs targeted for CO₂ storage may be residual hydrocarbon fields or saline aquifers. Within one reservoir, CO₂ will be stored in four principal forms (Figure 1). The proportions of these forms will change within time, with a tendency to increased storage security.

Figure 1: Both the proportion of CO₂ & the security of that stored volume increases with time (left to right) from an injected fluid to a mineral precipitate
At typical reservoir depths, CO\textsubscript{2} will be injected in the supercritical state. Thus sequestration scenarios need to model both scCO\textsubscript{2} and the associated property changes when

\begin{itemize}
  \item a) CO\textsubscript{2} migrates through the host rock in buoyancy driven plumes.
  \item b) CO\textsubscript{2} dissolves into the in situ reservoir fluids.
  \item c) Dissolved CO\textsubscript{2} sinks in density-driven convection.
  \item d) Water/scCO\textsubscript{2} emulsions and dissolved CO\textsubscript{2} react with reservoir cap rock minerals
\end{itemize}

In geologic formations CO\textsubscript{2} will be interacting with several different fluids in several different phases. Not only will the CO\textsubscript{2} affect the behaviour of the reservoir fluids, the mixing components will influence the behaviour of the CO\textsubscript{2}, shifting the critical point to higher temperature and pressures. Given this, it is possible to have seven fluid phases present within a single field, Figure 2.

![Figure 2: The seven principal fluid phases likely to be present in a single reservoir, and the multiple mixing scenarios for CO\textsubscript{2} with pure H\textsubscript{2}O, brine & hydrocarbons](image)

**An Equation of State (EoS) for CO\textsubscript{2} and its mixtures:**

Conventional fluid properties used in reservoir models rely on mixing models based on cubic equations of state (EoS) for a single fluid, including, although not limited to, Peng-Robinson [2] or Soave-Redlich-Kwong [2]. These models are only valid for pure CO\textsubscript{2}, and their good accuracy (<5%) is restricted to conditions below or away from the critical point. They also produce unsatisfactory predictions for the deviant behaviour of CO\textsubscript{2} when mixing with other chemical species.

A well known exception to these mixing models is a CO\textsubscript{2}-specific EoS developed by Span & Wagner [3]. This EoS was developed to predict the behaviour of CO\textsubscript{2} at elevated temperatures and pressures for industrial means, including density and bulk modulus for pure CO\textsubscript{2} at temperatures and pressures past the critical point of 305 K (31.85 °C), 7 MPa, and up to 523 K (249.05 °C) and 30 MPa (~4350 psi) respectively. Although significantly more applicable that the preceding cubic EoS, the accuracy deviates close to the critical point and the model is limited when dealing with the mixtures of fluids likely to be present in a reservoir and the subsequent deviant properties of CO\textsubscript{2}.

An alternative to these more traditional cubic EoS is the Statistical Associating Fluid Theory (SAFT) developed from statistical mechanics. This is a Helmholtz free energy EoS that predicts the effects of intermolecular interactions on the bulk behaviour of the fluid, from the microscopic to the macroscopic [4]. It has been the most successful EoS to date for predicting phase behaviour close to the critical point and has many industrial applications as a result. Recent research has also focused on predicting the behaviour of water and salt mixtures for geologic purposes [5].
Thermodynamic expressions are mathematically manipulated to find bulk material properties, predict phase equilibria and other chemical properties. Both EOR and geologic sequestration are dynamic systems, and the chemical reaction between the fluid and the reservoir rock, or even within the fluid – e.g. precipitation of asphaltenes, must be accounted for. The flexibility of SAFT, which is unique to the specific attributes of individual fluid mixtures, provides a series of mathematical formulae which can address the fluid properties of an interacting CO₂ mixture under reservoir conditions.
Applications

The development of a SAFT EoS and mixing model for CO$_2$ within the current rock physics model has potential to greatly enhance the existing geophysical tool box and integrated workflows. The current SAFT module allows the user to predict fluid properties of CO$_2$ mixing with brines (of variable composition) at a given temperature and pressure. Using updated initial reservoir fluid properties in the rock physics model, gives a means to reliably assess sites and evaluate the dynamic properties of CO$_2$ (gas, liquid, scCO$_2$, aqueous and hydrocarbon solutions) through 2D & 3D time lapse studies. This is particularly important for CCS feasibility and monitoring:

Feasibility: The effects of reservoir composition (brine composition, residual hydrocarbons: type and their proportion) upon the injected CO$_2$ can be modelled, as can the effects of overpressure, temperature of injection, dispersion pathways etc. Understanding the variation in the state of CO$_2$ across the reservoir is integral to CCS site assessments.

Monitoring: Figure 1 illustrates how the principle form of CO$_2$ will change depending on the time in storage and the mixture in which it exists. As the fluid behaviour varies, significant changes in its acoustical signature may be detectable.

Example (Figure 3): We have used the SAFT function to model a scenario where supercritical CO$_2$ has been injected at depth into brine sand and become structurally trapped (at an undetermined time after injection). Over time a proportion of the injected volume will slowly dissolve into the reservoir fluids, and this CO$_2$ in solution is also modelled. Note a variation between the seismic response of CO$_2$ in solution and scCO$_2$, Figures 3 a) & b). Figure c) shows a residual plot of scenario b).

Summary

The SAFT EoS is an improved mixing model for CO$_2$ with water, brine and hydrocarbons. Unlike cubic EoSs, SAFT mixing rules allow accurate CO$_2$ modelling close to its critical point, and they account for the deviant behaviour caused by additional chemical species present in the reservoir. Thus, the SAFT mixing model offers a method to accurately predict, monitor and verify the properties of CO$_2$ over the lifetime of a CCS project.

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References

(a) Simple 2D anticline model containing blocky sands. Overburden consists of shale and brine saturated thin sands. An increase in acoustic impedance between the brine case and sands saturated with CO$_2$ in solution causes a prominent peak reflection.

(b) A fluid contact is added to the blocky sand. A scCO$_2$ cap is injected above the CO$_2$ in solution. The greater increase in acoustic impedance, due to the associated increase in Rho & Vp values for scCO2 causes a brightening of the positive peak. At the contact between scCO$_2$ and the less dense CO$_2$ in solution, a weak trough develops.

(c) A residual plot (b–a) reveals the scCO$_2$ case is ~15% brighter than CO2 in solution. A small negative residual across the contact results from the difference between a weak positive peak (a) and a weak negative trough (b).

**Figure 3** 2D model demonstrating the changing seismic response observable between scCO$_2$ and CO$_2$ in an aqueous solution. Reflectivity traces are $0^\circ$ incidence.