Modelling the Impact of Geochemical Reactions on Hydrocarbon Phase Behavior during CO₂ Gas Injection for Enhanced Oil Recovery

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Abstract

CO₂ injection in oil reservoirs offers the dual advantage of increasing oil recovery as well as storage to combat global warming. The injected CO₂, however, may react with ions present in the brine as well as the rock. In this research, we present a model that quantifies the impact of these geochemical reactions on the phase behavior of hydrocarbon mixtures. A Gibbs free energy model is proposed that unifies different phase descriptions - the Peng-Robinson Equation of State (PR EOS) description for hydrocarbon phase components, the Pitzer activity coefficient model for aqueous components and an ideal solid phase. In particular, we illustrate the use of this model to determine the impact of geochemical reactions, introduced by the presence of an aqueous phase with ions and a solid calcite phase, on the phase envelope of CO₂-nC₁₄H₃₀ mixture with different phase descriptions. The presented Gibbs free energy model is adaptable to different reservoir brines and can be used to assess the maximum impact of geochemical reactions during CO₂ injection in different hydrocarbon reservoirs.

Keywords: Gibbs free energy, hydrocarbon phase behavior, geochemical reactions, CO₂ sequestration, CO₂ EOR

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1. Introduction

The International Energy Association (IEA) has identified carbon capture and sequestration (CCS) technologies as integral to reducing CO₂ in the atmosphere to mitigate climate change. The CCS technologies are expected to contribute one-fifth of the total target of halving current levels of CO₂ emission by 2050 (1).

. CO₂ has been injected in oil reservoirs in West Texas for over 30 years to enhance oil recovery. If injected at appropriate conditions, the injected CO₂ develops miscibility with oil. Thus, CO₂ injection in oil reservoirs provides the dual benefit of sequestration as well as increasing recovery. Accordingly, efforts are underway to inject CO₂ in carbonate reservoirs (constituting 70% of all oil reservoirs) in The Middle East - a region that hold 62% of world's proven conventional oil reserves (2).

. Compositional simulations are routinely used in the oil and gas industry to predict oil recovery. The entire reservoir is described as a sum of gridblocks in these macroscopic simulations. Phase behavior computations are performed to obtain equilibrium compositions at every time step at different pressures but for a constant temperature in each gridblock. The oil recovery predictions from CO₂ injection is also modeled similarly.

. The injected CO₂ can react with the brine as well as calcite from the carbonate rocks. The geochemical reactions can have undesirable consequences - precipitation reactions could decrease flow while dissolution reactions could result in CO₂ leakage. The geochemical reactions change the overall mole numbers that can influence the number of phases and composition of components at equilibrium and hence, the oil recovery predictions (3).

. In this research, we propose the Gibbs free energy framework that can integrate geochemical reactions with phase behavior computations for use in compositional simulations. This framework is used to quantify the influence of

geochemical reactions on the phase behavior of hydrocarbons. We illustrate the
30 use of this model to quantify the influence of the aqueous phase as well as geo-
chemical reactions in a carbonate system on the phase envelope of $\text{CO}_2\text{-nC}_{14}\text{H}_{30}$
mixture.

. We begin with a review of available methods to integrate geochemical reac-
tions and phase behavior computations in compositional simulations. The
35 general Gibbs free energy model is introduced to obtain phase equilibrium com-
positions when different phase descriptions are used - activity coefficient for
aqueous phase components and EOS description for hydrocarbon components.
The model is used to obtain changes in the phase envelope of $\text{CO}_2\text{-nC}_{14}\text{H}_{30}$ mix-
ture in the presence of aqueous phase and geochemical reactions in subsequent
40 sections.

. The phase envelope obtained by including the effects of geochemical reac-
tions can be used directly in compositional simulations for predictions of oil
recovery. The model presented is generic and can be used to describe phase
behavior changes associated with CO_2 injection in carbonate reservoirs having
45 any hydrocarbon and brine compositions.

2. Previous Research

In this section, we review the limitation of simulators as well as previous ef-
fort to couple geochemical reactions with phase behavior computations. We also
review previous uses of the proposed Gibbs free energy minimization approach
50 in different fields to obtain equilibrium compositions.

2.1. Simulators

. Reactive flow simulators model flow and geochemical reactions between aque-
ous phase ions and the solid rock. PHREEQC (4), TOUGHREACT (5), PFLO-
TRAN (6; 7), UTCHEM (8) and IPARS (9; 10) are some of the frequently used

55 reactive flow simulators. These simulators do not include a provision for including hydrocarbons for equilibrium computations and hence, cannot describe the impact of geochemical reactions when CO_2 is injected in carbonate reservoirs.

. Compositional simulators, on the other hand, model flow and phase behavior computations but typically do not include reactions. Geochemical reactions
60 in CMG, a compositional simulator (CMG-GHG (11)) where the hydrocarbon phase behavior computations are performed by specifying partition coefficients (constant K values) in the aqueous, gas and the oil phase for each component (11). The phase behavior changes accompanying CO_2 injection in hydrocarbons cannot be adequately described using the partition coefficient approach (12). In
65 summary, there is a need to develop a framework that can couple flow, phase behavior and reactions to model CO_2 injection for enhanced oil recovery.

. Efforts are underway to integrate geochemical reactions with phase behavior calculations using Henry's law (13; 14). In this approach, phase behavior computations and geochemical reactions are decoupled and carried out sequentially. Also, the amount of CO_2 dissolved in aqueous phase is estimated using a
70 Henry's law coefficient and equilibrium composition arising out of geochemical reactions is obtained subsequently.

. The equilibrium composition arising out of geochemical reaction are dependent on the initial estimates of CO_2 in the aqueous phase. While Henry's law
75 estimates compare quite well with experimental values at low pressures, they are not accurate at high pressures of CO_2 injection (15; 16). Besides, decoupling phase equilibrium and geochemical reaction equilibrium computations results in different fugacities of CO_2 component in hydrocarbon phases and the aqueous phase.

80 . The Gibbs free energy minimization approach provides the advantage of obtaining compositions arising from not just phase equilibrium (no reactions) but also phase and chemical equilibrium (with reactions). This approach has been extensively used in many chemical engineering applications as well as petroleum

engineering applications like compositional simulation. In the next section, we
85 review the developments in the Gibbs free energy approach in these areas.

2.2. Gibbs free energy approach

The minimization of the Gibbs free energy function has been used to find
equilibrium compositions for several applications in distillation and chemical
separation. The RAND algorithm was developed to calculate equilibrium con-
90 centration using Newton's method for minimizing the Gibbs free energy function
(17). The system considered was a reactive set of ideal species in a single phase
and the Gibbs free energy function for such a single phase system with ideal
components is convex (18).

. However, the Gibbs free energy function for nonideal components (nonideality
95 expressed using activity coefficient models or equation of state models) in a sin-
gle phase or for multiphase systems need not be convex. Hence, the multiphase
multicomponent problem becomes increasingly difficult as the number of phases
and the component distribution, in those phases, at equilibrium are unknown.

. The phase splitting algorithm to predict equilibrium composition for multi-
100 component species in multiple phases was proposed in (19). This algorithm
begins by assuming all components to be present in a single phase and splits
phases depending on whether the splitting reduces the Gibbs free energy. This
splitting is continued as long as the Gibbs free energy of the system decreases.
For cases illustrated in the original paper, this step-by-step approach of increas-
105 ing phases to find minimum of Gibbs free energy works well even with poor
initial guesses.

. An alternative to the step-by-step approach is the global minimization ap-
proach (20; 21; 22). However, these approaches can be computationally ex-
pensive and hence not employed in compositional simulation. The Gibbs free
110 energy approach has been used for both phase stability calculation as well as
flash calculation to determine the composition of components in those phases
for compositional simulations.

. Baker *et al* (23) formulated the tangent plane distance function to separate local and global minima of the Gibbs free energy function. The tangent plane distance function is the distance between the tangent plane, at any extremum point (any identified minimum) in the Gibbs free energy function, and the Gibbs free energy function value of the entire phase at any other feasible point. This distance function is never negative if the tangent is constructed at the global minima. Michelsen (24) proposed a numerical implementation scheme to compute the tangent plane distance function and use it for phase stability calculations. Because all stationary points of the tangent plane distance function are not found, Michelsen suggests using different guesses as starting points.

. Trangenstein (25) also developed a minimization procedure using the Gibbs free energy function for both stability analysis and flash calculation. The numerical algorithm proposed was useful for phase behavior calculations near the critical points and thus, provides an advantage over successive substitution (26), more commonly used for flash calculations.

. The Gibbs free energy function has also been used in geochemistry to find equilibrium compositions arising out of mineralization reactions in aqueous phase (27). In this approach, the chemical potential was approximated to the second degree and Newton's method is used to find descent direction to reduce Gibbs free energy (27). The addition of solid phase, from precipitation, is formulated as a separate optimization problem. In comparison to the earlier discussed approaches, this application does not presume presence of all components in all phases. We use this as a basis in formulation of our proposed model.

3. Gibbs Free Energy Model

The Gibbs free energy function provides a framework to integrate different thermodynamic descriptions of phases - equation of state (EOS) models for hydrocarbon phases and activity coefficient models for water and ions present in the brine. We begin with a review of the Gibbs free energy framework and

subsequently present how the Gibbs free energy function is adapted to model the impact of aqueous phase as well as a separate case of aqueous phase with ions and geochemical reactions on phase equilibrium calculations.

3.1. Review of Gibbs free energy framework

. The total Gibbs free energy of a closed system (G^T) consisting of N_c components and N_p phases at a fixed temperature (T) and pressure (P) is the sum of the partial molar Gibbs free energy ($\bar{G}_{ij}$) of all components present in all the phases. The components are distributed between different phases so that the total Gibbs free energy of the system attains its global minimum at equilibrium. Equilibrium compositions then are the solution to the following minimization problem subject to an elemental balance constraint and given as,

$$\text{Minimize} \quad G^T(T, P) = \sum_{j=1}^{N_p} \sum_{i=1}^{N_c} n_{ij} \bar{G}_{ij}(T, P), \quad (1)$$

$$\text{Subject to} \quad \mathbf{A} \mathbf{N} = \mathbf{E} \quad \text{and} \quad n_{ij} \geq 0.$$

Here, $\mathbf{A}$ is the elemental matrix representing the number of specific elements in each component, $\mathbf{N}$ is the matrix comprising of moles of each component n_{ij} in each phase (unknowns) while $\mathbf{E}$ is formed by the total number of moles of each element. Because elements are conserved for both phase equilibrium (no reactions) as well as phase and chemical equilibrium (with reactions), the Gibbs free energy framework can be used to find equilibrium composition for either cases.

. The necessary conditions for a minimum are equal temperature and pressure of phases as well as the equality of partial molar Gibbs free energy (28), also referred to as the chemical potential, of the components in all the phases that they are present,

$$T_j = T_{N_p} \quad ; \quad P_j = P_{N_p} \quad \forall \quad j = 1, 2, \dots, N_p - 1. \quad (2)$$

$$\bar{G}_{i1} = \bar{G}_{i2} = \dots = \bar{G}_{iN_p} \quad \forall \quad i = 1, 2, \dots, N_c. \quad (3)$$

A reactive system with R reactions has additional relationships that can be given in terms of the stoichiometric coefficients (ν_{ik} for component i in k^{th} reaction),

$$\sum_{i=1}^{N_c} \nu_{i,k} \bar{G}_{ij} = 0; \quad \forall k = 1, 2, \dots, R. \quad j = 1, 2, \dots, N_p. \quad (4)$$

Because eqns 2 and 3 are sufficient but not necessary conditions, equating chemical potentials and using additional relationships like eq 4 for a reactive system to find equilibrium composition might not be the right approach. A solution thus obtained could correspond to the local minimum instead of the global minimum and hence, not the physical equilibrium composition. The equilibrium composition is the global minimum of the Gibbs free energy function for a system and holds true for a system with pure phase equilibrium (no reactions) as well as phase and chemical equilibrium (with reactions).

. The partial molar Gibbs free energy is defined with respect to a reference state value that varies depending on the thermodynamic description of the individual phases. In the model presented in this manuscript, we use the Peng Robinson EOS description for hydrocarbon phases, the Pitzer activity coefficient model for aqueous phase components and the solid phase is assumed to be ideal. The reference state value for EOS description is pure component ideal gas (G_i^{IG}) while the reference state value for a solute is its value in a unit molal solution ($\bar{G}_i^0$). The Gibbs free energy function is additive even when different reference states are used because the reference states are themselves related.³

. The expressions for chemical potential when the reference state is at the same pressure and temperature conditions as the mixture is given in Table 1. The reference state values at any T and P can be calculated from the National

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³Even though different reference states are used for some components like CO₂, depending on whether it is in the gas or aqueous phase, the total Gibbs free energy of the system is additive because the aqueous and gas phase reference states are themselves related by,

$$\bar{G}_1^0(T_o, P_o) = G_1^{IG} + (\Delta G)_{hydration}.$$

Table 1: Partial molar Gibbs free energy expressions for components in different phases

Component(s)	Phase	Chemical Potential Expression
Hydrocarbon/CO ₂	Hydrocarbon	$\bar{G}_{ig}(T, P) = G_{-i}^{IG}(T, P) + RT\ln(y_i\hat{\phi}_i).$
Solutes	Aqueous	$\bar{G}_{iw}(T, P) = \bar{G}_i^0(T, P) + RT\ln(x_i\gamma_i).$
Water	Aqueous	$\bar{G}_w(T, P) = G_w^0(T, P) + RT\ln(x_w\gamma_w).$
CaCO ₃	Solid	$\bar{G}_{is}(T, P) = G_{-i}^0(T, P) + RT\ln(z_i\delta_i);$ $= G_{-i}^0(T, P).$

Institute of Standards and Technology (NIST) tabulated values (29) at standard conditions of T_0 and P_0 (Appendix A). The calculated reference state values along with the expressions in Table B.5 can be used to simplify the Gibbs free
180 energy function in eq 1 depending on the components in the system. This is explained in the following sections.

3.2. Hydrocarbon phase equilibrium

The Gibbs free energy framework described in the previous section can be directly used to obtain the equilibrium composition for any hydrocarbon mixture.
185 Let the initial moles of each component be z_i . These moles are distributed in the hydrocarbon phases at equilibrium so that $z_i = \sum_{j=1}^{N_p} n_{ij}$ where n_{ij} is the number of moles of component i in phase j . Also, x_{ij} is the corresponding mole fraction. The Gibbs free energy function of the system can be written as,

$$\begin{aligned}
G^T(T, P) &= \sum_{i=1}^{N_c} \sum_{j=1}^{N_p} n_{ij} [G_{-i}^{IG}(T, P) + RT\ln(x_{ij}\hat{\phi}_i)] \\
&= \sum_{i=1}^{N_c} z_i \underbrace{\left[G_{-i}^{IG}(T_0, P_0) + RT\ln\left(\frac{P}{P_0}\right) + [H_{-i}]_{P_0, T_0} \left(1 - \frac{T}{T_0}\right) \right]}_{\text{a constant}} \\
&\quad + \underbrace{\sum_{i=1}^{N_c} \sum_{j=1}^{N_p} n_{ij} [RT\ln(x_{ij}\hat{\phi}_i)]}_{G_m^T(P, T)}. \tag{5}
\end{aligned}$$

Eqn B.8 was used to simplify eq 5. Because the first term is a constant, a new
 190 function G_m^T has the same minimum as G^T . Also, the function $G_m^T(T, P)$ is
 devoid of reference state values and hence, preferable over G^T for minimization
 to obtain equilibrium composition. However, the challenge of finding the global
 minimum from local minima persists. The elements of the system or components
 themselves can be in the constraint equation. This is illustrated for the CO₂-
 195 nC₁₄H₃₀ mixture discussed in section 4.1.

3.3. Hydrocarbon phase equilibrium in presence of aqueous phase

The Gibbs free energy framework can be used to obtain equilibrium com-
 position when aqueous phase is present in addition to the hydrocarbon phases.
 If the aqueous phase is described using an EOS approach, the G_m^T function,
 200 similar to eq 5 is obtained. If an activity coefficient model is used to describe
 the aqueous phase, the total Gibbs free energy of the entire system is,

$$\begin{aligned}
 G^T(T, P) = & \sum_{i=1}^{N_c} z_i \underbrace{\left[G_i^{IG}(T_0, P_0) + RT \ln\left(\frac{P}{P_0}\right) + [H_i]_{P_0, T_0} \left(1 - \frac{T}{T_0}\right) \right]}_{\text{a constant}} \\
 & + \underbrace{\sum_{i=1}^{N_c} \sum_{j=1}^{N_{hc}} n_{ij} [RT \ln(x_{ij} \hat{\phi}_i)] + n_w [\bar{G}_w^0(T, P) + RT \ln x_w \gamma_w]}_{G_m^T(P, T)} \quad (6)
 \end{aligned}$$

The $G_m^T(T, P)$ function in eq 6 is used as the objective function to obtain equi-
 librium compositions as it has the same minimum as G^T . Like all phase equi-
 librium computation, either elements or component themselves can be used in
 205 the constraint equation.

3.4. Hydrocarbon phase equilibrium with geochemical reactions

Geochemical reactions arising out of CO₂ injection in the presence of aqueous
 phase with ions as well as solid rock can be integrated with the hydrocarbon
 phase equilibrium computations using the Gibbs free energy framework. The
 210 following assumptions are made to adapt this framework -

1. Ions and undissociated components are present in the aqueous phase.

2. The aqueous phase always contacts the solid phase.
3. Geochemical reactions occur between the components in the aqueous phase and the solid phase and all reactions are at equilibrium.

215 Recognizing that not all components are present in all phases, the total N_c components are divided into two groups. Group A are N_{c1} components that participate in only phase equilibrium within the hydrocarbon phases. As an example, the heavy hydrocarbon components that have negligible solubility in water. Group B are N_{c2} components present in both hydrocarbon and aqueous
 220 phase as well as components present exclusively in aqueous phases. Light hydrocarbons like CH_4 , C_2H_6 as well as CO_2 are examples of components in both aqueous and hydrocarbon phases while ions are present only in aqueous phase. The total Gibbs free energy function is,

$$\begin{aligned}
 G^T(T, P) = & \underbrace{\sum_{i=1}^{N_{c1}} \sum_{j=1}^{N_{hc}} n_{ij} [G_i^{IG}(T, P) + RT \ln(x_{ij} \hat{\phi}_i)]}_{\text{group A}} \\
 & + \underbrace{\sum_{i=1}^{N_{c2}} \sum_{j=1}^{N_{hc}} n_{ij} [G_i^{IG}(T, P) + RT \ln(x_{ij} \hat{\phi}_i)]}_{\text{group B}} \\
 & + \underbrace{\sum_{i=1}^{N_{c2}} n_{iw} [\bar{G}_{iw}^0(T, P) + RT \ln x_i \gamma_i] + n_w [\bar{G}_w^0(T, P) + RT \ln x_w \gamma_w]}_{\text{group B}} \quad (7)
 \end{aligned}$$

Using argument presented in section 3.1, an equivalent G_m^T function that does
 225 not have the reference state values for group A components can be defined. Because the G_m^T function has the same minimum as G^T in eq 7, it is used as the objective function for obtaining equilibrium composition and is given as,

$$\begin{aligned}
 G_m^T(T, P) = & \sum_{i=1}^{N_{c1}} \sum_{j=1}^{N_{hc}} n_{ij} [RT \ln(x_{ij} \hat{\phi}_i)] + \sum_{i=1}^{N_{c2}} \sum_{j=1}^{N_{hc}} n_{ij} [G_i^{IG}(T, P) + RT \ln(x_{ij} \hat{\phi}_i)] \\
 & + \sum_{i=1}^{N_{c2}} n_{iw} [\bar{G}_{iw}^0(T, P) + RT \ln x_i \gamma_i] + n_w [\bar{G}_w^0(T, P) + RT \ln x_w \gamma_w] \quad (8)
 \end{aligned}$$

. The constraint equation for the minimization is modified to include group A components as base components in addition to the elements conserved in the system. The inclusion of group A components in the constraint equation helps define that these components do not participate in the reactions and separate them from group B components that do participate in reactions. This is illustrated for mixtures discussed in the next section.

. While any minimization algorithm can be used, the RAND algorithm (17) is used to find the equilibrium composition for cases discussed in this manuscript. The comparison with experimental values, wherever available, helps identify the global minimum from the local minima and hence, the equilibrium composition.

4. Results

The Gibbs free energy model presented in the previous section is used to obtain phase envelope for the $\text{CO}_2\text{-nC}_{14}\text{H}_{30}$ mixtures. Phase envelopes of the mixtures are obtained in the presence of the aqueous phase as well as geochemical reactions. Geochemical reactions are a result of including ions and having a solid calcite phase. A comparison is presented to identify important parameters that impact the influence of geochemical reactions on the phase envelope for this mixture.

. Mangone (30) performed experiments on the $\text{CO}_2\text{-nC}_{14}\text{H}_{30}$ system to obtain the two-phase envelope for this system. For a fixed composition, the pressure is varied and the bubble and the dew points are inferred from the volumetric measurement of phases. These experiments were performed at 343 K for different compositions and indicate the presence of two phases ($N_p = 2$) for this two component mixture ($N_c = 2$). Components in both phases are described using PR EOS.

4.1. Phase equilibrium

. The Gibbs free energy model was used to obtain phase envelope for the CO_2 ($i = 1$)- $\text{nC}_{14}\text{H}_{30}$ ($i = 2$) system for a fixed overall composition at 343 K. The

equilibrium composition is the global minimum of the equivalent objective function G_m^T (eq 5). For this case of two components and two phases ($j = 2$) is,

$$G_m^T = \sum_{i=1}^2 \sum_{j=1}^2 n_{ij} [RT \ln(x_{ij} \hat{\phi}_i)]. \quad (9)$$

The matrices in the elemental constraint equation for the conserved elements -
255 carbon (C), oxygen (O) and hydrogen (H) as base components is,

$$\begin{aligned} \mathbf{A} &= \begin{bmatrix} 1 & 14 & 1 & 14 \\ 2 & 0 & 2 & 0 \\ 0 & 30 & 0 & 30 \end{bmatrix}; \quad \mathbf{E} = \begin{bmatrix} e_C \\ e_O \\ e_H \end{bmatrix}; \\ \mathbf{N} &= \begin{bmatrix} n_{11} & n_{21} & n_{21} & n_{22} \end{bmatrix}^T. \end{aligned} \quad (10)$$

As this is a phase equilibrium problem without reactions, an equivalent constraint set can be written using the components, CO_2 and $\text{n-C}_{14}\text{H}_{30}$ directly as conserved base components. While $\mathbf{N}$ remains the same, $\mathbf{A}$ and $\mathbf{E}$ are,

$$\mathbf{A} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}; \quad \mathbf{E} = \begin{bmatrix} e_{CH_4} \\ e_{C_{14}H_{30}} \end{bmatrix}. \quad (11)$$

Equilibrium computations were performed for a fixed overall composition assuming two phases and the total Gibbs free energy of the system, G^T (or, equivalently G_m^T) is compared with that of a single phase system. The combination corresponding to lowest G^T is the equilibrium composition at that
260 temperature and pressure. Pressures are varied, keeping temperature constant, to obtain bubble point and dew point curves and plot the phase envelope for the $\text{CO}_2\text{-nC}_{14}\text{H}_{30}$ system. The binary parameters for PR EOS listed in Table 2 ($K_{C_{14}H_{30},CO_2} = 0.0889$ gives coefficient of determination⁴) $R^2 = -1.9447$

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⁴Coefficient of determination R^2 measures the variability of a data set consisting of model predicted values (y_i) and experimental values (f_i) in terms of mean of the data set $\bar{y}$ and sums of squares.

$$R^2 = 1 - \frac{\sum_i (y_i - f_i)^2}{\sum_i (y_i - \bar{y})^2}.$$

have been obtained to get a sufficient match between the model predictions and
 265 the experimental values as shown in Figure 1. In determining this parameter,
 priority was accorded to match the critical point region in the phase envelope.

4.2. Phase equilibrium in presence of H_2O

. Mangone (30) also performed an additional set of experiments in the pres-
 ence of water to obtain the phase envelope for the CO_2 - $nC_{14}H_{30}$ system in
 270 the presence of aqueous phase. There are two hydrocarbon phases ($N_{hc} = 2$;
 $j = 1, 2$) and an aqueous phase ($j = 3$) in this system. Also, all components -
 CO_2 ($i = 1$), $nC_{14}H_{30}$ ($i = 2$) and H_2O ($i = 3$) are distributed in all phases.
 The hydrocarbon phase components are described using the PR EOS while the
 aqueous phase is described using the Pitzer activity coefficient model. In the
 275 absence of any ions in the aqueous phase, the osmotic coefficient is used to cal-
 culate the activity coefficient of water (Appendix B). The global minimum of
 the equivalent objective function G_m^T (eq 6) can then be used to find equilibrium
 composition,

$$G_m^T(T, P) = \sum_{i=1}^3 \sum_{j=1}^2 n_{ij} [RT \ln y_i \hat{\phi}_i] + \sum_{i=1}^2 n_{i3} [\bar{G}_{i3}^0(T, P) + RT \ln x_i \gamma_i] + n_{33} [\bar{G}_3^0(T, P) + RT \ln x_3 \gamma_3]. \quad (12)$$

As explained in the previous section, the constraint can be written in terms of
 280 conserved elements or components themselves for a phase equilibrium problem.
 The matrices written for the conserved elements in this system are,

$$\mathbf{A} = \begin{bmatrix} 1 & 14 & 0 & 1 & 14 & 0 & 1 & 14 & 0 \\ 2 & 0 & 1 & 2 & 0 & 1 & 2 & 0 & 1 \\ 0 & 30 & 2 & 0 & 30 & 2 & 0 & 30 & 2 \end{bmatrix}; \quad \mathbf{E} = \begin{bmatrix} e_C \\ e_O \\ e_H \end{bmatrix};$$

$$\mathbf{N} = \begin{bmatrix} n_{11} & n_{21} & n_{31} & n_{12} & n_{22} & n_{32} & n_{13} & n_{23} & n_{33} \end{bmatrix}^T. \quad (13)$$

. The experimental measurements for the CO_2 - $nC_{14}H_{30}$ - H_2O mixture (30) were
 made for equal initial volumes of water and $nC_{14}H_{30}$. This corresponds to
 a constant mole ratio of 14.45 between total moles of H_2O and total moles

Table 2: Properties of components used in PR EOS for CO₂-nC₁₄H₃₀ and CO₂-nC₁₄H₃₀-H₂O mixtures

Component (i)	Critical Pressure (MPa)	Critical Temperature (K)	Accentric Factor (w)	BIP K_{i,H_2O} (tuned)	BIP K_{i,CO_2} (tuned)
nC ₁₄ H ₃₀	1.62	693	0.644	0.95	0.0889
CO ₂	7.376	304.2	0.225	0.4	0
H ₂ O	22.06	647	0.344	0	0.4

of nC₁₄H₃₀, calculated using the molecular weights and densities of H₂O and nC₁₄H₃₀. A comparison of model prediction for the CO₂-nC₁₄H₃₀-H₂O with experimental measurements, converted to a water-free basis, are also shown in Figure 1. As an example, consider a case of nC₁₄H₃₀ = 0.0157, CO₂ = 0.7582 and H₂O = 0.2261 (equal volume of nC₁₄H₃₀). The equivalent mole fraction excluding water, also referred to as the water free basis in this representation, corresponds to nC₁₄H₃₀ = 0.02 and CO₂ = 0.88.

. As in the previous case, the binary parameters for PR EOS listed in Table 2 have been obtained to get a sufficient match between the model predictions and the experimental values as shown in Figure 1. The binary interaction parameter $K_{C_{14}H_{30},CO_2} = 0.0889$ was retained while K_{CO_2,H_2O} was varied to obtain match with experimental data according priority to critical region in the two phase envelope of the mixture. A value of $K_{CO_2,H_2O} = 0.4$ resulted in a coefficient of determination $R^2 = 0.8154$.

. These parameters are further used for computations involving geochemical reactions (phase and chemical equilibrium). It can be seen that the presence of H₂O shifts the two-phase envelope of the hydrocarbon system towards lower moles of nC₁₄H₃₀. This shift occurs because some CO₂ enters the aqueous phase and the overall mole fraction of CO₂ in phase equilibrium with nC₁₄H₃₀ decreases. In the next section, we investigate how the presence of geochemical reactions and varying initial compositions further affect the phase envelope for

Figure 1: Two-phase envelope for $\text{CO}_2\text{-nC}_{14}\text{H}_{30}$ and $\text{CO}_2\text{-nC}_{14}\text{H}_{30}\text{-H}_2\text{O}$ mixtures at 343 K.

this system.

4.3. Phase behavior with geochemical reactions

The addition of ions, typically present in a carbonate system, in the aqueous phase and solid calcite phase to $\text{CO}_2\text{-nC}_{14}\text{H}_{30}$ mixture introduces geochemical reactions. These components, along with their thermodynamic properaties, are listed in Table C.8. The hydrocarbon phases are described using PR EOS while aqueous phase ions and undissociated components are described using Pitzer activity coefficient model. As mentioned earlier, the solid phase is calcite, single component and assumed ideal.

315 . As discussed in section 3.4, the first step is to classify components in groups A and B based on their solubility in the aqueous phase. The heavy hydrocarbon component ($\text{nC}_{14}\text{H}_{30}$) has negligible solubility in the aqueous phase and is a group A component. CO_2 is the group B component in this system. Hence, the changes in the hydrocarbon phase behavior occur as CO_2 enters the aqueous
320 phase and further participates in the geochemical reactions owing to the presence of other ions as well as solid calcite.

. No experimental data for this system comprising of CO_2 - $\text{nC}_{14}\text{H}_{30}$ mixture along with components in the aqueous phase and the solid calcite phase is available for comparison with model prediction. Hence, parameters obtained from
325 tuning experimental data of two subsystems - CO_2 - $\text{nC}_{14}\text{H}_{30}$ - H_2O and CO_2 - CaCl_2 - H_2O - CaCO_3 (solid) have been used for calculating equilibrium composition for this complete system.

. As described in sections 4.1.2, the binary coefficients listed in Table 2 are obtained by tuning the experimental data available for the CO_2 - $\text{nC}_{14}\text{H}_{30}$ - H_2O
330 mixture. The Pitzer binary and tertiary interaction parameters are obtained from the experimental data for CO_2 solubility in CaCl_2 solution (hence, CO_2 - CaCl_2 - H_2O system) and compare well with experimental data in presence of solid CaCO_3 (see Appendix B).

. The components in the hydrocarbon phases are $\text{nC}_{14}\text{H}_{30}$ ($i = 1$), CO_2 ($i = 2$)
335 and H_2O ($i = 3$). The aqueous phase components are ions typically present in a carbonate system - Ca^{2+} ($i = 4$), HCO_3^- ($i = 5$), CO_3^{2-} ($i = 6$), H^+ ($i = 7$), OH^- ($i = 8$), Cl^- ($i = 9$) as well as undissociated components - H_2CO_3 ($i = 10$), CaCO_3 ($i = 11$), CaCl_2 ($i = 12$), CO_2 ($i = 13$) and H_2O . The solid component CaCO_3 ($i = 14$) is assumed ideal. The equivalent objective function G_m^T (eq 8)
340 adapted for this mixture with $\text{nC}_{14}\text{H}_{30}$ as a group A component and CO_2 as a group B component and including a single hydrocarbon phase at equilibrium

can be written as,

$$\begin{aligned}
G_m^T(T, P) = & n_{11}[RT\ln(x_{11}\hat{\phi}_1)] + n_{21}[G_2^{IG}(T, P) + RT\ln(x_{21}\hat{\phi}_2)] \\
& + \sum_{i=4}^{13} n_{iw}[\bar{G}_{iw}^0(T, P) + RT\ln x_i \gamma_i] + n_{14}[\bar{G}_{14}^0] \\
& + n_3[\bar{G}_3^0(T, P) + RT\ln x_3 \gamma_3].
\end{aligned} \tag{14}$$

The elemental balance constraint for this system of phase and chemical equilibrium corresponding to a single hydrocarbon phase at equilibrium is written as the sum of conserved elements and additionally conserved group A component. This can be given as,

$$\mathbf{A} = \begin{bmatrix} 0 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 1 \\ 0 & 2 & 1 & 0 & 3 & 3 & 0 & 1 & 0 & 3 & 3 & 0 & 2 & 1 & 3 \\ 0 & 0 & 2 & 0 & 1 & 0 & 1 & 1 & 0 & 2 & 0 & 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 2 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}; \quad \mathbf{E} = \begin{bmatrix} e_C \\ e_O \\ e_H \\ e_{Ca} \\ e_{Cl} \\ e_{C_{14}H_{30}} \end{bmatrix}. \tag{15}$$

. In addition to the elements, the additional constraint on including nC₁₄H₃₀ as a separate base component in $\mathbf{E}$ helps indicate that it does not participate in reactions and the C and H elements in this component are not available for reactions. An additional hydrocarbon phase, with components CO₂ and nC₁₄H₃₀, may be present depending on the pressure and temperature conditions. The total system Gibbs free energy (G^T) for both cases are compared and the combination with the lowest G^T corresponds to the equilibrium concentration of the system that is used to plot the phase envelope for the CO₂-nC₁₄H₃₀ system with geochemical reactions.

5. Discussion

As equilibrium concentration of components for a reactive system depends on the initial concentration of components, the impact of geochemical reactions

on phase behavior of the hydrocarbon mixture can vary based on the initial mole number of components. A sensitivity study is done to determine how a change in initial mole numbers of the above identified parameters can change the phase envelope of the $\text{CO}_2\text{-nC}_{14}\text{H}_{30}$ hydrocarbon mixture.

. A base case is defined as the case where volume of water is equal to the volume of $\text{nC}_{14}\text{H}_{30}$ similar to the experiments for the $\text{CO}_2\text{-nC}_{14}\text{H}_{30}\text{-H}_2\text{O}$ system (30). This corresponds to a constant molar ratio of 14.45, obtained using densities and molecular weights of H_2O and $\text{nC}_{14}\text{H}_{30}$. Also, the number of moles of solid and water are equal in the base case. The concentration of CaCl_2 in the base case is taken as 10.1 mole % of water. Similarly, the Pitzer activity parameters for 10.1 % CaCl_2 solution, listed in Table B.4 and obtained by comparing experimental data for $\text{CO}_2\text{-CaCl}_2\text{-H}_2\text{O-CaCO}_3$ (solid) system (16; 31) are also used for the aqueous phase components. These parameter values are assumed constants for the sensitivity study discussed in the following sections.

. The moles of solid relative to the aqueous phase moles have no effect on the phase behavior of the hydrocarbon mixture. As solid is a pure component phase that is assumed ideal in the model, its fugacity is fixed by the pressure. At equilibrium, since the fugacity of CaCO_3 in the aqueous phase is equal to that of CaCO_3 solid the concentration of CaCO_3 in the aqueous phase is fixed. Hence, increasing solid moles do not have an effect on the hydrocarbon phase behavior.

. The equilibrium composition corresponding to this case of both phase and chemical equilibrium can depend on

1. CaCl_2 concentration in aqueous phase, which is representative of ionic concentration of species and is analogous to the salinity of the reservoir brine.
2. Volume ratio of H_2O and $\text{nC}_{14}\text{H}_{30}$ and hence, molar ratio. A volume ratio is preferable owing to analogous measurements of initial saturations of water and oil that is possible in an oil field.

. The Pitzer parameters obtained in Table B.4 as well as the binary interaction
 385 parameters in Table 2 are used for phase and chemical equilibrium computa-
 tions. Figure 2 shows the impact of geochemical reactions on the phase envelope
 for two different concentrations of CaCl_2 . The phase envelope of the hydrocar-
 bon mixture shifts further towards decreasing concentration of $\text{nC}_{14}\text{H}_{30}$ in the
 presence of geochemical reactions than just water. At an overall mole fraction
 390 of 0.2 mole % of $\text{nC}_{14}\text{H}_{30}$, the bubble point pressure of the CO_2 - $\text{nC}_{14}\text{H}_{30}$ mix-
 ture in the presence of water changes by about 5 % while in the presence of
 geochemical reactions, the bubble point pressure decreases by about 10 %.

. The volume ratio of H_2O and $\text{nC}_{14}\text{H}_{30}$ is an important parameter that may
 be determined in the field based on the saturation data. Figure 3 shows that
 395 the difference in phase envelope between cases of only phase equilibrium with
 no reactions and phase equilibrium with geochemical reactions when other pa-
 rameters are held constant as in the base case. The moles of solid are equal to
 the moles of water and the CaCl_2 is 10 % of H_2O in all cases considered.

. Figure 3 shows that the difference between the phase envelopes for cases with
 400 and without reactions increases as the initial ratio of H_2O to $\text{nC}_{14}\text{H}_{30}$ (Y)
 increases. The difference in phase envelopes for the case where $Y = 5$ is greater
 than that for $Y = 0.5$. If Y is larger, the geochemical reactions have a greater
 impact on the phase envelope of CO_2 - $\text{nC}_{14}\text{H}_{30}$ - H_2O system. At a $\text{nC}_{14}\text{H}_{30}$
 overall mole fraction of 0.2 %, the bubble point pressure decrease for $Y = 0.5$
 405 and in the presence of reactions is insignificant. However, at the same $\text{nC}_{14}\text{H}_{30}$
 overall mole fraction of 0.2 %, the decrease in bubble point pressure for $Y = 5$ is
 about 27 % in the presence of reactions. In summary, the initial volume ratio of
 H_2O and $\text{nC}_{14}\text{H}_{30}$ is an important parameter that influences the shift in phase
 envelope.

410 . An initial mole ratio of 5 between H_2O and nC_{14} was chosen to magnify the
 impact of geochemical reactions and study the effect of varying CaCl_2 concentra-
 tion. Also the amount of solid was taken equal to the amount of H_2O (as in the

Figure 2: Two-phase envelopes for CO_2 - $\text{nC}_{14}\text{H}_{30}$ system in presence of water (no reactions) as well as with 10.1 and 20.2 mole % of CaCl_2 solution at 343 K. The mole fraction of $\text{nC}_{14}\text{H}_{30}$ is on a water-free basis.

Figure 3: Two-phase envelopes for CO₂-nC₁₄H₃₀-H₂O system for varying initial mole ratios of H₂O and nC₁₄H₃₀ at 343 K.

base case). Figure 4 shows the phase envelope for different CaCl_2 concentration.

. The geochemical reactions, occurring because of CaCl_2 solution in the aqueous
415 phase along with solid CaCO_3 and all the aqueous phase ions associated with
the carbonate system, shift the phase envelope even further towards lower $n\text{C}_{14}$.
This has implications for oil recovery predictions using compositional simulations.
The equilibrium concentrations obtained as solution to the Gibbs free
energy minimization indicate that the aqueous concentration of CO_2 increases
420 as the concentration of CaCl_2 in the aqueous phase increases. The amount of
 CO_2 available for phase equilibrium with $n\text{C}_{14}$ decreases and hence, a shift is
observed. The decrease in bubble point pressure at 0.2 % overall mole fraction
of C_{14} is about 35% at 30% CaCl_2 concentration (Figure 4).

. The changes in two-phase envelope of the CO_2 - $n\text{C}_{14}\text{H}_{30}$ mixture has impli-
425 cations in oil recovery predictions. As an example, let point A in Figure 4
represent an overall mole fraction and pressure occurring during reservoir simu-
lation. As point A lies within the two phase envelope, two phases are present
at equilibrium and this is also obtained by flash calculations and stability anal-
ysis performed in compositional simulations. If no reactions are considered, the
430 vapor and liquid compositions at equilibrium are represented by points L_1 and
 V_1 , respectively. However, if the new two-phase envelope due to reactions (say
10.1 % CaCl_2) are considered, the equilibrium compositions are represented by
points L_2 and V_2 . While there is little difference between compositions repre-
sented by points V_1 and V_2 , the difference in composition represented by points
435 L_1 and L_2 , impacts liquid mole fractions at equilibrium and hence, oil recovery
predictions.

. Let point B in Figure 4 represent an overall mole fraction and pressure occur-
ing during reservoir simulation. If no geochemical reactions are occurring in the
system, a flash computation in compositional simulation will predict a two phase
440 system (as it lies within the two phase envelope for CO_2 - $n\text{C}_{14}$ system without
any reactions). If geochemical reactions are considered, point B lies outside the

Figure 4: Two-phase envelopes for $\text{CO}_2\text{-nC}_{14}\text{H}_{30}\text{-CaCl}_2\text{-H}_2\text{O-CaCO}_3$ system for varying CaCl_2 mole % in H_2O at 343 K. Initial mole ratio of H_2O to $n\text{-C}_{14}\text{H}_{30}$ (Y) is 5 for these cases.

Table 3: A summary of all mixtures considered for equilibrium computations in this study to obtain changes to $\text{CO}_2\text{-nC}_{14}\text{H}_{30}$ phase envelope at 343 K. Please note that HC means hydrocarbon phases in this table.

Mixture	Phases	Components
$\text{CO}_2\text{-nC}_{14}\text{H}_{30}$ (Figures 1 and 2)	Two HC phases (potential)	CO_2 , $\text{nC}_{14}\text{H}_{30}$.
$\text{CO}_2\text{-nC}_{14}\text{H}_{30}\text{-H}_2\text{O}$ (Figures 1, 2 and 3)	Two HC phases (potential) & aqueous phase	CO_2 , $\text{nC}_{14}\text{H}_{30}$, H_2O , H^+ , OH^- .
$\text{CO}_2\text{-nC}_{14}\text{H}_{30}\text{-CaCl}_2\text{-H}_2\text{O}$ (Figure 2)	Two HC phase (potential) & aqueous phase	CO_2 , $\text{nC}_{14}\text{H}_{30}$, H_2O , H^+ , OH^- , CaCl_2 , Ca^{2+} , Cl^- .
$\text{CO}_2\text{-nC}_{14}\text{H}_{30}\text{-CaCl}_2\text{-H}_2\text{O}\text{-CaCO}_3$ (Figure 4)	Two HC phases (potential), aqueous phase & solid phase	Group A: $\text{nC}_{14}\text{H}_{30}$. Group B: CO_2 , CaCl_2 , H_2O , H^+ , OH^- , Ca^{2+} , Cl^- , CO_3^{2-} , HCO_3^- , H_2CO_3 , CaCO_3 .

two-phase envelope so that only a single phase is present at equilibrium at that overall mole fraction and pressure. Thus, the changes in two-phase envelope impacts the equilibrium compositions at different mole fractions and pressures and hence, the oil recovery predictions. A summary of mixture components with phases considered for equilibrium compositions in this manuscript is listed in Table 3.

6. Conclusion

A Gibbs free energy model for phase equilibrium computations associated with CO_2 injection in carbonate reservoirs is presented in this manuscript. The Gibbs free energy function is a unifying function and a practical approach is presented that can be used to obtain changes in the phase envelope of hydrocarbons in the presence of an aqueous phase with geochemical reactions. The

two important parameters that impact the phase envelope for the example mixture CO₂-nC₁₄H₃₀ discussed in this manuscript, when geochemical reactions are incorporated, are volume ratio of the oil to brine (and hence, molar ratio) and the brine salinity.

. The advantage of this model is the ability to combine different thermodynamic models - EOS description for hydrocarbon components and activity coefficient model for aqueous phase description using the Gibbs free energy function. The division of system components in the model helps modify the Gibbs free energy function and eliminate the need to have the standard state Gibbs free energy values of heavy components for equilibrium computations. This is particularly relevant for any characterized real oil sample that has psuedo components not soluble in the aqueous phase (32)

. Experiments can help identify the brine components and their Pitzer parameters to characterize the CO₂ solubility in any brine composition. While synthetic nC₁₄H₃₀ was used as oil for illustration in this manuscript, real oil composition, typically characterized by the PR EOS, can be used. Also, saturation measurements can be used to calculate the initial molar ratios of oil and brine. These parameters can be directly used in the presented model to quantify the impact of CO₂ injection in any hydrocarbon containing carbonate reservoir with any brine composition. As any minimization algorithm can calculate equilibrium compositions, the presented framework can be added to compositional simulators.

. One of the limitations of this model is the lack of kinetics as the geochemical reactions are assumed to be at equilibrium in this model. Because of this assumption, the results from the model represent a maximum possible change in phase envelope owing to geochemical reactions during CO₂ injection. Additional research is needed to understand how geochemical reactions may impact the critical temperature and pressure of the mixtures as it directly impacts the minimum miscibility pressure for injection during gas EOR.

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Appendix A. Chemical Potential Expression for Components

The reference state values at any T and P can be related to the NIST tabulated values at standard conditions of T_0 and P_0 using the following equations,

$$\underline{G}_i^{IG}(T, P) = \underline{G}_i^{IG}(T_0, P_0) + RT \ln\left(\frac{P}{P_0}\right) + T \int_{T_0}^T - \left(\frac{\underline{H}_i}{T^2}\right)_P dT \quad (\text{A.1})$$

$$\bar{G}_{iw}^0(T, P) = \bar{G}_i^0(T_0, P_0) + \int_{P_0}^P (\bar{v}_i)_{T_0} dP + T \int_{T_0}^T - \left(\frac{\bar{H}_{iw}}{T^2}\right)_P dT \quad (\text{A.2})$$

$$\bar{G}_{is}^0(T, P) = \underline{G}_i^0(T_0, P_0) + \int_{P_0}^P (v_i)_{T_0} dP + T \int_{T_0}^T - \left(\frac{\underline{H}_i}{T^2}\right)_P dT \quad (\text{A.3})$$

$$\bar{G}_w^0(T, P) = \underline{G}_w^0(T_0, P_0) + \int_{P_0}^P (v_w)_{T_0} dP + T \int_{T_0}^T - \left(\frac{\underline{H}_w}{T^2}\right)_P dT \quad (\text{A.4})$$

Helgeson and co-workers (33; 34; 35) have developed EOS models for the partial molal volumes $\underline{v}$ as well as expressions for partial molal enthalpies $\underline{H}$ for aqueous solutes (CO₂, H₂S as well as ionic solutes) to evaluate the reference state values at high temperatures and high pressures (upto 1273 K and 500 MPa). The typical pressure range for CO₂ injection is less than 80 MPa. The molar volumes and enthalpies at T_0 and P_0 (tabulated in NIST database (29)) are assumed to be constants over the pressure and the temperature range of CO₂

injection. We can then simplify eqs A.1 - A.4 to obtain following expressions for different components in different phases,

$$\bar{G}_i^{IG}(T, P) = \bar{G}_i^{IG}(T_o, P_o) + RT \ln\left(\frac{P}{P_o}\right) + [\bar{H}_{i1}]_{P_o, T_o} \left(1 - \frac{T}{T_o}\right). \quad (\text{A.5})$$

$$\bar{G}_{iw}^0(T, P) = \bar{G}_i^0(T_o, P_o) + (\bar{v}_i^\infty)_{T_o} (P - P_o) + [\bar{H}_{iw}]_{P_o, T_o} \left(1 - \frac{T}{T_o}\right). \quad (\text{A.6})$$

$$\bar{G}_{is}^0(T, P) = \bar{G}_s^0(T_o, P_o) + (v_s)_{T_o} (P - P_o) + [\bar{H}_s]_{P_o, T_o} \left(1 - \frac{T}{T_o}\right). \quad (\text{A.7})$$

$$\bar{G}_w^0(T, P) = \bar{G}_w^0(T_o, P_o) + (v_w)_{T_o} (P - P_o) + [\bar{H}_w]_{P_o, T_o} \left(1 - \frac{T}{T_o}\right). \quad (\text{A.8})$$

The reference state values at any temperature and pressure is calculated and used in eq 1 to minimize the Gibbs free energy function of the entire system.

640 Appendix B. Pitzer activity coefficient model

The Pitzers activity coefficient is extensively used to model the impact of ions in geochemistry in high salinity brines. It is used for solutions when the ionic strength I is greater than 0.02. The ionic strength measures ionic activity where m_i and z_i as molality and charge of component i , respectively and given
645 as $I = 0.5 \sum_i z_i m_i^2$. The more popular Debye-Huckel activity coefficients and their extensions, are only used for solutions with ionic strengths less than 1.

. Harvie and co-workers (36) have adapted the Pitzer activity coefficient model for geochemical reactions modified the virial expansion of the activity coefficient (37) to include only two terms. The expression can be given as,

$$\ln \gamma_i = \ln \gamma_{DH} + \sum_j B_{ij}(I) m_j + \sum_{jk} C_{ijk}(I) m_j m_k \quad (\text{B.1})$$

Here, γ_{DH} is the Dubye-Huckel activity coefficient, m_i is the molality of species i while B_{ij} and C_{ijk} are the second and third virial activity coefficients respectively. These coefficients account for effects between like-charged ions at high
650 ionic activity as well as the solvent structure and use the same parametrization as interaction coefficients used by Pitzer (38; 39; 40).

. In this manuscript we assume that the interaction coefficients, originally defined for a system of aqueous ions and minerals (listed in (36)) are assumed to hold for a system that includes hydrocarbons in addition to aqueous ions and
655 rock. The mineral solubility data at different temperatures were used to find temperature dependent expressions for the interaction parameters (41; 36; 42). Although the interaction parameters are functions of temperature and pressure, the values at 25°C are used in all models at different temperatures and pressures discussed in this manuscript.

660 . The underlying equation for excess Gibbs free energy (G^E) in the Pitzer activity coefficient model is,

$$G^E/RT = n_w \left[f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \right] \quad (\text{B.2})$$

Here, m_i is the molality of species i (m_c for cation with charge z_c and m_a for anion with charge z_a). Also, M , c and c' represent cations while X , a and a' represent anions. Both the first term $f(I)$ is the Debye-Huckel coefficient and
665 the second coefficient in the virial expansion $\lambda_{ij}(I)$ are functions of the ionic strength, I , while the third coefficient μ_{ijk} is independent of I .

. The expression for G^E is used to derive expressions for osmotic coefficient and the activity coefficients of components. The activity of water (a_{H_2O}) is obtained from the osmotic coefficient (ϕ) and given as (43),

$$\ln a_{H_2O} = -0.0018 \left(\sum_i m_i \right) \phi. \quad (\text{B.3})$$

The osmotic coefficient measures the deviation of the solvent (water) from ideal behavior. The expression for osmotic coefficient (ϕ) for the Pitzer activity co-

efficient model is,

$$\begin{aligned} \phi - 1 = & \frac{2}{\sum_i m_i} \left[-\frac{A^\phi I^{3/2}}{1 + bI^{1/2}} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \right. \\ & + \sum_c \sum_{c'} m_c m_{c'} (\phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a}) \\ & \left. + \sum_a \sum_{a'} m_a m_{a'} (\phi_{aa'}^\phi + \sum_c m_c \psi_{aa'c}) \right]. \end{aligned} \quad (\text{B.4})$$

670 At 25°C, $A^\phi = 0.392$ and $b = 1.2$. In the above equation, $Z = \sum_i m_i z_i$. The activity coefficient expressions for cations (γ_M) and anions (γ_X) in the aqueous phase are,

$$\begin{aligned} \ln \gamma_M = & z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\phi_{Mc} + \sum_a m_a \psi_{Mca}) \\ & + \sum_a \sum_{a'} m_c m_{a'} \psi_{aa'M} + z_M \sum_c \sum_a m_c m_a C_{ca} \end{aligned} \quad (\text{B.5})$$

$$\begin{aligned} \ln \gamma_X = & z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_a m_a (2\phi_{Xa} + \sum_c m_c \psi_{Xac}) \\ & + \sum_c \sum_{c'} m_a m_{c'} \psi_{cc'X} + z_X \sum_c \sum_a m_c m_a C_{ca} \end{aligned} \quad (\text{B.6})$$

In eqns B.5 and B.6, F represents the Debye-Huckel term and the derivatives of the second coefficient with respect to ionic strength (I), and is given as,

$$\begin{aligned} F = & -A^\phi \left[\frac{\sqrt{I}}{I + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right] + \sum_c \sum_a m_c m_a B'_{ca} \\ & + \sum_c \sum_{c'} m_c m_{c'} \phi'_{cc'} + \sum_a \sum_{a'} m_a m_{a'} \phi'_{aa'} \end{aligned} \quad (\text{B.7})$$

675 As mentioned earlier, A^ϕ and b are considered constants with values 0.392 and 1.2 respectively. Also, B' , B , ϕ_{ij} , ϕ'_{ij} are coefficients of the binary interaction parameter and ψ_{ijk} is the coefficient for ternary interaction parameter. The expressions for coefficients B_{MX}^ϕ , B_{MX} and B'_{MX} in eqns B.4-B.7 for 1-1 valence

type ions are,

$$B_{MX}^{\phi} = \beta_{MX}^0 + \beta_{MX}^1 e^{-\alpha\sqrt{I}} \quad (\text{B.8})$$

$$B_{MX} = \beta_{MX}^0 + \beta_{MX}^1 g(\alpha\sqrt{I}) \quad (\text{B.9})$$

$$B'_{MX} = \beta_{MX}^1 g'(\alpha\sqrt{I})/I \quad (\text{B.10})$$

680 In eqns B.8-B.10, $\alpha = 2$ has been empirically found by Pitzer and $x = \alpha\sqrt{I}$.
Besides, $g(x)$ and $g'(x)$ are functions defined as,

$$g(x) = \frac{2[1 - (1+x)e^{-x}]}{x^2} \quad (\text{B.11})$$

$$g'(x) = -\frac{[1 - (1+x + \frac{1}{2}x^2)e^{-x}]}{x^2} \quad (\text{B.12})$$

The constants B_{MX}^{ϕ} , B_{MX} and B'_{MX} for 2-2 valence type ions ($\alpha_1 = 2$ and $\alpha_2 = 12$) are given by,

$$B_{MX}^{\phi} = \beta_{MX}^0 + \beta_{MX}^1 e^{-\alpha_1\sqrt{I}} + \beta_{MX}^2 e^{-\alpha_2\sqrt{I}} \quad (\text{B.13})$$

$$B_{MX} = \beta_{MX}^0 + \beta_{MX}^1 g(\alpha_1\sqrt{I}) + \beta_{MX}^2 g(\alpha_2\sqrt{I}) \quad (\text{B.14})$$

$$B'_{MX} = \beta_{MX}^1 \left(\frac{g'(\alpha_1\sqrt{I})}{I} \right) + \beta_{MX}^2 \left(\frac{g'(\alpha_2\sqrt{I})}{I} \right) \quad (\text{B.15})$$

The constants C_{MX} , ϕ_{ij}^{ϕ} and ϕ'_{ij} in eqns B.4-B.7 are,

$$C_{MX} = \frac{C_{MX}^{\phi}}{2\sqrt{z_M z_X}} \quad (\text{B.16})$$

$$\phi_{ij}^{\phi} = \theta_{ij} + {}^E\theta_{ij}(I) + I^E \theta'_{ij}(I) \quad (\text{B.17})$$

$$\phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad (\text{B.18})$$

$$\phi'_{ij} = {}^E\theta'_{ij}(I) \quad (\text{B.19})$$

685 Here, ${}^E\theta_{ij}$ and ${}^E\theta'_{ij}$ account for electrostatic unsymmetrical mixing effects and depend only on charges of ions i and j and the total ionic strength I . They are both zero if i and j are of the same charge. A complete list of binary interaction parameters for any two pairs of cations/anions ($\phi_{cc'}/\phi_{aa'}$) as well as ternary interaction parameters between two cations and one anion ($\psi_{cc'a}$) or two anions
690 and one cation ($\psi_{aa'c}$) are listed in Tables B.5 and B.7.

Table B.4: Tuned Pitzer activity coefficient parameter values for CO₂-CaCl₂-H₂O system

CaCl ₂ mole in H ₂ O	Tuned binary parameter ($\lambda_{CO_2-Ca^{2+}}, \lambda_{CO_2-Cl^-}$)	Tuned ternary parameter ($\xi_{CO_2-Ca^{2+}-Cl^-}$)	R ²
10.1 %	-0.02, -0.02	-0.0002	0.99
20.2 %	0.025, 0.025	-0.0002	0.99
30.2 %	0.061, 0.061	-0.0002	0.97

. The neutral species considered in our aqueous system for applications discussed in chapter 6 is CO₂ (aq). The Pitzer equations for activity coefficient for CO₂ (γ) to include its interaction with other ions is given as,

$$\log \gamma = \sum_c 2m_c \lambda_{CO_2-c} + \sum_a 2m_a \lambda_{CO_2-a} + \sum_c \sum_a m_c m_a \xi_{CO_2-c-a}. \quad (B.20)$$

The interaction parameters ($\lambda_{CO_2-Ca^{2+}}, \lambda_{CO_2-Cl^-}$ and $\xi_{CO_2-Ca^{2+}-Cl^-}$) in the Pitzer activity coefficient model are obtained by matching experimental data. The coefficient of determination (R^2) is used as a measure, the closer the value of R^2 to 1, the better the match between model and experimental data.

695 The tuned parameter values for different concentrations of CaCl₂ in H₂O are given in Table B.4. Figure B.5 a shows comparison of tuned model for CO₂ solubility with experimental data for 10.1 % CaCl₂ solution.

. The Pitzer activity coefficient along with the tuned interaction parameter values obtained from the above section are used to predict the solubility for a
700 complex system that contains calcite (CaCO₃ solid) in addition to the CaCl₂ solution. The presence of solid phase introduces additional components in the aqueous phase. The complete system then consists of three phases - gas phase ($j = 1$) with components CO₂ ($i = 1$), H₂O ($i = 2$), solvent H₂O, aqueous phase ($j = 2$) components CO₂, Ca²⁺ ($i = 3$), HCO₃⁻ ($i = 4$), Cl⁻ ($i = 5$), H₂CO₃
705 ($i = 6$), CaCO₃ ($i = 7$) and solid phase ($j = 3$) component CaCO₃. The equilibrium composition is obtained by minimization of G_m^T described in section 4.3. The model predictions compare well with the experimental observations

Table B.5: Pitzer binary interaction parameters between different cations and anions (36; 45)

Component (<i>i</i>)	Component (<i>j</i>)	β_{MX}^0	β_{MX}^1	β_{MX}^2	C_{MX}^ϕ
Na ⁺	Cl ⁻	0.0765	0.2664	-	0.00127
Na ⁺	SO ₄ ²⁻	0.01958	1.113	-	0.00497
Na ⁺	HCO ₃ ⁻	0.028	0.044	-	-
Na ⁺	CO ₃ ²⁻	0.036	1.512	-	0.0052
K ⁺	Cl ⁻	0.04835	0.2122	-	0.00084
K ⁺	SO ₄ ²⁻	0.04995	0.7793	-	-
K ⁺	HCO ₃ ⁻	-0.0107	0.048	-	-
K ⁺	CO ₃ ²⁻	0.129	1.433	-	0.0005
Mg ²⁺	Cl ⁻	0.35235	1.6815	-	0.00519
Mg ²⁺	SO ₄ ²⁻	0.221	3.343	-37.25	0.025
Mg ²⁺	HCO ₃ ⁻	0.03	0.8	-	-
Mg ²⁺	CO ₃ ²⁻	-	-	-	-
Ca ²⁺	Cl ⁻	0.3159	1.614	-	-0.00034
Ca ²⁺	SO ₄ ²⁻	0.2	2.65	-57.7	0
Ca ²⁺	HCO ₃ ⁻	0.2	0.3	-	-
Ca ²⁺	CO ₃ ²⁻	-	-	-	-

($R^2 = 0.77$ in Figure B.5).

. In summary, experimental values can be used to determine the Pitzer binary and tertiary interaction coefficients for CO₂ in any brine sample if its composition is known. The binary interaction parameter (λ) and the ternary interaction parameter (ξ) between CO₂ and different anions and cations at 25°C can be found in (36; 45) and are listed in Tables B.5-B.7.

Figure B.5: (a) Model prediction and tuning interaction parameters for match with experiments (44) for benchmarking case of 10.1 mole % CO₂-CaCl₂ system at 120°C. (b) Comparison of model prediction and experiments (44) for complex system of CO₂-CaCl₂ and solid CaCO₃ at 120°C.

Table B.6: Binary interaction coefficient between CO_2 and ionic component (45).

Component (j)	$\lambda_{\text{CO}_2} - j$
H+	-
Na ⁺	0.07748
K ⁺	0.04583
Ca ²⁺	0.19775
Mg ²⁺	0.1946
Cl ⁻	0.02021
SO ₄ ²⁻	0.1392

Table B.7: Pitzer binary (θ_{ij}) and ternary (ψ_{ijk}) interaction parameters for different cations and anions at 25°C (36; 45)

Component (i)	Component (j)	Component (k)	θ_{ij}	ψ_{ijk}
Na ⁺	K ⁺	Cl ⁻	-0.012	-0.0018
Na ⁺	K ⁺	SO ₄ ²⁻	-	-0.01
Na ⁺	Mg ²⁺	Cl ⁻	0.07	-0.012
Na ⁺	Mg ²⁺	SO ₄ ²⁻	-	-0.015
Na ⁺	Ca ²⁺	Cl ⁻	0.07	-0.014
Na ⁺	Ca ²⁺	SO ₄ ²⁻	-	-0.023
K ⁺	Mg ²⁺	Cl ⁻	-	-0.022
K ⁺	Mg ²⁺	SO ₄ ²⁻	-	-0.048
K ⁺	Ca ²⁺	Cl ⁻	0.032	-0.025
K ⁺	Ca ²⁺	SO ₄ ²⁻	-	-
Mg ²⁺	Ca ²⁺	Cl ⁻	0.007	-0.012
Mg ²⁺	Ca ²⁺	SO ₄ ²⁻	-	0.05
Cl ⁻	SO ₄ ²⁻	Na ⁺	0.02	0.0014
Cl ⁻	SO ₄ ²⁻	K ⁺	-	-
Cl ⁻	SO ₄ ²⁻	Mg ²⁺	-	-0.004
Cl ⁻	SO ₄ ²⁻	Ca ²⁺	-	-

Appendix C. Thermodynamic properties of components

715 The thermodynamic properties of components used for computations are given in this section.

Table C.8: Thermodynamic properties of components (46). Values are in kJ/moles except partial volume in cm^3 .

Component	Thermodynamic property at $T_0 = 25^\circ\text{C}$ and $P_0 = 1\text{atm}$	Value
Ca^{2+}	Partial molar Gibbs free energy of in the aqueous phase, $\bar{G}_1^0$	-553.04
	Partial molar enthalpy in the aqueous phase, $\bar{H}_{12}$	-542.96
Cl^-	Partial molar Gibbs free energy of in the aqueous phase, $\bar{G}_2^0$	-131.17
	Partial molar enthalpy in the aqueous phase, $\bar{H}_{22}$	-167.46
CO_3^-	Partial molar Gibbs free energy of in the aqueous phase, $\bar{G}_3^0$	-528.10
	Partial molar enthalpy in the aqueous phase, $\bar{H}_{32}$	-676.26
HCO_3^-	Partial molar Gibbs free energy of in the aqueous phase, $\bar{G}_4^0$	-587.06
	Partial molar enthalpy in the aqueous phase, $\bar{H}_{42}$	-691.11

CaCl ₂	Partial molar Gibbs free energy of	-816.05
	in the aqueous phase, $\bar{G}_5^0$	
	Partial molar enthalpy	-877.3
	in the aqueous phase, $\bar{H}_{52}$	
H ₂ CO ₃	Partial molar Gibbs free energy of	-623.42
	in the aqueous phase, $\bar{G}_6^0$	
	Partial molar enthalpy	-698.73
	in the aqueous phase, $\bar{H}_{62}$	
CO ₂	Gibbs free energy of an ideal gas, G_{11}^{IG}	-394.38
	Molar enthalpy in gas phase, H_1	-393.51
	Partial volume of at infinite dilution, $\bar{v}_1^\infty$	32.80
	Partial molar Gibbs free energy	
	of aqueous solute, $\bar{G}_1^0$	-386.23
	Partial molar enthalpy of solute	
	in aqueous phase, $\bar{H}_{12}$	-412.92
H ₂ O	Gibbs free energy of an ideal gas, G_{21}^{IG}	-228.57
	Molar enthalpy of in gas phase, H_2	-241.81
	Molar volume of H ₂ O, v_2	19
	Molar Gibbs free energy, G_2^0	-237.19
	Molar enthalpy of H ₂ O	
	in aqueous phase, H_{22}	-285.84
H ⁺	Partial molar Gibbs free energy	0
	in the aqueous phase, $\bar{G}_3^0$	
	Partial molar enthalpy of H ⁺	0
	in the aqueous phase, H_{32}	
OH ⁻	Partial molar Gibbs free energy	-157.3
	in the aqueous phase, $\bar{G}_4^0$	
	Partial molar enthalpy of OH ⁻	-229.94
	in aqueous phase, H_{42}	
CaCO ₃	Partial molar Gibbs free energy	-1099.39
	in the aqueous phase, $\bar{G}_7^0$	
	Partial molar enthalpy	-1196.62
	in the aqueous phase, $\bar{H}_{72}$	
	Molar Gibbs free energy	-1128.76
	in the solid phase, G_7	