A Thermodynamic Model to Predict the Aqueous Solubility of Hydrocarbon Mixtures at Two-Phase Hydrate-Liquid Water Equilibrium

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Understanding the fate and transport of hydrocarbons and hydrocarbon mixtures in the deep sea and underlying sediments requires accurate determination of the two-phase hydrate (H)-liquid water (L_w) thermodynamic equilibrium in the absence of a free gas phase. In addition to controlling hydrate formation directly from the aqueous phase, the H- L_w equilibrium provides the aqueous solubility of dissolving hydrate. The aqueous solubility of hydrocarbon mixture at H- L_w equilibrium was calculated based on the van der Waals and Platteeuw statistical thermodynamic model and the Holder model. Langmuir constants were calculated from cell potential parameters obtained from *ab initio* intermolecular potentials and thus the model contains no fitting parameters. The model accurately predicts pure methane, ethane, and propane experimental H- L_w equilibrium solubility data, including new data provided here for methane. We present hydrocarbon solubilities in water and seawater at H- L_w equilibrium at deep sea conditions for both methane and a thermogenic mixture based on the methane-ethane-propane ratio from the 2010 Macondo oil spill. We also present model predictions of the proportion of occupied large and small cages at H- L_w equilibrium for both systems, as well as hydrocarbon ratios in the hydrate phase for the thermogenic mixture.

Key words: Gas hydrates, Aqueous solubility of hydrocarbon mixtures, Hydrate cage occupancy, Hydrate-Liquid water two-phase thermodynamic equilibrium, Deep sea hydrates

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1.0 Introduction

Gas hydrates are non-stoichiometric crystalline solids formed from mixtures of host water molecules and enclathrated guest molecules under favorable temperature and pressure conditions[1]. In clathrate hydrates, polyhedral cavities (or cages) are formed from a hydrogen-bonded network of water molecules. The cavities are occupied by guest molecules whose presence stabilizes the water lattice through van der Waals forces[1]. Favorable conditions for the formation of naturally occurring hydrates can be found in permafrost regions and cold marine environments. Naturally occurring hydrates are present in vast quantities, primarily contain methane, and are being pursued as an energy source[1-2]. Methane is also a greenhouse gas. Release of large volumes of methane from hydrate instability into the ocean can result in transport to the surface, contributing to global warming[3-5].

Gas hydrates are known to occur in nature in three structural forms: structure I (sI), structure II (sII) and structure H (sH)[1]. Pure methane and pure ethane form sI hydrate, while pure propane and hydrocarbon mixtures form sII hydrate. In nature, biogenic hydrates are predominately methane and form sI hydrate, while thermogenic gas - including natural gas associated with industrial hydrocarbon production - contains a mixture of methane, ethane, propane, and isobutane, and forms sII hydrate. The unit crystal structure of sI hydrate is composed of two smaller pentagonal dodecahedrons (5^{12}) cavities and six larger tetrakaidecahedron ($5^{12}6^2$) cavities, while sII is composed of sixteen smaller 5^{12} cavities and eight larger hexakaidecahedron ($5^{12}6^4$) cavities. Thermodynamic conditions during hydrate formation determine the occupancy of small and large cages by each hydrate former present in the system[1]. At thermodynamic equilibrium hydrate cages are not fully occupied[1]. Instead, large and small cage occupancies change with the thermodynamic conditions. As a result, hydrates are non-stoichiometric molecules. At a molecular scale, bulk hydrate composition is the ratio of enclathrated hydrate-former molecules to lattice water molecules averaged over the complete set of unit lattices composing the bulk crystal. Thus, because thermodynamic conditions during hydrate formation control

the proportion of large and small cages occupied as well as the proportion of each cage type filled by each hydrate former, they also control bulk hydrate composition.

Hydrates can form in the absence of a vapor phase from a single aqueous phase system consisting of liquid water with dissolved hydrate former at appropriate temperature, pressure and dissolved hydrate former concentrations[6-8]. The temperature and pressure dependencies of the solubility of hydrate former in water are different at two-phase liquid water-vapor (L_w -V) equilibrium and two-phase hydrate-liquid water (H- L_w) equilibrium[9-10]. The solubility of hydrate-former in water at L_w -V equilibrium decreases with an increase in temperature at a given pressure, while at H- L_w equilibrium the solubility in water increases with an increase in temperature [7,10-12]. Two-phase H- L_w equilibrium conditions can occur at the same high pressure and cold temperature conditions as the three-phase hydrate-liquid water-vapor (H- L_w -V) equilibrium, which are common to Arctic regions, the deep sea, and underlying sediments. Knowledge of H- L_w equilibria is necessary for studying the formation and accumulation of subsea hydrates[13] and for modeling the dissolution rates of hydrate-covered bubbles through the deep sea[14-16]. The driving force for gas bubble dissolution with or without hydrate is the concentration difference between the hydrocarbon solubility at the interface and the bulk hydrocarbon concentration in the surrounding ocean. Accurate thermodynamic predictions of the solubility of hydrocarbon mixtures in seawater in the presence of hydrate is therefore necessary for modeling the dissolution rate of hydrate-covered bubbles as they transit the ocean. Hydrocarbon bubbles can originate from either natural seeps or from anthropogenic release. Therefore, bubble plume models require accurate thermodynamic predictions of nearly pure methane sI hydrates for biogenic seeps and mixed hydrocarbon sII hydrates for thermogenic seeps and anthropogenic releases.

Most of the available hydrate thermodynamic equilibrium experimental data are three-phase H- L_w -V equilibria[1]. Experimental two-phase H- L_w equilibrium data are comparatively scarce and limited to pure component methane, carbon dioxide, ethane and propane[1,7,10-12,17]. To our knowledge there are no reliable experimental data on the solubility of hydrocarbon mixtures containing

methane-ethane and propane in the aqueous phase at H-L_w equilibrium. Similarly, predictive solubility models of hydrate-forming species at H-L_w equilibrium have been limited to single components in water[6,9,11,18-20].

Hashemi et al.[9] developed a model for the calculation of methane solubility in water at H-L_w equilibrium based on the van der Waals and Platteeuw model. They used the Trebble-Bishnoi equation of state for fugacity calculations. Their model readjusts the reference chemical potential and reference enthalpy difference parameters with three phase H-L_w-V equilibrium experimental data to improve the accuracy of the model. When the parameters are fitted to the H-L_w-V experimental data, the model works well within the range of the fit, but fails when extended outside the range of fit and also for mixed hydrates[21], this will also be true for H-L_w system.

The Langmuir constant, which accounts for guest-host interactions, is an important term in the van der Waals and Platteeuw model. Parrish and Praustniz[22] used a spherical core Kihara-type potential to describe the interactions between a guest and surrounding water molecules. These Kihara potential parameters were obtained by empirical fitting to H-L_w-V equilibrium pressures. However, the parameter set of Parrish and Praustniz fails to accurately predict equilibrium pressures for gas mixtures and for pure components outside the range of the fitted data[23-25]. The use of these Langmuir constants by Mohammadi and Richon[19] in their H-L_w equilibrium model may account for deviations in their model's predictions from H-L_w experimental data. The Langmuir constant calculation has had several significant improvements including guest-host interactions beyond the first shell, evaluation of the full configurational integral and more realistic guest-host intermolecular potentials[25-27]. Sun and Duan[18] predicted the solubility of methane in water at H-L_w equilibrium using the van der Waals and Platteeuw model and angle-dependent *ab initio* intermolecular potentials. Their model prediction of methane solubility is as good as our model for methane, but does not predict ethane, propane, or mixed hydrate H-L_w equilibria. There are also other models for H-L_w equilibrium,[7-8,28] but these models require considerable efforts to fit experimental data. A recent detailed review of aqueous methane

solubility at H-L_w equilibrium conditions showed good agreement between experimental data and predictions from existing “off the shelf” thermodynamic models[20].

The objective of this work is to develop an accurate model with no fitting parameters to determine the solubility of pure hydrocarbons and methane-ethane-propane mixtures in water, when in equilibrium with hydrates (H-L_w). The van der Waals and Platteeuw[29] and the Holder et al.[30] models were employed to calculate the chemical potential of water in the hydrate and liquid phases respectively. The fugacity of each hydrocarbon hydrate former in the liquid water phase was calculated using the Poynting correction approach[6]. Langmuir constants were obtained from cell potential parameters. We have used different reference chemical potential difference parameters and reference enthalpy difference parameters for each guest molecule, and used hydrate composition-weighted reference parameters for hydrocarbon mixtures. Model predictions are compared with the available experimental data for pure methane, ethane and propane guest molecules solubility at H-L_w equilibrium. The solubility of a methane-ethane-propane mixture in water at H-L_w equilibrium is also predicted with the model.

2.0 Thermodynamic model

The thermodynamic model presented here is an extension and modification of a model we previously presented[31-33] that was limited in application to H-L_w-V. The method for predicting equilibrium is based on the criterion that the chemical potentials, μ , of each component in the coexisting phases are equal. So at equilibrium for water:

$$\mu_w^H(T, P) = \mu_w^L(T, P) \quad (1)$$

where $\mu_w^H(T, P)$ is the chemical potential of water (w) in the hydrate phase (H), and $\mu_w^L(T, P)$ is the chemical potential of water in the water rich liquid phase (L) at a given temperature, T , and pressure, P . Using the chemical potential of a hypothetical empty hydrate lattice, μ_w^β , as a reference condition, the equilibrium condition can be written as given in Eq. 2,

$$\Delta\mu_w^{\beta-H} = \Delta\mu_w^{\beta-L} \quad (2)$$

where $\Delta\mu_w^{\beta-H} \equiv \mu_w^\beta - \mu_w^H$, and $\Delta\mu_w^{\beta-L} \equiv \mu_w^\beta - \mu_w^L$.

The statistical thermodynamic model proposed by van der Waals and Platteeuw[29] for $\Delta\mu_w^{\beta-H}$, the difference in chemical potential of water in the empty hydrate lattice (μ_w^β) and that in filled hydrate lattice, is given as:

$$\Delta\mu_w^{\beta-H} = -RT \sum_{j=1}^2 v_j \ln(1 - \sum_i \theta_{ji}) \quad (3)$$

where R is the universal gas constant, T is the absolute temperature, reported in Kelvin throughout this paper, v_j is the number of j -type cavities per water molecule, and θ_{ji} is the fractional occupancy of j -type cavities occupied with i -type guest molecules. The cage occupancy, θ_{ji} , is calculated as given in Eq. 4

$$\theta_{ji} = \frac{C_{ji}f_i}{1 + \sum_i C_{ji}f_i} \quad (4)$$

where C_{ji} is the temperature-dependent Langmuir constant for hydrate forming species i in cavity j and f_i is the fugacity of hydrate forming species i in the phase with which the hydrate phase is in equilibrium. Langmuir constant and fugacity calculations are discussed in dedicated sections below.

The chemical potential difference, $\Delta\mu_w^{\beta-L}$, between the water in the hypothetical empty hydrate lattice and water in the liquid-rich phase is given by Holder et al.[30] as

$$\frac{\Delta\mu_w^{\beta-L}(T,P)}{RT} = \frac{\Delta\mu_w^0(T_0,0)}{RT} - \int_{T_0}^T \frac{\Delta H_w^{\beta-L}}{RT^2} dT + \int_0^P \frac{\Delta V_w^{\beta-L}}{RT} dP - \ln a_w \quad (5)$$

$\Delta\mu_w^0(T_0, 0)$ is the reference chemical potential difference between a hypothetical empty hydrate lattice and pure water at a reference temperature, T_0 , and zero absolute pressure. The reference temperature (T_0) is taken here as the ice point temperature, 273.15 K, for pure ethane and propane hydrates, and for pure methane hydrate, T_0 is taken as 272.9 °C[1]. The slight depression in the ice point temperature for methane hydrate is due to the solubility of methane in water. The temperature-dependent enthalpy difference between the empty hydrate and liquid water, $\Delta H_w^{\beta-L}$, is given by Eq. 6

$$\Delta H_w^{\beta-L} = \Delta H_w^0(T_0) + \Delta H_w^{\alpha-L}(T_0) + \int_{T_0}^T \Delta C_P dT \quad (6)$$

where $\Delta H_w^0(T_0)$ is the reference enthalpy difference between the empty hydrate lattice and a pure ice phase, denoted by α , at the reference temperature T_0 , $\Delta H_w^{\alpha-L}(T_0)$ is the latent heat of converting ice to liquid water, and ΔC_P is the heat capacity difference between the empty hydrate lattice and the pure water phase. The reference chemical potential and enthalpy differences, $\Delta\mu_w^0$ and ΔH_w^0 , vary with the size of each guest molecule as there is an increase in the lattice distortion with increasing guest molecule size.[34-35] Therefore, variable reference parameters were used to account for lattice distortion for each guest in each hydrate structure, instead of using the same reference parameter corresponding to hydrate structure for all the guests. Our group developed correlations for $\Delta\mu_w^0$ and ΔH_w^0 for each guest that are similar to the functional forms of Lee and Holder.[36] These correlations are a function of the molecular diameter of the guest, d_g . Garapati et al.[33,37] obtained correlation parameters using regression analysis on *ab initio* calculated reference parameters, $\Delta\mu_w^0$ and ΔH_w^0 , of CO₂[31-32] and CH₄[38] for sI hydrate and Ar[38] and N₂[37] for sII hydrate. The correlations for $\Delta\mu_w^0$ (J/mol), and ΔH_w^0 (J/mol) based on the guest size (d_g in Å) are given in Eq. 7 and 8 for sI and in Eq. 9 and 10 for sII.

$$\text{Structure I} \quad \Delta\mu_w^0 = 1197.279 \exp(0.0010933 d_g) \quad (7)$$

$$\Delta H_w^0 = 1061.589 \exp(0.0010933 d_g) \quad (8)$$

$$\text{Structure II} \quad \Delta\mu_w^0 = 974.033 \exp(0.026446 d_g) \quad (9)$$

$$\Delta H_w^0 = 1044.658 \exp(0.056329 d_g) \quad (10)$$

The reference parameters for mixed hydrates are calculated from the pure components using the following mixing rules:

$$\Delta\mu_{w,mix}^0 = \sum_i^N \Delta\mu_{w,i}^0 z_i \quad (11)$$

$$\Delta H_{w,mix}^0 = \sum_i^N \Delta H_{w,i}^0 z_i \quad (12)$$

where N is the number of guest components and z_i is the molar composition, of the i^{th} component in the hydrate phase on a water-free basis.

The heat capacity difference between the empty hydrate lattice and the pure water phase, ΔC_p , is also temperature dependent and is approximated as:

$$\Delta C_p = \Delta C_p^0(T_0) + b(T - T_0) \quad (13)$$

where $\Delta C_p^0(T_0)$ is the reference heat capacity difference between the empty hydrate and pure water phases at T_0 . The constant b represents the dependence of heat capacity on the temperature.

$\Delta V_w^{\beta-L}$ is the volume difference between an empty hydrate lattice and a pure water phase, is assumed to be constant for a hydrate structure. $\Delta V_w^{\beta-L}$ is calculated with reference to an ice phase as $\Delta V_w^{\beta-L} = \Delta V_w^{\beta-\alpha} + \Delta V_w^{\alpha-L}$, where $\Delta V_w^{\beta-\alpha}$ and $\Delta V_w^{\alpha-L}$ are the volume differences between an empty hydrate lattice and pure ice, and ice and liquid water respectively. The last term in Eq. 5 is the activity of water, a_w , defined as $a_w \equiv f_w^L / f_w$, where f_w^L is the fugacity of water in the water-rich aqueous phase and f_w is the water fugacity at the reference state, the pure water phase. Values of reference parameters used in this work are given in Table 1.

2.1 Langmuir constant calculation

The accuracy of the van der Waals and Platteeuw statistical thermodynamic model is most sensitive to the Langmuir constant term, C_{ji} . Most previous models for hydrates calculated the Langmuir constant from the Kihara potential model, with parameters arbitrarily adjusted to experimental phase equilibrium data. These potentials are aphysical and fundamentally not based on guest-host interactions. They work well within the range of the experimental data, but fail when extended outside, such as when applied to mixed hydrate[21]. C_{ji} is defined for a non-linear and non-spherical guest molecule as:

$$C_{ji} = \frac{z_{ji}}{kT} = \frac{1}{8\pi^2 kT} \int_V \exp\left(-\frac{\Phi(r, \theta, \phi, \alpha, \beta, \gamma)}{kT}\right) r^2 \sin \theta \, dr \, d\theta \, d\phi \, d\alpha \, d\beta \, d\gamma \quad (14)$$

where k is the Boltzmann constant and Z_{ji} is the full configurational integral, which depends on the total interaction potential, Φ , between the guest molecule and the host molecules surrounding it[26,38]. The total interaction potential, $\Phi = \sum \Phi_{ij}$, is pair-wise additive between the guest molecule and the surrounding water molecules and guest molecules. The contributions from guest-guest interactions are generally small and do not contribute much to the Langmuir constant calculations. However it was shown for methane hydrates that the guest-guest interactions can affect the total interaction energy[39-40]. The Langmuir constants used in this work were developed assuming on guest-guest interactions. These Langmuir constants with the van der Waals and Platteeuw thermodynamic model frame work were able to predict the three phase hydrate equilibrium very well[33,41]. Therefore, in this work the guest-guest interactions were not included in the calculation of Langmuir constant. Z_{ji} is a function of the polar coordinates r, θ, ϕ , of the center of mass of the guest molecule and the Euler angles, α, β, γ , that describe its orientation with respect to the hydrate lattice. The full configurational integral (Eq. 14) must be evaluated to accurately represent the total interaction potential[26]. Anderson et al.[38] calculated Langmuir constants from site-site *ab initio* intermolecular potentials by calculating the full six-dimensional integral for methane hydrates over five hydrate shells. The resulting Langmuir constants, computed from *ab initio* data, are fitted to the van't Hoff temperature dependence functional form[21], given by Eq. 15:

$$C_{ji}(\beta) = C_{0ji} \exp(m_{ji}\beta) \quad (15)$$

where the parameter β is defined as $\beta = 1/kT$, and C_{0ji} and m_{ji} are cell potential parameters that are specific to the guest molecule i and the cavity j occupied. The Langmuir constant is expressed in a temperature-dependent functional form to avoid evaluating the rigorous integral (Eq. 14) for each calculation.

For hydrate-forming species that occupy only the large cages of the two sets of cavities, e.g. ethane and propane, cell potential parameters can be obtained directly from experimental dissociation

data using the variable reference parameters given in Eqs. 7-8 and 9-10 for sI and sII respectively[21,37,42]. The cell potential parameters for each guest molecule used in this work are given in Tables 2 and 3 for sI and sII hydrates respectively.

2.2 Fugacity of hydrocarbon species in the aqueous phase

At three-phase H-L_w-V equilibrium, the fugacity of the hydrate-forming species, f_i , in the hydrate (f_i^H), liquid (f_i^L), and vapor (f_i^V) phases are equal:

$$f_i^H = f_i^L = f_i^V \quad (16)$$

The fugacity of the pure gas or gas mixture (f_i^V) can be calculated from a *PVTN* equation of state. In this work the Peng-Robinson equation of state[43] is used to calculate the vapor phase fugacity of the hydrate forming species..

At the two-phase H-L_w equilibrium where there is no vapor phase, the hydrate and liquid water phase fugacities of each hydrate-forming species are equal:

$$f_i^H = f_i^L \quad (17)$$

When only a single aqueous phase is present, the fugacity of each hydrocarbon is calculated using the thermodynamic method described by Holder et al.[6] as:

$$f_i^L(T, P, x_i) = f_i^{sat} \exp \left[\int_{P^{sat}}^P \frac{\bar{V}_i dp}{RT} \right] \quad (18)$$

where $\bar{V}_i$ is the partial molar volume of species i in the water phase, P^{sat} is the saturation pressure corresponding to a given solubility x_i , and f_i^{sat} is the fugacity of hydrocarbon at P^{sat} . We follow the common assumption that $\bar{V}_i$ is constant, and Eq. 18 can be modified as:

$$f_i^L(T, P, x_i) = f_i^{sat} \exp \left[\frac{\bar{V}_i(P - P^{sat})}{RT} \right] \quad (19)$$

$\bar{V}_i$ is corrected for temperature with reference to a standard state of 298 K using the approximation[44]:

$$\bar{V}_i(T) = \bar{V}_i(298 \text{ K}) \frac{V_w^0(T)}{V_w^0(298 \text{ K})} \quad (20)$$

where $V_w^0(T)$ and $V_w^0(298\text{ K})$ are the molar volume of water, $\bar{V}_l$ at 298 K for methane[45], ethane[46], and propane[46] are 0.0398, 0.0530, and 0.0710 m³/kmol, respectively. Henry's law is used to calculate the solubility of hydrocarbon in water, and Eq. 19 is modified as:

$$f_i^L(T, P, x_i) = \gamma_i x_i H_{iw} \exp \left[\frac{\bar{V}_l(P - P^{sat})}{RT} \right] \quad (21)$$

where γ_i and H_{iw} are the activity coefficient and Henry's constant of each hydrate forming species i . γ_i are taken as unity for pure water and for seawater are discussed in the seawater section below. H_{iw} in bars) for methane[44], ethane[47] and propane[48] are given in Eqs. 22, 23 and 24 respectively:

$$H_{iw} = \exp \left(5.135 + \frac{7837}{T} - \frac{1.5090 \times 10^6}{T^2} + \frac{2.06 \times 10^7}{T^3} \right) \times 0.01 \quad (22)$$

$$H_{iw} = 10^{151.901 - \frac{5768.3}{T} - 51.8593 \log T + 0.01741 T} \quad (23)$$

$$H_{iw} = \exp \left(552.64799 + 0.078453 T - \frac{21334.4}{T} - 85.89736 \ln T \right) \times 0.01 \quad (24)$$

P^{sat} occurs at the V-L_w phase boundary, i.e. the pressure required to obtain a given solubility x_i . The fugacities at V-L_w equilibrium are calculated using the Peng Robinson equation of state for the hydrocarbon rich phase and by the Henry's constant for the liquid water phase at a given solubility x_i .

2.3 Activity of water and activity coefficients in seawater

The solubilities of methane, ethane and propane in water are small, so we assume that the activity coefficient of water (γ_w) does not change with these gases and is taken as unity for pure water.

The activity of water (a_w) is given as

$$a_w = \gamma_w x_w = 1 - \sum_i x_i \quad (25)$$

where x_w is the mole fraction of water in the aqueous phase and x_i is the hydrocarbon solubility in pure water. The summation is performed over all the guest molecules present.

The presence of electrolytes in liquid water will change the activity of water and the solubility of hydrocarbons. The presence of electrolytes will not change the chemical potential of water in the hydrate phase, as they cannot enter the hydrate lattice. However, by changing the activity, and therefore

the chemical potential, of liquid water, electrolytes affect the hydrate thermodynamic equilibrium (Eq. 5). We model the activity of water in seawater using the Pitzer[49] model and is given as:

$$\ln a_w = -\phi M_{H_2O} \sum_i m_i \quad (26)$$

where m_i is the molality (mol/kg) of ions and M_{H_2O} is the molecular weight of water. ϕ is the osmotic coefficient. For completeness we include the equations and constants[50] used in the model in the Appendix. The aqueous solubilities of non-electrolytes such as alkanes are dependent on the concentration and type of salts present in solution. The activity coefficient of each neutral hydrocarbon species in electrolyte solutions, γ_i , is calculated from the Setschenow equation:

$$\ln \gamma_i = \sum_s k_s m_s \quad (27)$$

where k_s is the salting in or salting out coefficient and m_s is the molality of each salt species s . The Setschenow coefficients for methane[51], ethane[51] and propane[52] are given in Table 4. The propane activity coefficient is calculated using a brine of the specified salinity composed of NaCl and KCl at the NaCl:KCl ratio found in seawater. Seawater is typically approximately 3.5 wt% ions (35 salinity); the molalities of the major ions in seawater [53] are given in Table 5.

3.0 Methods

3.1 Experiments

Experiments to determine the H-L_w equilibrium conditions (T and P) of methane dissolved in fresh water were conducted in a stirred, 100-mL autoclave in a manner similar to that previously described to measure H-L_w equilibria for CO₂ in fresh water and artificial seawater[11]. Aqueous hydrocarbon concentrations were determined from the initial volumes of water and gas added to the autoclave. Water was purified by reverse osmosis and deionization (18 megaohm-cm). Densities of water and methane (99.99% purity) were obtained from the online NIST Webbook[54].

After filling and equilibration, the autoclave was then cooled and heated in an environmental chamber to form and then decompose the hydrate, respectively. This is referred to as one cycle, which was performed with a stirring speed of either 800 or 1000 rpm. The system was cooled and equilibrated from room temperature to just above 0 °C in less than 12 h. Hydrate would sometimes not form during cooling. When this occurred, the stirring was momentarily increased by 200 rpm, which caused hydrate to form. Heating was then staged to approach the H-L_w equilibrium point at 0.3 °C/h and to pass through it at 0.1°C/h. After this, the temperature was increased at 0.3 °C/h until the system was above the H-L_w-V point. Examples of three cooling and heating cycles from one experiment are shown in Figure 1. The cooling trend corresponds to the compressibility of the single phase system until hydrate formation occurs and the pressure decreases rapidly (approx. 1 MPa/min) at nearly constant temperature, as shown in Figure 1.

The H-L_w equilibrium point occurs when the heating curve returns to the cooling curve, which is indicated in Figure 1. As in the previous work with CO₂, the H-L_w equilibrium point is more accurately determined from a plot of dP/dT versus T, as shown in Figure 2 for the cycles shown in Figure 1. The specific heating rates are shown, as well as a vertical line representing the H-L_w-V equilibrium temperature. The smooth transition through the H-L_w-V point indicates no undissolved methane was present in the system. Also, note that the presence of a vapor phase would shift the divergence of the traces in Figures 1 and 2 to the H-L_w-V equilibrium temperature.

3.2 Model Implementation Algorithm

The solubility of the hydrocarbon (x_i) in water at H-L_w two-phase equilibrium is calculated by solving Eq. 2 for a given pressure (P) and temperature (T) by an iterative procedure (x_i from PT). First an initial guess is made for x_i , and the saturation pressure, P^{sat} , is calculated corresponding to x_i . Next we calculate the aqueous-phase hydrocarbon fugacity, f_i^L , from Eq. 21 and substitute to calculate

$\Delta\mu_w^{\beta-H}$ from Eqs. 3 and 4. Finally the pressure is calculated using Eqs. 2 and 5. If the relative difference between the calculated pressure and the specified pressure is within the tolerance limit then x_i is taken to be the solubility at that pressure and temperature. The tolerance limit for the results presented here was a normalized difference in pressures of 0.1%. If the pressure difference is outside the tolerance limits, then the guessed x_i is updated proportionally to the normalized difference in pressures and the procedure is repeated. Obtaining a unique solution for a hydrocarbon mixture requires specifying the molar ratio of the hydrocarbon species and then solving for total hydrocarbon solubility. To calculate equilibrium pressure for a given temperature (T) and solubility (x_i), i.e. P from Tx , we modify the algorithm accordingly. We guess an initial value for pressure rather than solubility, P^{sat} is calculated from the specified, not guessed, x_i , and the pressure-tolerance condition is based on comparing the guessed and calculated pressures rather than the calculated and specified pressures.

4.0 Results and Discussion

4.1 Experimental Results

The H-L_w equilibrium P and T conditions are shown in Table 6 for the two dissolved methane concentrations investigated. The data for the individual cycles are shown along with their respective averages. In one case, the experiment was able to be performed at two different pressures by releasing a small amount of the gas/water mixture through a series of valves as previously described[11]. The percent absolute deviations from concentrations calculated by the correlation of Lu et al. [12], and the model developed here are also shown. The percent absolute relative error (ARE) for these three data points respective to the model of Lu et al. and the model developed here are 4.13% and 1.05%, respectively.

The absolute relative error (ARE) and average absolute relative error (AARE) values with respective experimental and predicted results are calculated using Eq. 28 and Eq. 29 respectively.

$$\%ARE = \left(\frac{|experimental - predicted|}{experimental} \right) \times 100 \quad (28)$$

$$\%AARE = \frac{1}{N} \sum_1^N \left(\frac{|experimental - predicted|}{experimental} \right) \times 100 \quad (29)$$

4.2 H-L_w Equilibrium for Pure Components

Limited experimental data are available in the literature for the solubility of hydrocarbons in water at H-L_w equilibrium for comparison to the model's predictions. For the solubility of methane in water (x_{CH_4}) at H-L_w equilibrium, the data by Lu et al.[12], Servio and Englezos[10], Kim et al.[7] and Seo and Lee[55] are considered reliable[20,56]. Other experimental data[28] have been found to be erroneous when compared with other literature data and model predictions[7,12,56], and therefore are not used to evaluate the model accuracy in this work.

Comparison of the model predictions of x_{CH_4} with the four experimental data sets is given in Table 7. The model with no adjustable parameters predicts methane solubility for two phase H-L_w equilibrium with an AARE of 3.64 % for Servio and Englezos,[10] 5.82 % for Kim et al.[7], 6.92 % for Lu et al.[12], and 8.52 % for Seo et al.[55]. The predicted results are in agreement with the experimental data. Lu et al.[12] measured x_{CH_4} at H-L_w equilibrium using *in situ* Raman spectroscopy at deep sea pressures (10-40 MPa) and temperatures (276.55-294.55 K), and made more measurements of x_{CH_4} than all the other datasets combined[20]. Predictions from their simple expression for x_{CH_4} at H-L_w equilibrium as a function of P and T have been shown to be as good as any of the more complex models[20], making their model useful for comparative purposes for deep sea x_{CH_4} predictions. The solubility predictions by our model and the expression given by Lu et al.[12] are compared in Figure 3. Each nearly-vertical line in Figure 3 is the two-phase H-L_w equilibrium for an aqueous CH₄ concentration, or equivalently the solubility, for a series of pressure/temperature conditions.

Cage occupancy, the fraction of each type of cage occupied by each guest molecule, of hydrate at a temperature and pressure must be known to fully understand the thermodynamics of hydrate

formation and decomposition and to predict hydrate material properties such as bulk composition and density. θ_L and θ_S are calculated in Eq. 4 at a given P and T . The solubility of methane increases with increasing temperature and decreases with increasing pressure, while the effect of pressure on the solubility of methane in water in equilibrium with hydrate is small at a given temperature compared to the effect of temperature on the methane solubility at a given pressure. Methane forms sI hydrate and occupies both small and large cages. Direct measurements of cage occupancy are not available, but Huo et al.[57] and Seo et al.[55] have used Raman spectroscopy to measure the cage occupancy ratio (θ_L/θ_S) for methane hydrate at H-L_w equilibrium conditions. Table 8 shows θ_L/θ_S experimental data and predictions from this model and the Sun and Duan[18] model. Figure 4 shows that while both θ_L and θ_S increase with increasing pressure or temperature, their ratio, θ_L/θ_S , decreases with either increasing pressure or temperature (Figure 5). From figure 4, we can see that the large cage is almost fully occupied and when the temperature or pressure is increased, methane occupies more of small cages than large cages. Thus the θ_L/θ_S decreases with increase in temperature or pressure. This is similar to the trend predicted by Sun and Duan.[18]

Model predictions of the solubility of ethane in water at H-L_w equilibrium are compared to the limited available experimental data[7,58-59] in Table 9. For the data of Kim et al.[7,58], the prediction shows ARE less than 15% and the AARE is 11.5%. The high ARE for the Yang[59] data are likely due to the unreliability of the experimental data[19], with significant disagreement in P - T - x trends relative to the later Kim et al.[7,58] data sets from the same laboratory (Table 9).

There is only one experimental dataset for the solubility of propane in water at H-L_w equilibrium. Table 10 shows the experimental data measured by Gaudatte and Servio[17] and the corresponding predictions of this model. The model predictions have an AARE of 6.5% from the experimental data. Relative to the experimental uncertainties, this model is able to predict pure hydrocarbon solubility in water in equilibrium with a hydrate phase.

4.3 H-L_w Equilibrium for Mixed Components

A primary motivation for this work is to model prediction of the solubility of thermogenic hydrocarbon mixtures in the deep sea. Unfortunately, to our knowledge there are no experimental data available in the literature for hydrocarbon mixtures at two-phase H-L_w equilibrium conditions for model comparison. To demonstrate the model's ability to predict H-L_w conditions for hydrocarbon mixtures we calculated the solubility of a mixture for a representative thermogenic hydrocarbon mixture in fresh and seawater. Seawater results are discussed in a separate section below. For a representative thermogenic mixture, we selected the hydrocarbon composition of the Gulf of Mexico Macondo well[60-61], limited to the lightest three alkanes: 87.5% methane (C₁), 8.1% ethane (C₂), and 4.4% propane (C₃) molar concentrations. This C₁C₂C₃ mixture is also being used in ongoing laboratory experiments[62-63]. Figure 6 shows the prediction of $x_{C_1C_2C_3}$ at H-L_w equilibrium as well as the H-L_w-V equilibrium curve. These mixed hydrate predictions were made without any parameter fitting to any mixed hydrate data. It was shown for H-L_w-V system that the guest-guest interactions can have a significant effect on the Langmuir constant calculations and can influence the mixed hydrate phase equilibrium predictions[40]. This influence is also depends on the type of the guest molecules and the compositions used. In this model, the guest-guest interactions were not included in the prediction of two phase H-L_w predictions. The guest molecules considered in this work has weak guest-guest interactions but we cannot possibly rule out their influence in the prediction of H-L_w phase equilibrium. In order to have a true sense of how much these guest-guest interactions effect the H-L_w phase equilibrium predictions, the model predictions await experimental confirmations. Mixed hydrates form at lower pressures than pure methane hydrate and require lower hydrocarbon concentrations for hydrate formation (compare Figures 3 and 6) due to sII formation and increased large cage stabilization from the small amount of propane[1].

Mixtures of light alkanes form sII hydrate; the 16 small cages are occupied solely by methane while the eight large cages can be occupied by methane, ethane and propane. θ_S , θ_L , for each hydrocarbon are shown in Figure 7. Propane occupies 80-95% of the large cages, with the balance of large cages largely occupied by ethane, and only a small amount of methane (<2%). At lower $x_{C_1C_2C_3}$, the comparatively higher pressures needed for hydrate formation drive more hydrocarbon into the hydrate phase, resulting in increased θ_S and θ_L . The increase in θ_L is less than that for θ_S , primarily because the large cages are always nearly fully occupied. θ_S increases with increasing temperature, though $x_{C_1C_2C_3}$ in the coexisting liquid decreases (Figure 6). Figure 8 shows the mole fraction of each hydrocarbon in the hydrate phase. As either solubility decreases or temperature increases, the increase in pressure needed for hydrate stability increases methane occupancy of the 16 small cages (Figure 7), resulting in a net increase in the mole fraction of methane in the hydrate phase. The opposite is true for ethane, which is displaced by propane: Figure 7 shows that the decrease in large cage occupancy by ethane corresponds to an increase in propane occupancy, resulting in the decrease in the mole fraction of ethane shown in Figure 8.

4.4 H-L_w Equilibrium in Seawater

Salt concentration and species influence the solubility of hydrocarbons in water, altering H-L_w equilibria. H-L_w equilibrium phase diagrams were calculated for methane and the C₁C₂C₃ mixture in 35 salinity seawater and are given in Figures 6 and 9 to enable comparison to their respective fresh water phase diagrams. Also shown in Figures 6 and 9 are the seawater H-L_w-V equilibrium curves calculated using our model. Relative to the fresh water system, at a given x_i hydrates can form in seawater at lower pressures or higher temperatures. I.e., in the two-phase hydrate-liquid water equilibrium system, salt in seawater promotes hydrate formation rather than acting as an inhibitor. This phenomenon was first observed and described by Zhang et al.[11] in their experimental and theoretical study of the two-phase CO₂ hydrate-liquid water system. The opposite is well known in the three-phase H-L_w-V system

where salts acts as an inhibitor to hydrate formation, requiring higher pressures for hydrate formation compared to a fresh water system: compare the H-L_w-V equilibrium curves for seawater and pure water in Figures 6 and 9. For the hydrates formed from V-L_w system (three phase H-L_w-V equilibrium), the presence of salts in the seawater lowers the activity of water (a_w) in the aqueous phase. The reduction in a_w reduces the chemical potential of liquid water making the liquid phase more stable than hydrate phase at a temperature and pressure. The chemical potential of the hydrocarbon in the aqueous phase will not change as it has to be equal with the vapor phase chemical potential (salts do not enter in to the vapor phase); instead it reduces the solubility of hydrocarbon in aqueous phase to keep the chemical potential equal for V-L_w system. Therefore, the presence of salts inhibit the hydrate formation from the V-L_w system. In the case of hydrate formation from two phase H-L_w system there is no vapor phase present. When salts are added, the chemical potential of the hydrocarbons in the aqueous phase increases. As there is no vapor phase for the x_i value to change unlike in the V-L_w system the vapor phase acts as a source or a sink. Also the chemical potential of water in aqueous phase is reduced due to the presence of salts. But the reduction in the aqueous chemical potential is more than compensated by the increase in the hydrocarbon chemical potential in the aqueous phase causing the hydrate to be a stable phase, and thus salts promote hydrate formation in the H-L_w conditions[11]. As a result, for a given pressure and temperature, hydrates are formed at lower aqueous hydrocarbon concentrations in brine relative to the fresh water system.

5.0 Conclusions

A model with no fitting parameters has been used to calculate two-phase hydrate-liquid water equilibrium. The model is based on the van der Waals and Platteeuw and Holder models, solving for the equality of chemical potential differences. Variable reference chemical potential and enthalpy differences were used for each guest molecule and Langmuir constants were calculated from cell

potential parameters based on *ab initio* calculations, thus obviating the need for fitting parameters. Model predictions were within 3% of the limited pure hydrocarbon H-L_w equilibrium solubility experimental data. Phase diagrams, cage occupancies, and hydrate composition are presented for methane and a methane-ethane-propane mixture in fresh and sea water. Predicted cage occupancies increase with increasing temperature or pressure, while the predicted large cage to small cage occupancy ratio decreases with increasing temperature or pressure. The model results agree with previous experimental and theoretical observations that salt promotes hydrate formation relative to fresh water for the H-L_w system.

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Table 1: The values of reference properties for structure I and structure II hydrates

	Structure I		Structure II		Source
Component	$\Delta\mu_w^0$ (J/mol)	ΔH_w^0 (J/mol)	$\Delta\mu_w^0$ (J/mol)	ΔH_w^0 (J/mol)	
Methane	1203.00	1170.00	1093.07	1337.89	[38]
Ethane	1204.50	1195.59	1126.52	1431.90	[33]
Propane	-	-	1150.00	1488.00	
$\Delta V_w^{\beta-\alpha}$ (m ³ /mol)	3.0×10^{-6}		3.4×10^{-6}		[64]
$\Delta V_w^{\alpha-L}$ (m ³ /mol)	1.598×10^{-6}				[64]
$\Delta H_w^{\alpha-L}$ (J/mol)	-6009.5				[64]
$\Delta C_p^{\beta-L}$ (J/mol/K)	$-37.32 + 0.179 (T - T_0)$				[30]

Table 2. Cell potential parameters for structure I hydrate

	Small Cage		Large Cage	
Component	$\ln C_0$	m	$\ln C_0$	m
Methane	-11.6900	5.6454	-10.2200	5.6650
Ethane	-	-	-12.5402	8.2236
Propane	-	-	-	-

Table 3. Cell potential parameters for structure II hydrates

	Small Cage		Large Cage	
Component	$\ln C_0$	m	$\ln C_0$	m
Methane	-11.689	5.5140	-8.6930	4.9616
Ethane	-	-	-10.9615	8.9579
Propane	-	-	-14.8015	12.4594

Table 4. Salting coefficients for methane[51], ethane[51] and propane[52] in electrolyte solution at 25 °C

Salts	k_s, CH_4	$k_s, \text{C}_2\text{H}_6$	$k_s, \text{C}_3\text{H}_8$
NaCl	0.319	0.391	0.216
Na ₂ SO ₄	0.836	1.26	
KCl	0.233	0.375	0.121
NaHCO ₃	0.468	0.586	
CaCl ₂	0.497	0.723	
MgCl ₂	0.435	0.659	

Table 5. Molality (mol/kg H₂O) of ions in 35 wt % seawater

Ions	Molality
Na ⁺	0.4850
Mg ²⁺	0.0552
Ca ²⁺	0.0106
K ⁺	0.0106
Cl ⁻	0.5658
SO ₄ ²⁻	0.0293
HCO ₃ ⁻	0.0024

Table 6. Experimental results for H-L_w equilibrium conditions at two different concentrations of methane dissolved in water.

			x_{CH_4}	Absolute Relative Error, %	
Cycle	T, K	P, MPa	This work	Lu, et al.*	This work
<u>$x_{CH_4}=0.00144$ mole fraction</u>			1.444E-03	2.16	0.27
I	278.94	17.18			
II	278.84	17.16			
III	278.96	17.20			
IV	278.96	17.19			
Average	278.93	17.18			
Std Dev	0.06	0.015			
<u>$x_{CH_4}=0.00210$ mole fraction</u>			2.083E-03	4.41	0.81
I	284.80	18.54			
II	284.56	18.45			
III	284.58	18.44			
Average	284.65	18.48			
Std Dev	0.13	0.055			
<u>$x_{CH_4}=0.00210$ mole fraction</u>			2.048E-03	5.83	2.48
I	283.55	8.64			
II	283.75	8.75			
Average	283.65	8.69			
Abs. Dev.	0.10	0.055			

*With respect to x calculated from the correlation of Lu et al.[12]

Table 7. Experimental methane solubility data at H-L_w equilibrium

T range (K)	P range (MPa)	Number of points	Reference	% AARE
274.15-286.15	6.0-20.0	13	[55]	8.52
274.35-280.15	3.5 - 6.5	6	[10]	3.64
276.20-281.70	5.0-14.4	16	[7]	5.82
276.55-294.55	10.0-40.0	17	[12]	6.92

$$\%AARE = \frac{1}{N} \sum_{i=1}^N \left(\frac{experimental - predicted}{experimental} \right) \times 100$$

Table 8. Occupancy ratio, (θ_L/θ_S) , of methane sI hydrate at H-L_w equilibrium

Temperature (K)	Pressure (MPa)	Experimental value (θ_L/θ_S)	Sun and Duan[18]	This model
274.15	10	1.053[55]	1.066	1.099
275.15	30	1.167[57]	1.050	1.078

Table 9. Solubility of ethane in water at H-L_w equilibrium

Temperature (K)	Pressure (MPa)	Experimental mole fraction, $x_{C_2H_6} \times 10^4$	This model $x_{C_2H_6} \times 10^4$	%ARE
Experimental data from Yang et al.[59]				
273.10	51	4.12	3.40	17.48
277.82	101	4.12	2.56	37.86
278.46	151	4.12	1.94	52.91
Experimental data from Kim et al.[7]				
277.3	10.1	4.37	3.79	13.27
277.8	15.1	4.37	3.84	12.13
278.5	20.1	4.37	3.96	9.38
Experimental data from Kim et al.[58]				
277.7	10.1	3.53	3.93	11.33
278.9	10.1	4.00	4.38	9.50
280.0	10.1	4.50	4.84	7.56
278.4	15.1	3.54	4.05	14.41
279.5	15.1	3.97	4.48	12.85
280.7	15.1	4.52	4.99	10.40

$$\% \text{ Absolute Relative Error (ARE)} = \left(\frac{\text{experimental} - \text{predicted}}{\text{experimental}} \right) \times 100$$

Table 10. Solubility of Propane in water at H-L_w equilibrium.

Temperature (K)	Pressure (MPa)	Experimental[17]	This model	%ARE
		Mole fraction, $x_{C_3H_8}, \times 10^4$	Mole fraction, $x_{C_3H_8}, \times 10^4$	
274.16	0.301	1.440	1.443	0.21
274.23	0.253	1.439	1.458	1.32
274.33	0.358	1.546	1.483	4.08
275.20	0.302	1.572	1.704	8.40
275.20	0.352	1.572	1.704	8.40
276.16	0.355	1.642	1.890	15.10

Figure 1: Pressure versus temperature history for three cycles of an experiment in which hydrates were formed and decomposed in a single-phase solution with a methane mole fraction of 0.00210. Arrows indicate the history of the experiment. Data for VLH equilibrium from the literature [1] are shown with a 4th order polynomial fit in this temperature region (273 to 297 K). The H-L_w equilibrium points are located where the heating curves return to their respective cooling curves. The vertical line at 292.1 K represents the three-phase H-L_w-V temperature based on the literature VLH data.

Figure 2: dP/dT versus temperature for portions of the cooling and heating sections for the three cycles shown in Figure 1 for the experiment with 0.00210 mole fraction of methane. Only the data for the cooling curve for Cycle II are shown. The $H-L_w$ equilibrium point is indicated. It is at the first intersection of the heating trace (solid line) with the cooling trace (dashed line). The heating rates used during the experiments are indicated by color and arrows. Temperature oscillations increase at slower heating rates owing to the 0.1 K step size of the environmental chamber. The $H-L_w-V$ line is indicated at 292.1 K.

Figure 3. Comparison of mole fraction of methane in water at H-L_w equilibrium predicted by this model (solid lines) and by the correlation given by Lu et al.[12] (dashed lines). The bottom solid line is the H-Lw-V equilibrium for methane hydrate, plotted from the data obtained from Sloan.[1] The H-Lw equilibrium region exists at pressures higher than the H-Lw-V equilibrium. V-Lw equilibrium region exists at pressures lower than the H-Lw-V equilibrium.

Figure 4. Model predictions of cage occupancy of sI methane hydrate at H-L_w equilibrium.

Figure 5. Cage occupancy ratio (θ_L/θ_S) of sI methane hydrate at H-L_w equilibrium predicted by this model.

Figure 6. Dissolved hydrocarbon concentration in the aqueous phase in equilibrium with hydrates at different temperatures and pressures for fresh water and seawater. The nearly-vertical solid (—) and dashed lines (---) are for fresh water and seawater respectively. Each vertical line is for a total hydrocarbon mole fraction ($x_{c_1c_2c_3}$) in the aqueous phase for an 87.5% methane, 8.1% ethane, and 4.4% propane hydrocarbon mixture. The bottom solid and dashed black lines are the H-L_w-V equilibrium curves for fresh water and seawater respectively.

Figure 7. Hydrate cage occupancies at two phase equilibrium (L_w -H). The lines are for different total hydrocarbon solubility in water with composition, $C_1 = 87.5\%$, $C_2 = 8.1\%$ and $C_3 = 4.4\%$ when in equilibrium with hydrate phase.

Figure 8. Hydrate phase composition at two phase equilibrium (L_w -H). The lines are for different total hydrocarbon solubility in water with composition, $C_1 = 87.5\%$, $C_2 = 8.1\%$ and $C_3 = 4.4\%$ when in equilibrium with hydrate phase.

Figure 9. Effect of salinity on the formation of H-L_w methane hydrate from dissolved methane. Vertical solid lines (—) indicate the dissolved concentrations necessary for hydrate formation from pure water, while vertical dashed lines (---) indicate the equivalent pressures and temperatures for formation from seawater. The H-L_w-V equilibrium curves are shown as solid and dashed black line at the bottom for pure water and seawater respectively.

Appendix A

The notation and variable definitions in the Appendix follow the conventions typically used to present the Pitzer model rather than the conventions typically used for hydrate thermodynamic models.

The activity of water (a_w) is given by the Pitzer [49] model as:

$$\ln a_w = -\phi M_{H_2O} \sum_i m_i \quad (A.1)$$

where m_i is the molality (mol/kg) of ions and M_{H_2O} is the molecular weight of water. ϕ is the osmotic coefficient, given as:

$$\sum m_i (\phi - 1) = 2 \left[\frac{-A^\phi I^{1.5}}{1+1.2I^{0.5}} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + Z C_{ca}) + \sum_{c<} \sum_{c'} m_c m_{c'} (\Phi_{cc'}^\phi + \right. \\ \left. a m_a \Psi_{cc'a}) + a < a' m_a m_{a'} (\Phi_{aa'}^\phi + c m_c \Psi_{aa'c}) \right] \quad (A.2)$$

where I is the ionic strength and the subscripts c and a represent cation and anion respectively. A^ϕ is the Debye-Hückel limiting slope given as

$$A^\phi = \frac{1}{3} \left[\frac{2\pi N_0 \rho_w}{1000} \right] (e^2 / DkT)^{3/2} \quad (A.3)$$

where N_0 is Avogadro's number, ρ_w is the density of water, D is the dielectric constant of water, e is charge of electron, k is Boltzmann constant and T is temperature in K. The ionic strength, I , is defined as:

$$I = 1/2 \sum_i m_i z_i^2 \quad (A.4)$$

where z_i is the charge of ion. The function Z in Eq. (A.2) is defined as:

$$Z = \sum_i m_i |z_i| \quad (A.5)$$

B and Φ are measurable combinations of the second Virial coefficients. C and Ψ are measurable combinations of the third Virial coefficients. The neutral-neutral atom interactions and neutral-electrolyte interactions contributions in the activity of water calculations are ignored in this work, as their contributions to the activity of water are negligible.

The ionic strength dependence of the second virial coefficients, B_{ca}^ϕ , is defined as

$$B_{ca}^\phi = \beta_{ca}^0 + \beta_{ca}^1 e^{-\alpha_{ca}\sqrt{I}} \quad (\text{A.6})$$

β_{ca}^0 and β_{ca}^1 are binary interaction parameters. When either c or a is univalent then $\alpha_{ca} = 2$. For 2-2 or higher valence pair $\alpha_{ca} = 1.4$. The third virial electrolyte, C_{ca} , is defined as

$$C_{ca} = \frac{C_{ca}^\phi}{2\sqrt{|z_c z_a|}} \quad (\text{A.7})$$

The second virial coefficient, Φ , which accounts for the interactions of like atoms are defined as

$$\Phi_{ij}^\phi = \theta_{ij} + {}^E\theta_{ij}(I) + I^E\theta_{ij}(I) \quad (\text{A.8})$$

The binary interaction parameters, $\beta_{ca}^0, \beta_{ca}^1$ and C_{ca}^ϕ for each cation-anion pair and tertiary interaction parameters $\Psi_{aa'c}$, θ_{ij} and $\Psi_{cc'a}$ are represented as a temperature dependent with the empirical equation given in Eq. (A.9) and (A.10) respectively and the constant values a_1 to a_6 b_1 to b_5 are given in Table A.1 and A.2 respectively. The effect of pressure on the activity of water is small and so can be ignored[65].

$$Parameter(T) = a_1 + a_2T + \frac{a_3}{T} + a_4 \ln T + a_5T^2 + a_6T^3 \quad (\text{A.9})$$

$$Parameter(T) = b_1 + b_2T + \frac{b_3}{T} + b_4 \ln T + b_5T^2 \quad (\text{A.10})$$

Table A.1: The temperature dependence of the Debye-Huckel and binary interaction parameters of the Pitzer model[49] determined by Spencer et al.[50]

	a_1	a_2	a_3	a_4	a_5	a_6
A Φ	8.66836498E+01	8.48795942E-02	-1.32731477E+03	-1.76460172E+01	-8.88785150E-05	4.88096393E-08
Na, Cl						
$\beta^{(0)}$	7.87239712E+00	-8.38640960E-03	-4.96920671E+02	-8.20972560E-01	1.44137740E-05	-8.78203010E-09
$\beta^{(1)}$	8.66915291E+02	6.06166931E-01	-1.70460145E+04	-1.67171296E+02	-4.80489210E-04	1.88503857E-07
C^ϕ	1.70761824E+00	2.32970177E-3	-1.35583596E+00	-3.87767714E-01	-2.46665619E-06	1.21543380E-09
K, Cl						
$\beta^{(0)}$	2.65718766E+01	9.92715099E-03	-7.55707220E+02	-4.67300770E+00	-3.62323330E-06	-6.28427180E-11
$\beta^{(1)}$	1.69742977E+03	1.22270943E+00	-3.28684422E+04	-3.28813848E+02	-9.99044490E-04	4.04786721E-07
C^ϕ	-3.27571680E+00	-1.27222054E-03	9.07747666E+01	5.80513562E-01	4.71374283E-07	1.11625070E-11
Ca, Cl						
$\beta^{(0)}$	-5.62764702E+01	-3.00771997E-02	1.11730349E+03	1.06664743E+01	1.05630400E-05	3.33316260E-09
$\beta^{(1)}$	3.4787000E+00	-1.54170000E-02	0.0	0.0	3.17910000E-05	0.0
C^ϕ	2.64231655E+01	2.46922993E-02	-4.18098427E+02	-5.35350322E+00	-2.48298510E-05	1.22421864E-08
Mg, Cl						
$\beta^{(0)}$	3.13852913E+02	2.61769099E-01	-5.53133381E+03	-6.21616862E+01	-2.46268460E-04	1.15764787E-07
$\beta^{(1)}$	-3.18432525E+04	-2.86710358E+01	5.24032958E+05	6.40770396E+03	2.78892838E-02	-1.32797050E-05
C^ϕ	5.95320000E-02	-2.49949E-04	0.0	0.0	2.41831000E-07	0.0
Na, SO ₄						
$\beta^{(0)}$	-3.32486330E+03	-2.92973530E+00	5.53958527E+04	6.66660369E+10	2.80243670E-03	-1.31688300E-06
$\beta^{(1)}$	-3.57406160E+03	-3.00112060E+00	6.09716482E+04	7.11613120E+02	2.73660950E-03	-1.21917100E-06
C^ϕ	3.68520478E+02	3.16243995E-01	-6.22607913E+11	-7.35844094E+01	-2.95372760E-04	1.35491104E-07
K, SO ₄						
$\beta^{(0)}$	4.07908797E+01	8.26906675E-03	-1.41842998E+03	-6.74728848E+00	0.0	0.0
$\beta^{(1)}$	-1.31669510E+01	2.35793239E-02	2.06712594E+03	0.0	0.0	0.0
C^ϕ	-1.88000000E-02	0.0	0.0	0.0	0.0	0.0
Ca, SO ₄						
$\beta^{(0)}$	1.50000000E-01	0.0	0.0	0.0	0.0	0.0
$\beta^{(1)}$	3.00000000E+00	0.0	0.0	0.0	0.0	0.0
$\beta^{(2)}$	-1.29399287E+02	4.00431027E-01	0.0	0.0	0.0	0.0
Mg,SO ₄						
$\beta^{(0)}$	5.40078490E+03	4.90576884E+00	-8.80664146E+04	-1.08839565E+03	-4.80489750E-03	2.31126994E-06
$\beta^{(1)}$	2.78730869E+00	4.30077440E-03	0.0	0.0	0.0	0.0
C^ϕ	-5.88623653E+02	-5.05522880E-01	1.02002016E+04	1.17303808E+02	4.82776570E-04	-2.30298380E-07

Table A.2: The temperature dependence of mixed electrolyte parameters of the Pitzer model[49] determined by Spencer et al.[50]

	b_1	b_2	b_3	b_4	b_5
$\theta_{\text{Na,K}}$	-1.82266741E+01	-3.69038470E-03	6.12415011E+02	3.02994981E+00	0.0
$\Psi_{\text{Na,K,Cl}}$	6.48108127E+00	1.46803468E-03	-2.04354019E+00	-1.09448043E+00	0.0
$\Psi_{\text{Na,K,SO}_4}$	3.48120E-02	0.0	-8.21660E+00	0.0	0.0
$\theta_{\text{Na,Ca}}$	5.0E-02	0.0	0.0	0.0	0.0
$\Psi_{\text{Na,Ca,Cl}}$	-7.6398E+00	-1.299E-02	0.0	1.8475E+00	1.1060E-05
$\Psi_{\text{Na,Ca,SO}_4}$	-1.20E-02	0.0	0.0	0.0	0.0
$\theta_{\text{Na,Mg}}$	7.0E-02	0.0	0.0	0.0	0.0
$\Psi_{\text{Na,Mg,Cl}}$	-3.10987E-02	5.44647800E-05	1.99404210E+00	0.0	0.0
$\Psi_{\text{Na,Mg,SO}_4}$	1.175052E-01	0.0	-4.19862E+01	0.0	0.0
$\theta_{\text{K,Ca}}$	2.36571E+00	-4.54E-03	-2.849400E+02	0.0	0.0
$\Psi_{\text{K,Ca,Cl}}$	-5.930602E+00	2.54280E-04	-1.34390E+01	0.0	0.0
$\theta_{\text{K,Mg}}$	1.1670E-01	0.0	0.0	0.0	0.0
$\Psi_{\text{K,Mg,Cl}}$	5.0362230E-02	-8.75082E-06	-2.89909E+01	0.0	0.0
$\Psi_{\text{K,Mg,SO}_4}$	-1.36791570E+00	4.24016653E-03	0.0	0.0	0.0
$\theta_{\text{Ca,Mg}}$	5.31274136E+00	-6.34242480E-03	-9.83113847E+02	0.0	0.0
$\Psi_{\text{Ca,Mg,Cl}}$	4.1579022E+01	1.30377312E-02	-9.81658526E+02	-7.4061986E+00	0.0
$\theta_{\text{Cl,SO}_4}$	7.0E-02	0.0	0.0	0.0	0.0
$\Psi_{\text{Cl,SO}_4,\text{Na}}$	4.0209775E+00	1.1286005E-03	-1.01169260E+02	-7.060798E-01	0.0
$\Psi_{\text{Cl,SO}_4,\text{K}}$	-2.124815E-01	2.8469833E-04	3.75619140E+00	0.0	0.0
$\Psi_{\text{Cl,SO}_4,\text{Ca}}$	-1.8E-02	0.0	0.0	0.0	0.0
$\Psi_{\text{Cl,SO}_4,\text{Mg}}$	-1.839158E-01	1.429444E-04	3.2630E+01	0.0	0.0