METHANE SOLUBILITY IN WATER UNDER HYDRATE EQUILIBRIUM CONDITIONS: SINGLE PORE AND PORE NETWORK STUDIES

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ABSTRACT

In this work we perform a series of mass-balance-type calculations, in order to estimate the minimum volume of liquid water required to dissolve, completely, a single methane-gas bubble, located inside different types of domains that are under hydrate equilibrium pressure/temperature conditions. We examine the case of bubble dissolution in the bulk, along with the cases of bubble dissolution within simple networks of pores with the same pore/throat size. In our calculations we consider experimental values for the equilibrium solubilities of methane in water, under hydrate forming conditions, as well as, values obtained from predictive tools that are based on thermodynamic models. As a result of the relatively low solubility of methane in water, large volumes of water are required for complete dissolution of a methane bubble.

Keywords: gas hydrates, dissolution, methane solubility, hydrate equilibrium, porous medium.

NOMENCLATURE

\( L \) length  
\( MW \) molecular weight  
\( n \) number of moles  
\( P \) pressure  
\( R \) gas constant  
\( r \) radius  
\( T \) temperature  
\( V \) volume  
\( x \) mole fraction  
\( z \) compressibility factor  
\( \rho \) density  
\( \Phi \) constant  
\( \Psi \) geometrical factor  
\( \Omega \) proportionality constant  
\( \beta \) proportionality constant  
\( \gamma \) interfacial tension  
\( \zeta \) coordination number  
\( \eta \) proportionality constant  
\( \nu \) proportionality constant  

Greek

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\( \Psi \) geometrical factor  
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Superscripts  
\( eq \) equilibrium  
\( PM \) porous medium

Subscripts  
\( b \) bubble  
\( c \) capillary  
\( g \) gas  
\( H \) hydrate  
\( l \) liquid  
\( p \) pore  
\( t \) throat  
\( w \) water

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INTRODUCTION

Upward gas migration due to buoyancy forces and immiscible fluid displacement inside a porous medium are important processes occurring in the subsurface. Consider the schematic depicted in Figure 1a. Two gas-phase clusters that occupy several pores migrate upward, as a result of buoyancy forces, displacing during the migration process the liquid phase that is present in the porous medium. The mole fraction of the gas component in the liquid phase is initially (at time $t=0$) equal to $x_g^\infty$. For a given system (temperature, pressure, and salinity) corresponds a value $x_g^{eq}$ such that the system is at thermodynamic equilibrium. As long as, $x_g^\infty < x_g^{eq}$ (i.e. the liquid phase becomes undersaturated), the gas cluster continues to dissolve in the liquid phase until the point that $x_g^\infty = x_g^{eq}$ (i.e. the liquid phase is saturated). On the other hand, if $x_g^\infty > x_g^{eq}$ (i.e. the liquid phase is supersaturated), then the gas phase can grow, as a result of the gas component that comes out of the liquid solution. This process is known as gas-bubble growth resulting from “solution-gas-drive” [1-2] to the petroleum industry.

Under appropriate conditions of pressure, temperature and salinity the migrating gas phase can form solid hydrates inside a porous medium. Of significant interest is the case of methane migration in the subsurface, and the possible formation of methane hydrate. Oceanic or permafrost, naturally-occurring, methane hydrates are important because they are considered a possible source of methane for energy uses [3], a possible environmental threat (due to sudden release in the atmosphere of methane which is a “green-house” gas) [4], a geologic hazard (creation of a tsunami resulting from ocean-floor collapse as a result of sudden hydrate dissociation), and a drilling hazard for offshore oil/gas platforms [4].

During methane hydrate formation inside oceanic sediments the gas phase can be of either biogenic origin [5], produced locally by microorganisms inside the Hydrate Stability Zone (HSZ), or of thermogenic origin, produced deep in the subsurface and subsequently migrating into the HSZ [6]. In either case, part of the methane gas dissolves into the liquid water phase to saturate it for the prevailing pressure and temperature conditions, part is consumed to form hydrate, and part could remain as a free gas phase (provided adequate amounts of gas are present). If during the hydrate formation process inside a porous domain, a subdomain of the HSZ exists, such that the liquid water present there is undersaturated, then part of the formed hydrate can dissociate [7-11]. The hydrate dissociation continues up to the point that all the liquid becomes saturated with methane and the three phases (liquid/gas/hydrate) are at thermodynamic equilibrium. Therefore, methane solubility in the liquid phase is an essential parameter to be determined (either experimentally or computationally), if one needs to calculate correctly the amount of hydrate formed from a given amount of gas phase present inside a porous medium. Methane solubility in water at hydrate formation conditions has been studied extensively using theoretical [12-17] and experimental methods [18-22]. Here we reported only some representative works in the area.

Figure 1. Schematics: (a) Gas-bubble upward migration inside a porous medium driven by buoyancy forces. (b) Spherical gas bubble in a bulk phase.
The objective of the paper is to calculate the minimum volume of liquid required to dissolve completely, a single methane-gas bubble, located inside different types of domains that are under hydrate equilibrium pressure/temperature conditions.

This paper is organized as follows: Initially, we present the mathematical formulation for the case of a gas bubble in a bulk phase, namely in the absence of interference with any solid material. Next, the case of a gas bubble inside a regular pore network is described. Then, we present and discuss the results for both aforementioned cases, and finally, we end with the conclusions.

**MATHEMATICAL FORMULATION: BULK PHASE**

Consider a spherical gas (CH\textsubscript{4}) bubble with a radius \(r_b\) and volume \(V_b\) placed inside an aqueous (H\textsubscript{2}O) liquid phase, located in a container of arbitrary shape that has a volume \(V_{\text{box}}\). Such a system is shown in Figure 1b for the particular case of a square container. The pressure \(P_g\) in the gas bubble is given by the ideal gas law, corrected with the compressibility factor \(z\), in order to account for the non-idealities of the gas phase at higher pressures.

\[
P_g V_b = z n_g R T
\]

where \(R\) is the gas constant, \(T\) is the temperature and \(n_g\) the number of gas moles. In the current study we used the component-specific Equation of State developed by Duan et al. [24] to calculate the compressibility factor of methane.

The pressure inside the gas phase of the spherical bubble, \(P_g\), is also related to the capillary pressure, \(P_c\), and the pressure in the surrounding liquid phase, \(P_l\), as follows:

\[
P_g = P_c + P_l = \frac{2 \gamma}{r_b} + P_l
\]

where \(\gamma\) is the interfacial tension, which is a function of temperature and pressure. In the current study \(\gamma\) is calculated using the methodology reported in [25]. Emphasis is placed in values of pressure along the methane hydrate equilibrium curve \(P_{\text{eq}} = f(T_{\text{eq}})\). Therefore, we take the pressure in the container as \(P_l = P_{\text{eq}}\) for the calculations presented in this study.

Figure 2 shows the capillary pressure as a function of temperature for various gas bubbles with radii in the range \(10^{-9}–10^{-3}\) m. The dashed-dotted line shows the hydrate equilibrium curve for methane hydrate [26].
of methane near the bubble decreases and becomes $x_g < x_g^eq$ as time evolves, which then creates an additional driving force for further gas dissolution in the liquid phase. Gas dissolution continues as long as $x_g < x_g^eq$, and stops when $x_g = x_g^eq$. The transient dissolution process ends with one of the following two scenarios: (i) with complete dissolution of the gas phase if $x_g^eq < x_g^eq$, and (ii) with undissolved gas phase still present in the container if $x_g^eq = x_g^eq$.

The solution of the transient problem is an interesting research topic, however, it is beyond the scope of this study. Our concern is the state of the system when it has equilibrated and no further changes can be observed. In particular, we are interested for the case when at the end of the process there is complete dissolution of the gas bubble. We ask the question: “What is the minimum volume of the liquid phase, $V_w$, that is required to completely dissolve a single methane-gas bubble of a given radius at pressures and temperatures along the hydrate equilibrium curve?” Therefore, we need a volume of water such that at the end of the process: $n_g = x_g^eq / (n_g + n_w)$. Equivalently, in order for complete dissolution of a single methane bubble to occur, the number of methane moles inside the bubble should be equal to:

$$n_g = n_w \left( \frac{x_g^eq}{1 - x_g^eq} \right)$$  \hspace{1cm} (3)

where the number of moles of water are given by

$$n_w = \frac{\rho_w V_w}{MW_w}$$  \hspace{1cm} (4)

and $\rho_w$ and $MW_w$ denote the density and molecular weight of water respectively. For all the calculations presented in this study, liquid densities for water are obtained from Wagner and Pruss [27].

In order to solve the problem we make the following assumption: $V_w = \Omega V_b$, where $\Omega$ is the proportionality constant that needs to be calculated in order to answer the aforementioned question. By combining Equations (1-4), and introducing the previous assumption we can obtain an equation for $\Omega$ as follows:

$$\Omega = \frac{2\gamma + P_H^eq}{\rho_b \left( \frac{x_g^eq}{1 - x_g^eq} \right) \frac{P_w}{MW_w}}$$  \hspace{1cm} (5)

Once $\Omega$ is calculated for a particular radius of a gas bubble through Eq. (5), we can compute $V_w$ as $V_w = \Omega V_b$. During the methane dissolution process in water we assumed that there is no change in the temperature $T$ of the system, which remains equal to $T^eq$.

**MATHEMATICAL FORMULATION: PORE NETWORK**

In the previous section we developed an expression for the minimum volume required to dissolve completely a gas bubble for the case when the gas bubble is located in a large container (i.e. in the bulk). Namely, this result holds in the absence of any interactions between the bubble and the solid walls of the container. Of interest also is the case when the gas bubble is under confinement (i.e. located within a porous medium). In the current section we develop an expression for the minimum volume required to dissolve completely a gas bubble inside a regular pore network.

Initially, we describe the construction of the pore network. Consider the schematic shown in Figure 3a. At the center of a cubic solid block, with side-length $L_{UPB}$, we place a pore space (void) that is made up of a spherical pore body with radius $r_p$ and a number $\zeta$ of pore throats with radius $r_t$. $\zeta$ is known as the coordination number. The coordination number could have values in the approximate range 1-6. Alternatively, other geometrical shapes can be adopted for pore bodies (e.g. cubic, cylindrical, etc.). However, we limit the discussion in this study, to spherical pore bodies only.

The pore bodies provide the main storage capacity and the pore throats the secondary storage capacity. In addition, pore throats provide the connections between neighboring pore bodies. Pore throats also provide the resistance to flow, as a result of the capillary threshold that needs to be exceeded, in order for the throats to be penetrated.
The combination of solid and void spaces described above consists of a Unit Porous Block (UPB). This porous unit can be repeated in the three dimensions to create a 3-D pore network. In real porous media, both pore bodies and pore throats can have sizes that follow appropriate size distributions.

The total volume of the pore space inside each UPB should take into account the contribution of the volume of the pore body, $V_p$, and the volume of each throat, $V_{ti}$, among all the $\zeta$ pore throats that are connected to the pore. The total volume of the pore space is given as follows:

$$V_{UPB} = V_p + \sum_{i=1}^{\zeta} V_{ti} = V_p + \zeta V_{ti}$$  \hspace{1cm} (6)

The total volume of each UPB (including both solid and void spaces), $V_{UPB}$, is equal to: $V_{UPB} = (L_{UPB})^3$. We define the porosity of the system such that: $\varphi = V_{UPB} / V_{UPB}$. We can make the assumption that $V_p = \eta V_{ti}$ where $\eta$ is given by:

$$\eta = \psi \left( \frac{2 \beta^2}{\nu - 2} \right)$$  \hspace{1cm} (7)

where $\psi$ is a geometrical factor depending on the geometry of the pore throat used. In particular for the cases of pore throats examined in this study, and assuming a spherical pore body, we have:

$$\psi = \begin{cases} 
\frac{4}{3} & \text{for cylindrical throats} \\
\frac{\pi}{3} & \text{for rectangular throats}
\end{cases}$$  \hspace{1cm} (8)

By substituting into Eq. (6) we find that the total volume of the void (pore) space inside each UPB is given by:

$$V_{UPB}^{PM} = V_p \left( 1 + \frac{\zeta}{\eta} \right) = V_p \Phi$$  \hspace{1cm} (9)

where

$$\Phi = 1 + \frac{\zeta}{\eta}$$  \hspace{1cm} (10)
As $\Phi \to 1$ the contribution to the volume $V_{UPB}^{PM}$ originates only from the contribution of the pore body. When $\Phi > 1$ the pore throats begin to contribute to the volume $V_{UPB}^{PM}$. In order to solve the problem, for the volume required to dissolve a gas bubble occupying completely a single pore body with volume $V_p$, we make the assumption that $V_w = \Omega V_p = \epsilon V_{UPB}^{PM}$, where $\Omega$ is the parameter that was calculated in the previous section. Therefore, the new proportionality constant $\epsilon$ that needs to be calculated is given by:

$$\epsilon = \frac{\Omega}{\Phi}$$

(11)

Note that in the limiting case when $\nu \to 2$, essentially when there are no pore throats in the system, which is equivalent to the case of the gas bubble in the bulk fluid, then $\Phi \to 1$ and $\epsilon \to \Omega$, as one should expect. Essentially, $\epsilon$ denotes the number of UPB’s required to dissolve a given gas bubble.

RESULTS AND DISCUSSION

Thermodynamic issues

In this study we are interested in the methane solubility in water under pressure and temperature conditions along the methane hydrate equilibrium curve. Figure 4a shows the $P,T$ hydrate equilibrium curve as calculated: (i) by the correlation of Moridis [26], and (ii) by using the commercial code CSMGem [23]. Also shown in Figure 4a are the $P,T$ conditions where measurements for the methane solubility in the liquid phase, $x_g$, under hydrate formation conditions are available [18-22]. Figure 4b shows the methane solubility in the liquid phase, along the hydrate equilibrium curve, as calculated by using the CSMGem model. Figure 4b shows also available experimental methane solubilities under hydrate equilibrium conditions. In most cases, the experiments were performed at pressures that are higher than the $P_{H}^{eq} = f(T_{H}^{eq})$ (see also Figure 4a). Very good agreement is obtained between the available experimental values along the hydrate equilibrium curve and those calculated from CSMGem, as clearly shown in Table 1 for some representative cases. Therefore, the solubility values from CSMGem are used in Eq. (5) in order to calculate $\Omega$.

Figure 4. (a) The two lines denote the hydrate equilibrium curve for methane hydrate calculated by different methods (solid line: CSMGem [23], and dashed line: Moridis [26]). The experimental data show the $P,T$ conditions where measurements are available for the methane solubility in the liquid phase, $x_g$, under hydrate formation conditions. (b) Methane solubility in the liquid phase vs. temperature, along the hydrate equilibrium curve, using the CSMGem model and comparison with experimental data. (Experimental data used. A: Servio and Englezos, [20]; B: Kim et al., [21]; C: Seo et al., [22]; D: Yang et al., [19]; E: Bergeron and Servio, [18]).
Table 1. Comparison between experimental and calculated values for the mole fraction of methane in water under hydrate equilibrium conditions.

<table>
<thead>
<tr>
<th>$T_{H^2}$ (K)</th>
<th>$P_{H^2}$ (bar)</th>
<th>$x_{g}^{\text{exp}}$</th>
<th>Ref</th>
<th>$x_{g}^{\text{calc}}$</th>
<th>% dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>276.25</td>
<td>35.00</td>
<td>0.001240</td>
<td>20</td>
<td>0.001240</td>
<td>0.0</td>
</tr>
<tr>
<td>279.65</td>
<td>50.00</td>
<td>0.001600</td>
<td>20</td>
<td>0.001520</td>
<td>5.0</td>
</tr>
<tr>
<td>282.05</td>
<td>65.00</td>
<td>0.001850</td>
<td>20</td>
<td>0.001753</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Bulk Phase

Figure 5 shows the calculated values for $\Omega$ as a function of temperature and for various bubble radii in the range $10^{-9} – 10^{-3}$ m. We observe that for bubble radii with $r_b > 10^{-5}$ m, the values of $\Omega$ essentially collapse on a single curve, showing no effect of $\Omega$ vs. $T$. On the other hand, for bubble radii with $r_b < 10^{-5}$ m, the values of $\Omega$ increase significantly as $r_b$ decreases (for a given $P, T$ along the methane hydrate equilibrium curve). This should be expected since the contribution of $P_c$ to the total gas pressure $P_g$ becomes important as $r_b$ decreases (see also Figure 2).

![Figure 5](image1.png)

Figure 5. Calculated values of $\Omega$ vs. $T$ for various bubble radii in the range: (a) $10^{-9} – 10^{-5}$ m. (b) $10^{-6} – 10^{-3}$ m.

![Figure 6](image2.png)

Figure 6. Calculated values for $\Phi$ for rectangular pore throats as a function of $\beta$ and $\nu$ and two different pore network coordination numbers: (a) $\zeta=6$. (b) $\zeta=3$. 

(a)

(b)
Pore Network

Figure 6 shows the calculated values for \( \Phi \) corresponding to the case of rectangular pore throats. The values of \( \Phi \) are plotted as a function of \( \beta \) and \( \gamma \), and two different pore network coordination numbers (i.e. \( \xi = 6 \), \( \xi = 3 \)). As can be seen the values of \( \Phi \) are in the range 1-7 approximately. Similar results are obtained for the case of cylindrical pore throats with the values of \( \Phi \) being in the range 1-5.5 approximately.

Figure 7 shows the calculated values for \( \varepsilon \) as a function of temperature for various radii of gas bubbles, located inside a single spherical pore body. Three cases are considered for \( \Phi \). In particular curves are plotted for \( \Phi = 1, 4, 7 \). Higher values of \( \Phi \) imply increased contribution to the volume of the UPB from pore throats and therefore, less UPB’s are required to dissolve the same size of a gas bubble.

CONCLUSIONS

In this work we have performed analytical calculations to estimate the minimum volume of liquid water required to dissolve, completely, a single methane gas bubble, located inside different types of domains that are under hydrate equilibrium pressure/temperature conditions. Initially we considered the case of a single gas bubble dissolving in the bulk. In addition, we examined the case of gas bubble dissolution inside a regular pore network.

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