Measurements and Predictions of Phase Equilibria for Water + Ethane in Hydrate-Forming Conditions

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Introduction

- **Gas Hydrate (Clathrate Hydrate)**
  - a solid solution of water and light gases through hydrogen bonding

- **Researches on the gas hydrate**
  - Methane hydrates as a future resource of energy
  - Carbon dioxide sequestration as hydrates in deep ocean
  - Process problems in petroleum industry
    - Effects of inhibitors on hydrate-forming condition
    - Prediction of phase equilibria for mixed hydrates
What are gas hydrates?

- Crystalline solids consisting of a guest(s) component(s) and water
- Hydrates can form at conditions above the normal freezing point of water by the hydrogen bonding.
- Three cavities in gas hydrates

(a) Pentagonal Dodecahedron(5^{12}) (b) Tetrakaidecahedron(5^{12}6^{2}) (c) Hexakaidecahedron(5^{12}6^{4})

(Reproduced from “Clathrate Hydrates of Natural Gases”, Sloan, 1998)
Structures of gas hydrates

- Structure I(a) and II(b) form with relatively small guests, e.g., methane, ethane, nitrogen, etc.
- Structure I and II contains 48 and 136 water molecules, respectively.
- Structure H(c) is only known to form with at least one small guest (i.e., methane) and one large guest, e.g., cyclooctane, methylcyclohexane, etc.
Studies on Ethane Hydrate

- **H-L\textsubscript{W}-V\textsubscript{C2H4}** and **H-I-V\textsubscript{C2H4}**
  - Roberts et al. (1940) …

- **H-L\textsubscript{W}-L\textsubscript{C2H4}**
  - Ng and Robinson (1985)

- **H- Π\textsubscript{C2H4}**
  - Sloan (1986)
  - Song and Kobayashi (1994)

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**Figure 1. Phase diagram of H\textsubscript{2}O - C\textsubscript{2}H\textsubscript{6}**

Temperature / K

Pressure / MPa

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>Pressure / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>0.1</td>
</tr>
<tr>
<td>270</td>
<td>1</td>
</tr>
<tr>
<td>280</td>
<td>10</td>
</tr>
<tr>
<td>290</td>
<td>10</td>
</tr>
</tbody>
</table>

Q\textsubscript{1}(H-I-L-V)

Q\textsubscript{2}(H-Lw-Lc-V)
Models on Gas Hydrate

- Van der Waals and Platteeuw [1959]
  - Statistical model of hydrate cavities similar to gas adsorption model by Langmuir

- Holder et al.[1980]
  - The chemical potential difference between the hypothetical empty hydrate and the fluid phase or ice is calculated by classical thermodynamic relations

- Klauda and Sandler(2000)
  - Fitting the vapor pressure of the empty hydrate for each guest component
Purpose

- Experimental determination of H-L\textsubscript{W} equilibria
  - Effect on ethane solubility by existence of NaCl

- EOS approach available on
  - three-phase equilibria (H-I-V\textsubscript{C2H6}, H-L\textsubscript{W}-V\textsubscript{C2H6}, H-L\textsubscript{W}-L\textsubscript{C2H6})
  - two-phase equilibria (H-L\textsubscript{W}, H-L/V\textsubscript{C2H6})

- Applicability of Nonrandom Lattice Fluid Theory (NLF-HB) and Gibbs energy model on hydrate containing equilibria
NLF-HB Equation of State

- Nonrandom Lattice Fluid Hydrogen Bonding Theory
  - NLF EOS by You et al. [1993 a, b]
  - Expansion to associating system using Veytsman statistics[1990] by Yeom et al. [1999]
  - A normalization of Veytsman statistics by Lee et al. [2000]

- Parameters for pure species
  \[
  \frac{\epsilon_{ii}}{k} = \epsilon_a + \epsilon_b (T - 273.15) + \epsilon_c [T \ln(273.15 / T) + (T - 273.15)]
  \]

  \[
  r_i = r_a + r_b (T - 273.15) + r_c [T \ln(273.15 / T) + (T - 273.15)]
  \]

- Hydrogen-bonding energy and entropy for H₂O-H₂O interaction
  - \( E_{HB}^0 = -15.5 \text{ kJ/mol} \), \( S_{HB}^0 = -16.5 \text{ J/mol-K} \) by Luck [1980]
NLF-HB Equation of State

- **Expression for Pressure**

\[
P = \frac{1}{\beta V_H} \left\{ \left( \frac{z}{2} \right) \ln \left[ 1 + \left( \frac{q_M}{r_M} - 1 \right) \rho \right] - \ln(1 - \rho) - v_{HB} \rho \right\} - \left( \frac{z}{2} \right) \theta^2 \left( \frac{\varepsilon_M}{V_H} \right)
\]

\[
\varepsilon_M = (1/\theta^2) \sum_i \sum_j \theta_j \varepsilon_{ij} + (\beta/2\theta^2) \sum_i \sum_j \sum_k \theta_j \theta_k \theta_i \varepsilon_{ij} (\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk})
\]

\[
\rho_i = N_i r_i / (N_0 + \sum_{i=1}^C N_i r_i) \quad \theta_i = N_i q_i / (N_0 + \sum_{i=1}^C N_i q_i)
\]

\[
v_{HB} = \left( \sum_{k=1}^K \sum_{l=1}^L N_{HB}^{kl} - \sum_{k=1}^K \sum_{l=1}^L N_{HB0}^{kl} \right) / \sum_{i=1}^C N_i r_i
\]

- **Expression for chemical potential**

\[
\frac{\mu_i^{II} - \mu_i^{II0}}{RT} = -\ln \left( \frac{V_H}{RT} \right) + r_i \ln \left[ 1 + \left( \frac{q_M}{r_M} - 1 \right) \rho \right] - r_i \ln(1 - \rho) + \ln \left( \frac{\theta_i}{q_i} \right) + \left( \frac{z\beta q_i \varepsilon_M \theta^2}{2} \right)
\]

\[
\times \left[ 1 - \frac{r_i}{q_i} - \frac{2 \sum \theta_k \varepsilon_{ik}}{\varepsilon_M \theta^2} + \beta \sum \sum \sum \theta_j \theta_k \theta_i \varepsilon_{ij} (\varepsilon_{ij} + 2\varepsilon_{kl} - 2\varepsilon_{ik} - \varepsilon_{jk}) \right] + \sum_{k=1}^m \frac{N_{kB}}{N_{k0}} + \sum_{k=1}^n \frac{N_{0k}}{N_{0kB}}
\]
Thermodynamic Model for Hydrate Phase Equilibria

- Hydrate phase by van der Waals and Platteeuw model (1959)

\[ \mu_w^H = \mu_w^{EH} + RT \sum_j \nu_j \ln [1 - C_{i,j} f_i^{\Pi} / (1 + C_{i,j} f_i^{\Pi})] \]

\[ f_i^{\Pi} = P^0 \exp \left[ (\mu_i^{\Pi} - \mu_i^{\Pi 0}) / RT \right] \]

\[ C_{ki} = \frac{4 \pi}{kT} \int_0^R \exp \left( -\frac{W(r)}{kT} \right) r^2 dr \]

- Chemical potential difference between empty hydrate and reference fluid state

\[ \mu_w^{EH} = \mu_w^{\Pi 0} (T_o, P_o) + \int_{T_o}^T \frac{\Delta H_w^{HIP} / RT^2}{dT} dT + \int_{P_o}^P \frac{\Delta V_w^{HIP} / RT}{dP} dP \]

\[ \mu_w^{EH} = \mu_w^{\Pi 0} + RT \ln \left[ f_{pureW}^{EH} / f_{pureW}^{\Pi} \right] \]

\[ = \mu_w^{\Pi 0} + RT \ln \left[ f_w^{EH} \phi_w^{EH} / P \phi_{pureW}^{\Pi} \right] + \Delta V_w^{EH} [ P - P_w^{EH} ] \]

\[ \ln [P_w^{satEH} / atm] = 17.410 - 6072.3 / [T / K] \]
Chemical Equility

- **Three-phase equilibria**
  \[ \mu_i^{(1)} = \mu_i^{(2)} \]
  \[ \mu_w^H - \mu_w^{P0} = \mu_w^H - \mu_w^{P0} \]
  \[ \mu_w^H - \mu_w^{P0} = RT \sum_j \nu_j \ln[1 - C_{i,j} f_i^H / (1 + C_{i,j} f_i^H)] \]
  \[ + RT \ln[P_w^{EH} \phi_{w}^{EH} / P \phi_{pure}^{P0}] + \Delta V_w^{EH} [P - P_w^{EH}] \]

- **Two-phase equilibria**
  \[ \mu_w^H - \mu_w^{P0} = \mu_w^H - \mu_w^{P0} \]

- **Phase equilibria for containing electrolyte**
  \[ \mu_i^L = \mu_{i,Eos} + RT \ln a_i^E \]
Pure parameters for NLF-HB EOS

- Pure parameter regression
  - Vapor pressure and saturated liquid & vapor density

Table 1. Pure parameters for NLF-HB EOS

<table>
<thead>
<tr>
<th></th>
<th>( \varepsilon_a )</th>
<th>( \varepsilon_b )</th>
<th>( \varepsilon_c )</th>
<th>( r_a )</th>
<th>( r_b \times 10^3 )</th>
<th>( r \times 10^3_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O</td>
<td>134.022</td>
<td>7.8\times10\textsuperscript{-5}</td>
<td>-0.229</td>
<td>1.727</td>
<td>-0.002</td>
<td>-3.749</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{6}</td>
<td>76.378</td>
<td>-4.9\times10\textsuperscript{-7}</td>
<td>-0.110</td>
<td>5.091</td>
<td>-0.007</td>
<td>10.384</td>
</tr>
</tbody>
</table>

\( \varepsilon_{ii} / k = \varepsilon_a + \varepsilon_b (T - 273.15) + \varepsilon_c [T \ln(273.15/T) + (T - 273.15)] \)

\( r_i = r_a + r_b (T - 273.15) + r_c [T \ln(273.15/T) + (T - 273.15)] \)

- Hydrogen-bonding parameters for H\textsubscript{2}O-H\textsubscript{2}O interaction

\( E_{HB}^0 = -17.95 \text{ kJ/mol} \quad S_{HB}^0 = -16.6 \text{ kJ/mol} \)
Gibbs Energy Model (Lee et al., 1996)

- Pure parameter
  - Solvent or non-ionic molecule: 2 parameters
  - Ion: 3 parameters

<table>
<thead>
<tr>
<th>Components</th>
<th>( r_{s,j}[\text{Å}] )</th>
<th>( r_{j}[\text{Å}] )</th>
<th>( \varepsilon_{ii}[\text{kJ/mol}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>-</td>
<td>2.500</td>
<td>2.062</td>
</tr>
<tr>
<td>Ethane</td>
<td>-</td>
<td>6.3056</td>
<td>0.1733</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>2.327</td>
<td>2.554</td>
<td>5.521</td>
</tr>
<tr>
<td>Cl(^+)</td>
<td>3.017</td>
<td>0.484</td>
<td>1.362</td>
</tr>
</tbody>
</table>

- \( \text{H}_2\text{O} - \text{C}_2\text{H}_6 \) interaction parameter

\[
k_{ij} = 0.6276 - 187.123/T[\text{K}]
\]
Experimental Apparatus

● System accuracy
  ◆ Pressure: ±0.06 MPa
  ◆ Temp.: ±0.05 K
  ◆ Mole fraction: 5.3%
  ◆ Reproducibility of syringe pump: 0.5%

Figure 2. The experimental apparatus for measurement of the equilibrium pressure and the solubility of dissolved gas in the hydrate containing equilibria

(1) vacuum pump; (2) magnetic stirrer; (3) sampling cell; (4) sampling valve; (5) sampling loop; (6) metering pump; (7) density transducer; (8) water bath; (9) equilibrium cell; (10) flask; (11) syringe pump; (12) line filter; (13) gas bomb; (14) pressure gauge (15) McHugh type variable volume view cell
Thermodynamics & Properties Lab.

V\textsubscript{CH4}-L\textsubscript{W} equilibria

- Binary parameter for C\textsubscript{2}H\textsubscript{6}-H\textsubscript{2}O
  
  \[ k_{ij} = 0.90994 - 195.56/T \]

Table 2. Calculated L\textsubscript{W}-V\textsubscript{C2H6} equilibrium composition

<table>
<thead>
<tr>
<th>NaCl</th>
<th>pts</th>
<th>AADx [%]</th>
<th>P range [bar]</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8</td>
<td>4.3</td>
<td>13.7-35.4</td>
<td>a</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>11.0</td>
<td>24.4-36.1</td>
<td>b</td>
</tr>
<tr>
<td>1 M</td>
<td>3</td>
<td>26.7</td>
<td>32.2-57.4</td>
<td>a</td>
</tr>
</tbody>
</table>

- a) Mole fraction of ethane in water rich phase
- b) Mole fraction of water in ethane rich phase

**Figure 3. Isothermal vapor-liquid equilibria for water +ethane system at 298.15 K**
Three-phase equilibria

Table 4. Kihara potential for ethane hydrate

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon/k$ [K]</th>
<th>$\sigma$ [Å]</th>
<th>$a^{a)}$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_6$</td>
<td>144.7597</td>
<td>3.2606</td>
<td>0.5651</td>
</tr>
</tbody>
</table>

a) Radius of the spherical core $(a)$ was from Sloan (1998)

Table 5. Comparison of calculated 3-phase equilibrium pressure

<table>
<thead>
<tr>
<th>Phase</th>
<th>pts</th>
<th>Calculated error $a)^{a)}$</th>
<th>Present</th>
<th>Sloan</th>
<th>Klauda</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-I-$V_{C2H6}$</td>
<td>7</td>
<td>2.8</td>
<td>6.8</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>H-L$<em>W$-$V</em>{C2H6}$</td>
<td>61</td>
<td>2.6</td>
<td>9.0</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>H-L$<em>W$-$L</em>{C2H6}$</td>
<td>17</td>
<td>15.4</td>
<td>35.8</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

a) Absolute Average Deviation in pressure

Figure 4. Comparison of experimental and calculated equilibrium pressure of ethane hydrate in three-phase equilibria.
H-Π\textsubscript{C2H6} Equilibria

Table 6. Comparison of calculated Water content in ethane rich phase

<table>
<thead>
<tr>
<th>Phase</th>
<th>pts</th>
<th>Sloan\textsuperscript{a)} [%]</th>
<th>Present\textsuperscript{a)} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-V\textsubscript{C2H6} \textsuperscript{b)}</td>
<td>3</td>
<td>69.3</td>
<td>21.6</td>
</tr>
<tr>
<td>H-L\textsubscript{C2H6} \textsuperscript{b)}</td>
<td>4</td>
<td>14.0</td>
<td>16.1</td>
</tr>
<tr>
<td>H-L\textsubscript{C2H6} \textsuperscript{c)}</td>
<td>6</td>
<td>16.6</td>
<td>29.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} absolute Average Deviation in mole fraction
\textsuperscript{b)} Song and Kobayashi(1994)
\textsuperscript{c)} Sloan et al.(1986)

Figure 5. Comparison of calculated water contents in ethane-rich phase of H-L/V\textsubscript{C2H6} equilibria with data of Sloan et al. (1986) and Song and Kobayashi (1994)
H-Lw equilibria

Table 7. Comparison of calculated Ethane solubility in water phase

<table>
<thead>
<tr>
<th>NaCl</th>
<th>pts</th>
<th>AAD$^a$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3</td>
<td>0.09</td>
</tr>
<tr>
<td>1 M</td>
<td>3</td>
<td>4.84</td>
</tr>
</tbody>
</table>

a) Absolute Average Deviation in temperature (K)

Figure 6. Comparison of present calculation and experimental data of H-Lw equilibria of ethane hydrate
Figure 7. Comparison of calculated isobaric solubility of ethane in liquid water phase of H-Lw equilibria with experiments at 100 bar
Conclusion

- H-Lw Equilibrium compositions of ethane were experimentally determined.

- Recently proposed NLF-HB EOS was applied to various hydrate-containing phase equilibria.

- Effects of salt on hydrate-containing phase equilibria were experimentally determined for H-Lw equilibria and predicted for three-phase \((H-I-V_{C2H6}, H-L_w-V_{C2H6}, H-L_w-L_{C2H6})\) and two-phase \((H-L_w)\) equilibria.