L_W-H Equilibrium Measurements and Unified Predictions of Hydrate-Containing Phase Equilibriafor Methane, Ethane, Propane and Their Mixtures

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Motivation

- The methane hydrate as a possible energy resource or the CO_2 hydrate as a deep-ocean sequestration
  - Necessity for reliable **solubility data in water-rich phase** of hydrate-containing systems ($H\text{-}L_W$).
  - Measurement of solubility using **indirect method** for sparingly soluble gas components.

- Necessity for comprehensive calculation methods
  - Unified method to the hydrate-containing systems
  - The applicability of *Nonrandom lattice fluid hydrogen bonding* theory (You et al. 1994a, 1994b; Lee et al., 2001)

Computation of Hydrate Phase Equilibria

- Equality of Chemical potential(or fugacity)

◆ $\mu_i^H = \mu_i^\alpha \left(= \mu_i^\beta\right)$ or $\mu_i^H - \mu_i^{EH} = \mu_i^\alpha - \mu_i^{EH} \left(= \mu_i^\beta - \mu_i^{EH}\right)$

◆ $f_i^H = f_i^\alpha \left(= f_i^\beta\right)$ where α or β denotes V, L_W, L_C or Ice phase.

◆ $\mu_i^{\alpha \text{ or } \beta}$ is obtained from EOS and μ_W^{EH} and μ_W^{Ice} from vapor pressure and saturated molar volume(Sloan et al., 1976)

  - H-L_W-V, H-I-V, H-L_W-L_C : Yang et al.(2000), **Present work (Mixture)**
  - H-L_W-V, H-I-V : Klauda and Sandler (2000)
  - H-Lc, H-V, H-L_W : Yang et al.(2000, 2001), **Present work (Mixture)**
  - H-Lc, H-V : Sloan(1976)

Computation of Hydrate Phase Equilibria

- $\mu_W^{\alpha \text{ or } \beta} - \mu_W^{EH}$ is obtained from $\Delta\mu_W^{EH}(T_0, P_0), \Delta H_W^{EH}(T)$, and $\Delta V_W^{EH}(P)$ (Holder et al.,1980)

$$\frac{\mu_W^{EH} - \mu_W^{\Pi}}{RT} = \frac{\Delta\mu_W^{EH}(T_o, P_o)}{RT} - \int_{T_o}^{T} \frac{\Delta H_W^{EH}}{RT^2} dT + \int_{P_o}^{P} \frac{\Delta V_W^{EH}}{RT} dP - \ln x_w \gamma_w$$

  - H-L$_W$-V, H-I-V : Holder et al.(1980), Sloan (1998)
  - H-V, H-L$_C$: Anderson and Prausnitz(1986), Munck et al.(1988)

- $\mu_W^{H} - \mu_W^{EH}$ is obtained from the statistical model by van der Waals and Platteeuw (1959).

$$\mu_W^{H} = \mu_W^{EH} - RT \sum_m \nu_m \ln[1 + \sum_j C_{j,m} f_j^{\Pi}]$$

Chemical Potential in Fluid Phase

- *Nonrandom Lattice Fluid Hydrogen Bonding Theory*
  - NLF EOS by You et al. [1994 a, b]
  - Expansion to associating system using Veytsman statistics[1990] by Yeom et al. [1999]
  - A normalization of Veytsman statistics by Lee et al. [2001]

- Parameters for NLF-HB theory
  - Pure species : energy and size parameters
  - Hydrogen-bonding energy and entropy for H_2O-H_2O interaction
  - Binary interaction parameter for interactions between molecules

Chemical Potential of Water in Hydrate Phase

- Statistical model by van der Waals and Platteeuw(1959)
  - $\mu_W^H = \mu_W^{EH} - RT\sum_m \nu_m \ln[1+\sum_j C_{j,m} f_j^{\Pi}]$
  - f_j^{Π} is the fugacity of a component *j* in the equilibrium fluid phase.

$$f_j^{\Pi} = P^0 \exp[(\mu_j^{\Pi} - \mu_j^0)/RT]$$

  - $C_{j,m}$ is the Langmuir constants.

$$C_{j,m}(T) = \frac{4\pi}{kT}\int_0^{R_i} \exp\left(-\frac{W(r)}{kT}\right) r^2 dr$$

    - Calculated from the Kihara potential function
    - Kihara potential parameters are fitted from the three-phase equilibrium pressure for each guest species.

Chemical Potential of Empty Hydrate

- $$\mu_W^{EH} = \mu_W^0 + RT\ln\left(P_W^{satEH}\phi_W^{satEH}\right) + V_W^{satEH}\left(P - P_W^{satEH}\right)$$
  - ϕ_W^{satEH} of the empty hydrate is assumed to be unity.
  - Vapor pressure of empty hydrates
    - Fitted to equilibrium pressures of multi-guest and simple hydrates
    - Structure I :
      $$\ln[P_W^{satEH}/atm] = 17.410 - 6072.25/T$$
    - Structure II :
      $$\ln[P_W^{satEH}/atm] = 17.515 - 6121.34/T$$
  - Molar volume of empty hydrates
    - Correlated equation regressed by Avlonitis (1994)
    - $V_W^{satEH} = V_0[1 + k_1(T - T_0) + k_2(T - T_0)^2 + k_3(T - T_0)^3]$

Chemical Potential of Ice

- If saturated vapor pressure and molar volume of ice are known

$$\mu_W^I = \mu_W^0 + RT\ln\left(P_W^{satI}\phi_W^{satI}\right) + V_W^{satI}\left(P - P_W^{satI}\right)$$

  - Fugacity coefficient of ice, ϕ_W^{satI} is assumed to be unity.
  - Saturated vapor pressure is obtained from subcooled water properties(Perry et al., 1989)

$$\ln[P_W^{satI}/bar] = 17.9247 - \frac{6415.37}{T + 5.5171}$$

  - Molar volume of ice use the correlation equation regressed by Avlonitis (1994)

Experiments

- Direct method for small gas solubility
  - Applicable to salt-containing systems
  - Measurements by expansion of a liquid sample
  - Mole fraction of gas calculated by pressure changes in expansion chamber
    - Yang, S. O., Yang, I. M., Kim, Y. S. and Lee, C. S., "Measurement and prediction of phase equilibria for water+CO_2 in hydrate forming conditions", *Fluid Phase Equilib.*, **175** (2000), 79-85
    - Yang, S. O., Cho, S. H., Lee, H. and Lee, C. S., "Measurement and prediction of phase equilibria for water+methane in hydrate forming conditions", *Fluid Phase Equilib.*, **185** (2001), 53-63
  - Not applicable to **very sparingly soluble hydrocarbons**

Experiments

- Indirect method for very small gas solubility
    - With known composition of liquid phase, the phase transition point is detected by visual inspection.
        - Rumph, B. and Maurer, G., “An Experimental and Theoretical Investigation on the solubility of Carbon Dioxide in Aqueous Solutions of Strong Electrolytes”, *Ber. Bunsenges. Phys. Chems*., **97**(1993), 85-97
    - **Present study for water + methane or ethane in hydrate-forming conditions**

Experimental Apparatus

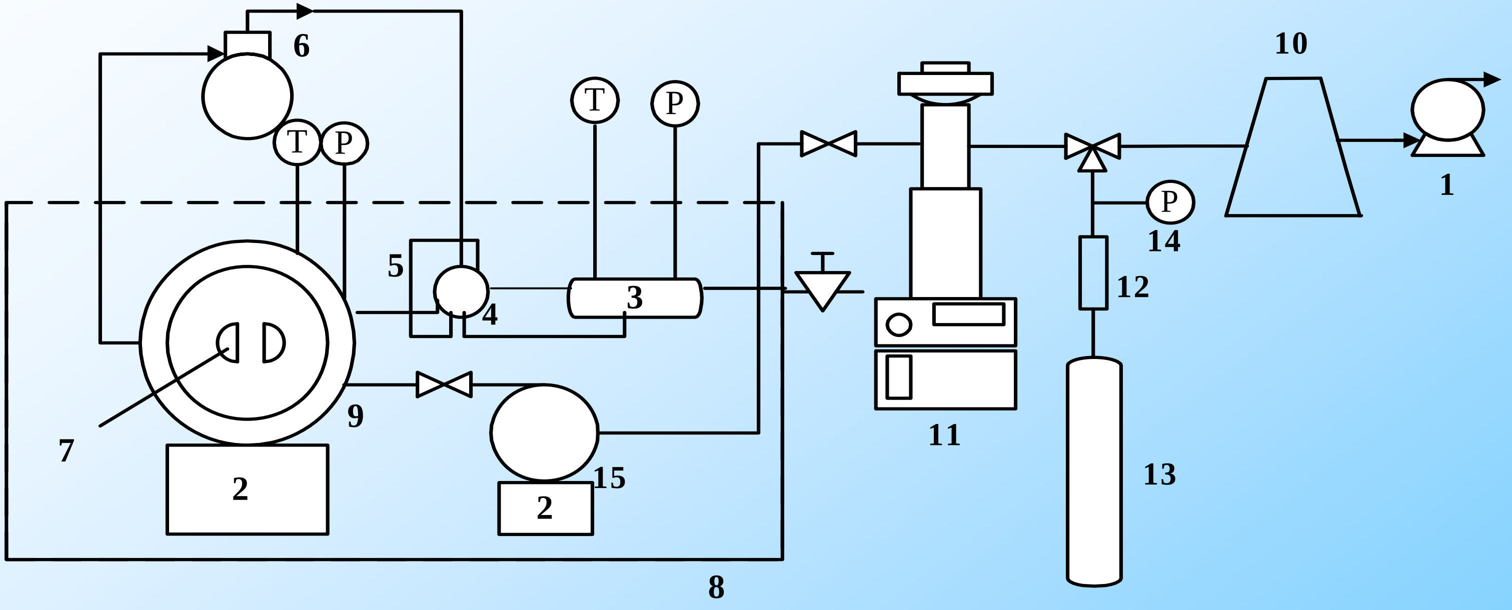


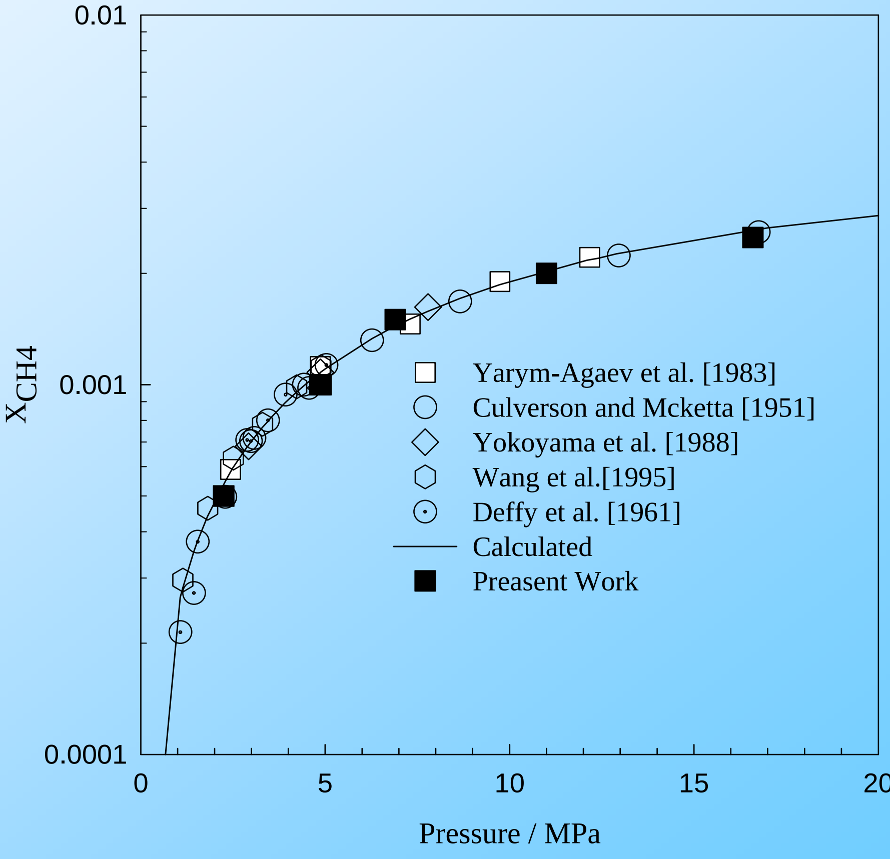
Figure 1. The experimental apparatus for measurement of the equilibrium pressure and the solubility of dissolved gas in the hydrate containing equilibria

(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

The Reliability of the Experimental Procedure

- Comparison between present methane solubility in water and those of DECEHEMA series

- The accuracy in mole fraction
  - Present work : 4.8 % AAD
  - DECHEMA : 5.3 % AAD



Three Phase Equilibria for Methane Hydrates

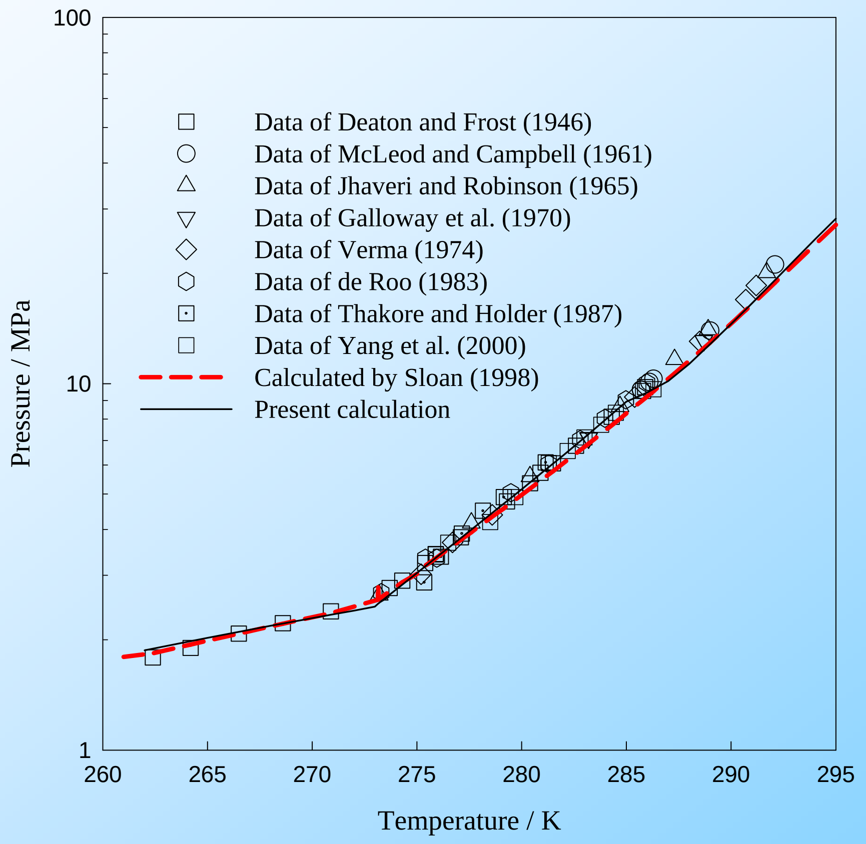


Figure 2. Comparison of experimental and calculated equilibrium pressure of methane hydrate in three phase equilibria

Three Phase Equilibria for Ethane Hydrates

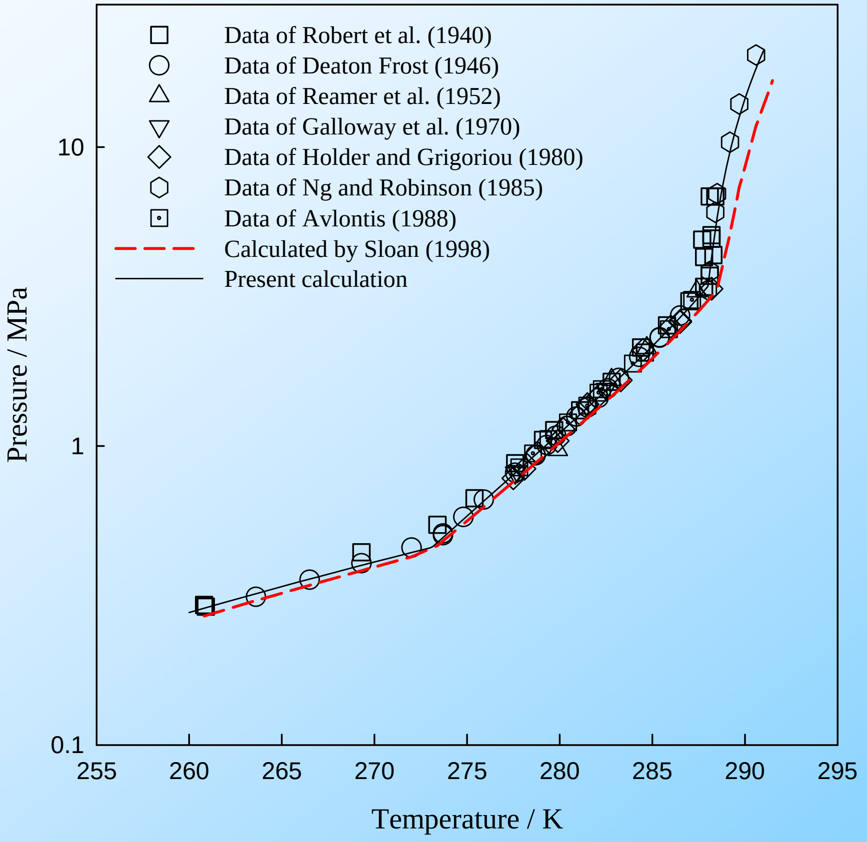


Figure 3. Comparison of experimental and calculated equilibrium pressure of ethane hydrate in three phase equilibria

Three Phase Equilibria for Propane Hydrates

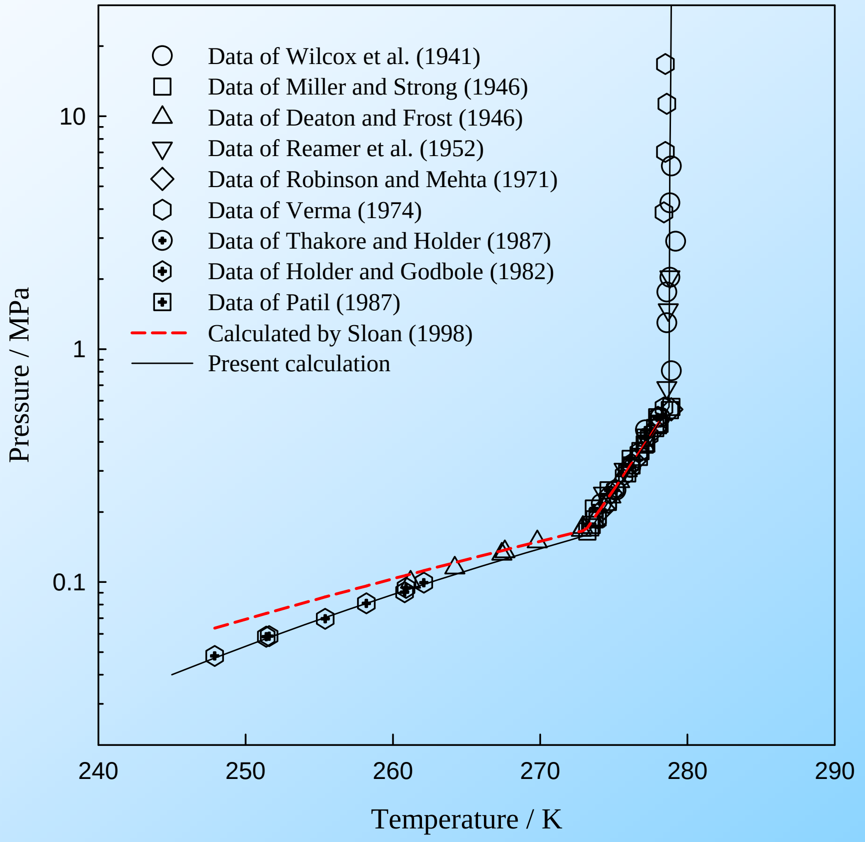


Figure 4. Comparison of experimental and calculated equilibrium pressure of propane hydrate in three phase equilibria

Three Phase Equilibria for Mixed Hydrates

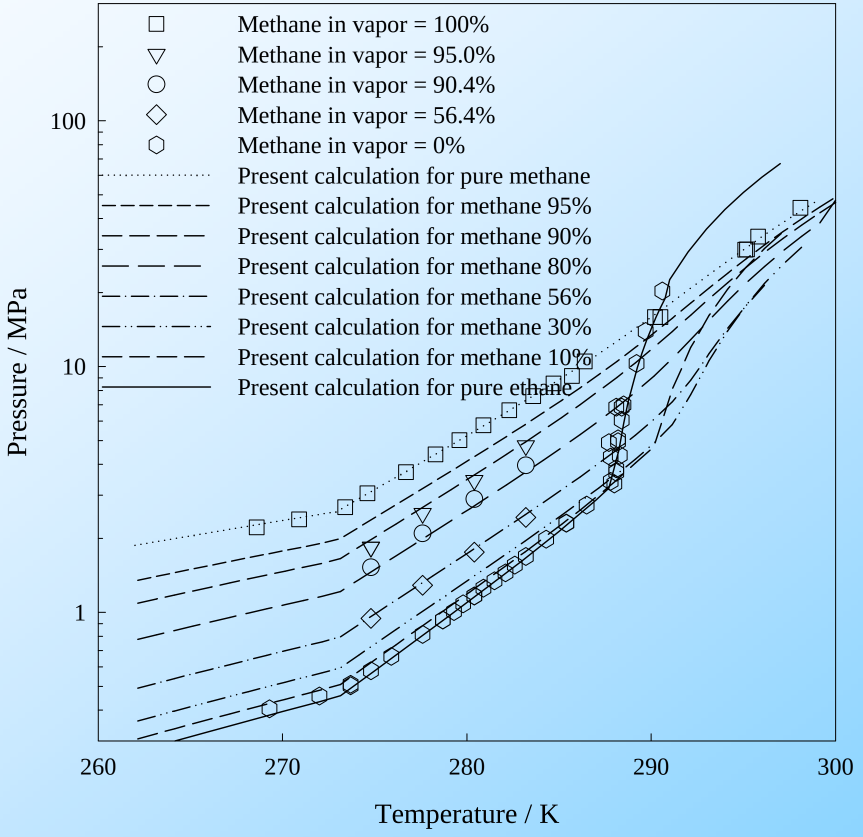


Figure 5. Comparison of calculated dissociation pressure of methane+ethane hydrate with measurements by Deaton and Frost (1946) for structure I

Three Phase Equilibria for Mixed Hydrates

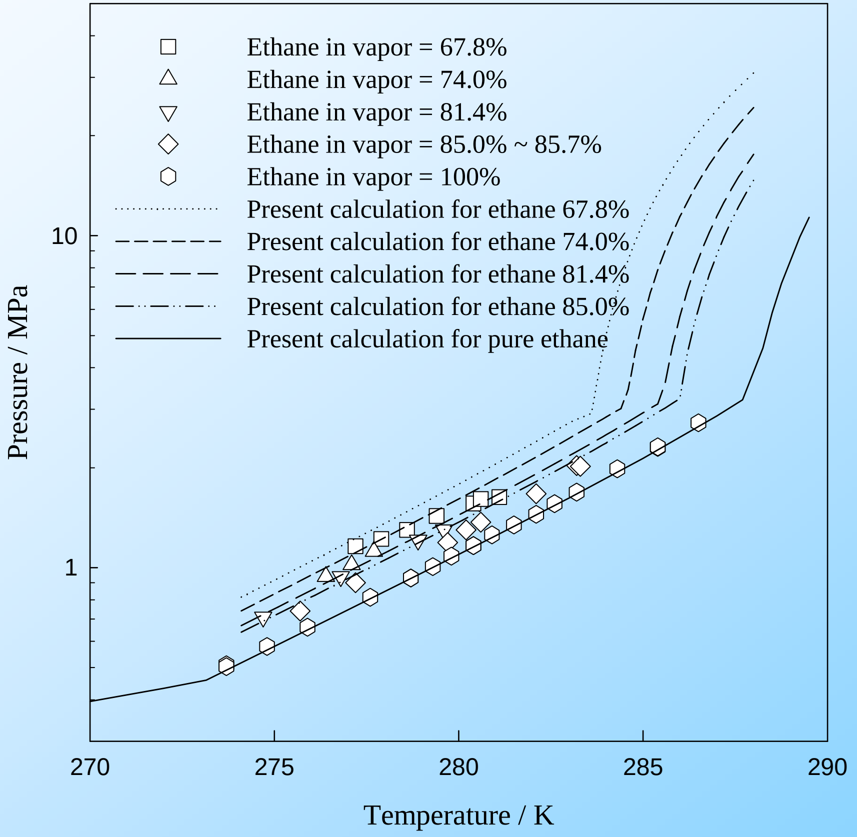


Figure 6. Comparison of calculated equilibrium pressure of ethane + propane hydrate with measurements for structure I hydrate

Three Phase Equilibria for Mixed Hydrates

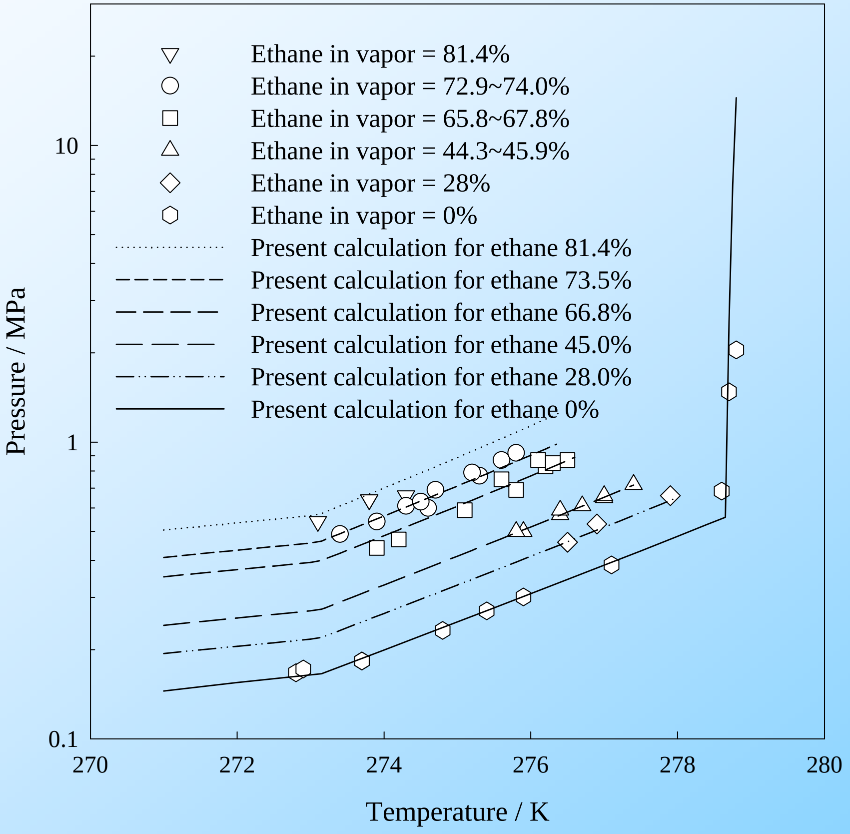


Figure 7. Comparison of calculated equilibrium pressure of ethane + propane hydrate with measurements for structure II hydrate

Solubility of Methane in H-L_w Equilibria

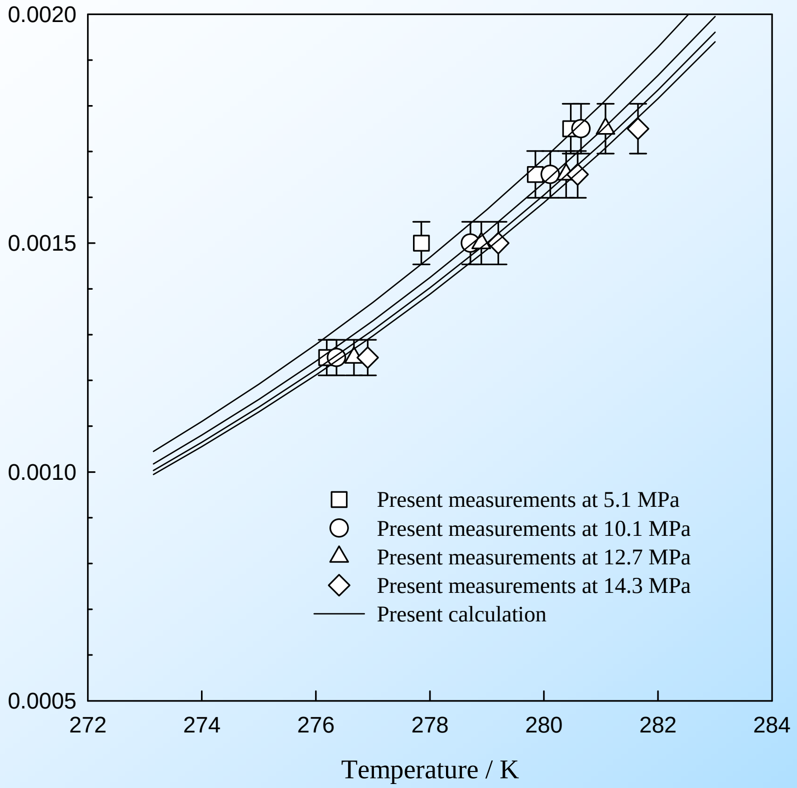


Figure 8. Comparison of calculated methane solubility in liquid water phase of H-L_w equilibria with present experimental data

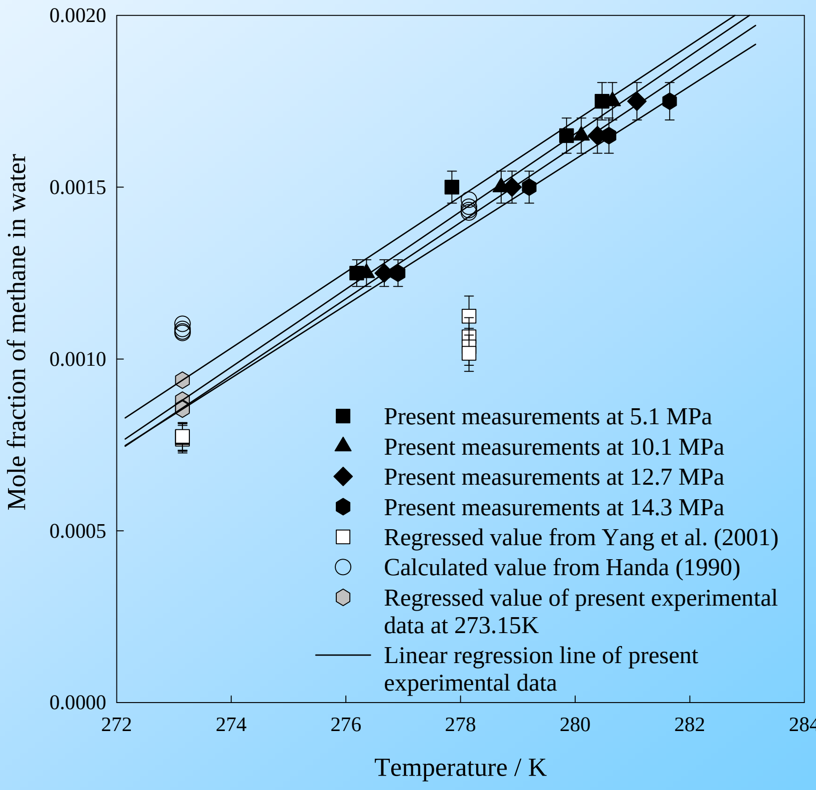


Figure 9. Comparison of present experimental methane solubility in liquid water phase of H-Lw equilibria with experimental data by Yang et al. (2001) and Handa's prediction (1990)

Solubility of Ethane in H-L_w Equilibria

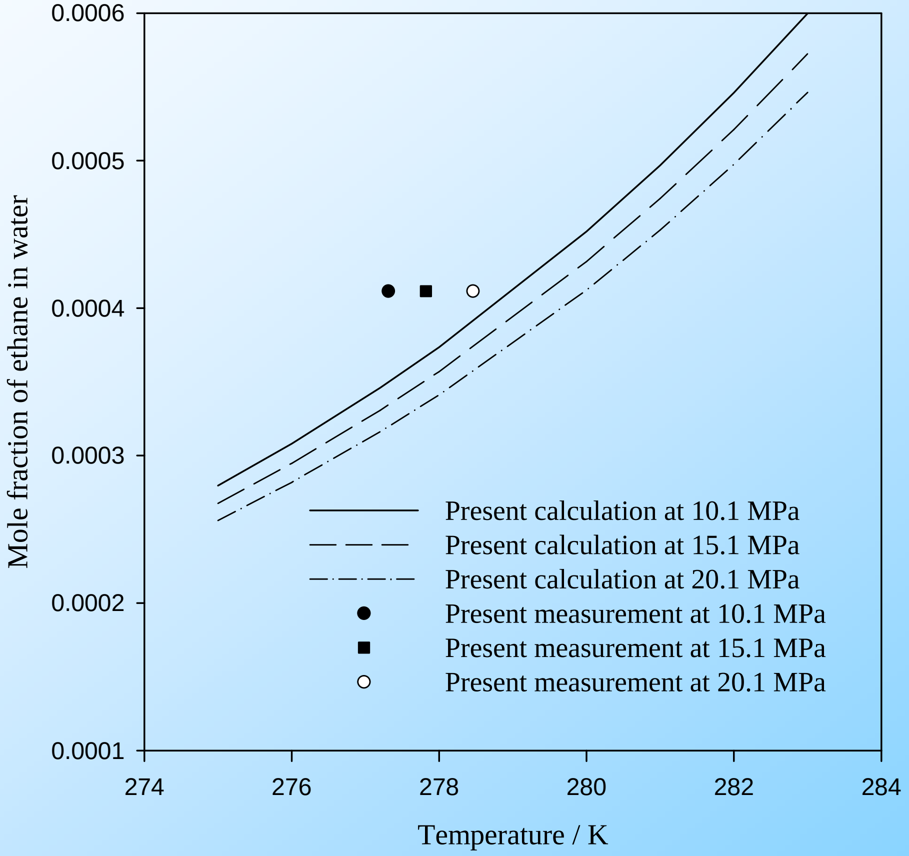


Figure 10. Comparison of calculated ethane solubility in liquid water phase of H-L_w equilibria with present experimental data

Water Content of Hydrocarbon-Rich Phase in H-Π_i Equilibria

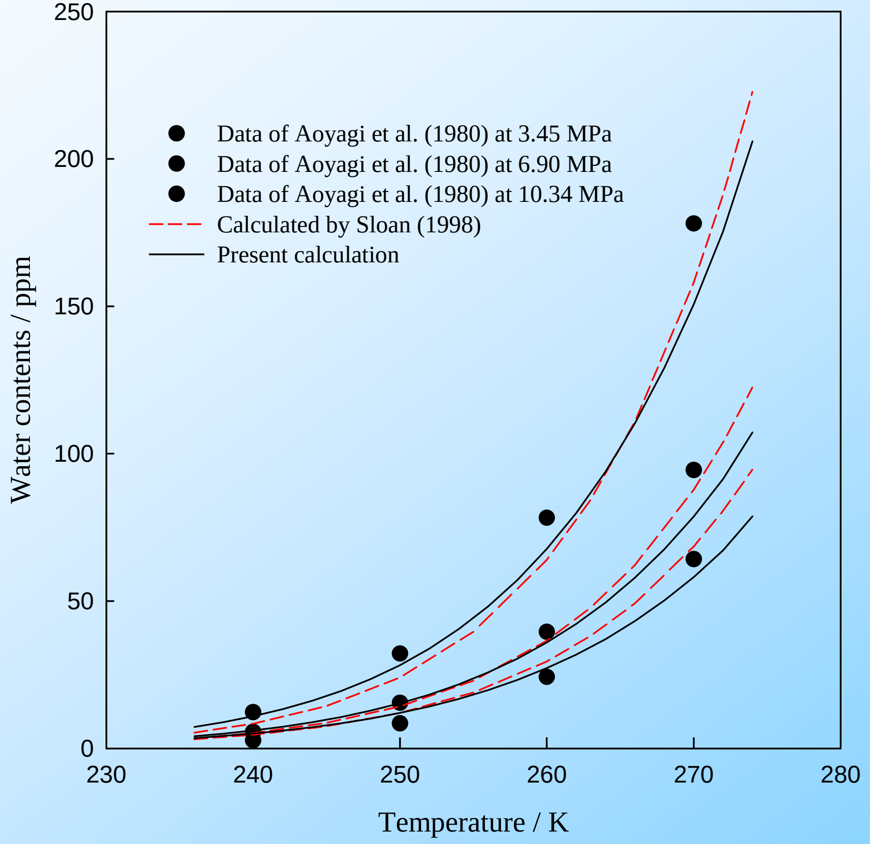


Figure 11. Comparison of calculated water contents in methane-rich phase of H-V equilibria with isobaric experimental data by Aoyagi et al. (1980) and Sloan's calculation (1998)

Water Content of Hydrocarbon-Rich Phase in H-Π_i Equilibria

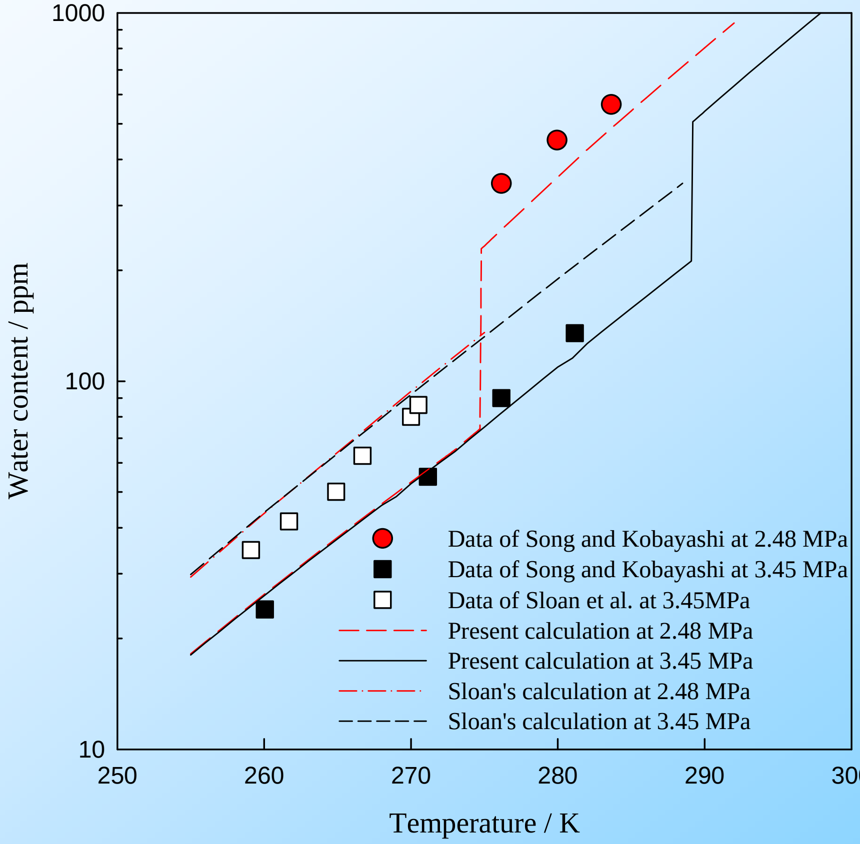


Figure 12. Comparison of calculated water contents in ethane-rich phase of H-Π_{C2H6} equilibria with Sloan et al. (1986) and Song and Kobayashi (1994).

Water content of hydrocarbon-rich phase in H-Π_i equilibria for mixed hydrate

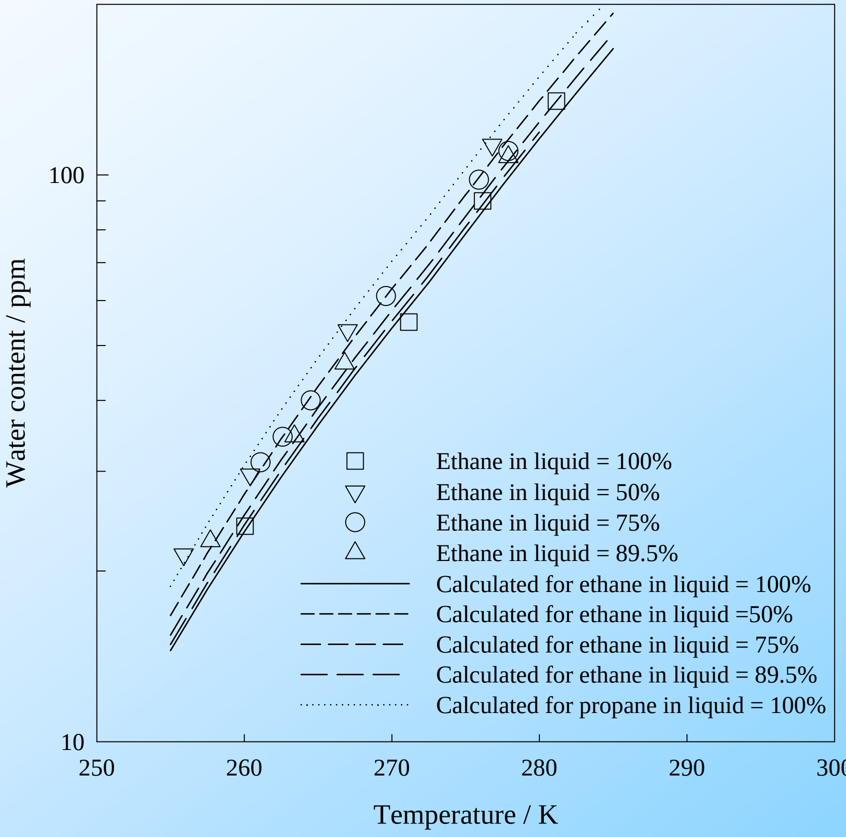


Figure 13. Comparison of calculated water contents in hydrocarbon-rich phase of H-L equilibria with isobaric experimental data of Song and Kobayashi (1994) for water+ethane+propane system at 3.45 MPa

Water content of hydrocarbon-rich phase in H-Π_i equilibria for mixed hydrate

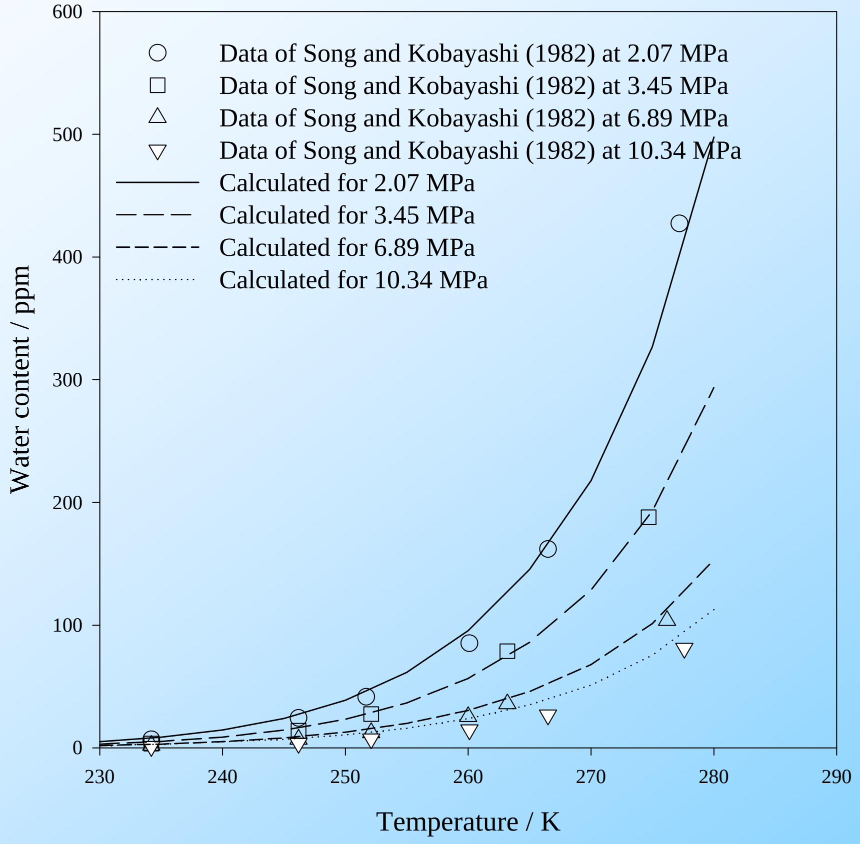


Figure 14. Comparison of calculated water content in hydrocarbon-rich phase of H-V equilibria with isobaric experimental data of Song and Kobayashi (1982) for water + methane + propane system, mole fraction of propane in vapor phase is 0.0531

Conclusions

- Solubilities in water-rich phase of H-L_W for methane and ethane hydrate were obtained with the accuracy of 3.1 % and 5.3 % in mole fraction, respectively.

- A unified calculation method was investigated with the nonrandom lattice fluid hydrogen bonding theory. The Kihara parameters in vdWP model and the vapor pressure of the empty hydrate were optimized.

- With a single binary parameter and hydrogen bonding energy, various phase equilibria of simple hydrate and mixed hydrate were calculated with good accuracy.