MEASUREMENT AND PREDICTION OF CARBON DIOXIDE-HYDRATE FORMATION IN AQUEOUS ELECTROLYTE SOLUTION

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Keywords : equation of state, carbon dioxide, electrolyte, experimental data , solid-fluid equilibria

ABSTRACT

Three phase equilibria involving clathrate hydrate and fluid phases were measured for carbon dioxide -water mixtures in the presence of sodium chloride. The pressure range was from 2 to 20Mpa and temperature range from 277K to 285K. A variable volume view cell was used with a magnetic stirrer inside. The experimental results were compared with predictions. In the prediction, an equation of state based on an approximate nonrandom lattice theory of fluids by You et al., a statistical model for hydrate chemical potential by van der Waals and Platteeuw, a recent electrolyte solution model for mixed electrolyte and mixed solvent systems by Lee et al. were used. Good agreements between calculated and experimental results were obtained.

INTRODUCTION

Since the early nineteen century water molecules have been known to form clathrate hydrates when stabilized by guest molecules occupying cavities in the crystal even above the freezing point of water. After a period of scientific interest clathrate hydrates became a practical concern for the natural gas industry. The history and the recent status of clathrate hydrate research are well documented in Sloan, Jr.′s book[1]. Clathrate hydrate of carbon dioxide attracted attention recently as a means of disposal[2] of the gas in deep sea. It has also been known that the formation of clathrate hydrates is inhibited by the presence of salts or methanol, for example.

Phase equilibria involving clathrate hydrates have been important problems in applications. Since the pressure range of interest is usually more than 50 bar, an equation of state approach is required in principle. However, for lack of a suitable equation of state liquid phase presents difficulties in most methods developed for equilibrium calculation. In the present study we investigate the applicability of lattice fluid equation of state of You et al.[3,4] for three phase equilibria involving clathrate hydrates. We also study the inhibition effect of salts in near sea water condition experimentally.

THEORY

Above the melting temperature of ice, the carbon dioxide and water mixture may exhibit vapor phase(V), water rich liquid phase(L_W), carbon dioxide rich liquid phase(L_{CO2}), and clathrate hydrate phase(H). Various phase equilibria involving these phases may be calculated once chemical potentials or fugacities of components for different phases are calculated. This thermodynamic-based method is similar to those described by Sloan[1], Holder[5] and Englezos[6] for L_W-H-V equilibria, but different in

defining reference properties. In the present study we use the lattice fluid equation of state by You et al.[3,4] which is accurate in both liquid and vapor phase. Therefore liquid phase non-ideality can be described without using activity coefficients, the use of which is limited to low pressures. In the lattice fluid theory chemical potential is conveniently evaluated and is used extensively instead of fugacity.

Van der Waals and Platteuw[7] derived the expression for the chemical potential of water in hydrate phase, μ_W^H. Since pure carbon dioxide form structure I as simple hydrates[1] , the general expression reduces to

$$\Delta\mu_W^H = \mu_W^H - \mu_W^{EH} = RT\sum_i \nu_i \ln[1 - C_{CO2,i} f_{CO2}^{\Pi} / (1 + C_{CO2,i} f_{CO2}^{\Pi})] \qquad (1)$$

where i denotes two kinds of cavities CO_2 molecules can occupy, Π denotes an equilibrium fluid phase, μ_W^{EH} is the chemical potential of empty hydrates, ν_i is the number of type i cavities per water molecule. The Langmuir constant, $C_{CO2,i}$, for each kind of cavities is a function of temperature and empirically represented by,

$$C_{CO2,i} = (A_{CO2,i} / T)\exp(B_{CO2,i} / T) \qquad (2)$$

These constants are available in the literature[8]. For the hydrate structure CO_2 molecules can occupy, these constants are A=2.474×10^{-4}, B=3.410×10^{3}, ν_1=1/23 for small cavities and A=4.246×10^{-2}, B=2.813×10^{3}, ν_2=3/23 for large cavities respectively. The fugacity of CO_2 is calculated from the chemical potential,

$$f_{CO2}^{\Pi} = P^0 \exp[(\mu_{CO2}^{\Pi} - \mu_{CO2}^{\Pi 0}) / RT] \qquad (3)$$

where $\mu_{CO2\Pi}^{0}$ is the fugacity of CO_2 at P^0=1 bar and at the system temperature which is assumed ideal gas.

When equating chemical potentials for equilibrium calculation between a fluid and hydrate phase, the difference of reference states should be considered. We define $\Delta\mu_W$,

$$\Delta\mu_W^{H\Pi}{}_W = \mu_W^{EH} - \mu_{pure\,W}^{\Pi} = RT\ln[f_{pure\,W}^{H} / f_{pure\,W}^{\Pi}]$$

$$= RT\ln[P_W^{sat\,EH}\phi_W^{sat\,EH} / P\phi_{pure\,W}^{\Pi}] + V_W^{sat\,EH}[P - P_W^{sat\,EH}] \qquad (3)$$

This relation requires the vapor pressure of the empty hydrate, $P_w^{sat\,EH}$.

Now we write the two phase equilibrium relation involving hydrate phase. For water

$$\Delta\mu_W^{\Pi} = \mu_W^{\Pi} - \mu_{pure\,W}^{\Pi} = \Delta\mu_W^{H} + \Delta\mu_W^{H\Pi} \qquad (4)$$

Three phase equilibrium relations can be written similarly. For L_W-H-V equilibria,

$$\Delta\mu_W^{LW} = \Delta\mu_W^{V} = \Delta\mu_W^{H} + \Delta\mu_W^{H\Pi}; \quad \mu_{CO2}^{LW} = \mu_{CO2}^{V} \qquad (5)$$

and for L_W-H-L_{CO2} equilibria we have

$$\Delta\mu_W^{LW} = \Delta\mu_W^{LCO2} = \Delta\mu_W^{H} + \Delta\mu_W^{H\Pi}; \quad \mu_{CO2}^{LW} = \mu_{CO2}^{V} \qquad (6)$$

In both cases the chemical potential of CO_2 in equilibrium phases affects the chemical potential of water in hydrates via eqn (1) and (2).

When nonvolatile strong electrolytes are present in aqueous phase, the chemical potential and the fugacities of the liquid phase are affected. The effects of electrolytes can be reflected accurately if a suitable equation of state is available. If the pressure dependence is neglected the effect may also be accounted for semi-empirically by the change of activity. This approach has been adopted by various investigators[2, 6].

$$\mu_i^{LE} = \mu_i^{L} + RT\ln x_j^{E}\gamma_j^{E} \qquad (7)$$

where the superscript *E* denotes quantities in the presence of electrolytes. The correction term reflects the change of mole fractions and activity coefficients due to the presence of electrolytes.

Eqn (5) may be solved by iteration for L_W-H-V equilibria and eqn (6) for L_W-H-L_{CO2} equilibria. Lattice fluid theory of You et al.[3,4] provides necessary expressions and they are summarized in appendix. For a fluid phase at given composition, temperature and

pressure, r is calculated by eqn (A5) and m_i from eqn (A7).

EXPERIMENTAL

All the experiments were performed using the apparatus shown in Fig. 1. A variable volume view cell with a magnetic stirrer inside was used. The cell was connected to an external circulation loop and the aqueous phase were circulated by a high-precision metering pump to enhance mixing. The cell and the circulation loop were immersed in a temperature-controlled bath. The apparatus and method is similar to that used by Adisasmito et al.[9] except for the mixing method. Valcom(model VPRT-350K) pressure gauge with the claimed accuracy of 0.1 bar was used after calibration with Heise gauge. Temperature was measured by Cole Parmer(model 8436-00) with an accuracy of 0.01K.

Approximately 80 ml of solution (NaCl 0.5 M) was charged into the cell. After the dissolved gases were removed, carbon dioxide gas was introduced. The system was pressurized with the hand pump until a desired pressure was reached while the temperature in the cell was maintained 3-4K below the expected three phase equilibrium temperature. Once the hydrates were formed, they were allowed to decompose by raising the temperature. Near the complete decomposition, the system was maintained at the temperature for 8 hours. When no pressure change was detected, the condition was taken as the equilibrium condition. Subsequently, a different pressure was selected, and the procedure was repeated to obtain the incipient hydrate formation temperature. Temperature measurements were found reproducible within 0.1K. The experimental data are listed in table 1.

RESULTS AND DISCUSSION

The main difference of present method in the equilibrium calculation is that we used the lattice equation of state for both vapor and liquid phases consistently. Parameters ε_{ii}/k and V_i^* in eqn (A1) and (A2) are pure component parameters and fitted to density and vapor pressure in the liquid phase or to PVT data in gas phase. They are listed in table 2. The binary energy parameter l_{ij} (=-0.16) in eqn (A1) was determined from two phase equilibria. We use literature value for $V_w^{sat\ EH}$ [10]. The only other property was the vapor pressure of empty hydrates $P_w^{sat\ EH}$ which we fitted data for both L_W-H-V and L_W-H-L_{CO2} equilibria. They are shown in Fig. 2 and represented by the relation,

$$\ln P_W^{sat\ EH} = 18.345 - 6261.2 / T \qquad (8)$$

Sloan, Jr. used this quantity below the freezing temperature of water[1]. Above the freezing temperature one need to use an equation of state for liquid phase for eqn (3) as we did in the present study. An alternative approach is to fit three phase equilibrium data using the relation,

$$\Delta\mu_W^{H\Pi} = \Delta\mu_W^{H\Pi}(T_0, P_0) + \int_{T_0}^{T} (\Delta H_W^{H\Pi} / RT^2) dT + \int_{P_0}^{P} (\Delta V_W^{H\Pi} / RT) dP \qquad (9)$$

as adopted by most other investigators. Still this method is not readily applied to L_W-H-L_{CO2} equilibria. Without an adequate equation of state one cannot use eqn (1).

The results of calculation are compared with data and with those of other calculation methods in Fig. 3. The present method is seen to give somewhat better results. It should be noted that the L_W-H-L_{CO2} branch is properly represented by the present method.

The inhibition effect of sodium chloride was calculated by eqn (7) and shown in the same figure. The activity coefficient of water may be calculated by the method of Lee et

al.[11]. Since concentration of CO_2 is very low, the activity coefficient is in good agreement with experimental values in aqueous electrolyte solutions[12]. Good agreements are observed. No L_W-H-L_{CO2} data with electrolytes are known to the authors.

CONCLUSION

L_W-H-V and L_W-H-L_{CO2} equilibrium data for water-CO_2-hydrate and water-NaCl-CO_2-hydrate were measured and calculated. Lattice fluid equation of state was used in the calculation for both liquid and vapor phases. For the chemical potential difference of empty hydrates and pure water the vapor pressure correlation of empty hydrates was determined. The effect of electrolytes was corrected with experimental activity coefficients of water. Good agreements between observed and calculated results were obtained

AKNOWLEDGEMENT

Authors are grateful to Korea Science and Engineering Foundation(94-0562-06-01-3) for financial support.

NOTATIONS

A = parameter for the calculation of Langmuir constant, K/atm

B = parameter for the calculation of Langmuir constant, K

C = Langmuir constant, 1/bar

N_a = Avogardro′s number.

q_i = surface area parameter for molecule i

r_i = number of segment per molecule i

V_i^* = molecular hard core volume of molecule i, cm^3/mol

V_H = lattice cell volume, cm^3/mol

z = lattice coordination number

Greek Letters

β = reciprocal temperature, $1/kT$

ε_{ij} = molecular interaction energy

ϕ = fugacity coefficient

γ_i = activity coefficient

λ_{ij} = binary energy parameter

μ= chemical potential

ν_i = number of cavities of type i

θ = surface area fraction of sites

ρ = molar density

Subscript

0 = hole

M = mixture quantity

Superscript

E = electrolyte

EH = empty hydrate

sat = saturated

π = fluid phase

^{o} = reference state

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APPENDIX

The lattice fluid theory of You et al.[3,4] uses two temperature dependent parameters for pure species, ϵ_{ii} and V_i^*, and one binary energy parameter, k_{ij}.

$$\varepsilon_{ii} / k = \varepsilon_a + \varepsilon_b T + \varepsilon_c \ln T \; ; \; \varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1 - k_{ij}) \tag{A1}$$

$$V_i^* = V_a + V_b T + V_c \ln T \tag{A2}$$

r_i is calculated from V_i^* by the relation,

$$V_i^* = r_i N_a V_H \tag{A3}$$

and q_i is related to r_i.

$$z q_i = (z-2) r_i + 2 \tag{A4}$$

where z and V_H are constants which are equal to 10 and 9.75 cm^3/mol, respectively, and N_a is the Avogardro′s number.

The expressions for equation of state and chemical potential are

$$P = \left(\frac{1}{\beta V_H}\right)\left\{\left(\frac{z}{2}\right)\ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] - \ln(1-\rho)\right\} - \left(\frac{z}{2}\right)\rho^2\left(\frac{\varepsilon_M}{V_H}\right) \tag{A5}$$

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

$$\times [1 - \frac{r_i}{q_i} - \frac{2\sum \theta_j \varepsilon_{ij} + \beta \sum\sum\sum \theta_k \theta_l \theta_m \varepsilon_{ik}(\varepsilon_{ik} + \varepsilon_{lm} - \varepsilon_{kl} - \varepsilon_{il})}{\theta^2 \varepsilon_M}] \tag{A6}$$

where

$$\varepsilon_M = \left(\frac{1}{\theta^2}\right)\left[\sum\sum \theta_i \theta_j \varepsilon_{ij} + \left(\frac{\beta}{2}\right)\sum\sum\sum\sum \theta_i \theta_j \theta_k \theta_l \varepsilon_{ij}\left(\varepsilon_{ij} + 3\varepsilon_{kl} - 2\varepsilon_{ik} - 2\varepsilon_{jk}\right)\right] \tag{A7}$$

$$q_M = \sum x_i q_i \qquad r_M = \sum x_i r_i \qquad \sum X_i = 1 \tag{A8}$$

$$\theta_i = x_i q_i / (x_0 + q_M) \qquad x_0 = N_0 / \sum N_i \qquad \theta = \sum \theta_i \tag{A9}$$

$$V = V_H (\sum N_i)(x_0 + r_M) \qquad \rho = \sum V_i^* / V \tag{A10}$$

Here N_i is the number of molecules of species i. The sum is over all molecular species and subscript 0 denotes holes.

Table 1. Experimental data of the three phase equilibrium for water-carbon dioxide-hydrate system

NaCl/mol	Temp/K	P(exptl)/bar	NaCl/mol	Temp/K	P(exptl)/bar
0.0	277.50	21.99	1.0	277.52	24.45
0.0	278.419	24.35	1.0	278.51	27.88
0.0	279.50	28.00	1.0	279.52	32.02
0.0	280.47	31.83	1.0	280.62	37.45
0.0	281.49	36.55	1.0	281.48	42.63
0.0	282.55	42.65	1.0	282.17	82.47
0.0	282.95	53.18	1.0	282.60	129.67
0.0	283.20	92.83	1.0	283.10	180.70
0.0	283.90	131.2			
0.0	284.48	195.14			

Table 2. Parameters for equation of state [3,4]

	Energy Parameters			Volume Parameters		
	ϵ_a	ϵ_b	ϵ_c	V_a	V_b	V_c
water	0.2255	-1.1563	132.025	111.325	0.07229	-20.155
CO_2	745.191	0.3371	-133.481	-56.874	-0.0090	16.923

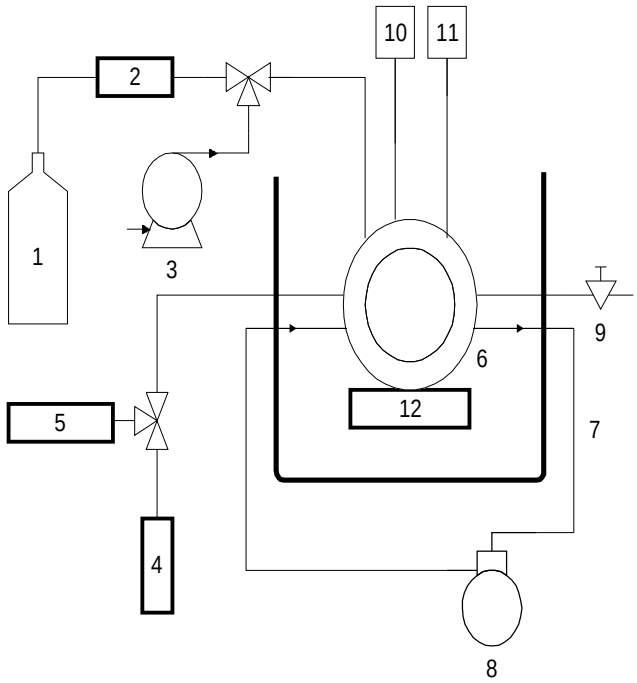
$\epsilon_{ii} / k = \epsilon_a + \epsilon_b T + \epsilon_c \ln T$; $V_i^* = V_a + V_b T + V_c \ln T$

FIGURE CAPTIONS

Figure 1. Schematic diagram of gas hydrate apparatus: (1) carbon dioxide cylinder; (2) line filter; (3) vacuum pump; (4) water reservoir; (5) hand pump; (6) equilibrium cell; (7) circulation loop; (8) metering pump; (9) vent; (10) temp. gauge; (11) press. gauge; (12) magnetic stirrer

Figure 2. Comparisons of calculated empty hydrate vapor pressures with fitted values

Figure 3. Comparisons of the three phase equilibrium data with calculated results for water-carbon dioxide-hydrate system


10
11
2
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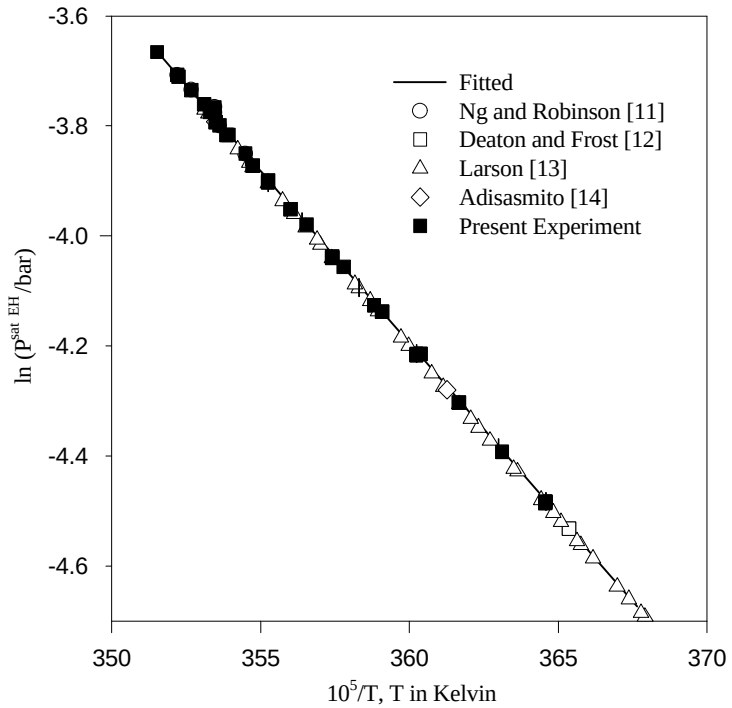
-3.6
-3.8
-4.0
-4.2
-4.4
-4.6
ln (P^sat EH /bar)
350
355
360
365
370
10^5/T, T in Kelvin
Fitted
Ng and Robinson [11]
Deaton and Frost [12]
Larson [13]
Adisasmito [14]
Present Experiment

Fig.2

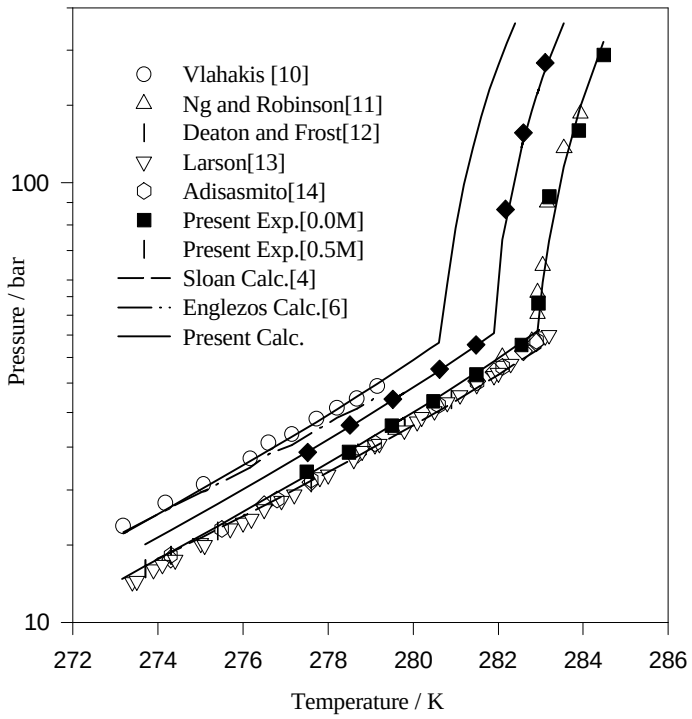
Vlahakis [10]
Ng and Robinson[11]
Deaton and Frost[12]
Larson[13]
Adisasmito[14]
Present Exp.[0.0M]
Present Exp.[0.5M]
Sloan Calc.[4]
Englezos Calc.[6]
Present Calc.
100
10
Pressure / bar
272
274
276
278
280
282
284
286
Temperature / K

Fig.3