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Prediction of Gas Hydrate Formation Conditions for
Carbon Dioxide in the Presence of Electrolytes

by

Cecilia Wai-Kam Tse

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "Prediction of Gas Hydrate Formation Conditions for Carbon Dioxide in the Presence of Electrolytes" submitted by Cecilia Wai-Kam Tse in partial fulfillment of the requirements for the degree of Master of Science.

P.R. Bishnoi

Supervisor, Dr. P.R. Bishnoi
Department of Chemical and Petroleum Engineering

N. Kalogerakis

Dr. N.E. Kalogerakis
Department of Chemical and Petroleum Engineering

Richard D. Rowe

Dr. R.D. Rowe
Department of Mechanical Engineering

Aug. 6, 1993
Date

ABSTRACT

This study deals with the thermodynamic modelling of CO₂ gas hydrates in the presence of electrolytes. Existing methods of hydrate calculation are not able to account for gases with considerable solubilities. This study has been undertaken to examine various thermodynamic models for their ability to account for the solubility of gases and the non-ideal behaviour due to the presence of electrolytes in the liquid phase for the calculation of incipient hydrate equilibrium conditions.

A methodology for the prediction of gas hydrates involving CO₂ and its mixtures with CH₄ was formulated. The method utilizes the statistical thermodynamic model of van der Waals and Platteeuw (1959) to describe the solid hydrate phase. Three thermodynamic liquid models were examined for hydrate calculations, namely Chen and Evans (1986), Zuo and Guo (1991) and Aasberg-Petersen et al. (1991). A mixing rule was proposed for handling mixed electrolyte systems for the models of Chen and Evans (1986) and Zuo and Guo (1991). It was found that the model of Zuo and Guo (1991) provided the best results when compared to experimental data for CO₂ gas hydrates.

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LIST OF SYMBOLS

A_{ij} B_{ij}	fitted constants in eqn. 8
A	parameter defined in eqn. 31
A_ϕ	Debye-Hückel constant
a_w	activity
a, b, c	equation of state parameters
B	parameter defined in eqn. 28 and 31
C	Langmuir constant, 1/Pa
C_j	= Z_j for ions and = 1 for molecules
C_p	heat capacity, J/mol K
F	moles of feed, mol
f_j	fugacity of component j, Pa
f	empirical parameter = 6.0
g^{ex}	excess Gibbs free energy
h	enthalpy, J/mol
h_{is}	regressed interaction coefficient
I	ionic strength
K_i	equilibrium constant
k	Boltzmann's constant, 1/K
L	moles of liquid, mol
M_s	molecular weight, g/mol
M_m	salt-free mixture molecular weight, g/mol
N	moles of volatile components in feed, mol

N_a	Avogadro's number
n	number of experimental data points
n_i	moles of ionic species i , mol
P	pressure, Pa
p	salt-specific interaction parameter
R	universal gas constant, J/mol K
$RMSD$	root mean square deviation
r	distance from centre of cavity, m
S	moles of ionic species
T	temperature, K
tc	total number of components in feed
V	moles of vapor
V_w	molar volume, m ³ /mol
vc	number of volatile components in feed
$W(r)$	cell potential function, J
w_j	mole fraction of j in S
X_j	effective mole fraction of j in liquid
x_i	mole fraction of i in liquid
y_i	mole fraction of i in vapor
Z_j	ionic charge of ionic species j
z_i	mole fraction of i in N

Greek Letters

α	NRTL nonrandomness factor
β	V/N

γ	activity coefficient
ϵ	ionic energy, J
μ	chemical potential
ν_i	number of cavities of type i
ξ_i	interaction parameter for common ion i
σ	ionic diameter, m
τ	binary interaction energy parameter
ϕ	fugacity coefficient
ψ	S/N
ϵ	ionic energy, J

Subscripts

a, a', a''	anion
c, c', c''	cation
<i>exp</i>	experimental
<i>i</i>	index
<i>j</i>	index
<i>k</i>	index
<i>m</i>	index
<i>o</i>	reference conditions
<i>pred</i>	predicted
<i>m</i>	molecule
<i>w</i>	water

Superscripts

<i>DH</i>	Debye-Hückel
<i>EL</i>	electrostatic term
<i>EOS</i>	equation of state
<i>H</i>	hydrate
<i>lc</i>	local composition
<i>MT</i>	empty lattice
<i>o</i>	pure liquid water at reference conditions
<i>pdh</i>	Pitzer-Debye-Hückel
<i>sl</i>	solution

1. INTRODUCTION

1.1 Description of Gas Hydrates

Gas hydrates are crystalline solids that are formed when water is contacted with low molecular weight gases at low temperatures and high pressures. The water molecules, through hydrogen bonding, form a lattice structure with cavities. These cavities are occupied by gas molecules with diameters smaller than the cavity diameters. The interactions between the gas molecules and the water molecules are of the van der Waals type dispersion forces. Gas hydrates may form in two different structures called structure I and structure II. Structure I has a unit crystal structure of a body centered cubic whereas the unit crystal structure for structure II is a diamond lattice. The structures of gas hydrates are illustrated in Figure 1.1 (Holder et al., 1988). Both structure I and structure II consist of small and large cavities which are polyhedra formed by the water molecules. The small cavities of both structure I and structure II have twelve pentagonal faces. The large cavities of structure I have twelve pentagonal and two hexagonal faces whereas the large cavities of structure II have twelve pentagonal and four hexagonal faces. The diameters of the lattice cavities are dependant on the structure formed. The cavity diameter is the main determining factor for the type of gases that will form gas hydrates. Table 1.1 (Holder et al., 1988) provides the general properties of the hydrate lattices. It has been found that gases such as nitrogen, carbon dioxide, oxygen, hydrogen sulfide, methane and ethane form structure I hydrates. Structure II hydrates are formed from larger gas molecules such as propane, iso-butane and n-butane. Detailed information on the structure of gas hydrates can be found in the literature. (Holder, 1988; Sloan, 1990).

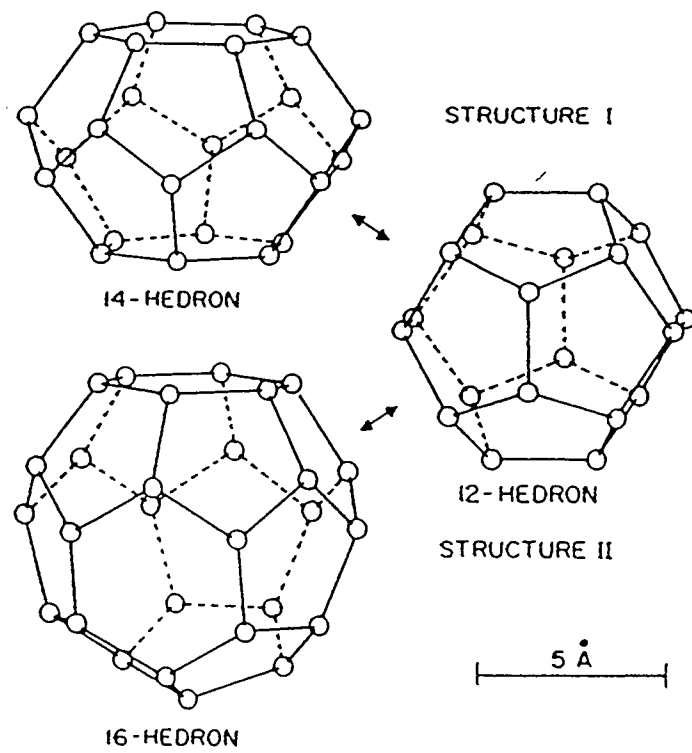


Figure 1.1 Structures of Gas Hydrates
[Reference: Holder et al. (1988)]

Table 1.1

Properties of Hydrate Lattices

	<u>Structure I</u>	<u>Structure II</u>
Unit Cell Size (A)	12.03	17.31
Number of Cavities per Unit Cell	2 Small Cavities 6 Large Cavities	16 Small Cavities 8 Large Cavities
Diameter of Cavities (A)		
Small	7.88	7.82
Large	8.60	9.46
Typical Hydrate Forming Gases	methane, ethane, carbon dioxide	propane, propylene, i-butane

Reference: Holder et al. (1988)

The study of gas hydrates is very important to the natural gas and petroleum industry. The formation of gas hydrates can create problems for natural gas handling, processing and transportation. The blocking of gas transportation pipelines was first discovered by Hammerschmidt (1934). Since then, the amount of work on hydrate research has increased tremendously. In order to avoid hydrate formation in pipelines, it is important to know the thermodynamic conditions at which gas hydrates will form. This knowledge can provide a guideline for operating conditions at which the processing equipment or pipelines should be operated. An alternative way to prevent the formation of gas hydrates in pipelines is the addition of inhibiting agents to the gas streams. A more detailed discussion on hydrate inhibition will be given in the next section.

Natural gas in the form of hydrates has been found in the permafrost regions and in the ocean floors of the world. These natural gas reserves will become increasingly important as the conventional gas reserves are depleted. In order to recover the natural gas hydrate reserves, research is needed to obtain economically feasible recovery methods. Gas hydrates has found application in the separation process. Musayev (1970) and Bukhgalter (1970) investigated the extraction of gases using hydrates. Wilson et al. (1990) found that hydrate formation improves near-critical and supercritical extraction equilibria. Gas hydrates is also becoming increasingly important in the environmental area. Carbon dioxide has been identified as a greenhouse gas contributing to global warming. Carbon dioxide introduced to the atmosphere comes from a variety of sources including power generation industry, automotive industry and petroleum sector. Once the carbon dioxide gas is removed from the source, it can be disposed through enhanced oil recovery or injection in disposal wells. Another disposal method is the fixation of carbon dioxide by hydrates

and then release of the hydrates on the ocean floor. Deep ocean carbon dioxide storage in the form of gas hydrates has been examined by several authors (Austvik and Loken, 1992; Dacey et al., 1992; Nishikawa et al., 1992; Saji et al., 1992). Recent studies in removal and deep ocean storage of carbon dioxide have been presented in the First International Conference On Carbon Dioxide Removal (1992). Another application of gas hydrates is in the desalination of seawater. The desalination of seawater using gas hydrates has been investigated by only a few researchers (Burduh et al., 1962; Knox et al., 1961; Smirnov, 1990). It is important to note that knowledge in the thermodynamic behaviour of gas hydrates is essential for all the above mentioned applications of gas hydrates.

1.2 Hydrate Inhibition

To overcome the gas hydrate problems in processing equipment and transportation pipelines, a common industrial practice is to use inhibitors. Inhibition of gas hydrates is commonly achieved using inhibitors such as methanol, ethylene glycol or salts. These inhibitors affect the thermodynamic behaviour of the aqueous phase because the activity of water is altered with the addition of inhibitors. The effect of inhibitors on the equilibrium hydrate formation conditions is illustrated in Figure 1.2. Addition of inhibitors will shift the equilibrium curve for hydrate formation. At a specific pressure (constant P line), the temperature at which hydrates form will be lower with inhibitors (point A) than without inhibitors (point B). Similarly at a specific temperature (constant T line), the pressure at which hydrates form will be higher with inhibitors (point C) than without inhibitors (point D). Therefore, hydrate inhibition can prevent the formation of gas hydrates in the transportation pipelines at a particular set of operation condition.

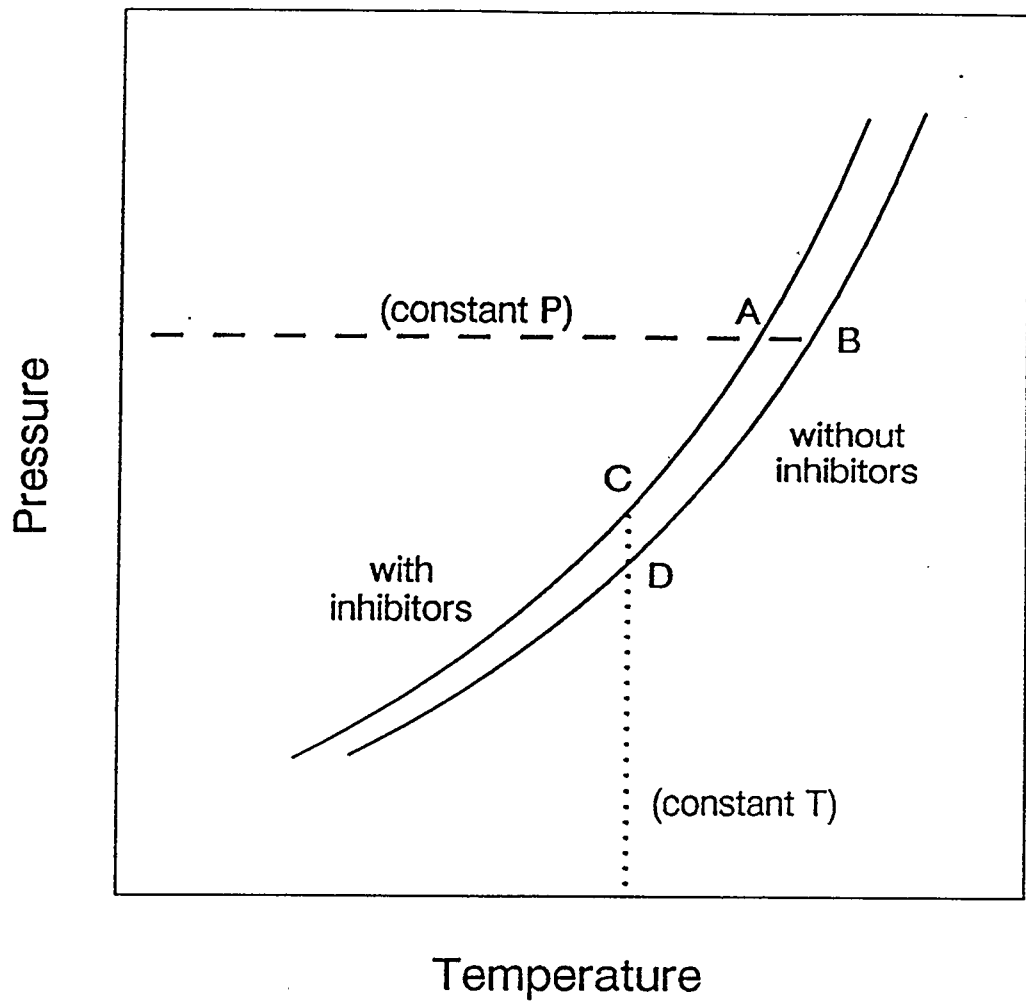


Figure 1.2 Effect of Inhibitors on the Hydrate Equilibrium Conditions

Research on gas hydrates has mainly focused on obtaining experimental data of equilibrium conditions for gas hydrates in the presence of different inhibitors. Studies investigating the inhibition of hydrate formation have been carried out by many researchers. Experimental equilibrium data for methane, ethane, propane, isobutane, carbon dioxide and hydrogen sulfide with inhibitors are summarized in Sloan (1990). The data are available for common inhibitors such as methanol, ethanol, ethylene glycol, sodium chloride and calcium chloride. The prediction of the equilibrium hydrate formation conditions is still a relatively new area of research. The goal of this research field is to have a predictive method for gas hydrate formation condition given a gas mixture and a liquid composition.

The fundamental model for calculating hydrate formation conditions is based on the model of van der Waals and Platteeuw (1959). These authors presented a statistical mechanical model for the chemical potential of water in the hydrate phase. The model was developed using the Lennard-Jones potential for the representation of the interaction between the gas molecule and the water molecule. The model was then modified using the Kihara potential to describe the interaction (McKoy and Sinanoglu, 1963). Using this model, Parrish and Prausnitz (1972) presented a method for prediction of hydrate equilibrium conditions in pure water. In order to predict the hydrate forming conditions from aqueous single salt solutions, a method was proposed by Menten et al. (1981). It was found that this method did not provide an accurate calculation of the water activity and extension to mixed salt solutions is not possible (Englezos, 1990). A computer implementable methodology for the prediction of incipient hydrate conditions was proposed by Englezos and Bishnoi (1988). This method is applicable for the prediction of hydrate conditions in systems containing light hydrocarbon gases in aqueous single or mixed electrolytes. The

method showed good results for gases with negligible solubility such as CH_4 , C_2H_6 and C_3H_8 . However, their method is not valid for gases with considerable solubility in the aqueous phase, e.g. carbon dioxide. In this work, the prediction of carbon dioxide gas hydrates formation conditions is examined. Much work has been done on obtaining experimental data for carbon dioxide gas hydrates equilibrium conditions in pure water (Deaton and Frost, 1946; Larson, 1955; Robinson and Mehta, 1971; Ng and Robinson, 1985; Adisasmito et al., 1991). However, the experimental data on carbon dioxide gas hydrates in aqueous electrolyte solutions is limited. Vlahakis et al. (1972) provides some data on the equilibrium conditions for formation of carbon dioxide gas hydrates in aqueous sodium chloride solutions. Recently, Dholabhai et al. (1991, 1993) presented data on carbon dioxide gas hydrate equilibrium conditions in single and mixed electrolyte systems containing sodium chloride, potassium chloride and calcium chloride. Bishnoi and Dholabhai (1993) and Dholabhai and Bishnoi (1993) provided experimental data on hydrate equilibrium conditions for gas mixtures of carbon dioxide and methane in single and mixed electrolyte systems.

1.3 Scope of the Study

The main objective of this work is to examine the methodology for predicting the incipient hydrate formation conditions for gas hydrates. The purpose of this work is to develop a calculation procedure for the prediction of carbon dioxide hydrate formation. The calculation procedure should be able to provide predictions for the following systems:

- (1) carbon dioxide gas in single salt solutions such as sodium chloride, potassium chloride and calcium chloride.

- (2) carbon dioxide gas in mixed salts solutions such as mixtures of sodium chloride and calcium chloride.
- (3) gas mixtures of carbon dioxide and methane in single salt solutions such as sodium chloride, potassium chloride and calcium chloride.
- (4) gas mixtures of carbon dioxide and methane in mixed salt solutions such as mixtures of sodium chloride and potassium chloride.

In order to perform the calculations of hydrate formation conditions for the above outlined systems, different thermodynamic models will be examined for their ability to describe the aqueous phase containing soluble gases and salts.

2. COMPUTATION OF HYDRATE EQUILIBRIUM CONDITIONS

2.1 Methodology

For a system in which the gas, liquid and hydrate phases co-exist at equilibrium, the equilibrium condition is given by

$$\mu_w^H = \mu_w^{sl} , \quad (1)$$

where μ_w^H and μ_w^{sl} are the chemical potentials of water in the hydrate and aqueous solution phases respectively. It is assumed that the amount of water in the vapor phase is negligible. If μ_w^{MT} is the chemical potential of water in an empty (unoccupied) hydrate lattice, then the equilibrium criterion stated in Equation (1) can also be written as

$$\Delta \mu_w^H = \Delta \mu_w , \quad (2)$$

where

$$\Delta \mu_w^H = \mu_w^{MT} - \mu_w^H , \quad \text{and} \quad \Delta \mu_w = \mu_w^{MT} - \mu_w^{sl} . \quad (3)$$

Using the model proposed by van der Waals and Platteeuw (1959), $\Delta \mu_w^H$ in Equation (3) is given by

$$\Delta \mu_w^H = R T \sum_i \nu_i \ln (1 + \sum_j C_{ij} f_j) , \quad (4)$$

where ν_i is the number of cavities of type i per water molecule, C_{ij} are the Langmuir constants, and f_j is the fugacity of the gas hydrate former j . The Langmuir constants, C_{ij} , describe the interaction between the gas and the surrounding water molecules and are obtained from the following expression (Holder et al., 1988),

$$C_{ij} = \frac{4\pi}{kT} \int_0^R \exp \left(-\frac{W(r)}{kT} \right) r^2 dr , \quad (5)$$

where k is the Boltzmann's constant, R is the cavity radius, r is the distance of the gas molecule from the center of the cavity, and $W(r)$ is the potential energy function for the interaction between the gas and the water molecules. Equation (5) assumes that the cavity is perfectly spherical and that the water molecules which form the cavity are smeared evenly over the surface of this sphere. McKoy and Sinanoglu (1963) suggested using the Kihara potential function to represent the gas-water interaction. Using the Kihara core pair potential for the gas-water interaction, the cell potential is given by

$$W(r) = 2Z\epsilon \left[\frac{\sigma^{12}}{R^{11}r} \left(\delta^{10} + \frac{a}{R} \delta^{11} \right) - \frac{\sigma^6}{R^5 r} \left(\delta^4 + \frac{a}{R} \delta^5 \right) \right] , \quad (6)$$

where

$$\delta^n = \frac{1}{n} \left[\left(1 - \frac{r}{R} - \frac{a}{R} \right)^{-n} - \left(1 + \frac{r}{R} - \frac{a}{R} \right)^{-n} \right] . \quad (7)$$

In equations (6) and (7), Z is the coordination number of the cavity, ϵ is the Kihara intermolecular well depth parameter and a is the core radius. In the temperature region of 260 to 300 K, Parrish and Prausnitz (1972) present the following empirical correlation to calculate the Langmuir constants in equation (5),

$$C_{ij} = \frac{A_{ij}}{T} \exp \left(\frac{B_{ij}}{T} \right) , \quad (8)$$

where A_{ij} and B_{ij} are fitted constants.

In equation (3), $\Delta \mu_w$ is the difference in chemical potential of water in an empty hydrate lattice and the aqueous solution phase. Holder et al. (1980) provide the following relationship for determining $\Delta \mu_w$,

$$\frac{\Delta \mu_w}{RT} = \frac{\Delta \mu_w^o}{RT_o} - \int_{T_o}^T \frac{\Delta h_w}{RT^2} dT + \int_0^P \frac{\Delta V_w}{RT} dP - \ln a_w \quad (9)$$

In the above equation, a_w is the activity of water and its calculation will be discussed in a subsequent section. $\Delta \mu_w^o$ is the chemical potential difference of water between the empty hydrate lattice and pure water at the reference temperature, $T_o = 273.15$ K and zero absolute pressure. This term is referred to as the reference chemical potential and must be determined experimentally. The terms Δh_w and ΔV_w are the enthalpy and volume differences respectively between the empty hydrate lattice and pure water. The enthalpy term, Δh_w , is given by

$$\Delta h_w = \Delta h_w^o + \int_{T_o}^T \Delta C_{p_w} dT \quad , \quad (10)$$

where Δh_w^o is the reference enthalpy difference at $T_o = 273.15$ K and ΔC_{p_w} is the heat capacity difference between the empty hydrate lattice and the water phase. The heat capacity difference is temperature dependent and is obtained by

$$\Delta C_{p_w} = \Delta C_{p_w}^o + b (T - T_o) \quad , \quad (11)$$

where $\Delta C_{p_w}^o$ is a reference heat capacity difference experimentally determined at $T_o = 273.15$ K, and b is a fitted constant.

The equilibrium criterion of Equation (2) can be rewritten in an alternative form by combining Equations (4) and (9). The result is as follows:

$$\frac{\Delta \mu_w^o}{RT_o} - \int_{T_o}^T \frac{\Delta h_w}{RT^2} dT + \int_0^P \frac{\Delta V_w}{RT} dP - \ln a_w - \sum_i \nu_i \ln(1 + \sum_j C_{ij} f_j) = 0 \quad . \quad (12)$$

For a specific temperature, T , Equation (12) contains one unknown which is the

pressure, P . This equation can be solved iteratively for the equilibrium hydrate pressure at a given temperature. The various constants in Equation (12) are obtained from Parrish and Prausnitz (1972).

2.2 Computation Procedure

Using the methodology outlined in the preceding section, the computational procedure for calculating the incipient hydrate formation conditions is shown in Figure 2.1. At a given temperature, gas, water and salt mixture, an initial guess of pressure is supplied to the computer program. At the specified temperature and estimated pressure, an isothermal-isobaric flash is performed to obtain the mole fraction of water in the liquid phase, x_w , the activity coefficient of water, γ_w , and hence the activity of water in the aqueous phase, a_w . Three different liquid models were examined in this work for the calculation of water activity. These models will be discussed in detail in the next chapter. Once the water activity, a_w , is known, $\Delta \mu_w$ can be calculated using Equation (9) along with Equations (10) and (11). The chemical potential difference $\Delta \mu_w^H$ is determined using Equation (4) with either Equations (5) - (7) or Equation (8). If the estimated pressure is the incipient hydrate equilibrium pressure at the specified pressure, equilibrium condition of Equation (2) will be satisfied. Otherwise, the pressure, P , can be updated using a Newton-Raphson procedure. The outlined computational procedure is repeated until the equilibrium conditions are satisfied.

2.3 Flash Calculation

One of the parameters required in the computation of gas hydrate incipient formation conditions is the activity of water in the aqueous liquid phase. In order

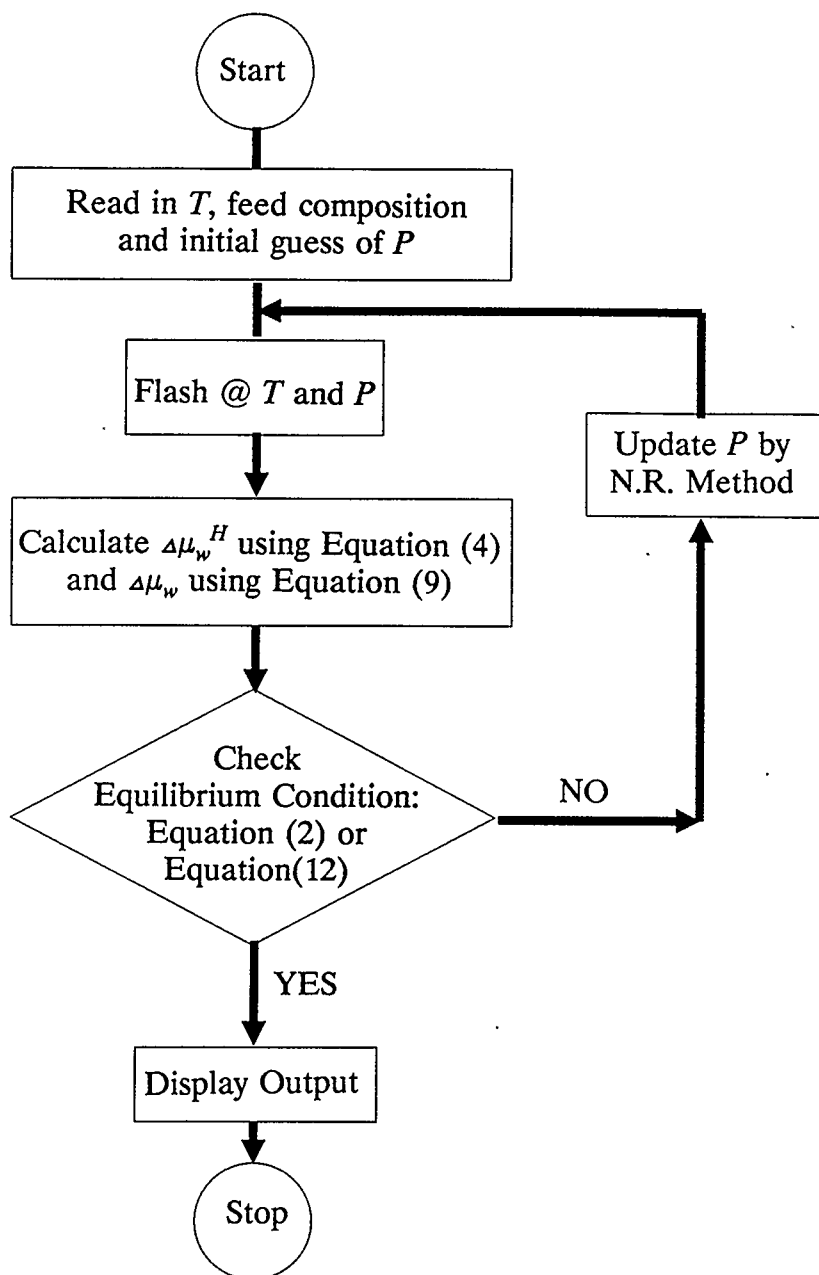


Figure 2.1 Computational Procedure for Calculation of CO₂ Gas Hydrates in the Presence of Electrolytes

to determine the activity of water, an isobaric-isothermal flash calculation is required for a given gas, liquid and salt mixture. In this section, the flash condition for a system involving salts will be outlined. For a mixture containing salts, a simplified flash calculation which involves only the volatile components can be carried out. The feed, vapor and liquid balances are:

$$F = N + S \quad , \quad (13a)$$

$$V = \beta N \quad , \quad (13b)$$

$$L = (1 - \beta)N + S \quad . \quad (13c)$$

In equation (13), F is the total moles of feed, N is moles of non-salt (volatile) components in the feed, S is moles of ionic species in the feed, V is moles of vapor, L is moles of liquid, and β is defined as $\beta = V/N$. The component balance for any volatile component, i , is given by

$$Nz_i = Lx_i + Vy_i \quad . \quad (14)$$

Also, the component balance for any ionic species, j , is given by

$$Sw_j = Lx_j \quad , \quad (15)$$

where w_j is the mole fraction of ionic species j in the feed containing ionic species only. The equilibria condition for any volatile component, i , can be written as

$$y_i = K_i x_i \quad . \quad (16)$$

On combining Equations (14) - (16) and defining $\psi = S/N$, the flash condition becomes

$$f(\beta) = \sum_{i=1}^{vc} y_i - \sum_{i=1}^{vc} x_i - \sum_{j=vc+1}^{ic} x_j = 0 \quad , \quad (17a)$$

$$\text{or } f(\beta) = \sum_{i=1}^{vc} \frac{(K_i - 1)z_i}{1 + \beta(K_i - 1) + \psi} - \sum_{j=vc+1}^{ic} \frac{w_j \psi}{(1 - \beta) + \psi} = 0 \quad , \quad (17b)$$

and the corresponding Newton-Raphson algorithm is

$$\beta^{(1)} = \beta^{(0)} + \frac{\sum_{i=1}^{vc} \frac{(K_i - 1)z_i}{1 + \beta(K_i - 1) + \psi} - \sum_{j=vc+1}^{tc} \frac{w_j \psi}{(1 - \beta) + \psi}}{\sum_{i=1}^{vc} \frac{(K_i - 1)^2 z_i}{[1 + \beta(K_i - 1) + \psi]^2} + \sum_{j=vc+1}^{tc} \frac{w_j \psi}{[1 - \beta + \psi]^2}} \quad (18)$$

A starting value of $\beta = 1$ is used to converge β in the Newton-Raphson procedure. The flash condition is used to calculate the compositions of the vapor and liquid phases along with the activity of water in the flash program. Different liquid models have been examined for the representation of the aqueous liquid phase containing salts. These models will be discussed in detail in the next chapter.

3. DESCRIPTION OF EXAMINED LIQUID MODELS

The calculation of water activity is important in the computation of gas hydrate equilibrium conditions. If the aqueous phase is pure water (i.e. salt-free), then it is generally assumed that the liquid phase behaves like an ideal solution and the water activity is equal to the mole fraction of water in the liquid phase. For light hydrocarbon gases such as methane, ethane and propane, their solubilities in the liquid water phase can be assumed to be negligible. This leads to a further simplification where the mole fraction of water in the liquid phase can be assumed to be unity. When the aqueous phase contains electrolytes, the liquid phase can no longer be considered as an ideal solution. Englezos and Bishnoi (1988) proposed that the water activity can be computed using electrolyte models such as Pitzer and Mayorga (1973) or Meissner and Kusik (1972). For the method of Englezos and Bishnoi (1988), these authors assumed that the solubility of gases is negligible in the aqueous electrolyte solution. This assumption is valid for light hydrocarbon gases but not for gases with considerable solubility in water such as carbon dioxide or hydrogen sulfide. For these gases, a liquid model is required to account for both the solubility of the gas and the influence of the dissolved gases along with electrolytes on the activity of water. This work has been taken up to formulate a methodology for the determination of incipient hydrate conditions for systems containing soluble gases, water and salts since there are no predictive methods available for this computation. In the following sections, a detailed description of three electrolyte liquid models will be presented. In the subsequent chapter, the ability of these models to represent the liquid phases will be examined and also the result of the prediction of carbon dioxide hydrate equilibrium conditions in aqueous electrolyte solutions using these models

will be presented.

3.1 Chen and Evans Model

The model by Chen and Evans (1986) represents the excess Gibbs energy and activity coefficients for aqueous multicomponent electrolyte systems. It is based on the local composition concept. The model has two assumptions regarding the liquid lattice structure of electrolyte systems. They are the like-ion repulsion assumption and the local electro-neutrality assumption. The like-ion repulsion assumption states that the local composition of anions around anions are zero and similarly for cations. This implies that the repulsive forces between ions of same charges are significantly large compared to the attractive forces between them. The local electro-neutrality assumption states that the distribution of cations and anions around a central molecule is such that the net local ionic charge is zero.

Chen et. al. (1982) identified three types of interaction in an electrolyte system: ion-ion, molecule-molecule, and ion-molecule. These authors also proposed that the excess Gibbs energy is given by the sum of the long-range electrostatic forces between ions and the short-range forces between all the species. The Pitzer-Debye-Hückel (Pitzer, 1980) equation is used to represent the long-range ion-ion interactions and the nonrandom two-liquid (NRTL) originally developed by Rennon and Prausnitz (1968) is modified to represent the short-range contributions. Therefore, the excess Gibbs energy and activity coefficient expressions can be written as

$$\frac{g^{ex}}{RT} = \frac{g^{ex,pdh}}{RT} + \frac{g^{ex,lc}}{RT} , \quad (19)$$

and

$$\ln \gamma_i = \ln \gamma_i^{pdh} + \ln \gamma_i^{lc} . \quad (20)$$

In equations (19) and (20), g^{ex} is the excess Gibbs energy, γ_i is the activity coefficient of species i , pdh and lc denote Pitzer-Debye-Hückel and local composition contributions respectively. The long-range electrostatic forces between ions are accounted for using the Pitzer-Debye-Hückel (Pitzer, 1980) expression and is given by

$$\frac{g^{ex,pdh}}{RT} = - \left(\sum_k x_k \right) \left(\frac{1000}{M_s} \right)^{\frac{1}{2}} \left(\frac{4A_\phi I_x}{\rho} \right) \ln \left(1 + \rho I_x^{\frac{1}{2}} \right) , \quad (21)$$

where x_k is the liquid mole fraction of species k , M_s is the solvent molecular weight, A_ϕ is the Debye-Hückel constant, I_x is the ionic strength, and ρ is the closest approach parameter. The short-range interaction contribution is represented by the NRTL theory modified for electrolyte systems and the excess Gibbs energy expression is written as

$$\begin{aligned} \frac{g^{ex,lc}}{RT} = & \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{\sum_j X_j G_{jc,a'} \tau_{jc,a'}}{\sum_k X_k G_{kc,a'}} \\ & + \sum_a X_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{\sum_j X_j G_{ja,c'} \tau_{ja,c'}}{\sum_k X_k G_{ka,c'}} , \end{aligned} \quad (22a)$$

where

$$G_{ji,ki} = \exp \left(-\alpha_{ji,ki} \tau_{ji,ki} \right) , \quad \text{and} \quad (22b)$$

$$X_j = x_j C_j \quad (C_j = Z_j \text{ for ions and } C_j = \text{unity for molecules}) \quad (22c)$$

In equation (22), X is the effective liquid mole fraction, Z is the ionic charge, α is the NRTL nonrandomness factor, τ is the binary interaction energy parameter, subscripts a, c, m denote anion, cation and molecule respectively, and subscripts i, j, k denote any species. By taking appropriate derivatives of Equations (21) and (22), expressions for the activity coefficients of all species may be obtained. These expressions are given by Chen and Evans (1986) and are summarized in Appendix B.

The activity coefficient of any species i can be calculated using Equation (20). Once the activity coefficient of water is obtained, the water activity is given by

$$a_w = x_w \gamma_w \quad (23)$$

The calculation of water activity is needed for the computation of gas hydrate incipient equilibrium conditions as explained in the previous chapter.

3.2 Zuo and Guo Model

Zuo and Guo (1991) examined the feasibility of extending the widely used van der Waals type cubic equation of state to salt-containing electrolyte systems. In their development of the model, these authors extended the Patel-Teja (1982) equation of state for phase equilibrium calculations for electrolyte solutions by adding a Debye-Hückel electrostatic contribution term. The model assumes that ions are not present in the vapour phase, and the fugacity coefficient of species i in the liquid phase consists of two contributions. These contributions are the long-range inter-ionic forces and the short-range interactions. Hence, the fugacity coefficient relationship for any species i in the liquid phase is given by

$$\ln \phi_i = \ln \phi_i^{EOS} + \ln \phi_i^{DH} , \quad (24)$$

where ϕ_i is the fugacity coefficient of species i , and superscripts *EOS* and *DH* denote equation of state and Debye-Hückel terms respectively. The long-range forces are represented by the Debye-Hückel electrostatic term whereas the short-range interactions are accounted by an equation of state term. The equation of state term is calculated from a modified Patel-Teja (1982) equation of state which takes into account the presence of ionic species in the liquid phase. For molecular species, the parameters a , b , c in the equation of state term are calculated following the original work of Patel and Teja (1982). For ionic species, Zuo and Guo suggested to estimate the parameter a from the following relationship,

$$a = 2.57012\pi \epsilon N_a^2 \sigma^3 f , \quad (25)$$

where N_a is the Avogadro's number, σ is the ionic diameter, and f is an empirical parameter which was assigned a value of 6. The ionic energy ϵ is determined from dispersion theory (Mavroyannis and Stephen, 1962). The parameters b and c are empirically expressed as

$$b = \frac{2}{3}\pi N_a \sigma^3 , \quad (26)$$

$$\text{and} \quad c = b . \quad (27)$$

In the model of Zuo and Guo (1991), the authors suggested using the classical one-fluid van der Waals mixing rules for the parameters b and c . However, a mixing rule proposed by Kurihara et al. (1987) which takes into account the residual excess Gibbs free energy was suggested for the parameter a . In the present work, we found that the classical one-fluid van der Waals mixing rule for the parameter a is

satisfactory for the gas hydrate systems considered. Therefore, the classical one-fluid van der Waals mixing rule is used for all the equation of state parameters in our hydrate calculations. For the Debye-Hückel term in Equation (24), Zuo and Guo suggest using the expression given by Li and Pitzer (1986). Therefore, the fugacity coefficient for the Debye-Hückel term is written as

$$\ln \phi_i^{DH} = -A \left[\frac{2Z_i^2}{B} \ln \left(\frac{1 + BI^{1/2}}{1 + B/\sqrt{2}} \right) + \left(\frac{I^{1/2}Z_i^2 - 2I^{3/2}}{1 + BI^{1/2}} \right) \right] , \quad (28)$$

where I is the ionic strength, Z_i is the ionic charge (Z_i is zero for molecular species), A is the Debye-Hückel constant, B is a parameter dependent on temperature, density and dielectric constant of the solvent. Once the two fugacity coefficient terms on the right-hand side of Equation (24) are calculated, Equation (24) is used to calculate the fugacity coefficient of water in the liquid phase. The activity of water in the aqueous phase is then given by

$$a_w = \frac{f_w}{f_w^o} , \quad (29)$$

where f_w and f_w^o are the fugacity of water in the solution and the fugacity of pure water respectively.

3.3 Aasberg-Petersen et al. Model

Aasberg-Petersen et al. (1991) presented a model for the prediction of the solubilities of gases in aqueous electrolyte solutions at high pressures. The model states that the fugacity coefficient consists of two contributions, an equation of state term combined with an electrostatic contribution. Therefore, the fugacity coefficient

of component i in the liquid phase is written as

$$\ln \phi_i = \ln \phi_i^{EOS} + \ln \gamma_i^{EL} , \quad (30)$$

where ϕ_i is the fugacity coefficient of component i , γ_i is the activity coefficient of component i , superscripts EOS and EL denote contribution from an equation of state term and contribution from an electrostatic term respectively.

Aasberg-Petersen et al. (1991) suggest that the equation of state term in Equation (30) can be calculated using any equation of state model suitable for the correlation of gas-water equilibria. Therefore, the equation of state term is determined using the Trebble-Bishnoi equation of state (Trebble and Bishnoi 1987) in the present work. Following the approach of Aasberg-Petersen et al. (1991), this term is calculated in the liquid phase on a salt-free basis.

Aasberg-Petersen et al. (1991) proposes the following expression for the calculation of the electrostatic term in Equation (30),

$$\ln \gamma_i^{EL} = \frac{2Ah_{is}M_m}{B^3} f(BI^{1/2}) , \quad (31a)$$

$$\text{and } f(BI^{1/2}) = 1 + BI^{1/2} - \frac{1}{(1+BI^{1/2})} - 2 \ln(1+BI^{1/2}) . \quad (31b)$$

In equation (31), I is the ionic strength, M_m is the salt-free mixture molecular weight determined as a molar average, h_{is} is a regressed interaction coefficient between the dissolved salt and a nonelectrolytic component, A and B are parameters dependent on the temperature, density and dielectric constant of the salt-free liquid mixture. The interaction coefficients, h_{is} , between salt and water are determined from experimental vapour pressure lowering data. The salt-gas interaction coefficients are obtained from either high-pressure ternary gas-water-salt solubility data or low-

pressure salting out constants.

The calculation of water activity would involve calculating the fugacity coefficient of water in the liquid phase using Equation (30) combined with Equation (29). The activity of water can then be utilized for the calculation of the chemical potential difference of water in an empty hydrate lattice and aqueous solution phase as explained in Chapter 2.

3.4 Mixed Electrolyte Solutions

Both the Chen and Evans model (1986) and Zuo and Guo model (1991) have salt-specific parameters. In order to handle different salts containing a common ion in a mixed electrolyte system, we suggest the following mixing rule for calculating the interaction parameter for the common ion. It was found that the mixing rule provides good results for the prediction of gas hydrates in mixed electrolyte solutions,

$$\xi_i = \frac{\sum_j n_{ij} p_{ij}}{\sum_j n_{ij}} \quad (32)$$

In Equation (32), ξ_i is the required interaction parameter for the common ion i , n_{ij} is the moles of ionic species i from salt j , and p_{ij} is the salt-specific interaction parameter for salt j containing ionic species i .

3.5 Mixture Of Gases

For the computation of gas hydrate equilibrium pressure at a given temperature, the calculations for mixture of gases in aqueous electrolyte solutions are quite straightforward. Following the suggestion of Zuo and Guo (1991), the interaction parameters k_{ij} for molecule-molecule pairs are set equal to zero except

for gas-water pairs. The interaction parameters for gas-water pairs and salt-water pairs are given in the work of Zuo and Guo (1991) and are summarized in Table B.1 in Appendix B.

4. RESULTS AND DISCUSSION

4.1 Carbon Dioxide in Single Electrolyte Solution

Three different liquid models were used to calculate the equilibrium conditions of carbon dioxide gas hydrate in single electrolyte solutions. These models have been explained in Chapter 3 and they are the models of Chen and Evans (1986), Zuo and Guo (1991), and Aasberg-Petersen et al. (1991). The predictions of incipient carbon dioxide gas hydrate conditions were performed using the computational procedure outlined in section 2.2. The hydrate computation was carried out for carbon dioxide gas in three single salt solutions (sodium chloride, potassium chloride and calcium chloride). The accuracy of the hydrate equilibrium predictions was determined by comparison with experimental carbon dioxide hydrate data. The experimental hydrate data for carbon dioxide in pure water was taken from Robinson and Mehta (1971), Ng and Robinson (1985) and Dholabhai et al. (1991, 1993). For carbon dioxide in sodium chloride solutions, the experimental data were obtained from Dholabhai et al. (1991, 1993) for various weight percent of sodium chloride. In addition, Larson (1955) provided data at 5 weight percent and Vlahakis et al. (1972) gave data at 10 weight percent. The experimental data for carbon dioxide in potassium chloride and calcium chloride solutions were taken from Dholabhai et al. (1991, 1993).

4.1.1 Chen and Evans Model

For the prediction of carbon dioxide gas hydrates in single electrolyte solutions, the model of Chen and Evans (1986) was used for the liquid phase whereas the Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1987) was used for the

vapour phase. Figures 4.1 to 4.3 show the predicted equilibrium pressures at given temperatures for carbon dioxide in aqueous sodium chloride, potassium chloride and calcium chloride solutions. The solid lines in the figure are the predictions whereas the experimental data are represented with symbols. The accuracy of the predictions as compared to the experimental data is shown in Figures 4.4 to 4.6. As seen from these figures, the model of Chen and Evans (1986) seemed to over-predict the equilibrium pressures. Furthermore, the discrepancy between the predicted and experimental pressure increases with the pressure. The numerical values of the predicted carbon dioxide gas hydrate pressures are compared to the experimental data in Tables A.1 to A.3 (Appendix A). From these tables, the maximum percent deviations between the predicted and experimental pressures for NaCl, KCl and CaCl₂ were 12.2%, 9.6% and 16.0%. The corresponding percent root mean square deviations (RMSD) were 6.6%, 4.9% and 9.2%. The deviation and RMSD were obtained as follows:

$$\% \text{ deviation} = \frac{P_{\text{exp}} - P_{\text{pred}}}{P_{\text{exp}}} * 100 \quad , \quad (33)$$

$$\text{and} \quad \% \text{ RMSD} = \left[\frac{1}{n} \sum_n \left(\frac{P_{\text{exp}} - P_{\text{pred}}}{P_{\text{exp}}} \right)^2 \right]^{1/2} * 100 \quad . \quad (34)$$

In Equations (33) and (34), n is the number of experimental data points, P_{exp} and P_{pred} are the experimental and predicted pressures respectively.

4.1.2 Zuo and Guo Model

The predictions of carbon dioxide gas hydrate equilibrium conditions were also carried out using the model of Zuo and Guo (1991). Since this model is based

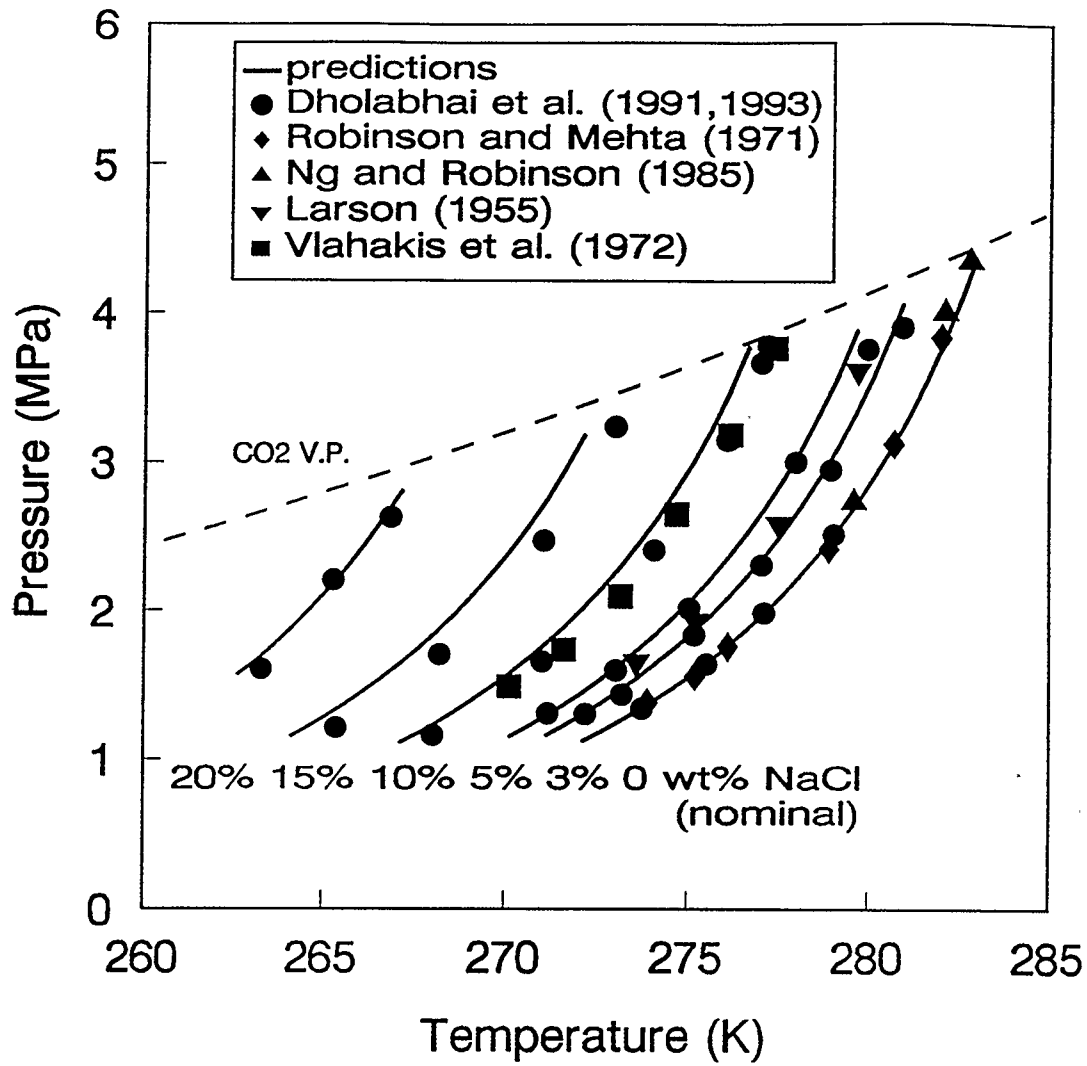


Figure 4.1 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Chen and Evans (1986) for Carbon Dioxide Gas in Aqueous NaCl Solution

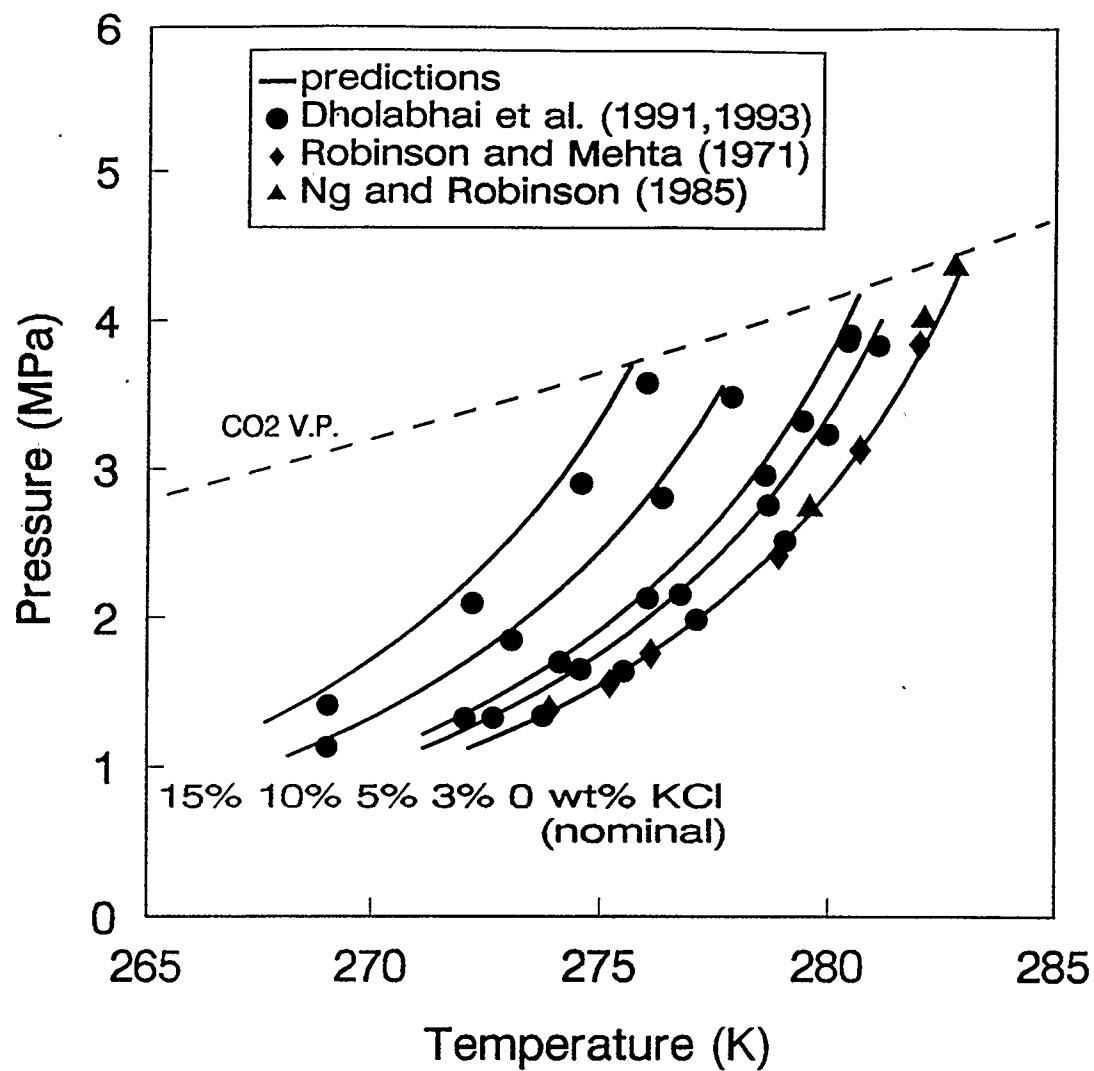


Figure 4.2 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Chen and Evans (1986) for Carbon Dioxide Gas in Aqueous KCl Solution

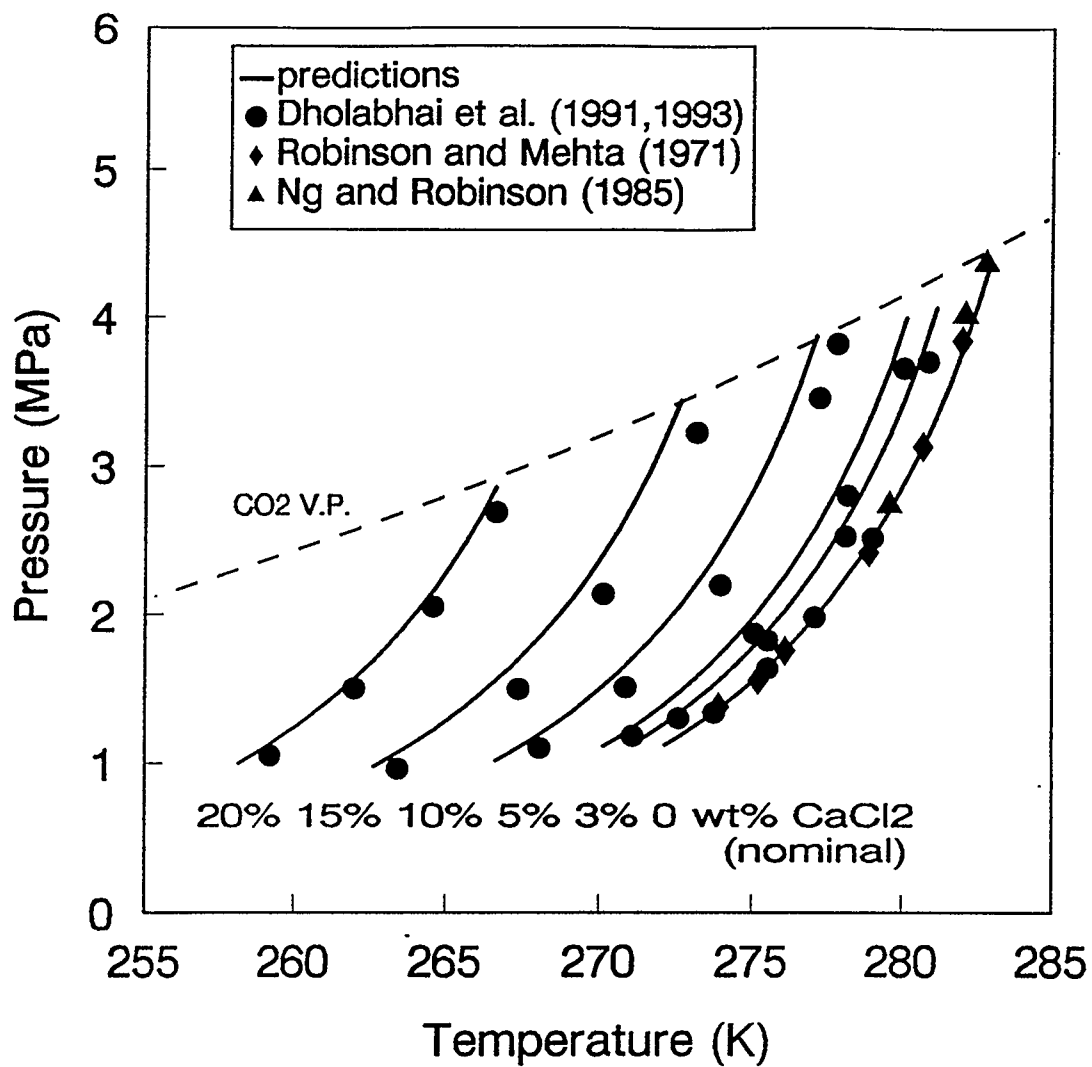


Figure 4.3 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Chen and Evans (1986) for Carbon Dioxide Gas in Aqueous CaCl₂ Solution

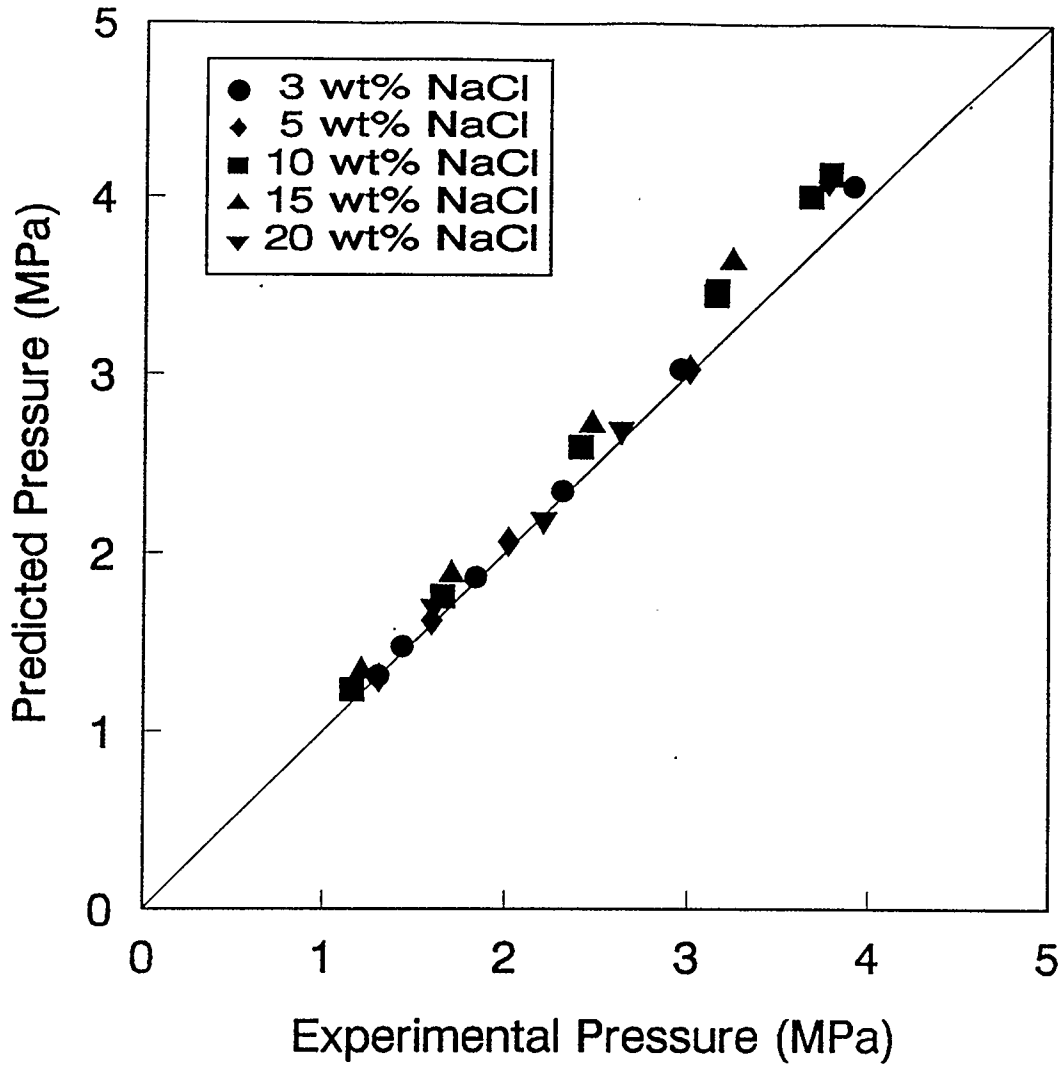


Figure 4.4 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Chen and Evans (1986) for Carbon Dioxide Gas in Aqueous NaCl Solution

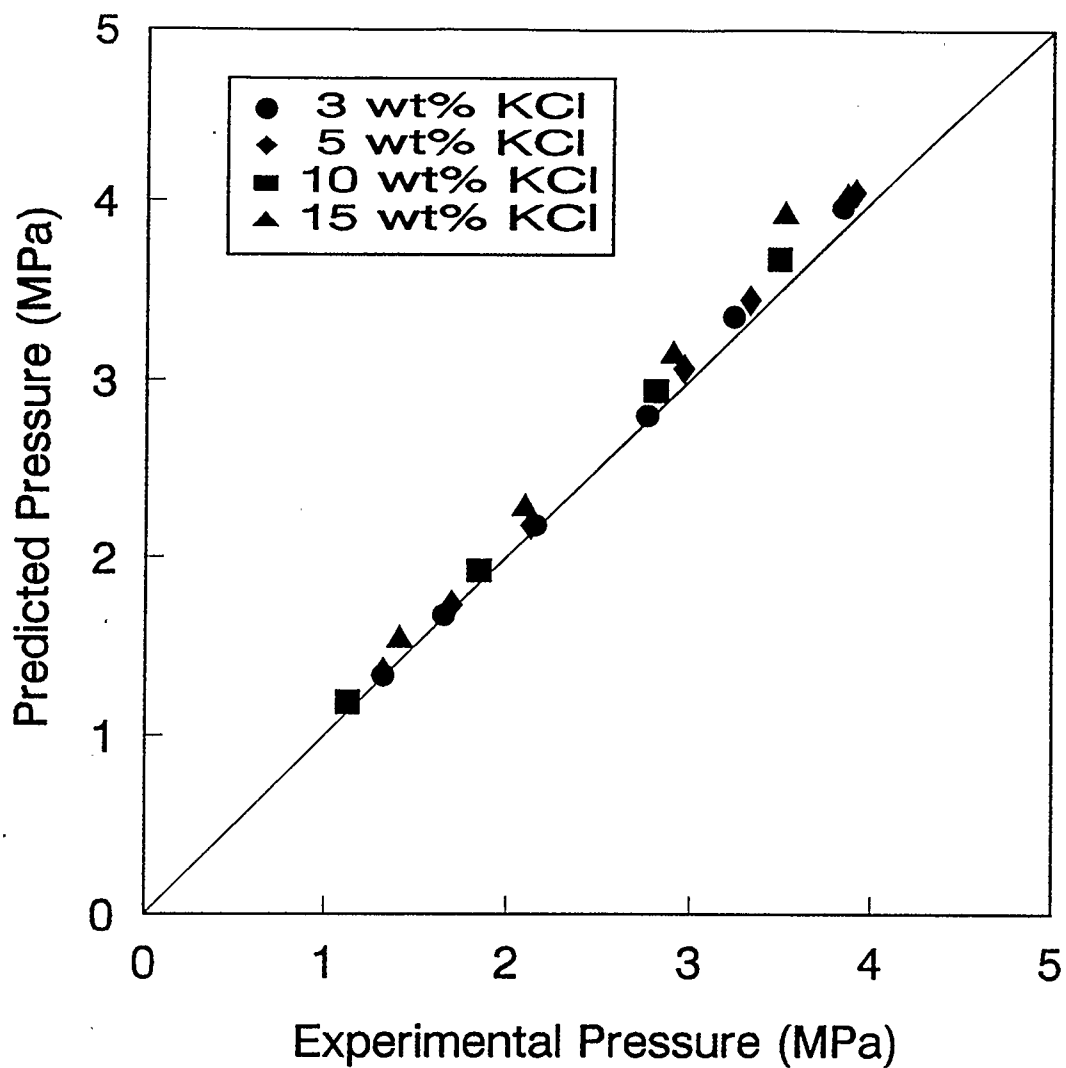


Figure 4.5 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Chen and Evans (1986) for Carbon Dioxide Gas in Aqueous KCl Solution

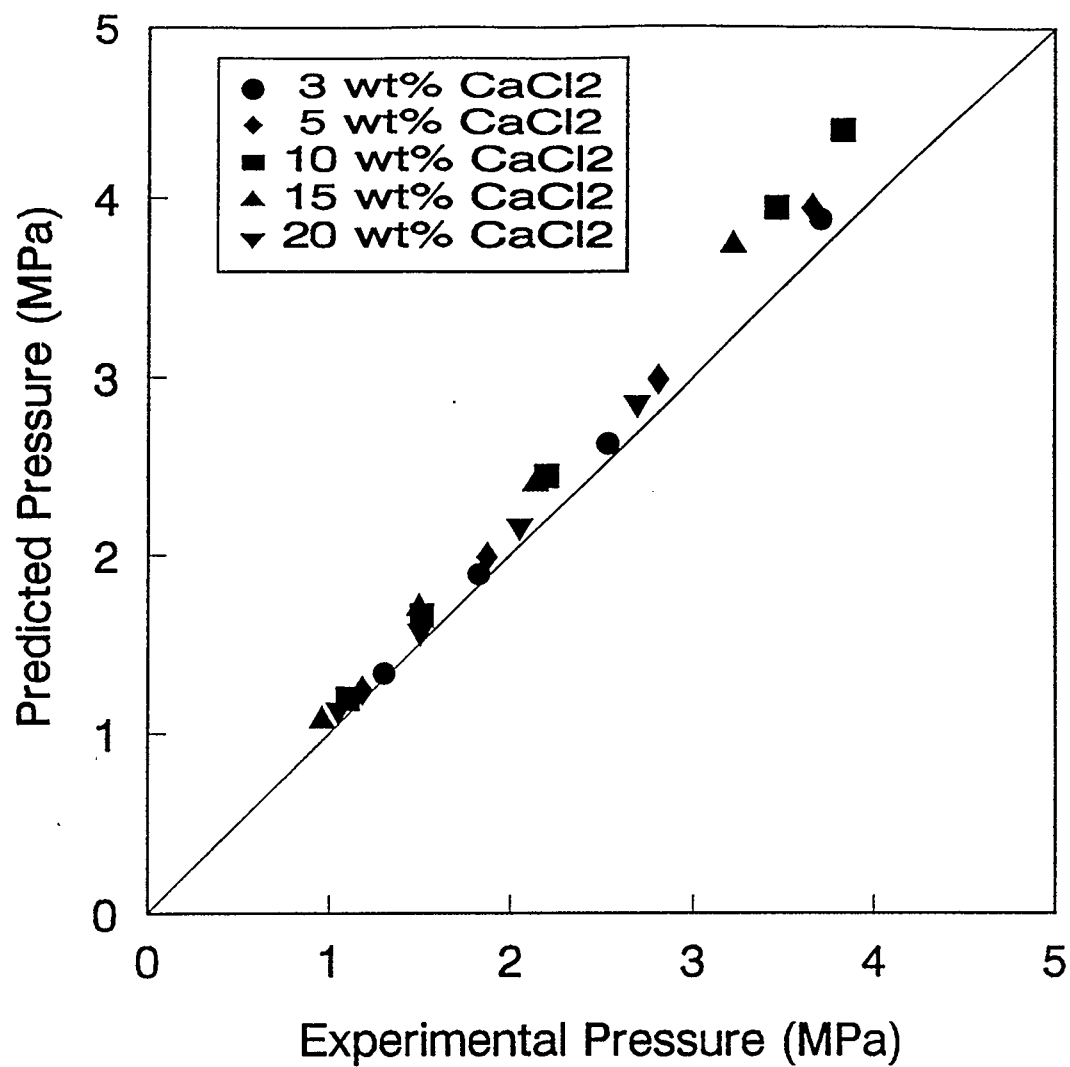


Figure 4.6 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Chen and Evans (1986) for Carbon Dioxide Gas in Aqueous CaCl₂ Solution

on the Patel-Teja equation of state (Patel and Teja, 1982), the same equation of state was used for the vapour phase. Figures 4.7 to 4.9 show the experimental and calculated inhibiting effect of sodium chloride, potassium chloride and calcium chloride on carbon dioxide gas hydrate formation. As seen from these figures, the calculated results are in good agreement with the experimental data. The inhibiting effect of electrolytes can be illustrated by comparing the hydrate formation pressures at any temperature at different salt concentrations. At a higher salt concentration, there is a notable increase in the pressure required for the formation of carbon dioxide gas hydrates. The model of Zuo and Guo (1991) seemed to under-predict the experimental pressures at higher salt concentrations as shown in Figures 4.10 to 4.12. The accuracy of the predictions decreases with increasing salt concentration. The comparison of the predicted pressures with the model of Zuo and Guo (1991) along with the deviations from the experimental data can be seen in Tables A.1 to A.3. The maximum percent deviations for NaCl, KCl and CaCl₂ were 15.6%, 4.8% and 10.3%. The corresponding RMSD were 5.0%, 3.0% and 4.3%. It can be seen that the model of Zuo and Guo (1991) provides a more accurate prediction of the carbon dioxide gas hydrate incipient equilibrium conditions in aqueous single electrolyte solutions.

4.1.3 Aasberg-Petersen et al. Model

The last model which was examined for its ability to represent the liquid phase for the prediction of carbon dioxide gas hydrates was the model of Aasberg-Petersen et al. (1991). Since these authors provided only the parameters for calcium chloride, the equilibrium hydrate conditions were calculated for calcium chloride only. The experimental and predicted carbon dioxide hydrate equilibrium conditions

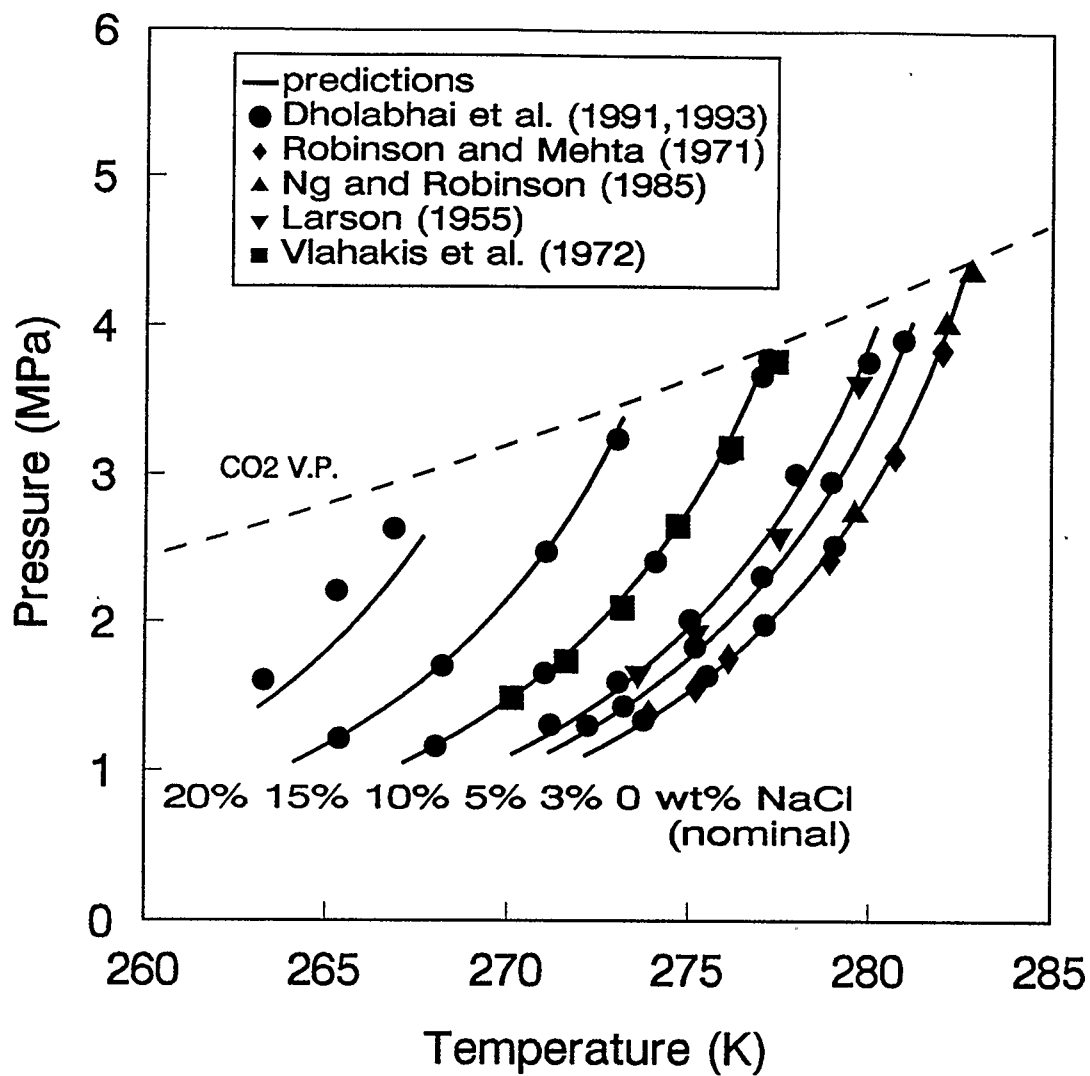


Figure 4.7 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous NaCl Solution

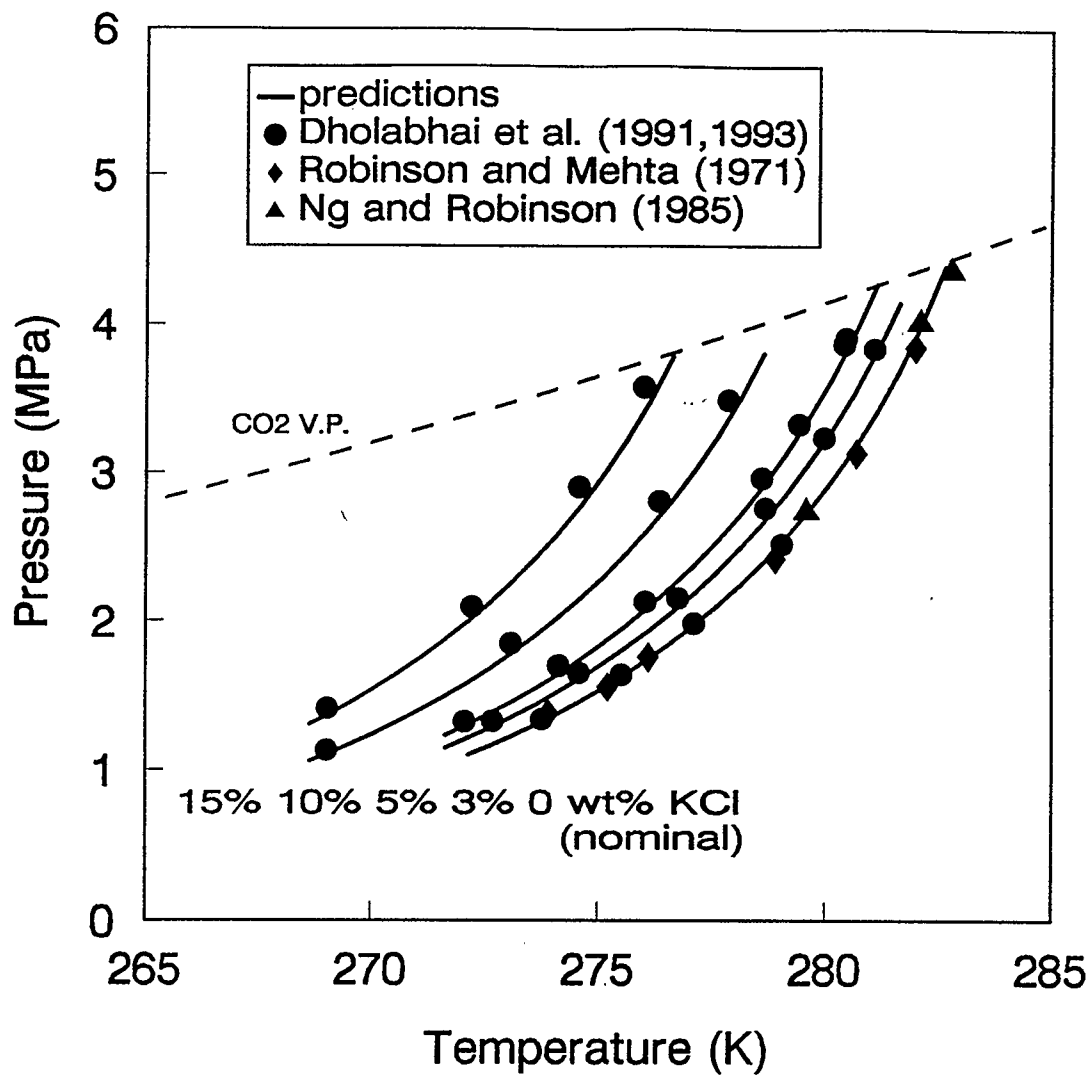


Figure 4.8 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous KCl Solution

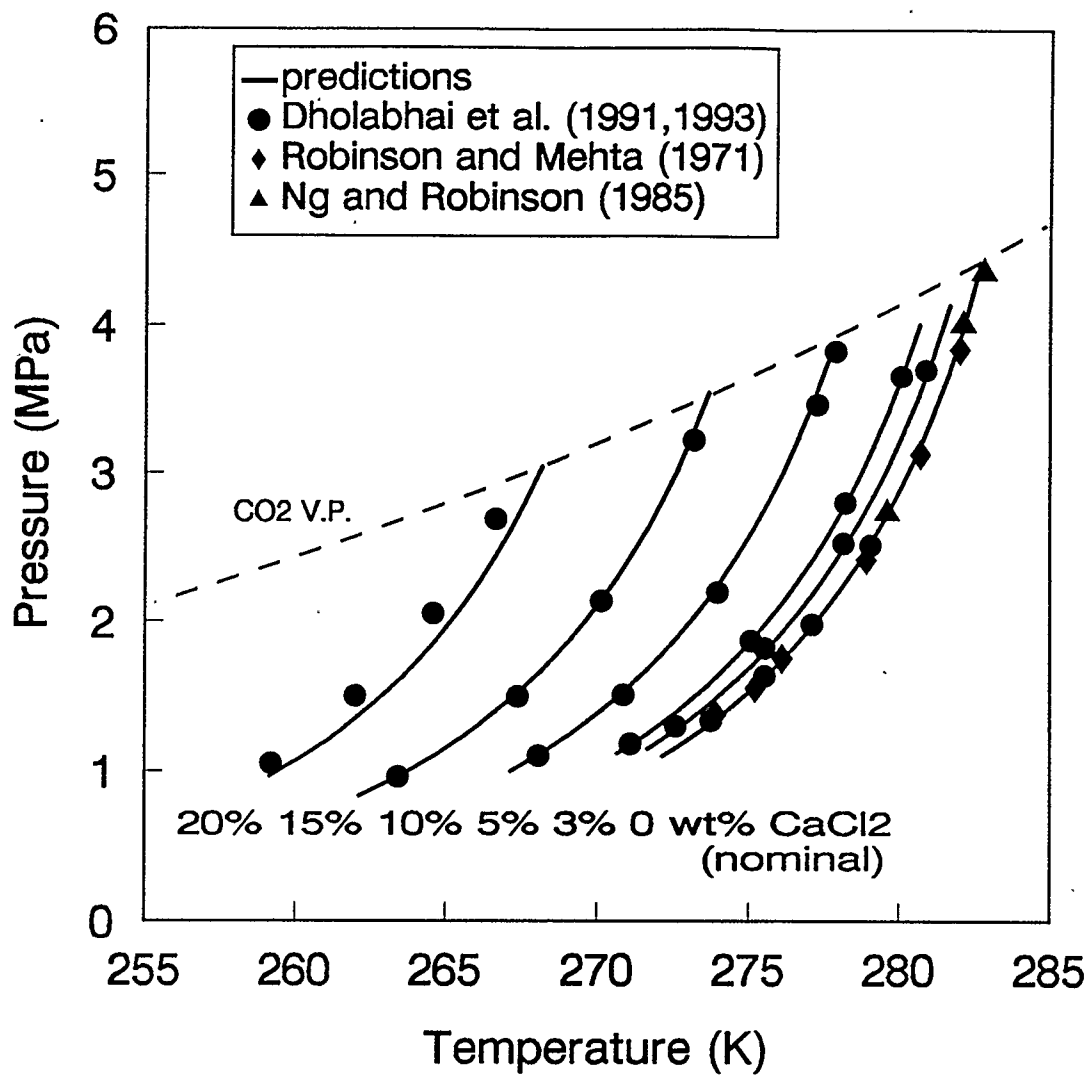


Figure 4.9 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous CaCl₂ Solution

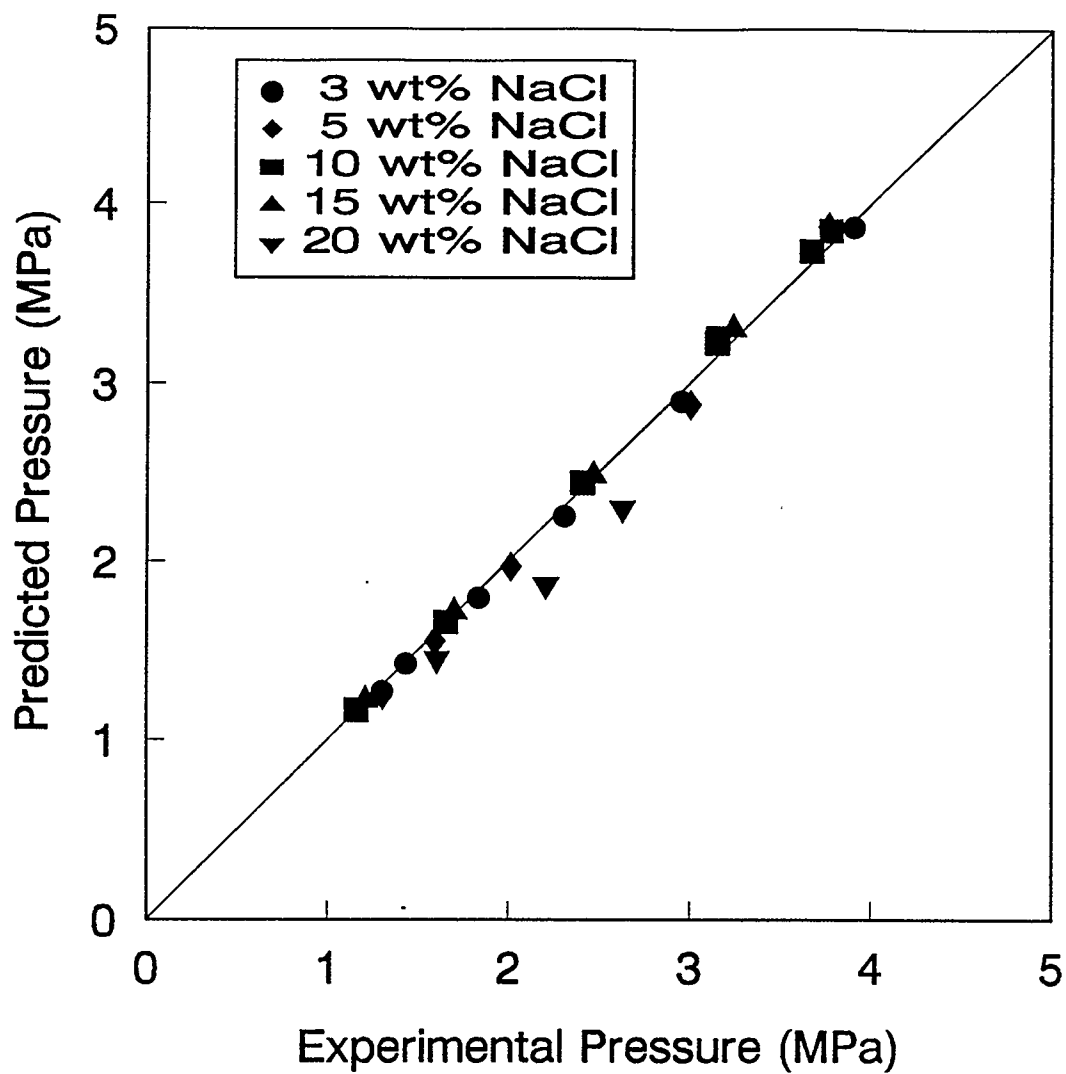


Figure 4.10 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous NaCl Solution

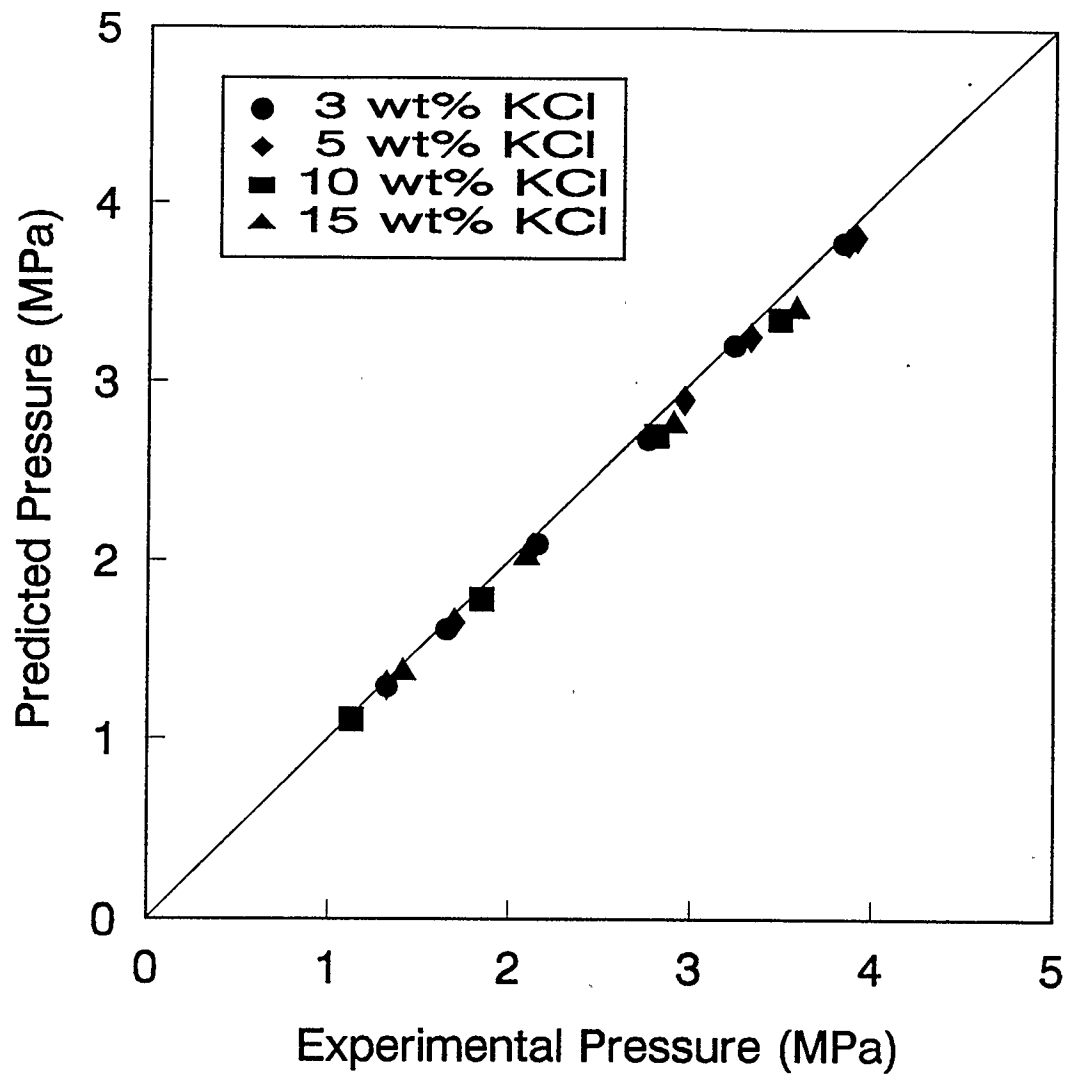


Figure 4.11 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous KCl Solution

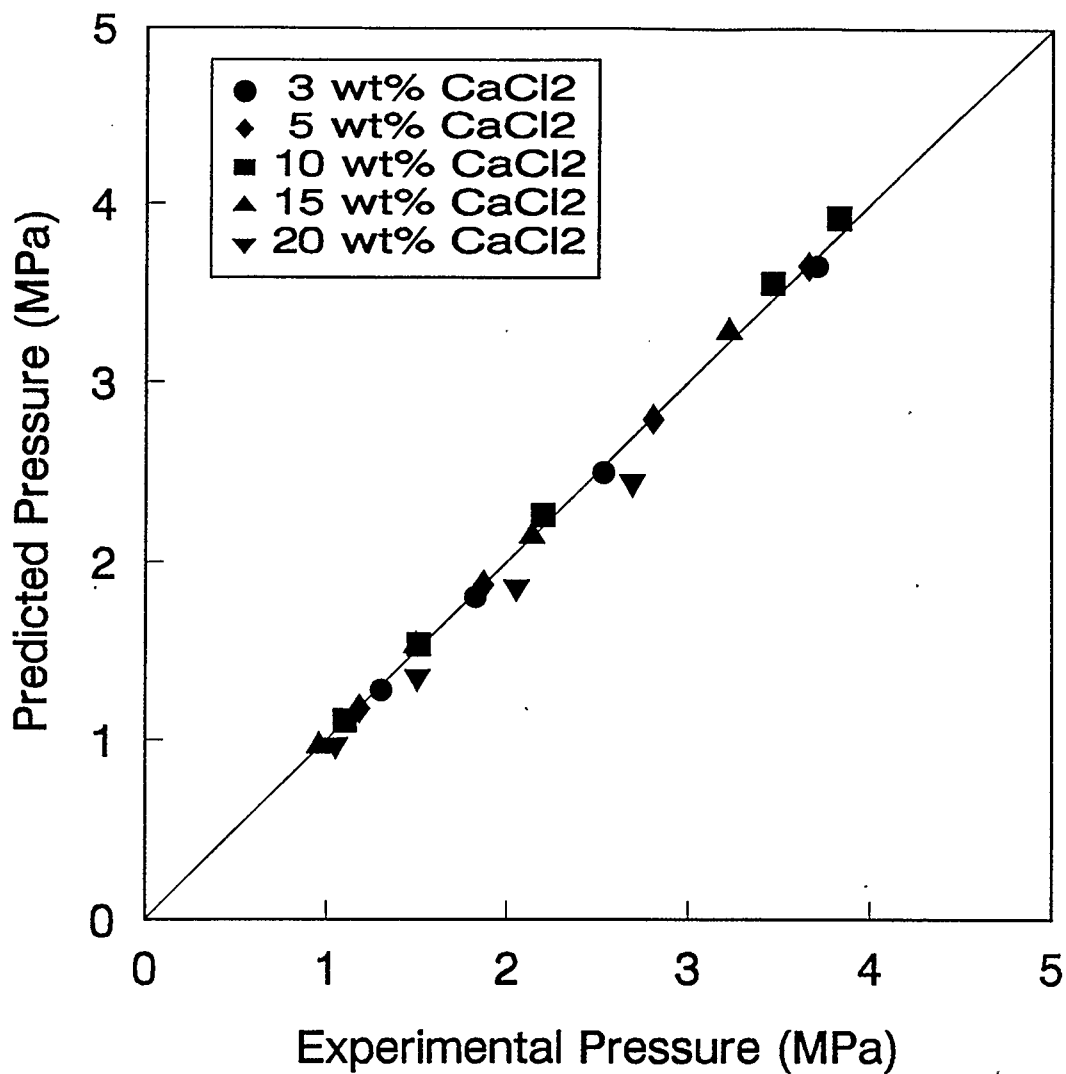


Figure 4.12 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous CaCl₂ Solution

using this model are shown in Figure 4.13. The accuracy between the calculated and the experimental pressures is illustrated in Figure 4.14. This model was capable of yielding accurate predictions for salt concentrations of 10 weight percent or less. Above the 10 weight percent of calcium chloride, this model gave poor results. As seen from Table A.3, the maximum percent deviation was 33.0% and the RMSD was found to be 14.2%. In the model of Aasberg-Petersen et al. (1991), the electrolytic interaction coefficients between salt and water were obtained by fitting the coefficients to match experimental vapour pressure lowering of a 1 m salt solution at a specific temperature. Since vapour pressure lowering is a function of salt concentration, the model should yield better results for salt concentrations close to 1 m. Above this concentration, the model provides poor predictions for the computation of hydrate equilibrium conditions.

4.2 Carbon Dioxide in Mixed Electrolyte Solution

The computation of the incipient hydrate formation conditions in mixed electrolyte solution was examined for the system containing carbon dioxide, sodium chloride and calcium chloride in an aqueous solution. Since the model of Aasberg-Petersen et al (1991) gave unacceptable results in the case of single electrolyte solution, it was not considered further for the mixed electrolyte solution. The inhibiting effect of sodium chloride and calcium chloride on hydrate formation conditions was investigated using the model of Chen and Evans (1986) and the model of Zuo and Guo (1991).

4.2.1 Chen and Evans Model

In Figures 4.15 and 4.16, the calculated results using the model of Chen and

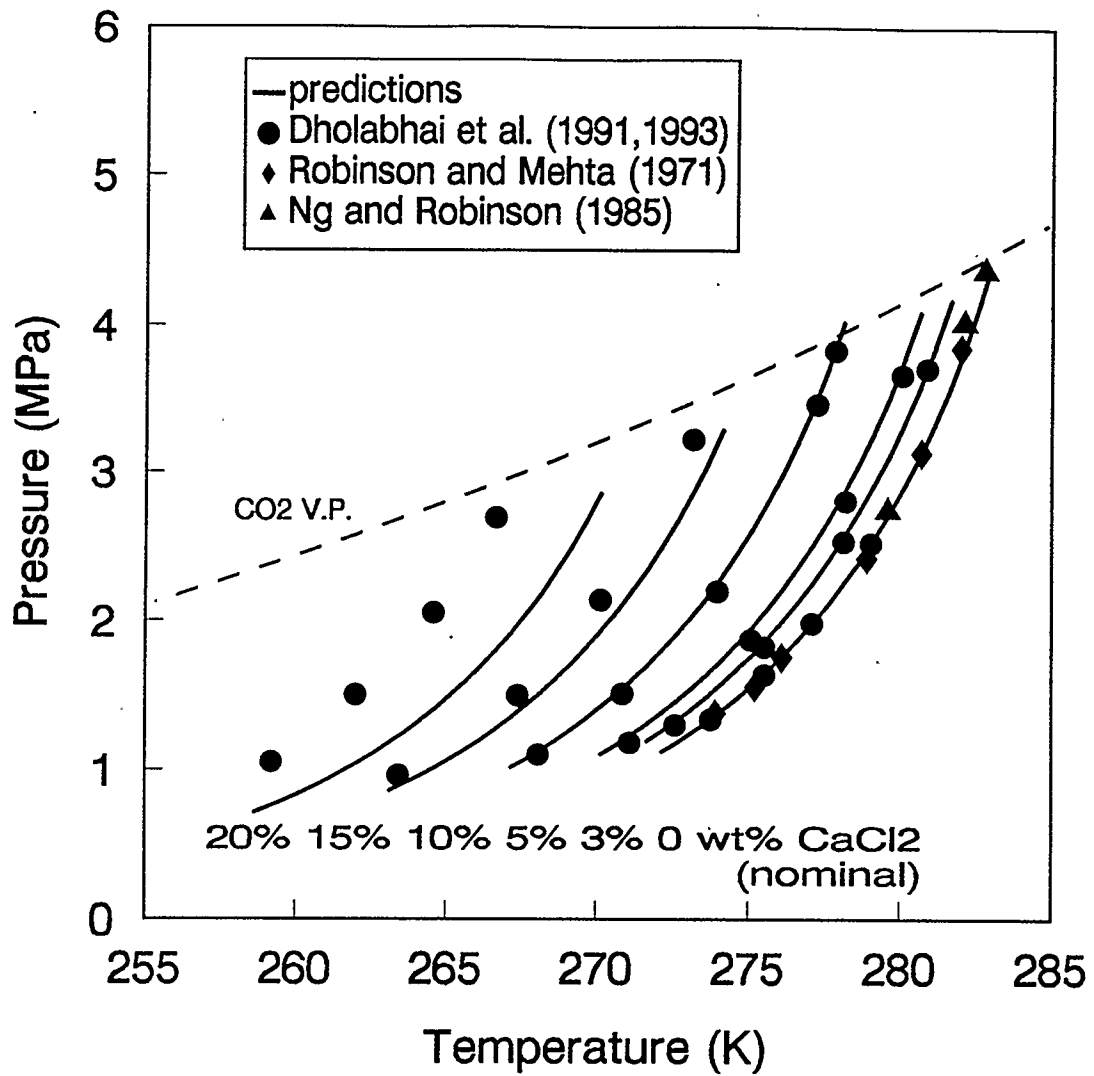


Figure 4.13 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Aasberg-Petersen et al. (1991) for Carbon Dioxide Gas in Aqueous CaCl₂ Solution

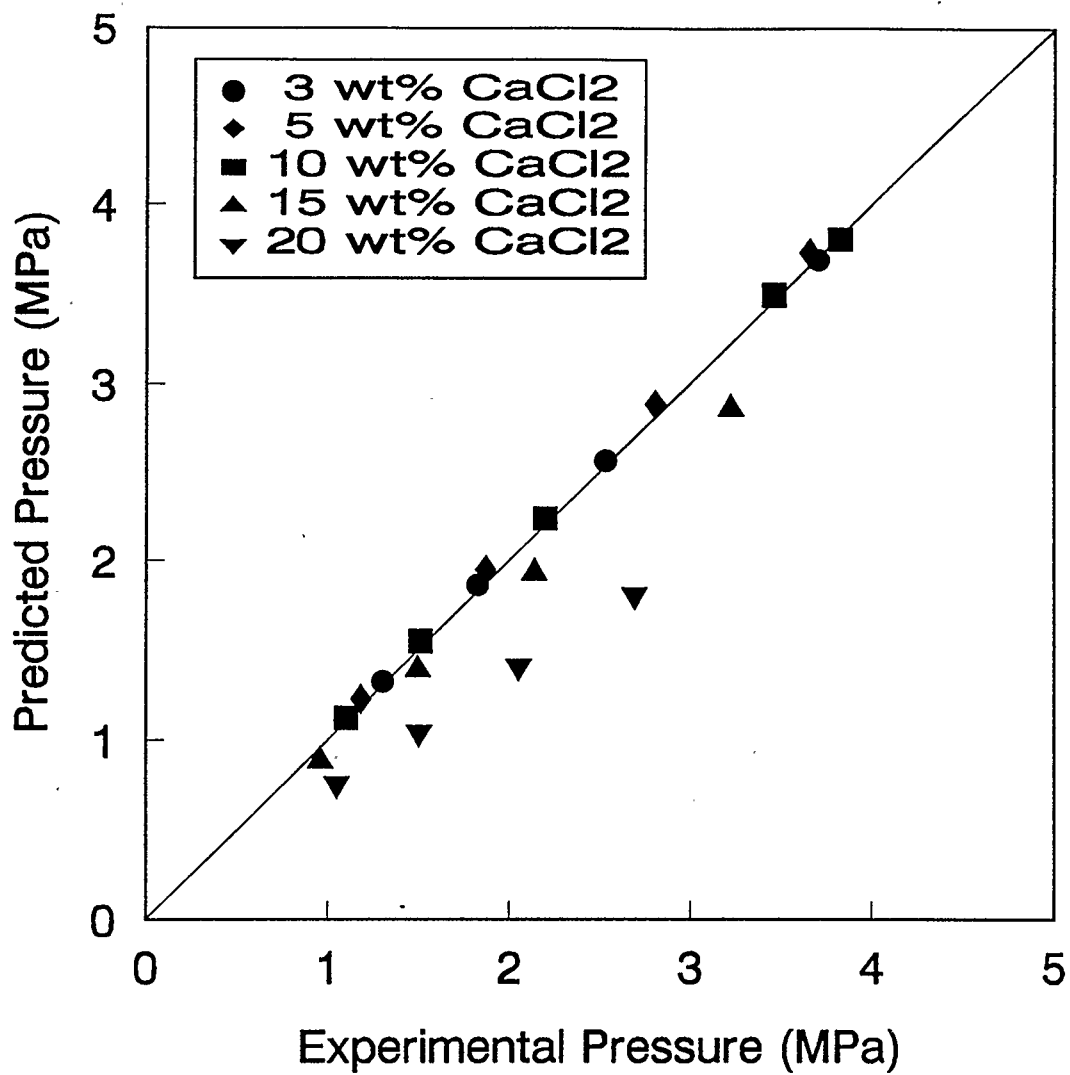


Figure 4.14 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Aasberg-Petersen et al. (1991) for Carbon Dioxide Gas in Aqueous CaCl₂ Solution

Evans (1986) and the comparison with the experimental pressures are shown respectively. The similarity in inhibiting effect for sodium chloride and calcium chloride can be seen in Figure 4.15. The total salt concentration on weight basis is the most important factor in determining the incipient hydrate formation conditions since both 8% NaCl / 2% CaCl₂ solution and 2% NaCl / 8% CaCl₂ solution on a weight basis yielded similar inhibiting effect. This observation is consistent with both the predictions by the model and the experimental hydrate data. The carbon dioxide experimental hydrate data in mixed electrolyte solutions is obtained from Dholabhai et al. (1991, 1993). The percent deviations between the predicted and experimental pressures are given in Table A.4. The maximum percent deviation with the model of Chen and Evans (1986) was 14.6% with a corresponding RMSD of 8.7%.

4.2.2 Zuo and Guo Model

The same computation was then carried out using the model of Zuo and Guo (1991). The calculated equilibrium hydrate formation pressures along with the experimental hydrate data are shown in Figures 4.17 and 4.18. The accuracy of the predictions for this model is also shown in Table A.4. The maximum percent deviation was 9.2% and the RMSD was 4.1%. Comparing these deviation values with those obtained from the model of Chen and Evans (1986) shows that the model of Zuo and Guo (1991) also provides better predictions for the case of aqueous mixed electrolyte solution of sodium chloride and potassium chloride. Using the model of Zuo and Guo (1991), predictions of carbon dioxide hydrate equilibrium conditions in aqueous solution of sodium chloride and potassium chloride were calculated. These results are given in Figure 4.19 and 4.20. Tabulated values along with the experimental data are summarized in Table A.5. The maximum percent

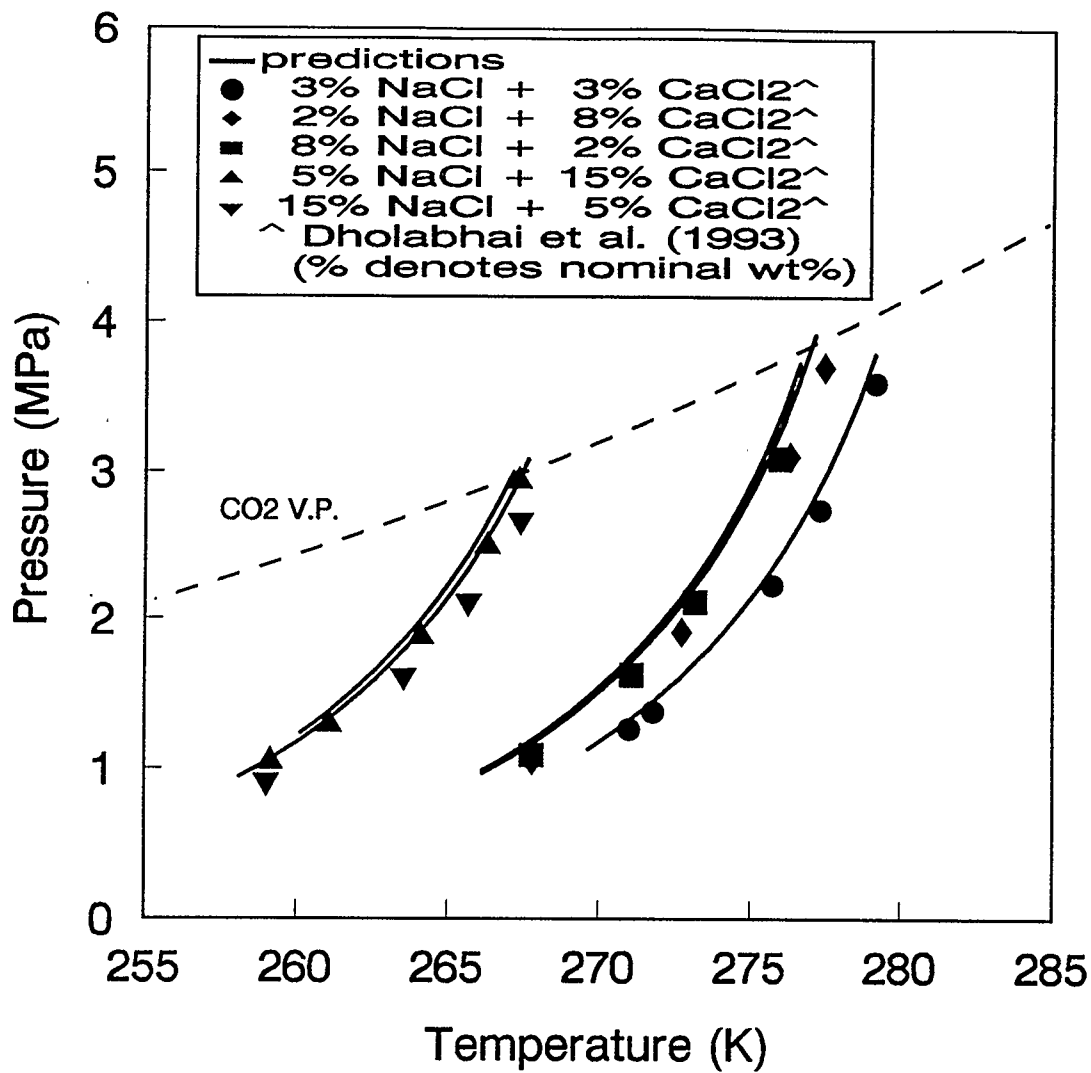


Figure 4.15 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Chen and Evans (1986) for Carbon Dioxide Gas in Aqueous NaCl and CaCl₂ Solution

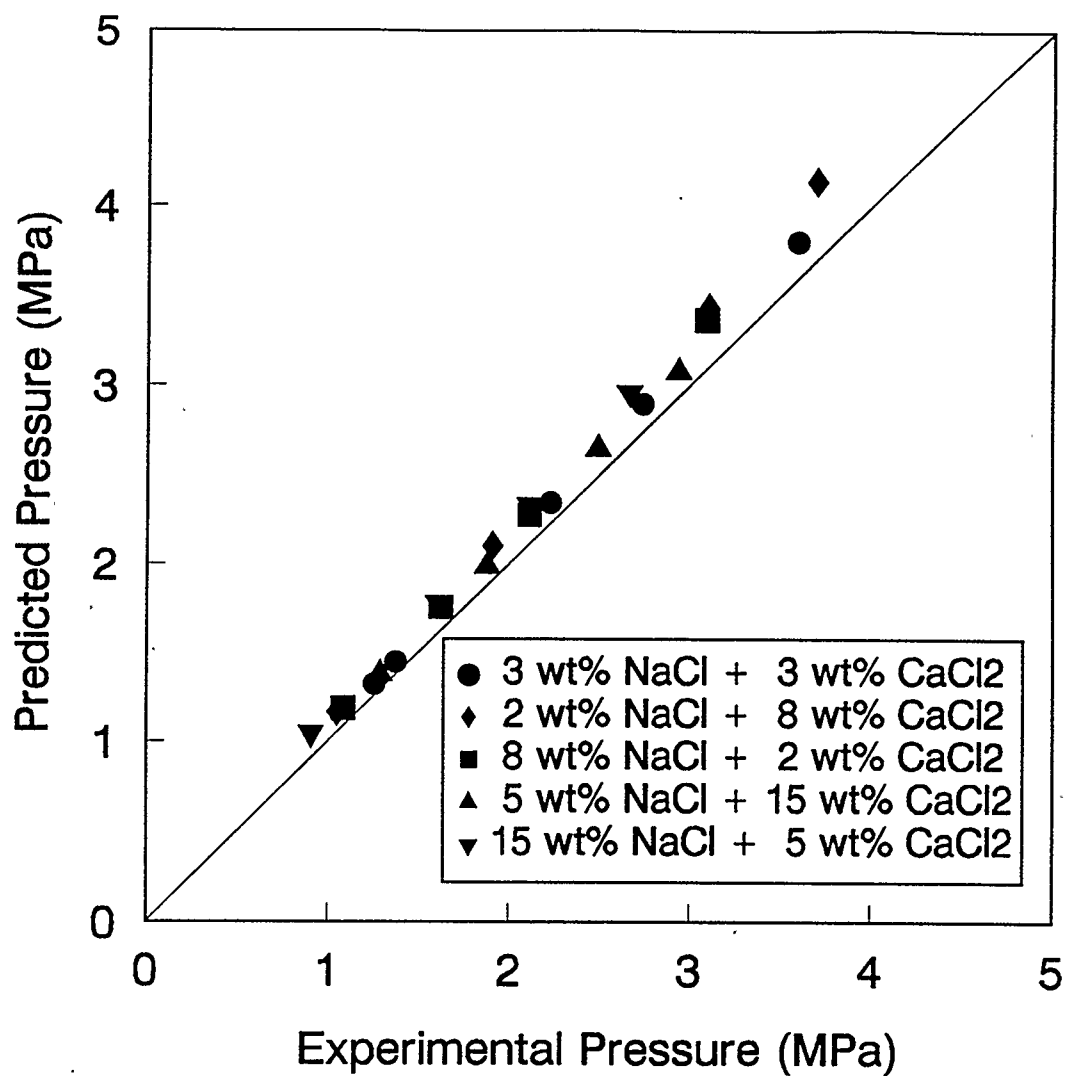


Figure 4.16 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Chen and Evans (1986) for Carbon Dioxide Gas in Aqueous NaCl and CaCl₂ Solution

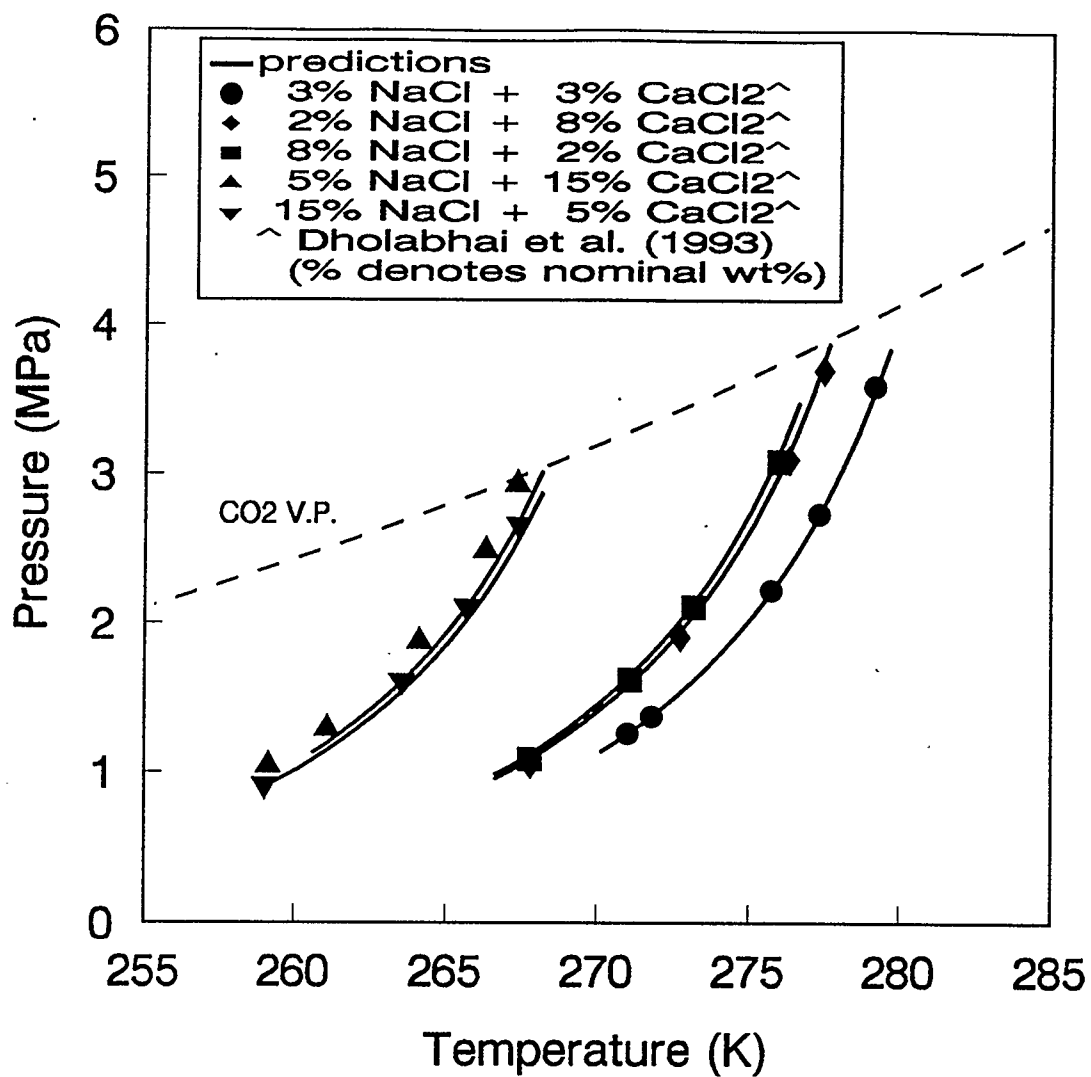


Figure 4.17 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous NaCl and CaCl₂ Solution

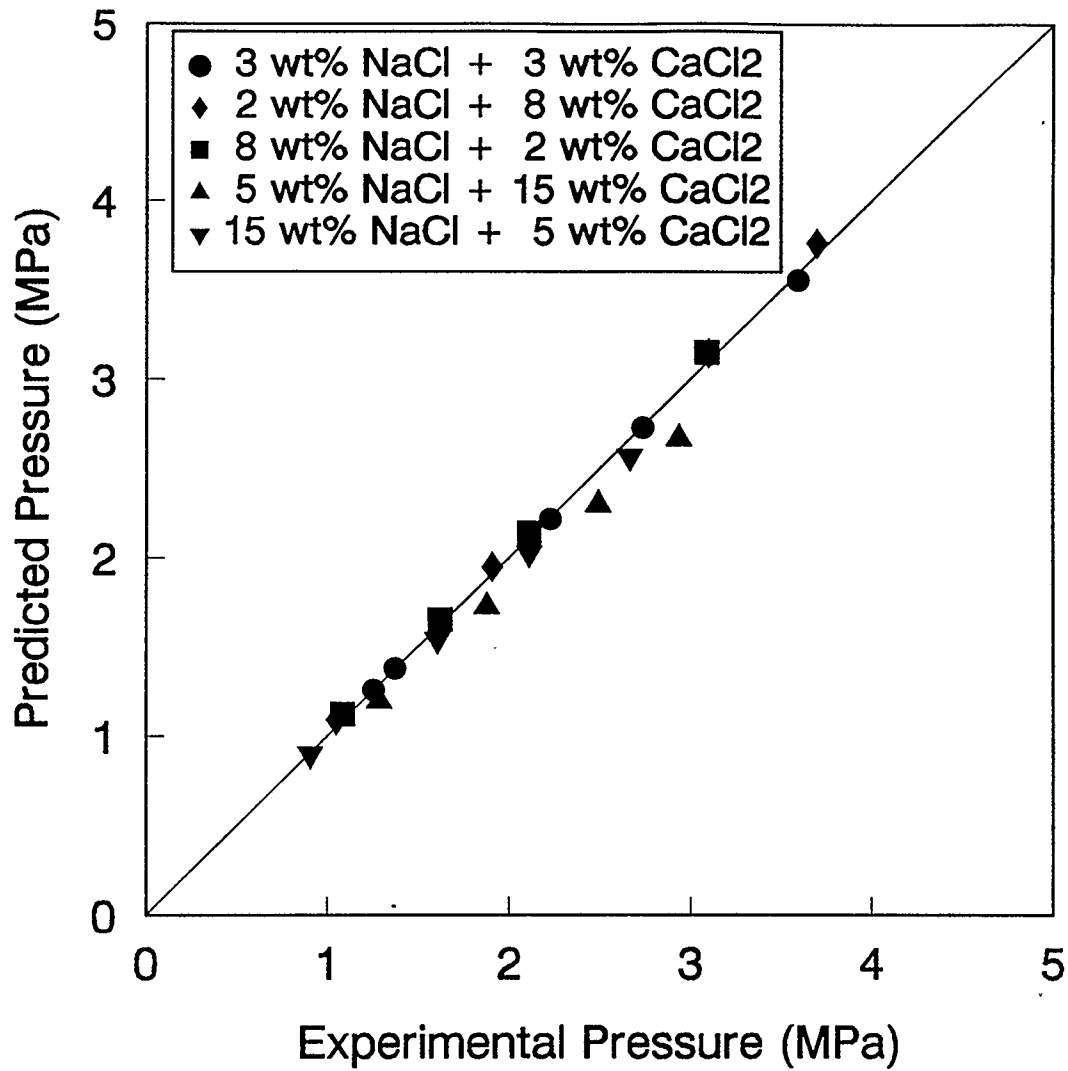


Figure 4.18 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous NaCl and CaCl₂ Solution

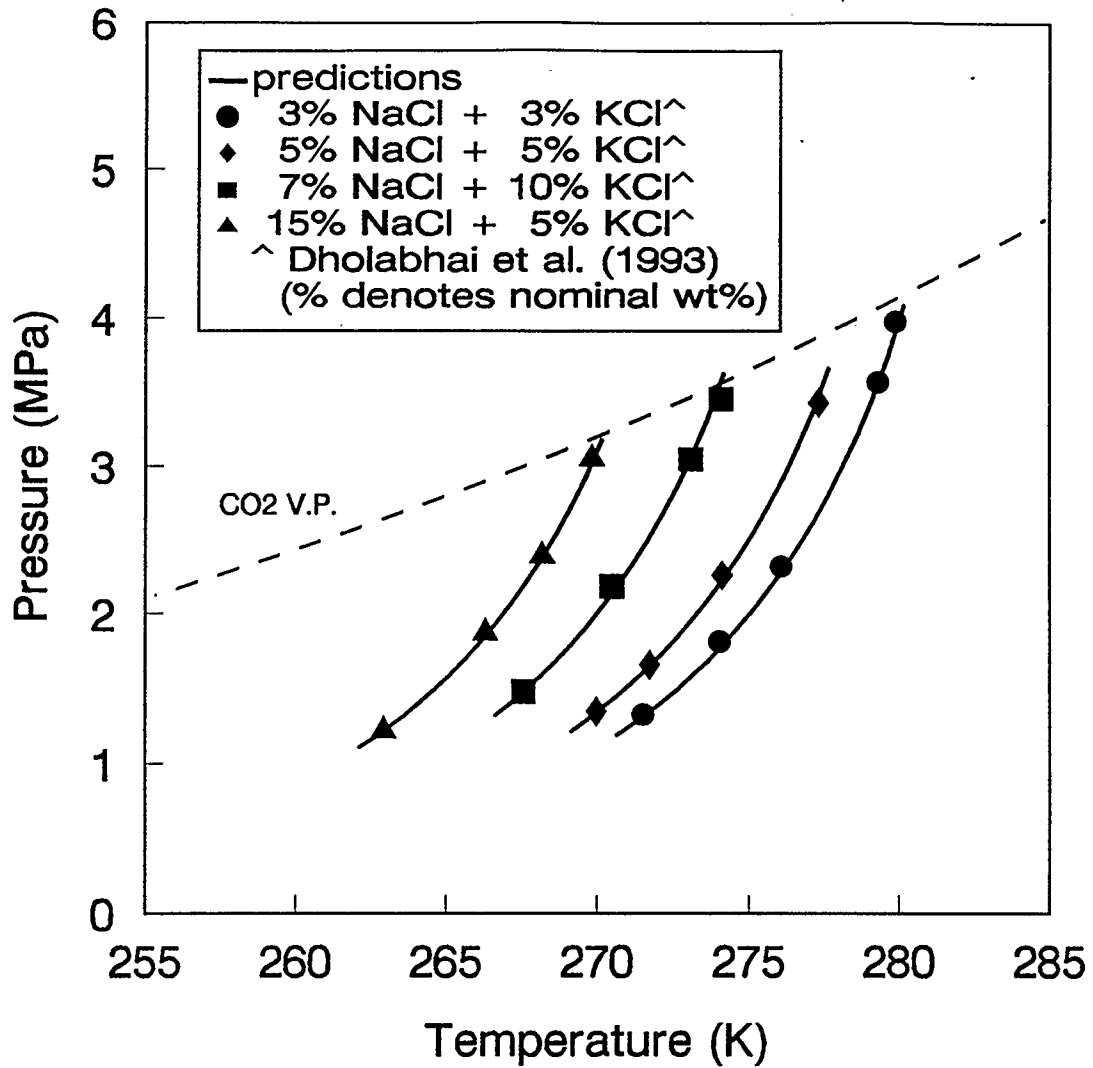


Figure 4.19 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous NaCl and KCl Solution

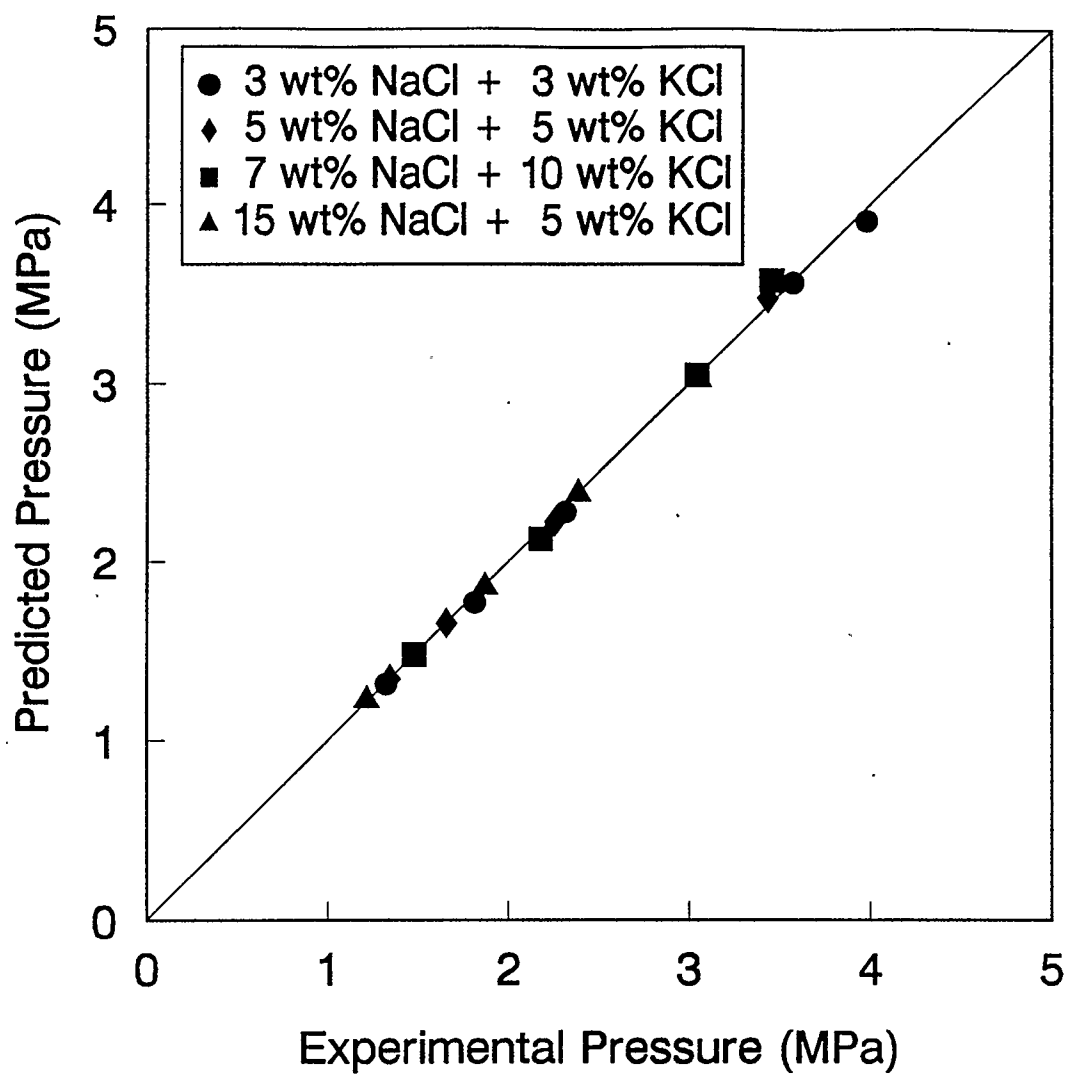


Figure 4.20 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for Carbon Dioxide Gas in Aqueous NaCl and KCl Solution

deviation was found to be 3.5% with the corresponding RMSD of 2.3%.

4.3 Gas Mixtures of Carbon Dioxide and Methane in Pure Water

Only the model of Zuo and Guo (1991) was used to compute the incipient hydrate formation conditions for gas mixtures in aqueous electrolyte solution. Since both Trebble-Bishnoi (1987) equation of state and Patel-Teja (1982) equation of state are cubic in nature, they would provide similar results for the vapor phase calculations. Therefore, the accuracy in the prediction of incipient hydrate equilibrium conditions depends primarily on the liquid model. It was found that the model of Zuo and Guo (1991) provided better results than the model of Chen and Evans (1986) for both single electrolyte solution and mixed electrolyte solution. Hence, the model of Zuo and Guo (1991) was utilized in the computation of methane - carbon dioxide gas mixtures in pure water. Furthermore, the model of Chen and Evans (1986) did not provide any binary parameters for methane - water interactions in the liquid phase. The computational procedure for the hydrate calculation with gas mixtures is shown in Figure 4.21. Since the mole fraction of CO_2 in the vapor phase, y_{CO_2} , is a variable in this calculation, the feed composition must be adjusted to obtain the desired y_{CO_2} . The predictions and the experimental data for a CO_2 - CH_4 gas mixture in pure water are shown in Figure 4.22. These predictions are compared to experimental data provided by Bishnoi and Dholabhai (1993), Adisasmito et al. (1991) and Dholabhai and Bishnoi (1993). It can be seen from Figure 4.23 that the predicted pressures are in excellent agreement with the experimental pressures. From Tables A.6 and A.7, the maximum percent deviation for this set of experimental data was 4.5% with a RMSD of 1.6%.

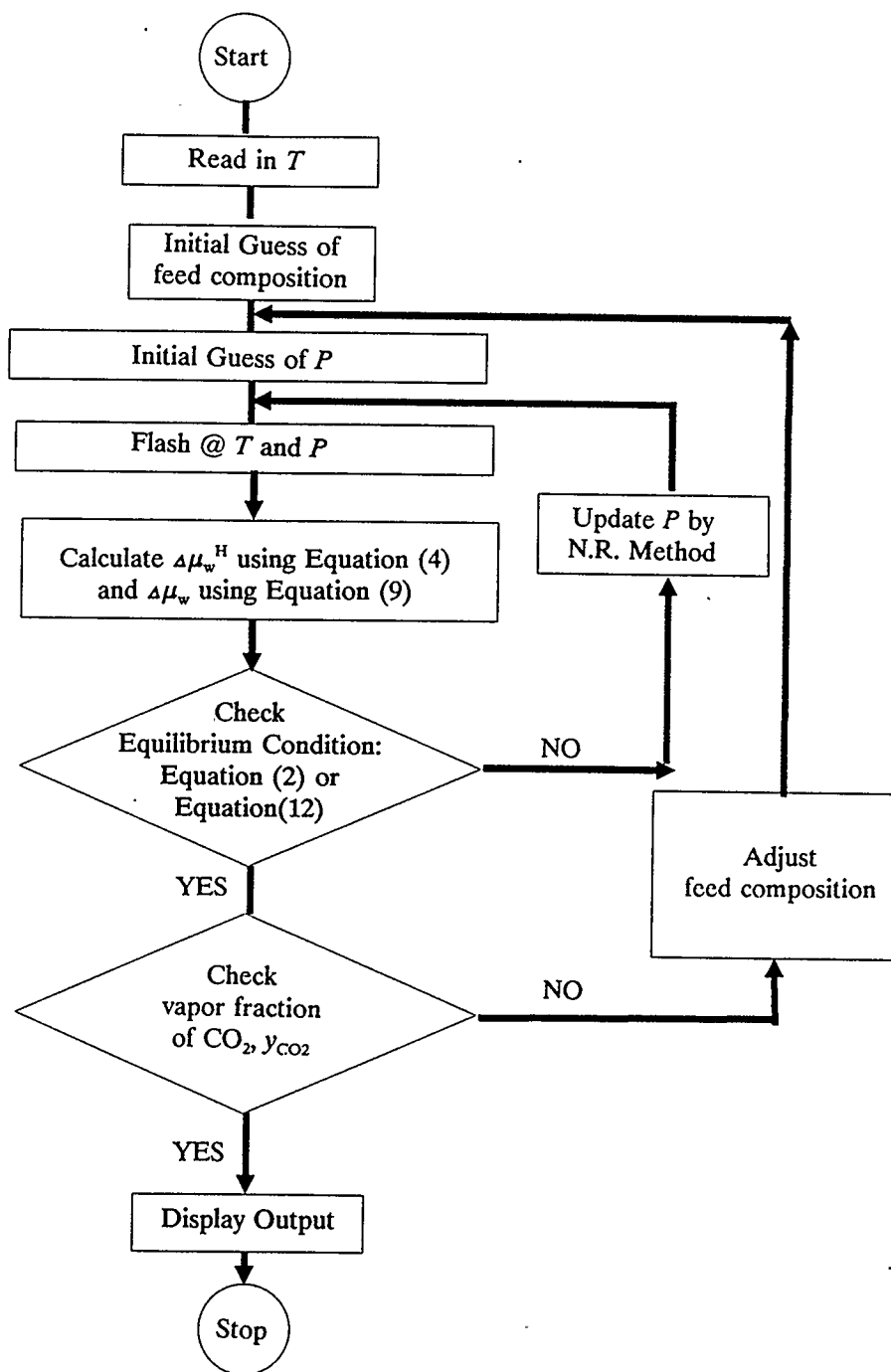


Figure 4.21 Computational Procedure for Calculation of Gas Mixtures of CO₂ and CH₄ in the Presence of Electrolytes

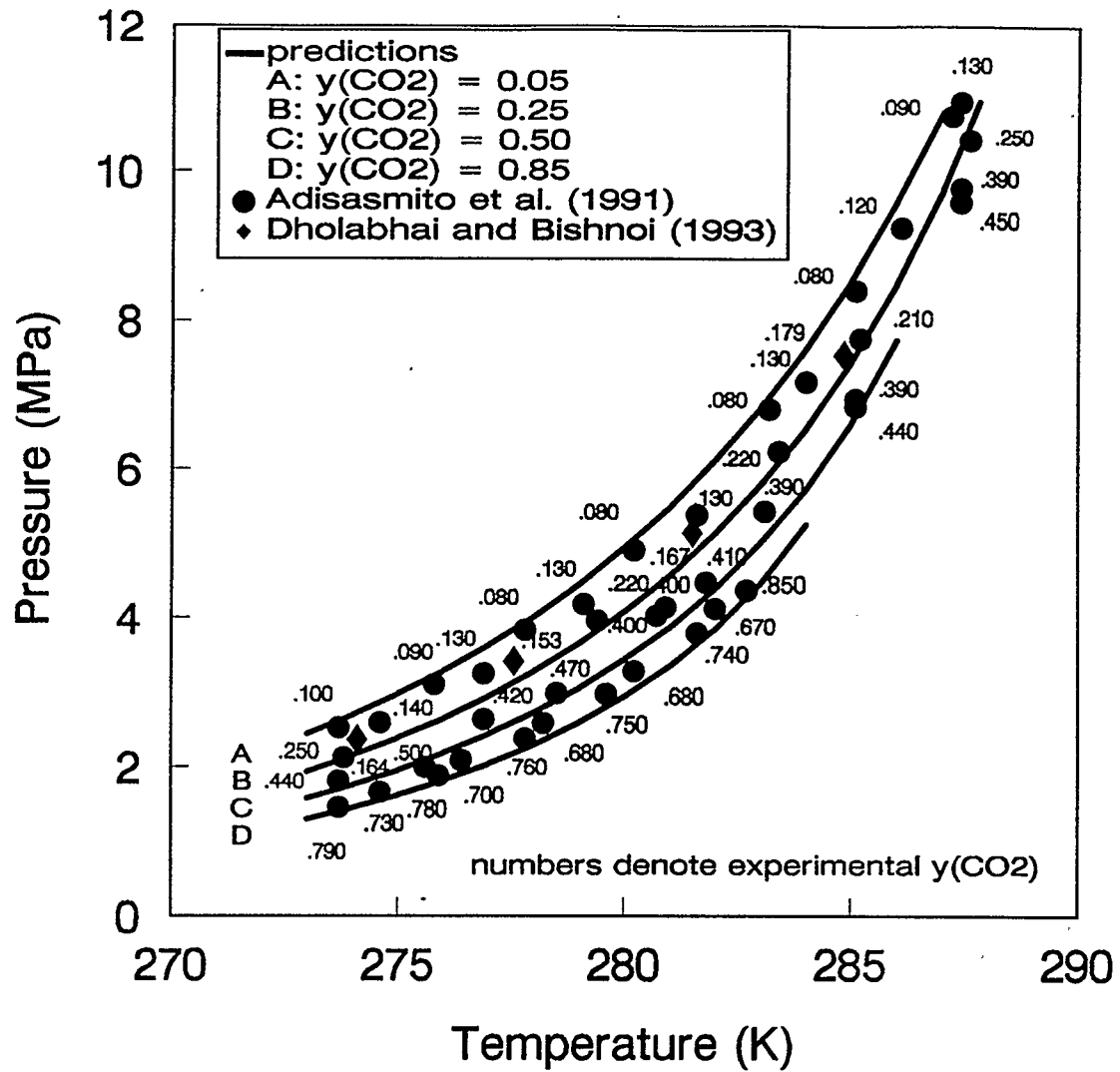


Figure 4.22 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for CH₄ - CO₂ Gas Mixtures in Pure Water

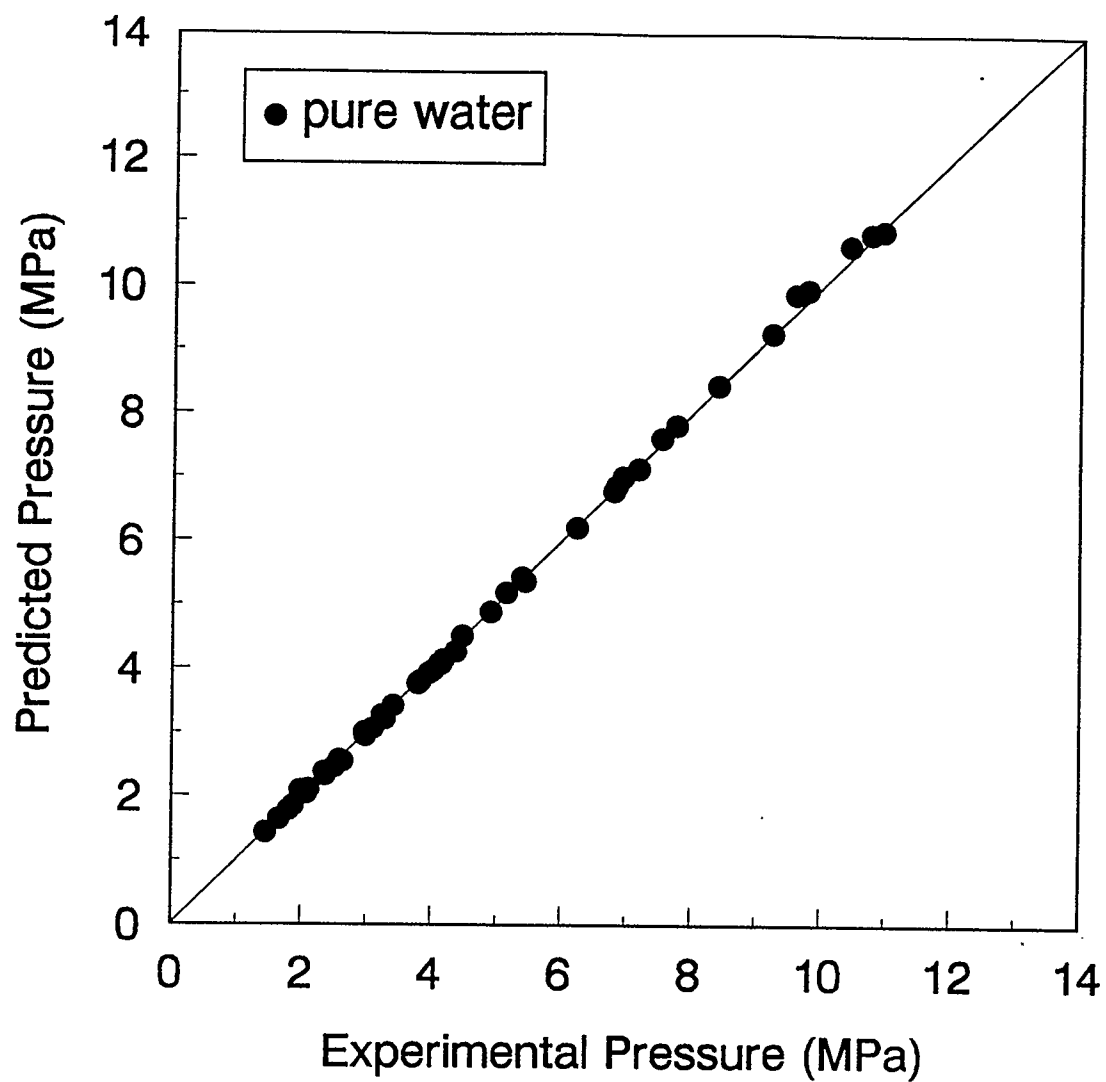


Figure 4.23 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for CH_4 - CO_2 Gas Mixtures in Pure Water

4.4 Gas Mixtures of Carbon Dioxide and Methane in Single Electrolyte Solution

The predictions along with the experimental data for a CO₂ - CH₄ gas mixture in 0, 5, 10, 15 and 20 weight percent aqueous sodium chloride solution are shown in Figure 4.24. The numerical values associated with each data point on the graph represents the mole fraction of CO₂ in the vapour phase at equilibrium. The predictions were obtained for 0.15 and 0.18 mole fraction of CO₂ in the vapour phase for the case of 0 and 5 weight percent NaCl. For the weight of 10, 15 and 20 percent, the predictions shown in the figure were obtained for 0.16 and 0.20 mole fraction of CO₂ in the vapour phase. There is not a notable difference in the predicted pressures at the various carbon dioxide vapour mole fraction considered for a specific salt concentration. The agreement between the experimental and the predicted values is shown in Figure 4.25. It can be noted that the agreement for low concentrations of NaCl is better than the high NaCl concentrations. The percent deviations between the predicted and experimental pressures are tabulated in Table A.7. The maximum deviation of CO₂ - CH₄ gas mixtures is 13.0% and the corresponding RMSD is 5.6%.

The next set of predictions is the CO₂ - CH₄ gas mixtures in aqueous potassium chloride solution. The incipient hydrate formation conditions were obtained for carbon dioxide mole fractions of 0.18 and 0.20 and are shown in Figure 4.26. The experimental data were taken from Bishnoi and Dholabhai (1993) and Dholabhai and Bishnoi (1993). The actual comparison between the experimental pressures with predicted pressures are given in Figure 4.27 and Table A.8. The maximum percent deviation and RMSD are 4.4% and 1.5% respectively.

In addition, the hydrate equilibrium conditions for gas mixture of CO₂ - CH₄ in aqueous calcium chloride are computed. The computations were performed for

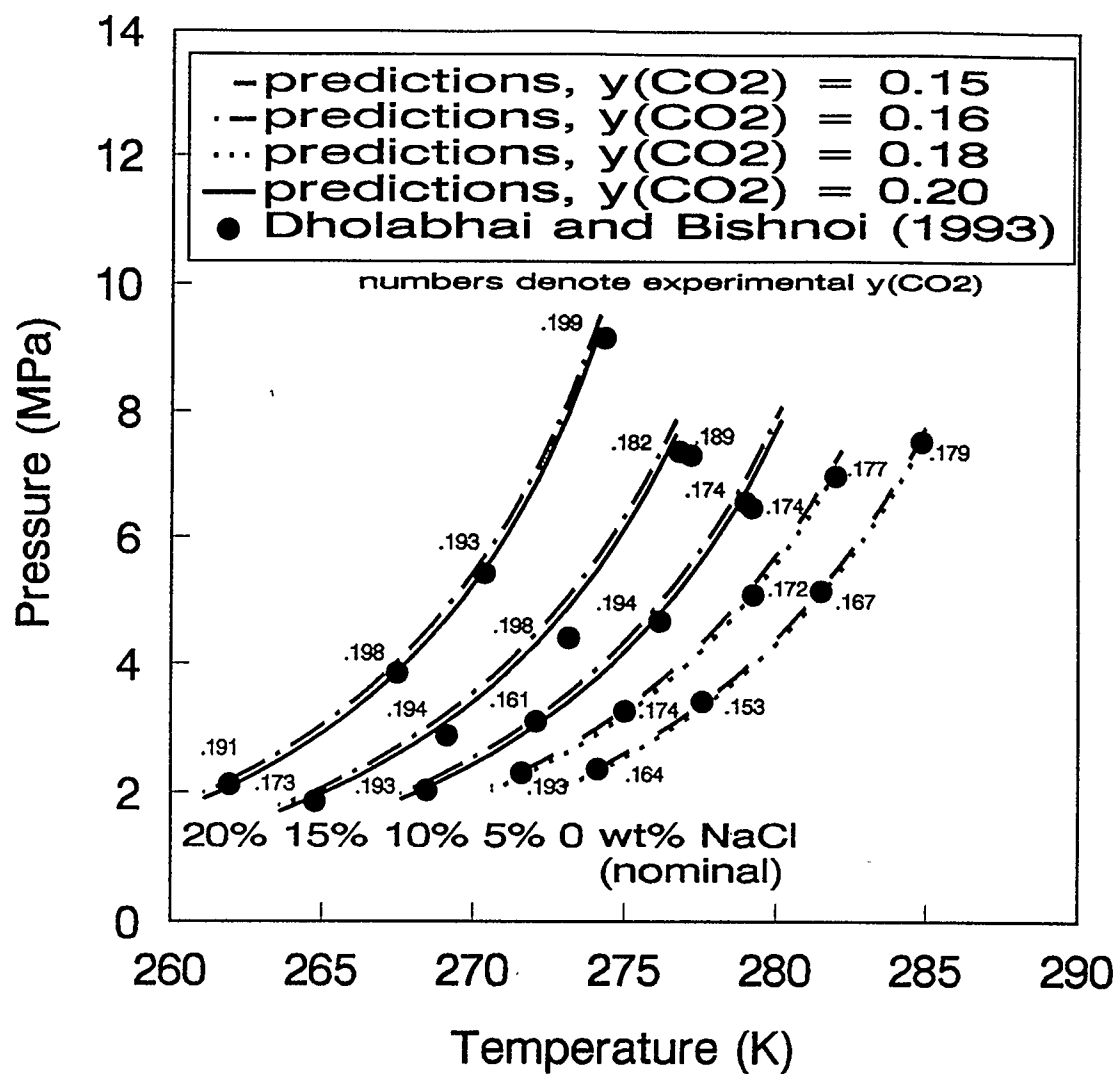


Figure 4.24 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for CH₄ - CO₂ Gas Mixtures in Aqueous NaCl Solution

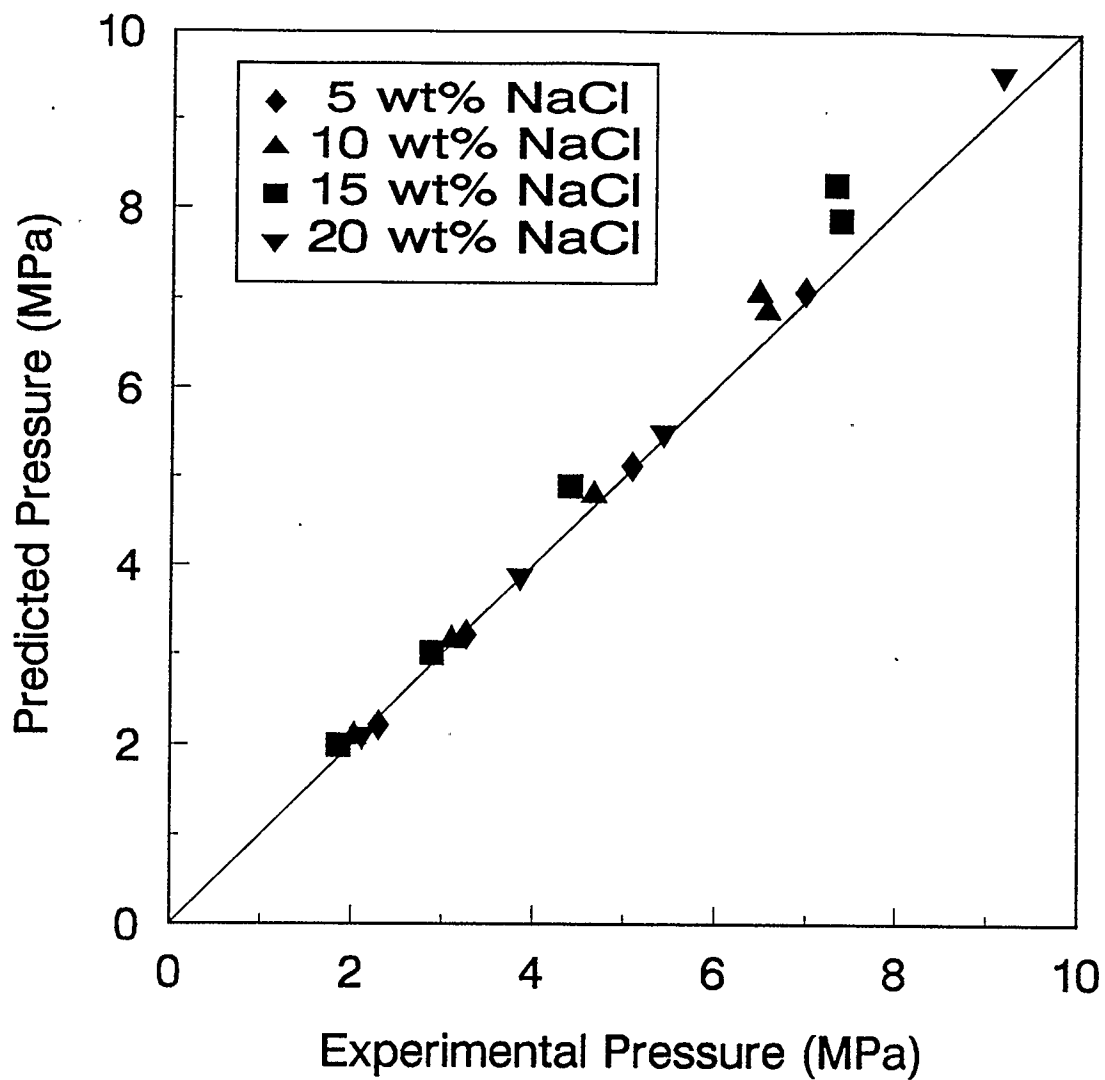


Figure 4.25 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for CH_4 - CO_2 Gas Mixtures in Aqueous NaCl Solution

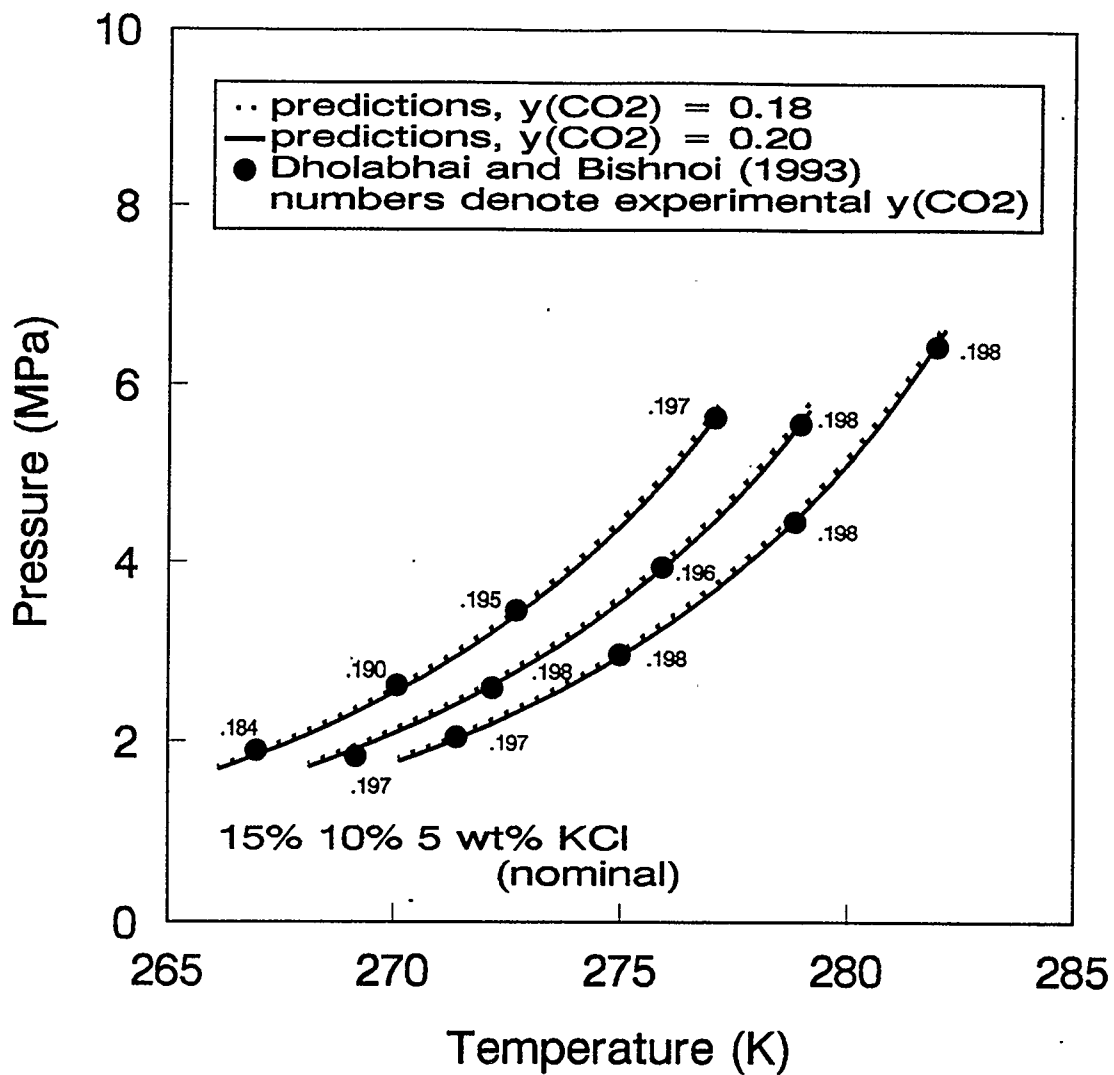


Figure 4.26 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for $\text{CH}_4 - \text{CO}_2$ Gas Mixtures in Aqueous KCl Solution

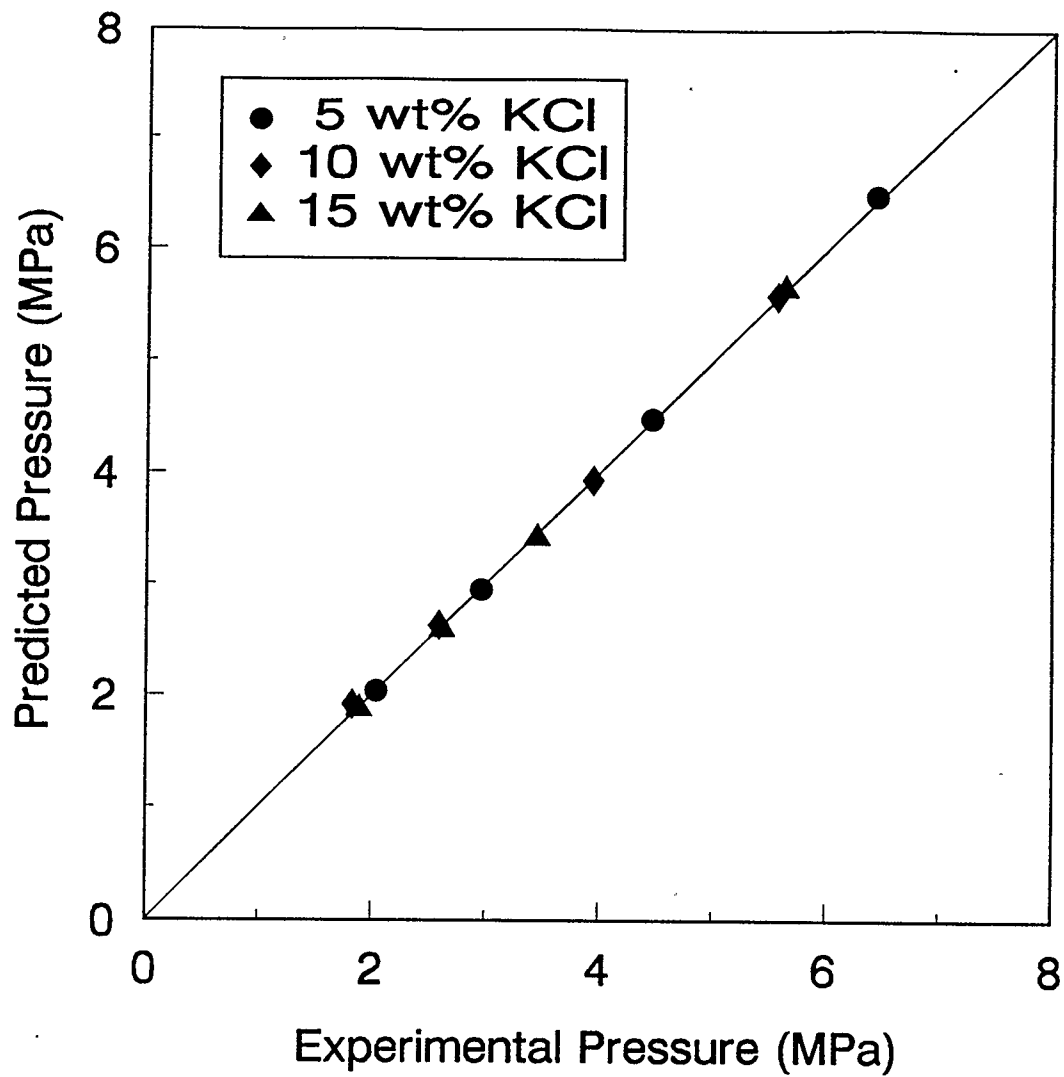


Figure 4.27 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for CH_4 - CO_2 Gas Mixtures in Aqueous KCl Solution

carbon dioxide mole fractions of 0.18 and 0.20 in the vapour phase at equilibrium. Figure 4.28 shows the equilibrium conditions for 10, 15 and 20 weight percent of CaCl_2 . It should be noted that the experimental data at 266.65K for 15% CaCl_2 seems questionable. Therefore, this particular data point is ignored for the consideration of maximum percent deviation and RMSD. The comparison between the experimental pressures and the predicted pressures is shown in Figure 4.29 and is summarized in Table A.9. The maximum percent deviation is 8.2% and the RMSD is 4.3%.

4.5 Gas Mixtures of Carbon Dioxide and Methane in Mixed Electrolyte Solution

Finally, the predictions of gas mixtures of carbon dioxide and methane in mixed electrolyte solutions are examined. The accuracy of these predictions are determined by comparison with the experimental data provided by Bishnoi and Dholabhai (1993) and Dholabhai and Bishnoi (1993). Figures 4.30 and 4.31 show the predictions of gas mixtures of approximately 20% CO_2 and 80% CH_4 in various binary salt solutions. The predictions shown in these figures have a vapour carbon dioxide mole fraction of 0.20 at equilibrium. The similarity in inhibiting effect of NaCl and CaCl_2 is again illustrated. The hydrate formation conditions for 5% CaCl_2 + 10% KCl are comparable with the conditions for 5% NaCl + 10% KCl . This behaviour can also be seen for the 5% CaCl_2 + 10% NaCl curve and 5% NaCl + 10% CaCl_2 . For gas mixtures of approximately 50% CO_2 and 50% CH_4 in binary electrolyte solutions, the predictions are shown in Figure 4.32. Predictions were obtained for CO_2 mole fractions of 0.46 and 0.50 whereas the mole fraction of CO_2 for the experimental data are given adjacent to the data points. The last set of predictions is for gas mixtures of CO_2 - CH_4 in an aqueous ternary solution

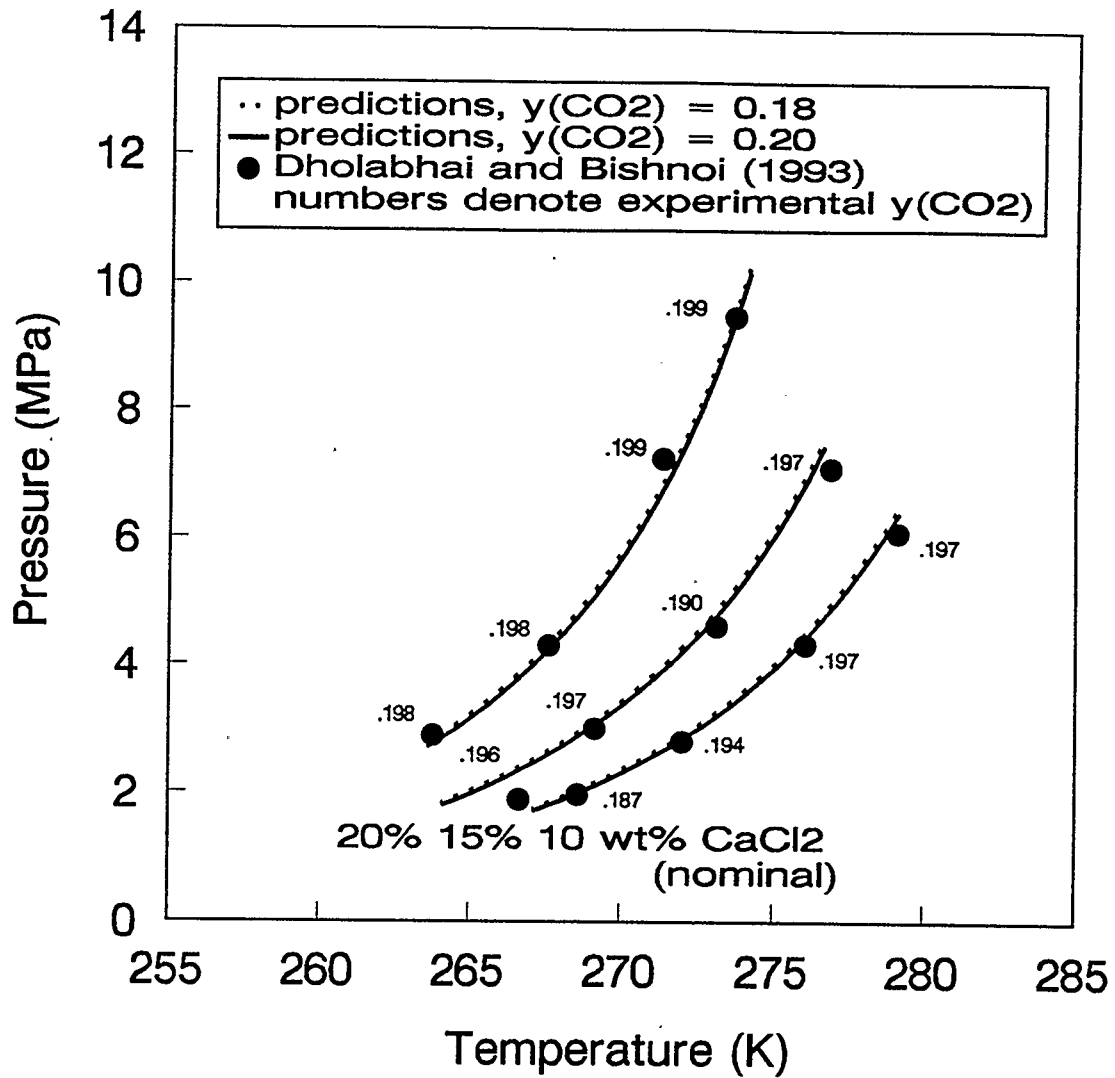


Figure 4.28 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for CH₄ - CO₂ Gas Mixtures in Aqueous CaCl₂ Solution

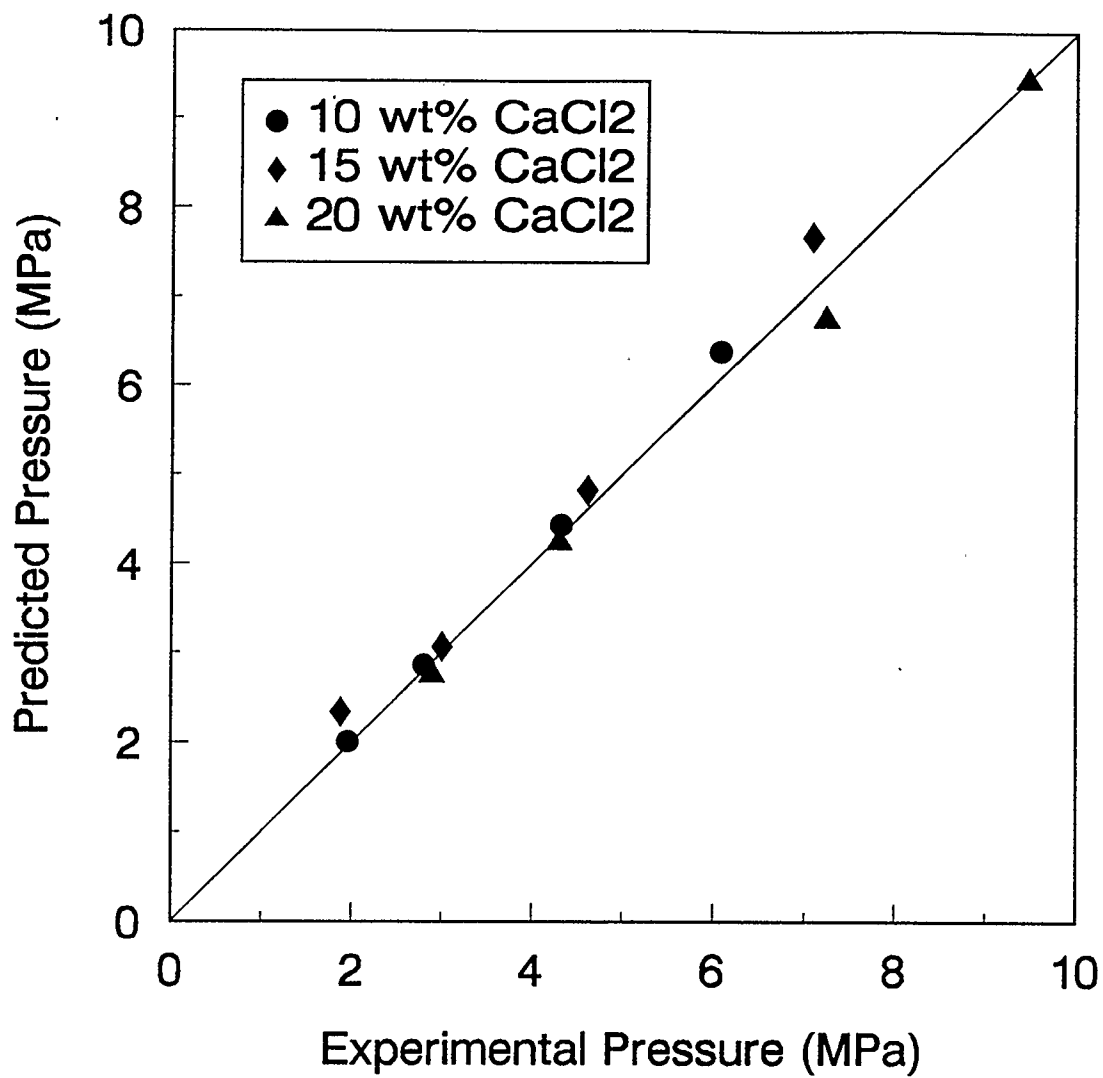


Figure 4.29 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for CH₄ - CO₂ Gas Mixtures in Aqueous CaCl₂ Solution

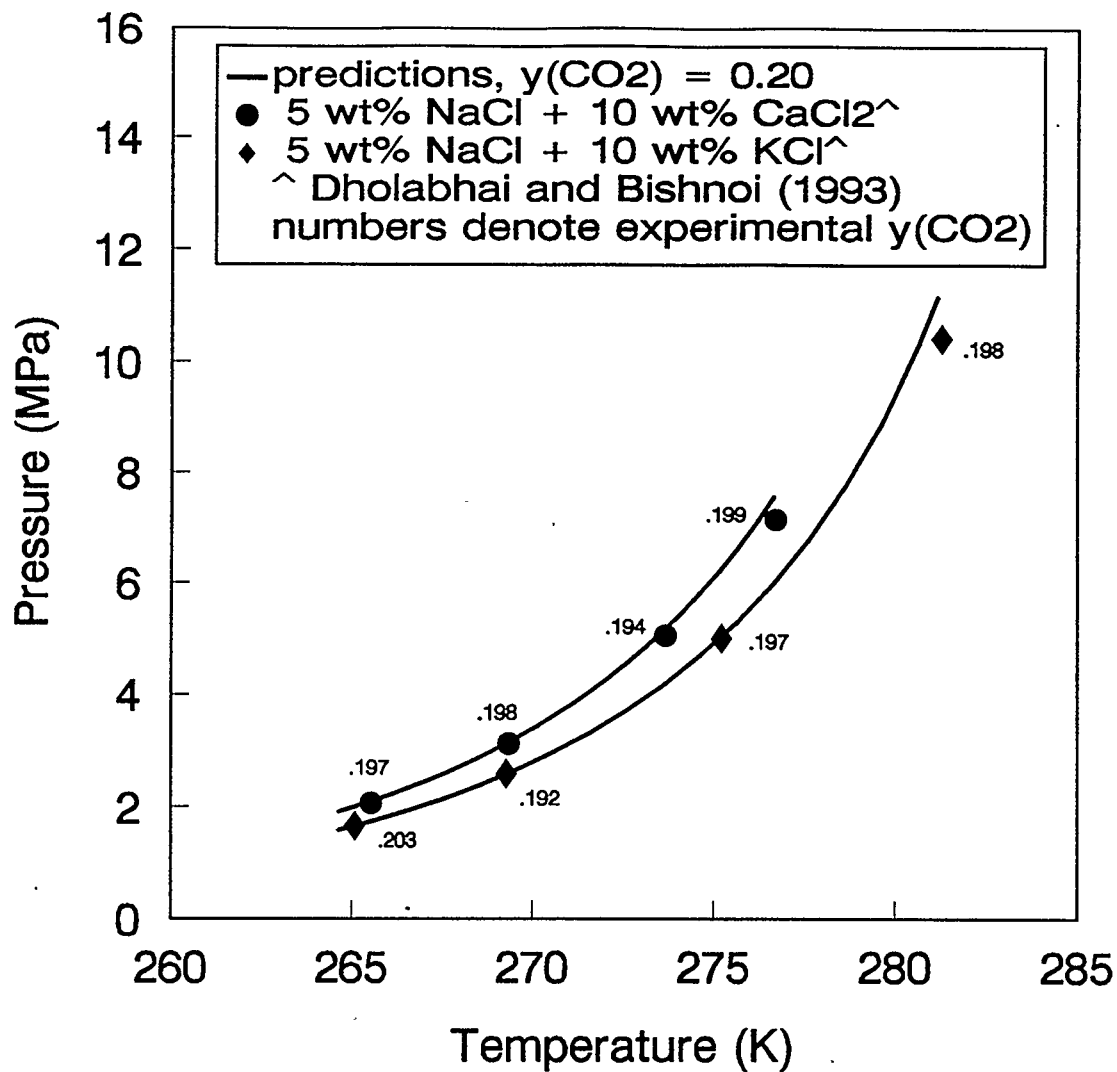


Figure 4.30 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for $\text{CH}_4 - \text{CO}_2$ Gas Mixtures in Aqueous Binary Electrolyte Solution

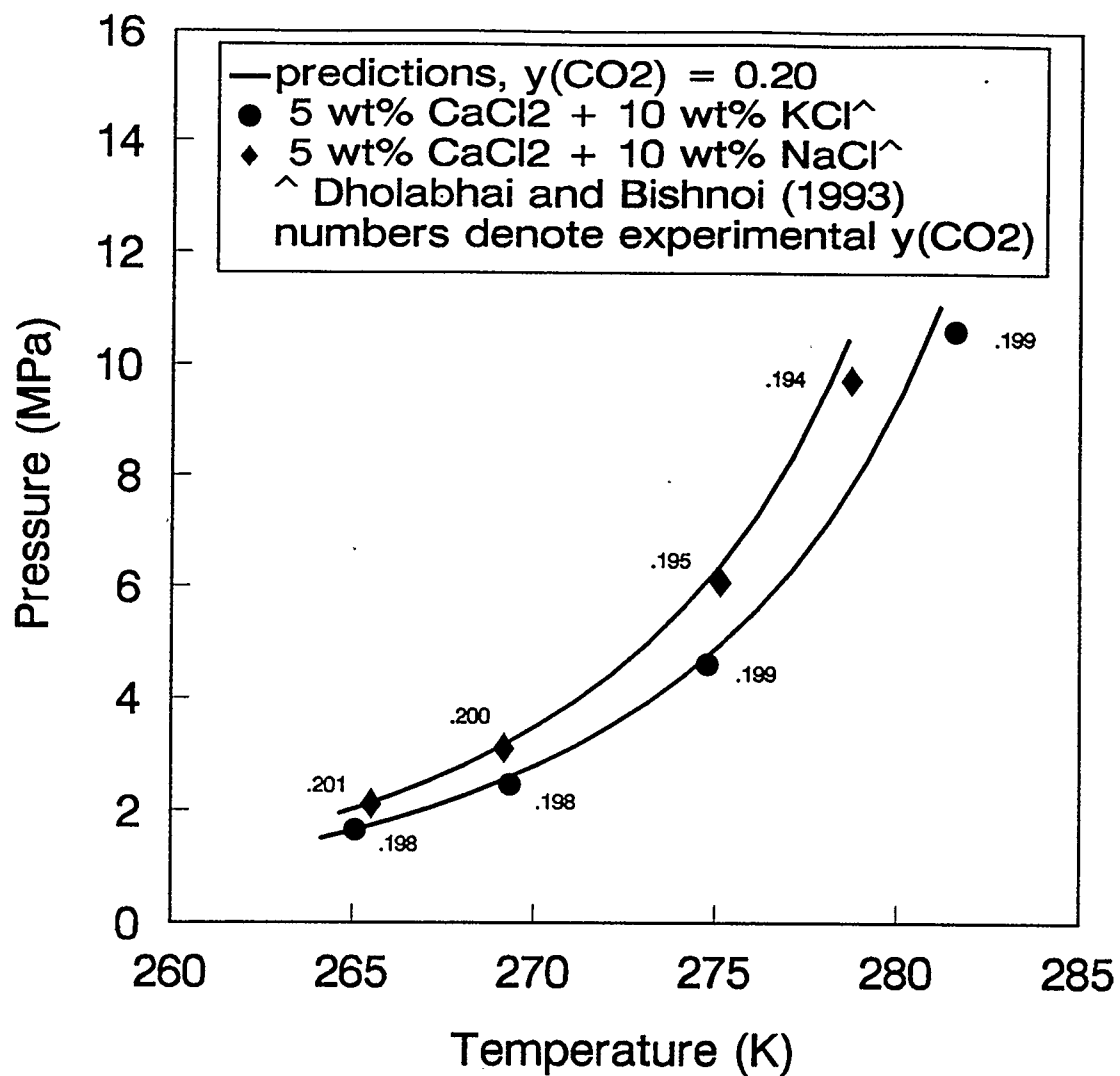


Figure 4.31 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for CH_4 - CO_2 Gas Mixtures in Aqueous Binary Electrolyte Solution

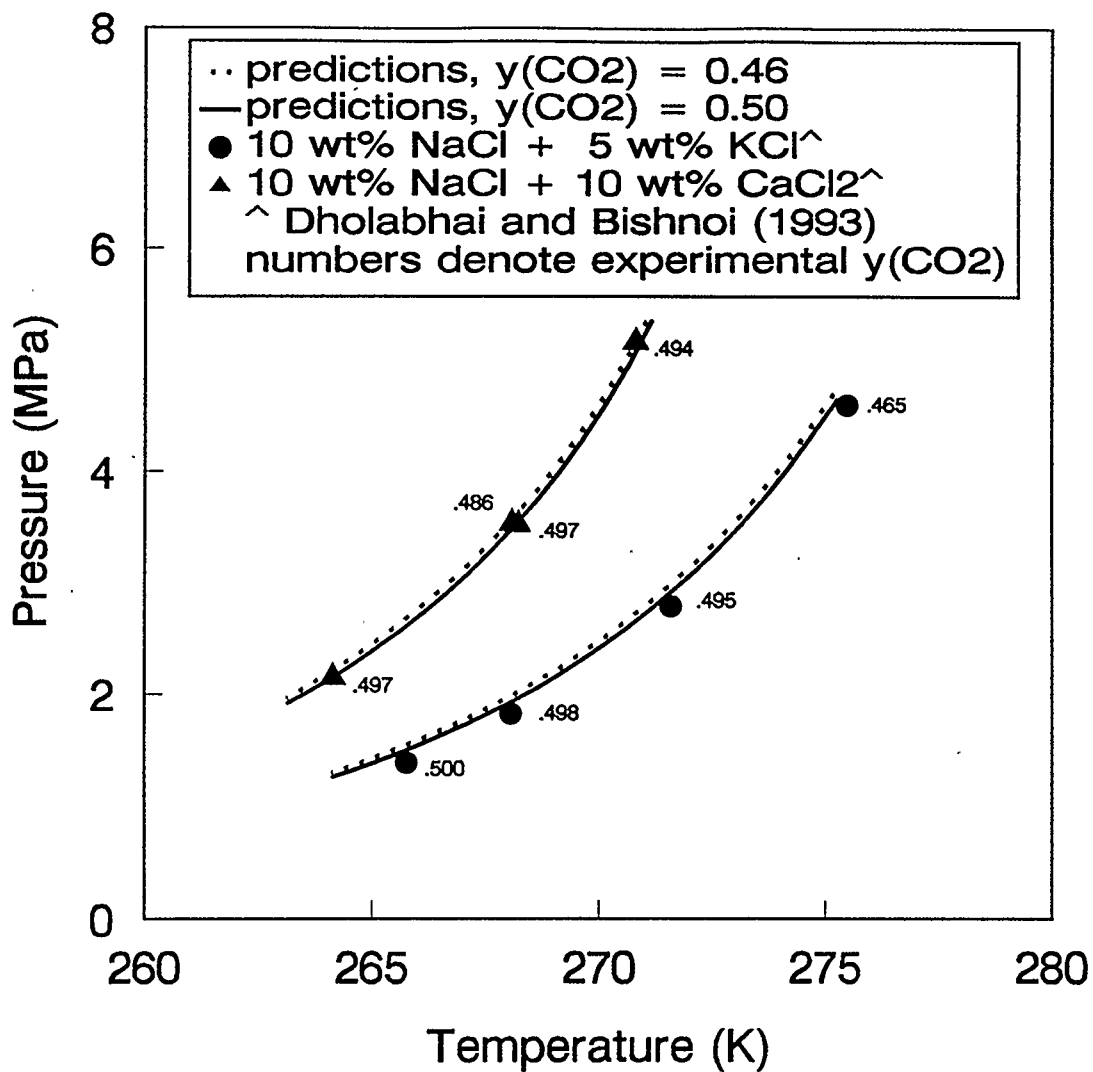


Figure 4.32 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for $\text{CH}_4 - \text{CO}_2$ Gas Mixtures in Aqueous Binary Electrolyte Solution

containing 4% CaCl₂, 5% KCl and 6% NaCl. These predictions can be seen in Figure 4.33. It may be noted that the hydrate formation pressure at a specific temperature increases with decreasing carbon dioxide mole fractions. The comparison between the predicted pressures and experimental pressures for CO₂ - CH₄ gas hydrate in mixed salt solutions is given in Table A.10 and in Figures 4.34 and 4.35. In general, the accuracy improves with decreasing equilibrium pressures. The maximum percent deviation is 11.1% and the corresponding RMSD is 5.4%.

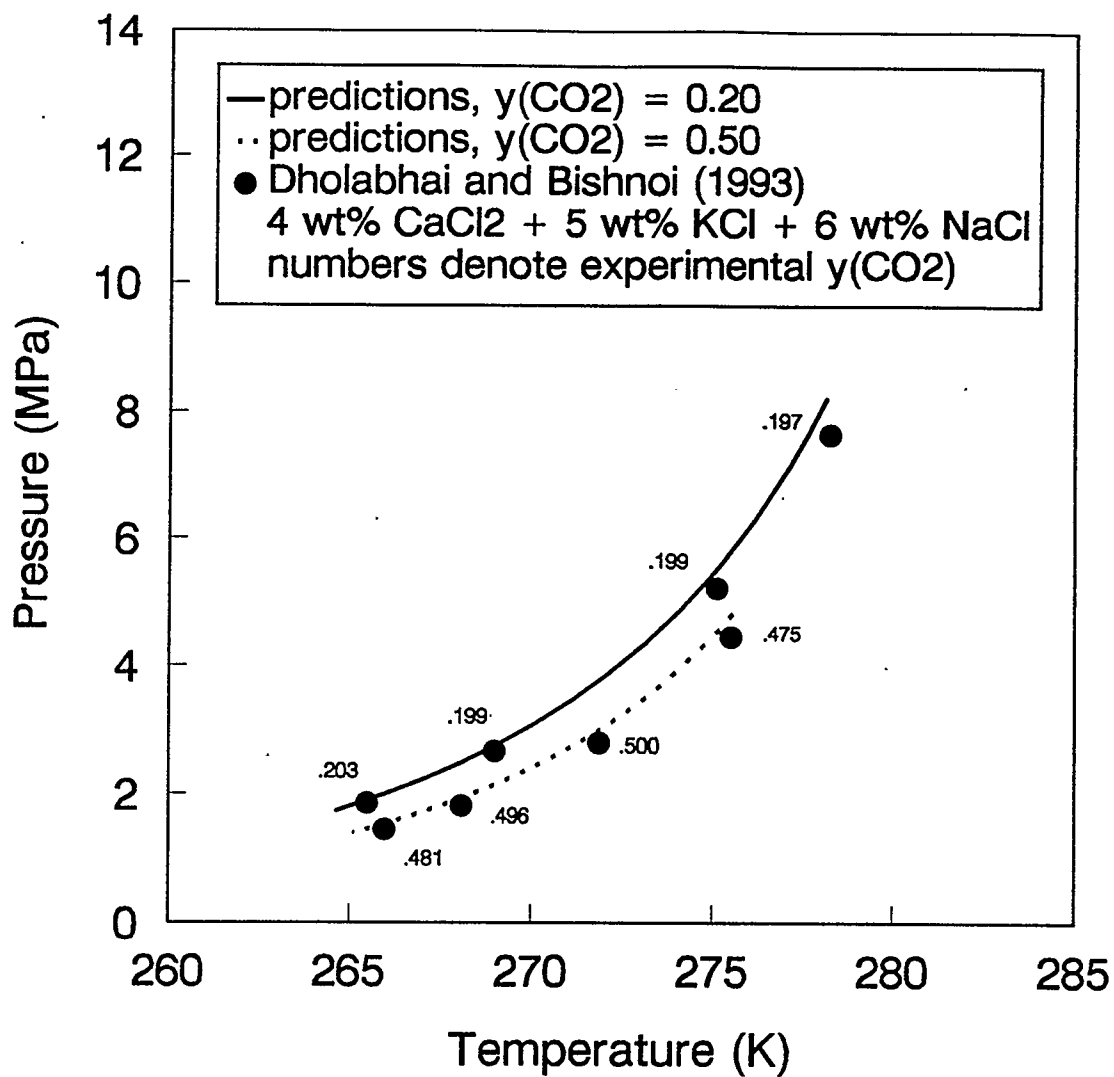


Figure 4.33 Experimental and Predicted Hydrate Equilibrium Conditions Using the Model of Zuo and Guo (1991) for CH_4 - CO_2 Gas Mixtures in Aqueous CaCl_2 , KCl and NaCl Solution

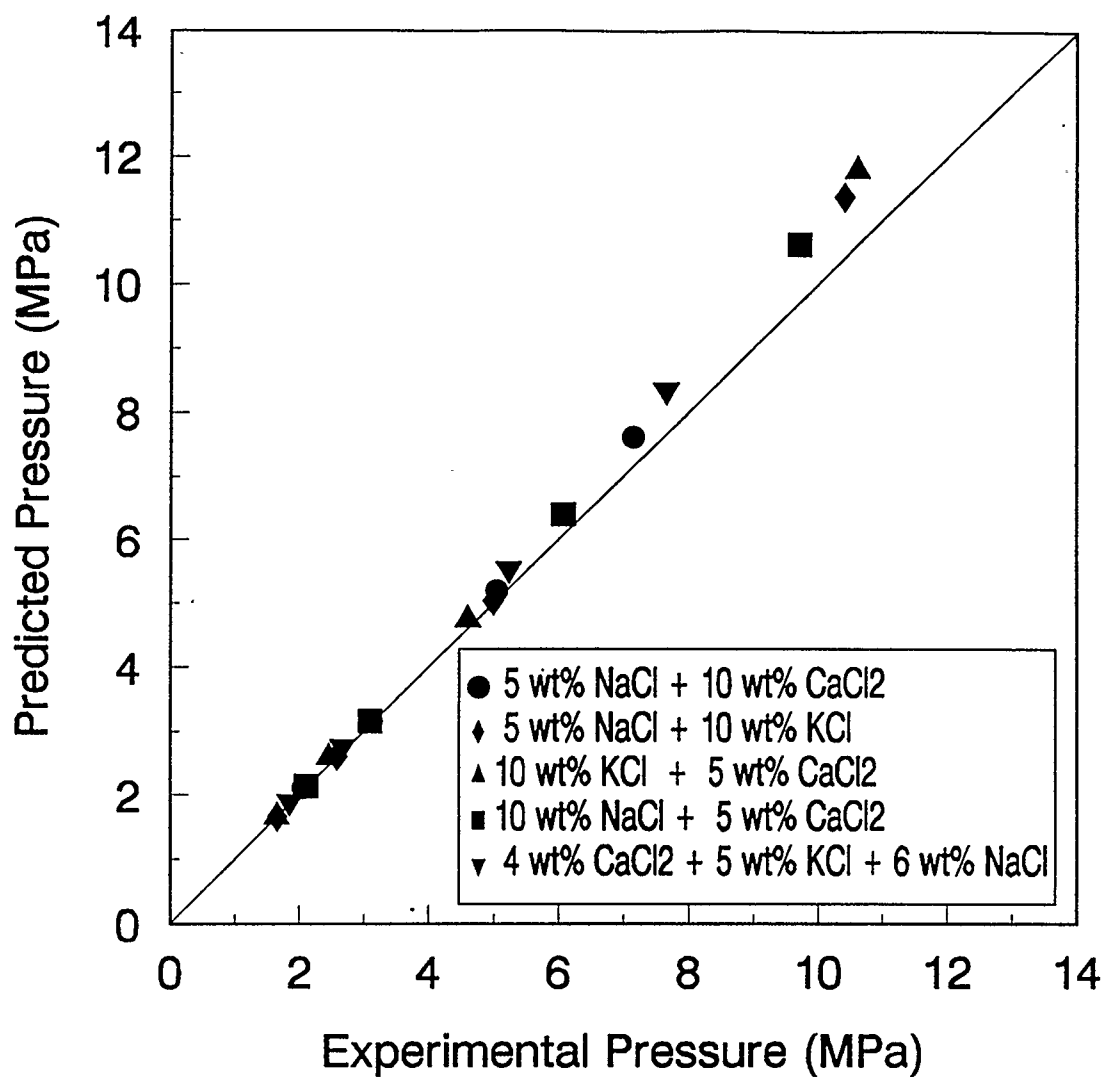


Figure 4.34 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for 80 mol% CH₄ - 20 mol% CO₂ Gas Mixtures in Aqueous Mixed Electrolyte Solution

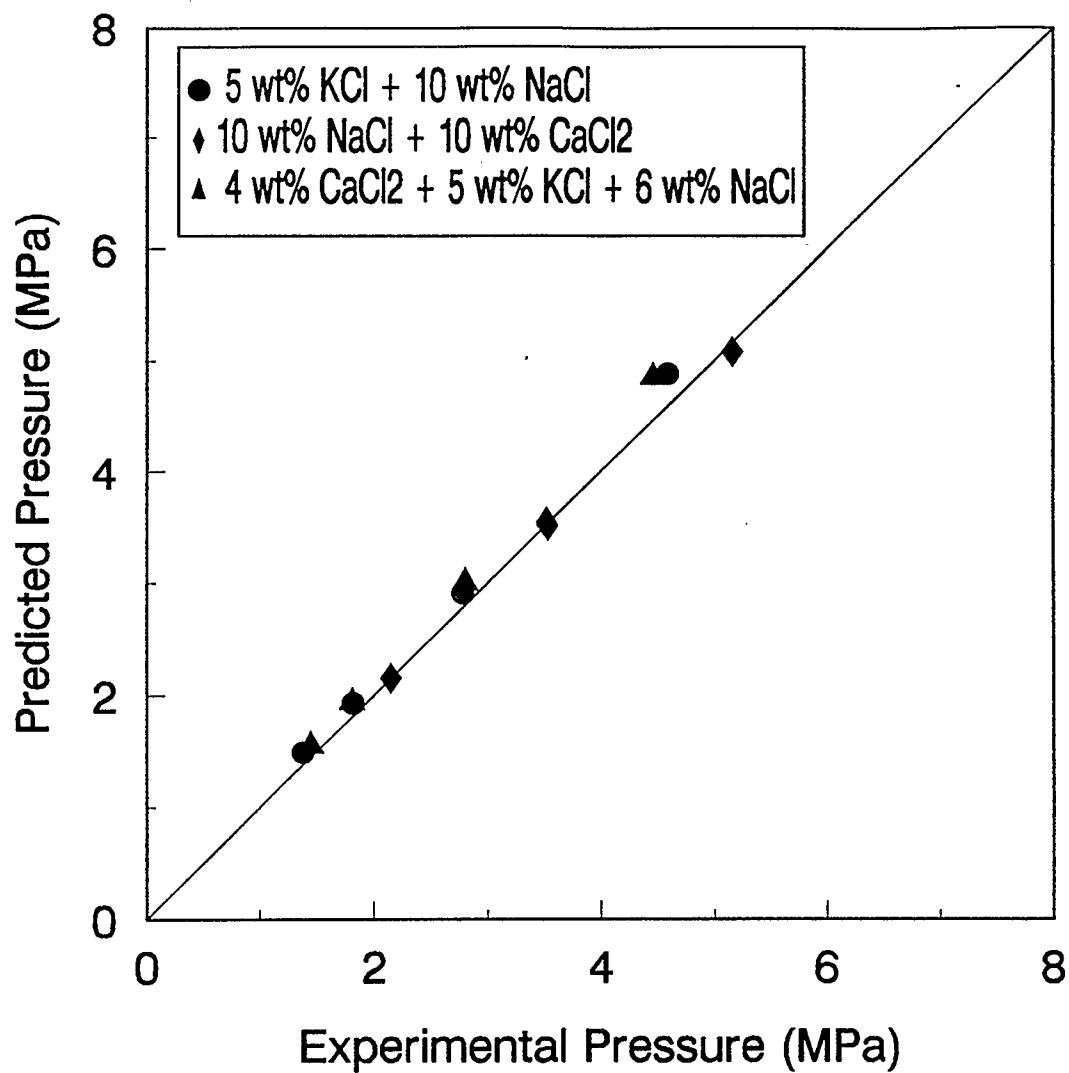


Figure 4.35 Comparison of Experimental and Predicted Hydrate Equilibrium Pressures Using the Model of Zuo and Guo (1991) for 50 mol% CH_4 - 50 mol% CO_2 Gas Mixtures in Aqueous Mixed Electrolyte Solution

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- A calculation procedure is outlined for the prediction of hydrate formation conditions in systems containing carbon dioxide, methane, and salts.
- Three thermodynamic models are examined for their ability to describe an aqueous phase containing soluble gases and electrolytes, namely the models of Chen and Evans (1986), Zuo and Guo (1991) and Aasberg-Petersen et al. (1991).
- Both the models of Chen and Evans (1986) and Zuo and Guo (1991) are able to predict the incipient hydrate equilibrium conditions for carbon dioxide in aqueous single and mixed electrolytes.
- A mixing rule is suggested for handling mixed electrolyte systems for using the models of Chen and Evans (1986) and Zuo and Guo (1991).
- The model of Aasberg-Petersen et al. (1991) is able to predict the incipient carbon dioxide hydrate equilibrium conditions in aqueous calcium chloride solution up to 10 weight percent. Above this concentration, the predictions are poor with deviations up to 30%.
- Comparison of the predictions with 88 experimental points in single and mixed electrolyte solutions shows that the percent root mean square deviation (RMSD) for the model of Chen and Evans (1986) is 7.5% whereas the RMSD for the model of Zuo and Guo (1991) is 4.2%.

- With a total of 119 experimental data points for gas mixtures of carbon dioxide and methane, the percent root mean square deviation between the experimental data and the predictions was found to be 4.0%.
- The experimental equilibrium hydrate formation conditions were accurately predicted using the outlined procedure with the model of Zuo and Guo (1991). This model can be used to represent both the gas and liquid phases.

5.2 Recommendations

- Extension of the calculation method to the case where the liquid phase contains solvents such as methanol. This is important as methanol is commonly used in industry to prevent hydrate formations. The objective is to predict the inhibiting effect of methanol on hydrate formations.
- The research on separation technology using gas hydrates depends on the capability of the thermodynamic model. Hence, efforts should be directed towards the examination of the thermodynamic model in handling a second liquid phase containing hydrocarbons.

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APPENDIX A

Table A.1 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Carbon Dioxide Gas in Aqueous NaCl Solution

Nominal Weight of NaCl (%)	Temperature (K)	Experimental Pressure* (MPa)	Chen and Evans (1986)		Zuo and Guo (1991)	
			Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)
3	272.20	1.304	1.309	-0.38	1.265	+2.99
	273.21	1.434	1.472	-2.65	1.422	+0.84
	275.17	1.837	1.860	-1.25	1.791	+2.50
	277.03	2.309	2.345	-1.56	2.253	+2.42
	278.95	2.955	3.026	-2.40	2.899	+1.89
5	280.92	3.907	4.062	-3.97	3.874	+0.84
	271.18	1.306	1.298	+0.61	1.247	+4.52
	273.05	1.597	1.617	-1.25	1.550	+2.94
	275.03	2.016	2.058	-2.08	1.967	+2.43
	277.97	3.004	3.026	-0.07	2.880	+4.13
	279.96	3.766	4.090	-8.60	3.876	-2.92

* Reference: Dholabhai et al. (1991, 1993)

Table A.1 (Continued)

Nominal Weight of NaCl (%)	Temperature (K)	Experimental Pressure* (MPa)	Chen and Evans (1986)		Zuo and Guo (1991)	
			Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)
10	268.03	1.162	1.231	-5.94	1.164	-0.17
	271.01	1.656	1.753	-5.86	1.655	+0.06
	274.08	2.409	2.593	-7.62	2.439	-1.24
	276.07	3.149	3.441	-9.27	3.226	-2.44
	276.12	3.155	3.468	-9.92	3.250	-3.01
	277.01	3.671	4.003	-9.04	3.739	-1.85
15	277.19	3.781	4.129	-9.20	3.853	-1.90
	265.38	1.212	1.333	-9.98	1.218	-0.50
	268.20	1.703	1.872	-9.92	1.712	-0.52
	271.05	2.469	2.715	-9.96	2.480	-0.44
	273.01	3.239	3.634	-12.2	3.304	-0.20
20	263.29	1.606	1.695	-5.54	1.447	+9.90
	265.29	2.208	2.180	+1.27	1.864	+15.58
	266.85	2.630	2.688	-2.20	2.295	+12.74

* Reference: Dholabhai et al. (1991, 1993)

Table A.2 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Carbon Dioxide Gas in Aqueous KCl Solution

Nominal Weight of KCl (%)	Temperature (K)	Experimental Pressure* (MPa)	Chen and Evans (1986)		Zuo and Guo (1991)	
			Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)
3	272.67	1.326	1.335	-0.68	1.289	+2.77
	274.57	1.654	1.669	-0.90	1.608	+2.77
	276.75	2.154	2.177	-1.07	2.092	+2.86
	278.68	2.760	2.795	-1.27	2.680	+2.91
	279.99	3.233	3.355	-3.77	3.209	+0.74
	281.09	3.834	3.965	-3.42	3.783	+1.33
5	272.06	1.325	1.351	-1.96	1.292	+2.49
	274.13	1.700	1.725	-1.47	1.646	+3.18
	276.03	2.129	2.178	-2.30	2.073	+2.63
	278.61	2.960	3.062	-3.44	2.901	+1.99
	279.43	3.324	3.445	-3.64	3.257	+2.01
	280.43	3.861	4.023	-4.20	3.790	+1.84
	280.47	3.905	4.050	-3.71	3.815	+2.30

* Reference: Dholabhai et al. (1991, 1993)

Table A.2 (Continued)

Nominal Weight of KCl (%)	Temperature (K)	Experimental Pressure* (MPa)	Chen and Evans (1986)		Zuo and Guo (1991)	
			Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)
10	269.02	1.130	1.184	-4.78	1.103	+2.39
	273.08	1.848	1.919	-3.84	1.778	+3.76
	276.34	2.807	2.935	-4.56	2.701	+3.78
	277.86	3.485	3.672	-5.36	3.356	+3.70
15	269.03	1.415	1.529	-8.06	1.365	+3.53
	272.22	2.095	2.270	-8.35	2.017	+3.72
	274.58	2.901	3.134	-8.03	2.761	+4.82
	276.01	3.575	3.917	-9.57	3.409	+4.64

* Reference: Dholabhai et al. (1991, 1993)

Table A.3 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Carbon Dioxide Gas in Aqueous CaCl₂ Solution

Nominal Weight of CaCl ₂ (%)	Temp. (K)	Experimental Pressure (MPa)	Chen and Evans(1986)		Zuo and Guo(1991)		Aasberg - Petersen	
			Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)
3	272.58	1.302	1.333	-2.38	1.276	+2.00	1.325	-1.77
	275.52	1.827	1.888	-3.34	1.800	+1.48	1.860	-1.81
	278.15	2.529	2.632	-4.07	2.498	+1.22	2.561	-1.26
	280.87	3.702	3.879	-4.78	3.651	+1.38	3.693	+0.24
5	271.08	1.184	1.237	-4.48	1.173	+0.93	1.227	-3.63
	275.06	1.872	1.985	-6.04	1.869	+0.16	1.944	-3.85
	278.21	2.805	2.990	-6.60	2.793	+0.43	2.879	-2.64
	280.07	3.657	3.942	-7.79	3.651	+0.16	3.730	-2.00
10	268.05	1.102	1.192	-8.17	1.107	-0.45	1.122	-1.81
	270.85	1.511	1.657	-9.66	1.531	-1.32	1.547	-2.38
	273.96	2.198	2.446	-11.28	2.244	-2.09	2.236	-1.73
	277.26	3.460	3.947	-14.08	3.554	-2.72	3.496	-1.04
	277.86	3.824	4.388	-14.75	3.922	-2.56	3.807	+0.44

* Reference: Dholabhai et al. (1991, 1993)

Table A.3 (Continued)

Nominal Weight of CaCl ₂ (%)	Temp. (K)	Experimental Pressure* (MPa)	Chen and Evans(1986)		Zuo and Guo(1991)		Aasberg - Petersen	
			Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)
15	263.42	0.960	1.069	-11.35	0.962	-0.21	0.885	+7.81
	267.37	1.497	1.698	-13.42	1.524	-1.80	1.389	+7.21
	270.12	2.138	2.402	-12.35	2.144	-0.28	1.928	+9.82
	273.17	3.221	3.737	-16.02	3.282	-1.89	2.856	+11.33
20	259.19	1.051	1.127	-7.23	0.968	+7.90	0.757	+27.97
	262.00	1.504	1.568	-4.26	1.349	+10.30	1.041	+30.78
	264.58	2.052	2.159	-5.21	1.855	+9.60	1.405	+31.53
	266.65	2.690	2.857	-6.21	2.443	+9.18	1.803	+32.97

* Reference: Dholabhai et al. (1991, 1993)

Table A.4 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Carbon Dioxide Gas in Aqueous NaCl and CaCl₂ Solution

Nominal Weight (%)	Temp. (K)	Experimental Pressure* (MPa)	Chen and Evans (1986)		Zuo and Guo (1991)	
			Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)
3% NaCl + 3% CaCl ₂	270.99	1.258	1.318	-4.77	1.255	+0.24
	271.78	1.375	1.445	-5.09	1.375	0.00
	275.73	2.227	2.343	-5.21	2.215	+0.54
	277.32	2.738	2.894	-5.70	2.727	+0.40
	279.17	3.595	3.797	-5.62	3.556	+1.08
2% NaCl + 8% CaCl ₂	267.79	1.053	1.164	-10.54	1.088	-3.32
	272.72	1.909	2.099	-9.95	1.947	-1.99
	276.32	3.101	3.429	-10.58	3.146	-1.45
	277.48	3.697	4.136	-11.87	3.762	-1.76
8% NaCl + 2% CaCl ₂	267.77	1.086	1.185	-9.12	1.120	-3.13
	271.07	1.623	1.751	-7.89	1.651	-1.72
	273.16	2.112	2.274	-7.67	2.140	-1.32
	276.00	3.089	3.365	-8.93	3.151	-2.01

* Reference: Dholabhai et al. (1991, 1993)

Table A.4 (Continued)

Nominal Weight (%)	Temp. (K)	Experimental Pressure (MPa)	Chen and Evans (1986)		Zuo and Guo (1991)	
			Predicted Pressure (MPa)	Percent Deviation (%)	Predicted Pressure (MPa)	Percent Deviation (%)
5% NaCl + 15% CaCl ₂	261.09	1.288	1.375	-6.75	1.193	+7.37
	264.11	1.878	1.985	-5.70	1.725	+8.15
	266.29	2.490	2.645	-6.22	2.298	+7.71
	267.34	2.935	3.075	-4.77	2.666	+9.16
15% NaCl + 5% CaCl ₂	259.02	0.909	1.042	-14.63	0.896	+1.43
	263.54	1.609	1.777	-10.44	1.534	+4.66
	265.67	2.112	2.330	-10.32	2.023	+4.21
	267.39	2.665	2.957	-10.96	2.566	+3.71

* Reference: Dholabhai et al. (1991, 1993)

Table A.5 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Carbon Dioxide Gas in Aqueous NaCl and KCl Solution

Nominal Weight (%)	Temp. (K)	Experimental Pressure* (MPa)	Zuo and Guo (1991)	
			Predicted Pressure (MPa)	Percent Deviation (%)
3% NaCl + 3% KCl	271.50	1.326	1.313	+0.98
	274.02	1.814	1.768	+2.54
	276.07	2.317	2.280	+1.60
	279.29	3.573	3.562	+0.31
	279.87	3.976	3.906	+1.76
5% NaCl + 5% KCl	269.97	1.347	1.341	+0.44
	271.72	1.660	1.651	+0.54
	274.11	2.258	2.222	+1.59
	277.32	3.432	3.478	-1.34
7% NaCl + 10% KCl	267.57	1.482	1.477	+0.34
	270.48	2.180	2.127	+2.43
	273.07	3.044	3.050	-0.20
	274.08	3.455	3.575	-3.47
15% NaCl + 5% KCl	262.93	1.218	1.221	-0.25
	266.30	1.872	1.854	+0.96
	268.18	2.388	2.382	+0.25
	269.82	3.050	3.027	+0.75

* Reference: Dholabhai et al. (1991, 1993)

Table A.6 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Gas Mixture of Methane and Carbon Dioxide in Pure Water

Nominal Weight (%)	Temp. (K)	Experimental Pressure* (MPa)	y_{CO_2}	Zuo and Guo (1991)	
				Predicted Pressure (MPa)	Percent Deviation (%)
pure water	273.7	2.52	.100	2.45	+2.78
	275.8	3.10	.090	3.06	+1.29
	277.8	3.83	.080	3.80	+0.78
	280.2	4.91	.080	4.88	+0.61
	283.2	6.80	.080	6.78	+0.29
	285.1	8.40	.080	8.43	-0.36
	287.2	10.76	.090	10.83	-0.65
	274.6	2.59	.140	2.56	+1.16
	276.9	3.24	.130	3.27	-0.92
	279.1	4.18	.130	4.13	+1.20
	281.6	5.38	.130	5.42	-0.74
	284.0	7.17	.130	7.13	+0.56
	286.1	9.24	.120	9.26	-0.22
	287.4	10.95	.130	10.88	+0.64
	273.8	2.12	.250	2.10	+0.94
	279.4	3.96	.220	3.92	+1.01
	283.4	6.23	.220	6.20	+0.48
	285.2	7.75	.210	7.81	-0.77
	287.6	10.44	.250	10.64	-1.92

* Reference: Adisasmito et al. (1991)

• mole fraction of CO₂ in vapor phase at equilibrium

Table A.6 (Continued)

Nominal Weight (%)	Temp. (K)	Experimental Pressure* (MPa)	$y^{\circ}_{\text{CO}_2}$	Zuo and Guo (1991)	
				Predicted Pressure (MPa)	Percent Deviation (%)
pure water	273.7	1.81	.440	1.77	+2.21
	276.9	2.63	.420	2.54	+3.42
	280.7	4.03	.400	3.97	+1.49
	283.1	5.43	.390	5.36	+1.29
	285.1	6.94	.390	7.00	-0.86
	287.4	9.78	.390	9.95	-1.74
	275.6	1.99	.500	2.08	-4.52
	278.5	2.98	.470	2.94	+1.34
	280.9	4.14	.400	4.06	+1.93
	281.8	4.47	.410	4.50	-0.67
	285.1	6.84	.440	6.86	-0.29
	287.4	9.59	.450	9.88	-3.02
	274.6	1.66	.730	1.63	+1.81
	276.4	2.08	.700	2.03	+2.40
	278.2	2.58	.680	2.52	+2.32
	280.2	3.28	.680	3.21	+2.13
	282.0	4.12	.670	4.07	+1.21
	273.7	1.45	.790	1.43	+1.38
	275.9	1.88	.780	1.84	+2.13
	277.8	2.37	.760	2.32	+2.11
	279.6	2.97	.750	3.00	-1.01
	281.6	3.79	.740	3.76	+0.79
	282.7	4.37	.850	4.26	+2.52

* Reference: Adisasmito et al. (1991)

• mole fraction of CO₂ in vapor phase at equilibrium

Table A.7 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Gas Mixture of Methane and Carbon Dioxide in Aqueous NaCl Solution

Nominal Weight (%)	Temp. (K)	Experimental Pressure (MPa)	$y^{\bullet}_{CO_2}$	Zuo and Guo (1991)	
				Predicted Pressure (MPa)	Percent Deviation (%)
pure water	274.10	2.36	.164	2.37	-0.42
	277.56	3.41	.153	3.42	-0.29
	281.50	5.14	.167	5.18	-0.78
	284.84	7.53	.179	7.61	-1.06
5% NaCl	271.59	2.30	.193	2.21	+3.91
	274.98	3.26	.174	3.21	+1.53
	279.23	5.08	.172	5.12	-0.79
	281.99	6.98	.177	7.08	-1.43
10% NaCl	268.46	2.03	.193	2.08	-2.46
	272.07	3.10	.161	3.15	-1.61
	276.14	4.66	.194	4.79	-2.79
	278.98	6.56	.174	6.86	-4.57
	279.19	6.47	.174	7.05	-8.96
15% NaCl	264.78	1.86	.173	1.99	-6.99
	269.12	2.88	.194	3.01	-4.51
	273.14	4.40	.198	4.89	-11.14
	276.79	7.37	.182	7.87	-6.78
	277.17	7.31	.189	8.26	-12.99
20% NaCl	261.95	2.12	.191	2.10	+0.94
	267.48	3.85	.198	3.87	-0.52
	270.37	5.42	.193	5.50	-1.48
	274.31	9.15	.199	9.53	-4.15

Reference: Dholabhai and Bishnoi (1993)

• mole fraction of CO₂ in vapor phase at equilibrium

Table A.8 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Gas Mixture of Methane and Carbon Dioxide in Aqueous KCl Solution

Nominal Weight (%)	Temp. (K)	Experimental Pressure* (MPa)	$y^{\bullet}_{CO_2}$	Zuo and Guo (1991)	
				Predicted Pressure (MPa)	Percent Deviation (%)
5% KCl	271.38	2.04	.197	2.03	+0.49
	274.97	2.96	.198	2.94	+0.68
	278.83	4.46	.198	4.48	-0.45
	281.98	6.43	.198	6.48	-0.78
10% KCl	269.16	1.83	.197	1.91	-4.37
	272.16	2.59	.198	2.62	-1.16
	275.90	3.94	.196	3.93	+0.25
	278.96	5.56	.198	5.58	-0.36
15% KCl	266.96	1.89	.184	1.87	+1.06
	270.07	2.62	.190	2.58	+1.53
	272.69	3.45	.195	3.41	+1.16
	277.07	5.63	.197	5.65	-0.35

* Reference: Dholabhai and Bishnoi (1993)

• mole fraction of CO₂ in vapor phase at equilibrium

Table A.9 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Gas Mixture of Methane and Carbon Dioxide in Aqueous CaCl₂ Solution

Nominal Weight (%)	Temp. (K)	Experimental Pressure (MPa)	$y^{\bullet}_{CO_2}$	Zuo and Guo (1991)	
				Predicted Pressure (MPa)	Percent Deviation (%)
10% CaCl ₂	268.59	1.96	.187	2.01	-2.55
	272.00	2.80	.194	2.86	-2.14
	276.04	4.32	.197	4.43	-2.55
	279.13	6.08	.197	6.38	-4.93
15% CaCl ₂	266.65	1.88	.196	2.34	-24.47
	269.13	3.00	.197	3.06	-2.00
	273.11	4.61	.190	4.82	-4.55
	276.88	7.09	.197	7.67	-8.18
20% CaCl ₂	263.78	2.89	.198	2.75	+4.84
	267.60	4.30	.198	4.24	+1.39
	271.34	7.24	.199	6.74	+6.91
	273.69	9.46	.199	9.44	+0.21

* Reference: Dholabhai and Bishnoi (1993)

• mole fraction of CO₂ in vapor phase at equilibrium

Table A.10 Comparison of Predicted and Experimental Hydrate Equilibrium Pressures for Gas Mixture of Methane and Carbon Dioxide in Aqueous Solution of Mixed Electrolytes

Nominal Weight (%)	Temp. (K)	Experimental Pressure* (MPa)	$y^{\bullet}_{CO_2}$	Zuo and Guo (1991)	
				Predicted Pressure (MPa)	Percent Deviation (%)
5% NaCl + 10% CaCl ₂	265.54	2.06	.197	2.10	-1.94
	269.35	3.12	.198	3.16	-1.28
	273.67	5.04	.194	5.19	-2.98
	276.71	7.14	.199	7.61	-6.58
5% NaCl + 10% KCl	265.09	1.66	.203	1.65	+0.60
	269.28	2.59	.192	2.60	-0.39
	275.21	4.99	.197	5.03	-0.80
	281.27	10.41	.198	11.37	-9.22
5% CaCl ₂ + 10% KCl	265.07	1.65	.198	1.65	0.00
	269.35	2.46	.198	2.59	-5.28
	274.76	4.60	.199	4.74	-3.04
	281.57	10.61	.199	11.79	-11.12
5% CaCl ₂ + 10% NaCl	265.52	2.11	.201	2.13	-0.95
	269.18	3.10	.200	3.16	-1.93
	275.13	6.07	.195	6.40	-5.44
	278.74	9.71	.194	10.62	-9.37
4% CaCl ₂ + 5% KCl + 6% NaCl	265.48	1.85	.203	1.89	-2.16
	268.99	2.67	.199	2.75	-3.00
	275.11	5.23	.199	5.53	-5.74
	278.25	7.65	.197	8.34	-9.02

* Reference: Dholabhai and Bishnoi (1993)

• mole fraction of CO₂ in vapor phase at equilibrium

Table A.10 (Continued)

Nominal Weight (%)	Temp. (K)	Experimental Pressure* (MPa)	y_{CO_2}	Zuo and Guo (1991)	
				Predicted Pressure (MPa)	Percent Deviation (%)
10% NaCl + 10% CaCl ₂	264.14	2.15	.497	2.15	0.00
	268.08	3.53	.486	3.51	+0.57
	268.21	3.52	.497	3.54	-0.57
	270.80	5.16	.494	5.08	+1.55
10% NaCl + 5% KCl	265.76	1.38	.500	1.49	-7.97
	268.04	1.82	.498	1.93	-6.04
	271.57	2.78	.495	2.91	-4.68
	275.48	4.59	.465	4.88	-6.32
4% CaCl ₂ + 5% KCl + 6% NaCl	265.97	1.45	.481	1.55	-6.90
	268.08	1.81	.496	1.94	-7.18
	271.86	2.80	.500	3.00	-7.14
	275.50	4.46	.475	4.85	-8.74

* Reference: Dholabhai and Bishnoi (1993)

• mole fraction of CO₂ in vapor phase at equilibrium

APPENDIX B

Expressions for the activity coefficients of all species:

Molecular species:

$$\begin{aligned} \ln \gamma_m^{lc} = & \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_{m'} \frac{X_{m'} G_{mm'}}{\sum_k X_k G_{km'}} \cdot \left(\tau_{mm'} - \frac{\sum_k X_k G_{km'} \tau_{km'}}{\sum_k X_k G_{km'}} \right) + \sum_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{X_c G_{mc,a'c}}{\sum_k X_k G_{kc,a'c}} \\ & \cdot \left(\tau_{mc,a'c} - \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right) + \sum_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{X_a G_{ma,c'a}}{\sum_k X_k G_{ka,c'a}} \cdot \left(\tau_{ma,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right) \end{aligned}$$

Cations:

$$\begin{aligned} \frac{1}{Z_c} \ln \gamma_c^{lc} = & \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{\sum_k X_k G_{ka,a'c} \tau_{ka,a'c}}{\sum_k X_k G_{ka,a'c}} + \sum_m \frac{X_m G_{cm}}{\sum_k X_k G_{km}} \cdot \left(\tau_{cm} - \frac{\sum_k X_k G_{km} \tau_{km}}{\sum_k X_k G_{km}} \right) \\ & + \sum_a \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{X_a G_{ca,c'a}}{\sum_k X_k G_{ka,c'a}} \cdot \left(\tau_{ca,c'a} - \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} \right) \end{aligned}$$

Anions:

$$\begin{aligned} \frac{1}{Z_a} \ln \gamma_a^{lc} = & \sum_{c'} \frac{X_{c'}}{\sum_{c''} X_{c''}} \frac{\sum_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}} + \sum_m \frac{X_m G_{am}}{\sum_k X_k G_{km}} \cdot \left(\tau_{am} - \frac{\sum_k X_k G_{km} \tau_{km}}{\sum_k X_k G_{km}} \right) \\ & + \sum_c \sum_{a'} \frac{X_{a'}}{\sum_{a''} X_{a''}} \frac{X_c G_{ac,a'c}}{\sum_k X_k G_{kc,a'c}} \cdot \left(\tau_{ac,a'c} - \frac{\sum_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}} \right) \end{aligned}$$

Table B.1 Binary parameters for Zuo and Guo model (1991).

Binary Pair	Interaction Parameter, k_{ij}
NaCl-H ₂ O	-0.1556
KCl-H ₂ O	-0.0972
CaCl ₂ -H ₂ O	-0.1801
CO ₂ -H ₂ O	$0.19235 - 93.953/T$
CH ₄ -H ₂ O	$0.68738 - 316.462/T$

Reference: Zuo and Guo (1991)