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INCIPIENT EQUILIBRIUM CONDITIONS FOR METHANE HYDRATE FORMATION

IN AQUEOUS MIXED ELECTROLYTE SOLUTIONS

by

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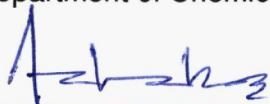
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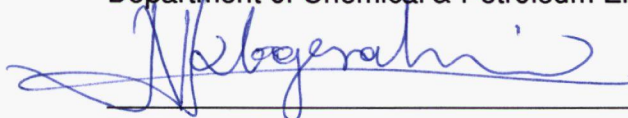
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ABSTRACT

Experimental studies on natural gas hydrates thermodynamics have concentrated on obtaining equilibrium data in pure water and in aqueous solutions containing inhibitors like alcohols and *single* electrolytes.

In this study methane hydrate equilibrium conditions have been experimentally obtained in solutions containing mixed electrolytes found in natural and sea waters.
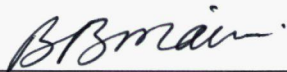
Methane gas and aqueous solutions were contacted in a stirred "reactor". A "pressure search" method was adapted in which the system pressure was manipulated to reach the equilibrium pressure at constant temperature. Data have been obtained for 5 mixtures of NaCl and KCl, 6 mixtures of NaCl and $CaCl_2$ and a mixture of eight electrolytes found in sea water. The ionic strength (in molality units) of the NaCl and KCl mixtures ranged from 1.70 to 4.72 and that of the NaCl and $CaCl_2$ mixtures from 1.27 to 3.90. The experimental temperatures ranged from 264 K to 284 K and the pressures from 2.5 MPa to 9.7 MPa.

Equilibrium pressures predicted using a recently proposed method (Englezos and Bishnoi, 1988) have been compared with the data obtained. The method uses the van der Waals-Platteeuw model (van der Waals and Platteeuw, 1959) for the hydrate phase. It also uses an equation derived

by Patwardhan and Kumar (1986) along with activity coefficient models already available in the literature (Pitzer and Mayorga, 1973; Meissner and Kusik, 1972) to compute the activity of water in a mixed electrolyte solution. In this study the model proposed by Pitzer and Mayorga (1973) has been used. Gas phase fugacities were calculated using the TB equation of state (Trebble and Bishnoi, 1988).

The study reveals that the method is able to predict the experimental equilibrium pressures very well. The largest prediction error for an experimental data point was 10.1%. The method predicted the equilibrium pressures with a root mean squared deviation of 6.06% for NaCl and KCl mixtures, 3.50% for the NaCl and $CaCl_2$ mixtures and 1.40% for the synthetic sea water. The deviations increase with increasing ionic strength.

The implementation of the model of van der Waals and Platteeuw requires the use of certain regressed constants, different values of which are in use in the literature. It has been shown in this study that the predictions of hydrate equilibrium conditions are sensitive to the particular set of these constants used.

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NOMENCLATURE

A_{ij} constant in Equation 21, K

A_ϕ Debye–Huckel coefficient

a difference between the heat capacities of water in the empty hydrate lattice and pure liquid water at 273.15 K, Equation 13, $J/mol\ K$

a_w activity of water

$a_{w,k}^0$ activity of water in a single electrolyte solution containing electrolyte k, the solution having the same ionic strength as that of a mixed electrolyte solution in which electrolyte k is one of the components

B_{ij} constant in Equation 21, K

b constant in Equation 13, $J/mol\ K^2$

C_{ij} Langmuir constant for hydrate former i in cavity type j

$\Delta C_{p,w}$ difference between the heat capacities of water in the empty hydrate lattice and pure liquid water, $J/mol\ K$

d_w density of water, g/cm^3

D dielectric constant for water

e electronic charge, 4.8029×10^{-10} e.s.u.

F degrees of freedom (Phase Rule)

f_j fugacity of hydrate former j, MPa

f_w fugacity of water in an aqueous solution, MPa

f_w^0 fugacity of pure water at the temperature and pressure of an

x

aqueous solution, *MPa*

Δh_W difference between the enthalpies of water in the empty hydrate lattice and pure liquid water, *J/mol*

Δh_W^0 Δh_W at 273.15 K, *J/mol*

I $= 1/2 \sum_i m_i z_i^2$, ionic strength in molality units

I_T ionic strength in molality units of a mixed electrolyte solution

k Boltzmann's constant, 1.38045×10^{-16}

m molality of an electrolyte in a single electrolyte solution, *mol/kg of water*

m_i molality of ion i, *mol/kg of water*

m_K molality of electrolyte k in a mixed electrolyte solution, *mol/kg of water*

m_K^0 molality of electrolyte k in a single salt solution having the same ionic strength as that of a mixed electrolyte solution in which electrolyte k is one of the components

N_0 Avogadro's number, 6.0232×10^{23}

n number of data points

n_s number of electrolytes in a solution

P Pressure, *MPa*

P_{exp} experimentally determined hydrate equilibrium pressure, *MPa*

P_0 zero absolute pressure

P_{pred} hydrate equilibrium pressure calculated from a model, *MPa*

P_{EQ}	hydrate equilibrium pressure, *MPa*
P_{SET}	Pressure at which the system is initially left for observation, *MPa*
P_H	"hydrate point", the constant pressure attained by the system at constant temperature with very little hydrates present, *MPa*
P_{NH}	"no-hydrate point", the constant pressure attained by the system at constant temperature with no hydrates present, *MPa*
ΔP_{CH}	the amount by which the system pressure is reduced after a "hydrate point" is obtained in order to confirm that the hydrates decompose at the lower pressure, *MPa*
P_H^t	hydrate equilibrium pressure at temperature T_2 calculated from an experimentally determined equilibrium pressure at temperature T_1 and the local slope of the P-T curve at T_1, *MPa*
$\Delta P / \Delta T$	slope of the P-T curve, *MPa/K*
R	gas constant
T	temperature, *K*
T_F	temperature at which the hydrate equilibrium conditions are to be calculated, *K*
T_0	reference temperature (273.15), *K*
Δv_W	difference between the molar volumes of empty hydrate lattice and pure liquid water, *L/mol*
x_W	mole fraction of water in the aqueous phase
z_+, z_-	charge numbers of cation and anion respectively
z_1	charge number of ion i in a summation over all cations and

anions present

GREEK SYMBOLS

β_i constants in activity coefficient model, i=0,1,2

μ_W^H chemical potential of water in the hydrate phase, *J/mol*

μ_W^{MT} chemical potential of water in the empty hydrate lattice, *J/mol*

μ_W^{sl} chemical potential of water in the aqueous solution, *J/mol*

μ_W^0 chemical potential of pure liquid water at the temperature and pressure of the system, *J/mol*

$\Delta\mu_W^0$ difference between chemical potentials of water in the empty hydrate lattice and pure liquid water at 273.15 K and zero pressure, *J/mol*

ν_i number of cavities of type i, i=1,2

ν_+, ν_- moles of cations and anions per mole of electrolyte respectively

θ_1, θ_2 defined by Equations 18 and 19 respectively

$\omega(r)$ cell potential

KEY TO SOLUTION ID/EXPERIMENT LABEL

NaXKY-ZZ, NaXCaY-ZZ

           Na   : electrolyte NaCl

           K   : electrolyte KCl

           Ca   : electrolyte $CaCl_2$

           X,Y : weight percent (abbreviated as wt%)

           ZZ   : experiment number

     Weight percent are on wet basis.

1. INTRODUCTION

1.1   Nature of gas hydrates

The discovery of gas hydrates dates back to 1810 when Davy (1811) formed the chlorine hydrate. By the end of the 19th century a number of investigations were published on the conditions of crystallisation of gas hydrates. Powell, while working with argon hydrates, named this class of compounds as "clathrate compounds" in which the "two or more components are associated without ordinary chemical union but through complete enclosure of one set of molecules in a suitable structure formed by another" (van der Waals and Platteeuw, 1959). When light non-polar gases are mixed with water at sufficiently high pressures and low temperatures, a solid clathrate hydrate phase can form in which water forms a lattice with cavities which are occupied by the molecules of the non-polar gas. Without the inclusion of the gas molecules, the lattice structure of water is unstable. The van der Waals type interaction between the enclosed gas molecules and the water molecules in the lattice structure stabilizes the clathrate.

Investigations on the hydrates formed by the components of natural gas gained momentum in the 1940s when gas pipelines became clogged in the cold weather, initially believed to be due to ice formation. An extensive historical background is provided by Berecz and Balla-Achs (1983).

Two different lattice structures, consisting of different number and sizes of cavities, are formed with light gases. These are called Structure I and Structure II. Smaller molecules like methane, ethane, carbon dioxide, nitrogen, oxygen, etc. form Structure I hydrates whereas larger molecules like propane and isobutane form Structure II hydrates. Structure I hydrate formers, when present in a mixture along with Structure II hydrate formers, can also occupy the cavities of the Structure II. Detailed information on the structures and properties of gas hydrates is available in the literature (Makogon, 1981; Berecz and Balla-achs, 1983).

It is now known that large amounts of hydrates are present in the marine sediments throughout the world and also in the oil deposits in the permafrost regions, where the oil has been "denuded" of the lighter hydrocarbons by hydrate formation (Holder et al, 1976). In fact, recent estimates indicate a reserve of about 10,000 trillion m^3 of natural gas trapped in the form of hydrates in the earth's crust, which is about 1,000 times the present known reserves. Knowledge of the properties of gas hydrates is thus of great importance if this reserve has to be tapped in the future. Moreover, the use of hydrates has been suggested in technologies such as the desalination of sea water and the storage of natural gas in salt-pits.

1.2 Thermodynamic and kinetic studies on gas hydrates

Research on gas hydrates prior to 1940 concentrated on "discovering" new hydrates formed from pure gases. From the beginning of

the 1940s, attention turned to hydrates formed from mixtures of gases. Katz and co-workers (Wilcox et al. 1949; Unruh and Katz, 1949; Kobayashi and Katz, 1949; Naoker and Katz, 1954) obtained data on natural gases, methane at high pressures and mixtures of methane with CO_2 and H_2S. Deaton and Frost (1949) reported data on natural gases and the effect of addition of inhibitors. Kobayashi and co-workers published a series of articles on hydrates at high pressures. Their work is summarized (with references) by Sloan and Nasir (1987). Robinson and co-workers (Otto and Robinson, 1960; Snell et al. 1961; Jhaveri and Robinson, 1965) constructed experimental hydrate equilibrium curves for systems containing mixtures of methane, nitrogen, ethylene and propylene. With the discovery of huge deposits of natural gas in the hydrate state in Siberia and Yakutia, Makogon and co-workers (Makogon, 1981) became actively involved in the research on gas hydrates, especially in the technological fields of exploration and transmission.

Experimental procedures commonly employed for the determination of the hydrate equilibrium conditions are described in section 4, "Experimental Procedure".

Von Stackelberg (1949) examined the hydrates using X-ray crystallography. This work permitted the determination of the structures of hydrates (Clausen, 1951; Pauling and Marsh, 1952).

Although a number of researchers had obtained experimental data

on gas hydrate formation, no reliable method was available to predict the hydrate formation conditions. Katz (1944) had published charts correlating the temperature, relative density and initial hydrate formation pressure to estimate the permissible expansion of natural gases. Katz and his co-workers had also published the solid-vapor equilibrium constant (K-value) charts for the hydrate formers from which the hydrate formation pressure could be calculated in a manner similar to that of dew point calculations. Because of their empirical nature, these charts could give errors if used for conditions outside those for which they were prepared.

Van der Waals and Platteeuw (1959) formulated for the first time a model based on Langmuir type adsorption theory to predict the hydrate equilibrium conditions. Based on the model, they computed the dissociation pressures of hydrates of eight polyatomic gases. Kobayashi and co-workers (Saito et al. 1964; Nagata and Kobayashi, 1966; Saito and Kobayashi, 1965) utilised the van der Waals-Platteeuw model to predict the dissociation pressures of binary and ternary systems from their own data. Parrish and Prausnitz (1972) developed a computer implementable algorithm for these calculations and published the required parameters which were fitted to the existing data. Later Ng and Robinson (1976) and Holder and co-workers (Holder et al. 1980; John and Holder, 1981, 1982; John et al. 1985) improved upon the procedure.

Musayev (1970) and Bukhgalter (1970) published studies on the

separation of hydrocarbon gases and liquids by means of hydrate formation. Gilliland (1955), Weigandt (1957), Hendrickson and Moulton (1956), Knox et al. (1961) and Kubota et al. (1984) studied sea water desalination by hydrate formation.

The missing link in the application of hydrate formation to technological processes such as sea water desalination was the kinetics of hydrate formation and decomposition. Bishnoi and co-workers have carried out systematic studies on the kinetics of hydrate formation and decomposition (Vysniauskas and Bishnoi, 1983, 1985; Englezos et al. 1987a, 1987b; Kim et al. 1987). They developed a mechanistic kinetic model with only one adjustable parameter which represents the intrinsic kinetic rate constant for hydrate formation. The model was tested successfully on methane, ethane and methane-ethane hydrate formation. Recently, the model was used to determine the effect of the presence of NaCl on the intrinsic rate constant for methane hydrate formation (Huang, 1989). In addition, by combining transport phenomena with the intrinsic kinetics, Bishnoi and co-workers have modeled the formation of a hydrate plug in natural gas pipelines and the decomposition of a hydrate core (Jamaluddin et al. 1988a, 1988b, 1989). A very useful computational scheme to calculate the *amounts* of the co-existing phases in equilibrium under hydrate forming conditions has been presented by Bishnoi et al. (1989a). Important characteristics of hydrate nucleation have been recently examined (Bishnoi et al. 1989b).

1.3   Inhibition of gas hydrate formation

Since the time hydrates were found to create problems in gas transmission lines, attention has centered on preventing their formation. Three methods have been in common industrial use :

1. Removal of water from streams where hydrate formation is a possibility;

2. Maintaining a temperature higher than that at which hydrates would start forming; and

3. Adding inhibitors like alcohols and electrolytes which lower the temperature at which hydrates start forming.

Hammerschmidt (1939) was the first to present an empirical method to calculate the effect of inhibitors on hydrate formation conditions and his method is still being used by industry to compute the amounts of inhibitors needed. Extensive research was also carried out by Makogon (1981), Bond and Russell (1949) and others on the effect of various inhibitors and their comparative effectiveness. Berecz and Balla–Achs (1983) discuss in detail the various investigations carried out on inhibitors. Menten at al. (1981) reported data on the effect of methanol on cyclopropane hydrate formation. Robinson and his co-workers have carried out systematic experimental study on the effects of methanol and glycols on hydrate formation from natural gas components (Ng and Robinson 1983, 1984; Ng et al. 1985, 1987).

Anderson and Prausnitz (1986) presented a method to calculate the

inhibiting effects of methanol utilizing the van der Waals–Platteeuw model (van der Waals and Platteeuw, 1959) for the hydrate phase, the Redlich–Kwong equation of state (Redlich and Kwong, 1949) for the vapor phase and the UNIQUAC model for the liquid phase. Englezos et al. (1988) presented a simple method for these calculations using the Trebble–Bishnoi equation of state (Trebble and Bishnoi, 1988) for the vapor *and* the liquid phases. Thus they eliminated the need for Henry's constants for gases dissolved in the aqueous phase and some empirical correlations for fugacity and molar volume calculations used by Anderson and Prausnitz (1986).

Despite the fact that all naturally occurring waters contain electrolytes dissolved in them, data on hydrate formation in systems containing electrolytes is scarce. All the data on electrolytes published so far, including those of Menten et al. (1981) and Roo et al. (1983), were on systems containing single electrolytes. Knox et al. (1961) and Kubota et al. (1984) studied sea water desalination using pure NaCl solutions to represent synthetic sea water.

The activity of liquid water in the presence of electrolytes can be significantly different from that of pure water. Menten et al. (1981) calculated the activity from experimental depression in freezing points. Their hydrate formation prediction method in the presence of electrolytes was limited to 1 molal solutions. Besides, in order to use their method, one has to have experimental freezing point data for every electrolyte

(or mixed electrolyte) concentration.

Recently, Englezos and Bishnoi (1988) presented a simple method to predict the hydrate equilibrium conditions in aqueous solutions of *single or mixed electrolytes*. It is based on the model developed by van der Waals and Platteeuw (1959) and the calculation schemes presented by Parrish and Prausnitz (1972) and Holder et al. (1980) for *pure water*. The activity of water in electrolyte solutions is calculated using the equation derived by Patwardhan and Kumar (1986) along with the activity coefficient models for salts in aqueous solutions which are already available in literature. The method is not limited to low concentrations and gives excellent results for single electrolyte solutions. However, no data were available to compare hydrate equilibrium conditions for mixed electrolytes. Almost concurrently, Munck et al. (1988) used UNIQUAC model to calculate activity coefficient of water in $CaCl_2$ solutions but did not compare the results with experimental data. They do not state whether their method can handle mixed electrolytes.

1.4   Scope

The goals of the present study were twofold :

1. to obtain experimental data on the equilibrium conditions for the incipient methane hydrate formation in the presence of mixed electrolytes; and

2. to test the validity of the method presented by Englezos and Bishnoi (1988) with the data obtained.

The experiments were carried out in a "reactor" in which methane and the aqueous solution were contacted under vigorous stirring to ensure a completely homogeneous liquid phase. The equipment is part of the assembly used by Bishnoi et al. (1985, 1986) for the study of kinetics of hydrate formation and decomposition. The procedure followed is a variation of the "pressure search" method (Englezos, 1988) in which the temperature of the contents of the reactor is kept constant, while manipulating the pressure to reach the equilibrium value with a very small amount of hydrates present. Once the equilibrium pressure is obtained the pressure is lowered slightly to confirm that the hydrates decompose.

Data have been obtained for the following mixed electrolytes : NaCl and KCl; NaCl and $CaCl_2$; and a mixture of eight electrolytes present in sea water. Table 1 gives the ranges of ionic strength (in molality units), temperature and pressure for each of the mixed electrolytes.

The equilibrium pressures predicted using the method of Englezos and Bishnoi (1988) have been compared with the data obtained.

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TABLE 1
Ranges of ionic strength, temperature and pressure
used in the experiments on mixed electrolytes

</div>

Mixture	Range		
	Ionic Str. molality	Temperature K	Pressure MPa
NaCl + KCl	1.70–4.72	264–281	2.6–9.4
NaCl + $CaCl_2$	1.27–3.90	266–282	2.5–9.7
Sea water	0.63	277–284	4.4–9.1

2. COMPUTATION OF HYDRATE EQUILIBRIUM CONDITIONS

2.1   Prediction method

For a system in which the gas, solid hydrate and aqueous liquid phases co-exist at equilibrium,

$$\mu_W^H = \mu_W^{sl} \qquad (1)$$

where μ_W^H and μ_W^{sl} are the chemical potentials of water in the solid hydrate and aqueous liquid phases respectively. This is true if it is assumed that the amount of water in the gas phase is negligible.

Van der Waals and Platteeuw (1959) derived the basic statistical thermodynamic equations for gas hydrates using a Langmuir-type adsorption theory. Based on this model, the difference between μ_W^{MT}, the chemical potential of water in the empty hydrate lattice, and μ_W^H is given by

$$\Delta\mu_W^H = \mu_W^{MT} - \mu_W^H = - RT_F \sum_i \nu_i \ln \left(1 + \sum_j C_{ij} f_j \right) \qquad (2)$$

where ν_i is the number of cavities of type i, f_j is the fugacity of the hydrate former j, T_F is the temperature at which the hydrate equilibrium properties are to be calculated and C_{ij} is the Langmuir constant for component j in cavity type i. The Langmuir constant is given by

$$C(T) = 4\pi / kT \int_0^\infty \exp \left[-\omega (r) / kT \right] r^2 \, dr \qquad (3)$$

where T is the temperature in degree K, k is the Boltzmann's constant and ω (r) is the spherically symmetric cell potential which is a function of the cell radius, the coordination number and the nature of gas-water interactions.

While using Equation (2), gas phase fugacities are substituted for f_j. Thus the equilibrium requirement of equal fugacities for the hydrate formers is also satisfied.

Defining

$$\Delta\mu_W = \mu_W^{MT} - \mu_W^{sl} \qquad (4)$$

it can be seen from Equations (1) and (2) that at equilibrium

$$\Delta\mu_W = \Delta\mu_W^H \qquad (5).$$

Equation (5) states that the difference between the chemical potentials of water in the empty hydrate lattice and that in the filled lattice ($\Delta\mu_W^H$) is the same as the difference between the chemical potentials of water in the empty lattice and that in the aqueous liquid phase ($\Delta\mu_W$).

The change in the chemical potential of water from its pure state to its state in a solution can be calculated by integrating

$$d\mu_W = RT_F \; d(\ln f_W)$$

at constant P and T. Integration yields

$$\mu_W^{sl} - \mu_W^0 = RT_F \; \ln (f_W / f_W^0) \qquad (6)$$

where μ_W^0 and f_W^0 are the chemical potential and fugacities of pure water, and f_W is the fugacity of water in the solution, all at the same pressure and temperature of the solution. Combining Equations (4) and (6),

$$\Delta\mu_W = \mu_W^{MT} - \mu_W^0 - RT_F \; \ln (f_W / f_W^0) \qquad (7)$$

If the aqueous phase contains only water with sparingly soluble gases dissolved in them, the mole fraction of water, x_W, in the solution can be assumed to be close to unity. The solution can then be considered ideal in the Lewis–Randall sense and one can make the following simplification :

$$f_W / f_W^0 = x_W \qquad (8)$$

In the presence of electrolytes, however, $f_W / f_W^0 = a_W$, the activity of water in the solution. Equation (7) then becomes

$$\Delta\mu_W = \mu_W^{MT} - \mu_W^0 - RT_F \; \ln a_W \qquad (9)$$

The presence of electrolytes is assumed in further discussions.

Since the electrolytes do not enter the hydrate lattice, the van der Waals and Platteeuw (1959) model is valid. Combining Equations (5), (2) and (9)

$$\frac{\mu_W^{MT} - \mu_W^0}{RT_F} - \ln a_W - \sum_i \nu_i \ln \left(1 + \sum_j C_{ij} f_j \right) = 0 \qquad (10)$$

The first term in Equation (10) refers to the empty hydrate lattice and pure water and is, therefore, unaffected by the identities of the other components in the system. The value of this term has been calculated at $T_0 = 273.15$ K and $P_0 = 0$ from experimental data on reference hydrates. This value at T_0, P_0 is then corrected to the system T and P for use in Equation (10). For example, Holder et al. (1980) give the following expression for this term :

$$\frac{\mu_W^{MT} - \mu_W^0}{RT_F} = \frac{\Delta\mu_W^0}{RT_0} - \int_{T_0}^{T_F} \frac{\Delta h_W}{RT^2} \, dT + \int_0^P \frac{\Delta v_W}{RT_F} \, dP \qquad (11)$$

where $\Delta\mu_W^0$ is the difference in the chemical potentials of water in the empty hydrate lattice and pure liquid water at $T_0 = 273.15$ K, and $P_0 = 0$ and Δv_W and Δh_W are the differences in molar volume and enthalpy respectively of water in the empty hydrate lattice and pure liquid water. The temperature dependence of Δh_W is given by

$$\Delta h_W = \Delta h_W^0 + \int_{T_0}^{T_F} \Delta C_{p,W} \, dT \qquad (12)$$

where $\Delta C_{p,W}$ is the heat capacity difference between the empty hydrate lattice and pure liquid water. Its temperature dependence is given by

$$\Delta C_{p,W} = a + b \, (T_F - T_0) \qquad (13)$$

where a and b are fitted constants.

Various researchers have used different values of the constants $\Delta\mu_W^0$, Δh_W^0, a and b ("hydrate model parameters") and these values are tabulated by Englezos et al. (1988).

Combining Equations (10) and (11)

$$\frac{\Delta\mu_W^0}{RT_0} - \int_{T_0}^{T_F} \frac{\Delta h_W}{RT^2} \, dT + \frac{\Delta v_W}{RT_F} P - \ln a_W - \sum_i \nu_i \ln \left(1 + \sum_j C_{ij} f_j\right) = 0 \qquad (14)$$

For gases with negligible solubility in the aqueous phase, and with only one electrolyte present in the aqueous phase, Englezos and Bishnoi (1988) calculate the activity of water in Equation (14) using one of the activity coefficient models available in the literature, e.g. Pitzer and Mayorga (1973). In addition, they have suggested that instead

of using the complex calculations involved in these models for mixed electrolytes, a very simple predictive equation proposed by Patwardhan and Kumar (1986) be used. The calculation of the activity of water is explained in the next section.

2.1.1 Calculation of the activity of water

The following equation, derived by Patwardhan and Kumar (1986), for the activity of water in a solution of mixed electrolytes is used to calculate a_W :

$$\ln a_W = \sum_k \left(m_k \, / \, m_k^0 \right) \ln a_{W,k}^0 \qquad (15)$$

where m_k is the molality of electrolyte k in the mixed electrolyte solution and m_k^0 and $a_{W,k}^0$ are the molality of electrolyte k and the activity of water respectively in a solution containing only electrolyte k with the same ionic strength I_T as that of the mixed electrolyte solution.

$a_{W,k}^0$ is calculated using the model developed by Pitzer and Mayorga (1973) :

$$\ln a_{W,k}^0 = - \frac{18\nu m}{1000} \left(1 + z_+ z_- \theta_1 + m\theta_2 + m^2\beta_2 \right) \qquad (16)$$

This equation is applicable to a single electrolyte $M_{\nu_+} A_{\nu_-}$ dissociating as

$$M_{\nu_+} A_{\nu_-} = \nu_+ M^{z_+} + \nu_- A^{z_-} \qquad (17)$$

In equation (16) m is the molality of electrolyte MA, $\nu = \nu_+ + \nu_-$ and θ_1, θ_2 are given by

$$\theta_1 = - \frac{A_\phi I^{0.5}}{1 + 1.2 I^{0.5}} \qquad (18)$$

and

$$\theta_2 = \beta_0 + \beta_1 \exp(-2 I^{0.5}) \qquad (19)$$

In equations (16) and (19) β_0, β_1 and β_2 are the adjustable parameters in the activity co-efficient model, I is the ionic strength and A_ϕ is the Debye-Huckel co-efficient given by

$$A_\phi^2 = \frac{1}{9} \frac{2\pi N_0 d_w}{1000} \left(\frac{e^2}{DkT_F}\right)^3 \qquad (20)$$

where :

N_0 - Avogadro's number = 6.0232×10^{23};

d_w - density of water, g/cm^3;

e - electronic charge = 4.8029×10^{-10} e.s.u;

D - dielectric constant for water; and

k - Boltzmann's constant = 1.38045×10^{-16} erg/deg.

In this study, the dielectric constant, D, was calculated using the correlation given by Bradley and Pitzer (1979).

2.2   Computer implementation

The hydrate equilibrium pressure at a given temperature for a gas or a gas mixture is calculated by solving equation (14) for pressure P. A computer program, based on the scheme given by Parrish and Prausnitz (1972) was written with an additional routine to calculate the activity of water.

The Langmuir constants C_{ij} in Equation (14) were calculated using the expression provided by Parrish and Prausnitz (1972) :

$$C_{ij} (T_F) = (A_{ij} / T_F) \exp (B_{ij} / T_F) \qquad (21)$$

In the above expression A_{ij}, B_{ij} are fitted constants taken from the above reference. The Langmuir constants calculated in the range 260 – 300 K with this expression deviate from those calculated with Equation 3 by a maximum of 0.2%.

The gas phase fugacities were calculated using the TB equation of state (Trebble and Bishnoi, 1988).

The following values for the hydrate model parameters appearing in Equations (14), (12) and (13) were used :

$$\Delta\mu_W^0 = 1264.0 \text{ J/mol};$$

$$\Delta h_W^0 = -4860.0 \text{ J/mol};$$

$$\Delta v_W = 0.0046 \text{ L/mol};$$

$$a = -38.13 \text{ J/mol K and}$$

$$b = 0.141 \text{ J/mol K}^2.$$

The program was checked with the data of Roo et al. (1983) for pure water and in NaCl solution. The results are shown in Figure 1 Each curve in the figure is for a different wt% NaCl in the solution. The maximum prediction error for pure water was 1.70% and the root mean squared deviation (RMSD) 1.15%. For the salt solution the maximum prediction error was −8.78% and RMSD 3.75%. The prediction error and RMSD are calculated as follows:

$$\% \text{ prediction error} = \frac{P_{exp} - P_{pred}}{P_{exp}} \times 100 \qquad (22)$$

$$\%\text{RMSD} = \left(\frac{1}{n} \sum \left(\frac{P_{exp} - P_{pred}}{P_{exp}} \right)^2 \right)^{1/2} \times 100 \qquad (23)$$

where P_{exp} and P_{pred} are the experimental and predicted pressures and n the number of points.
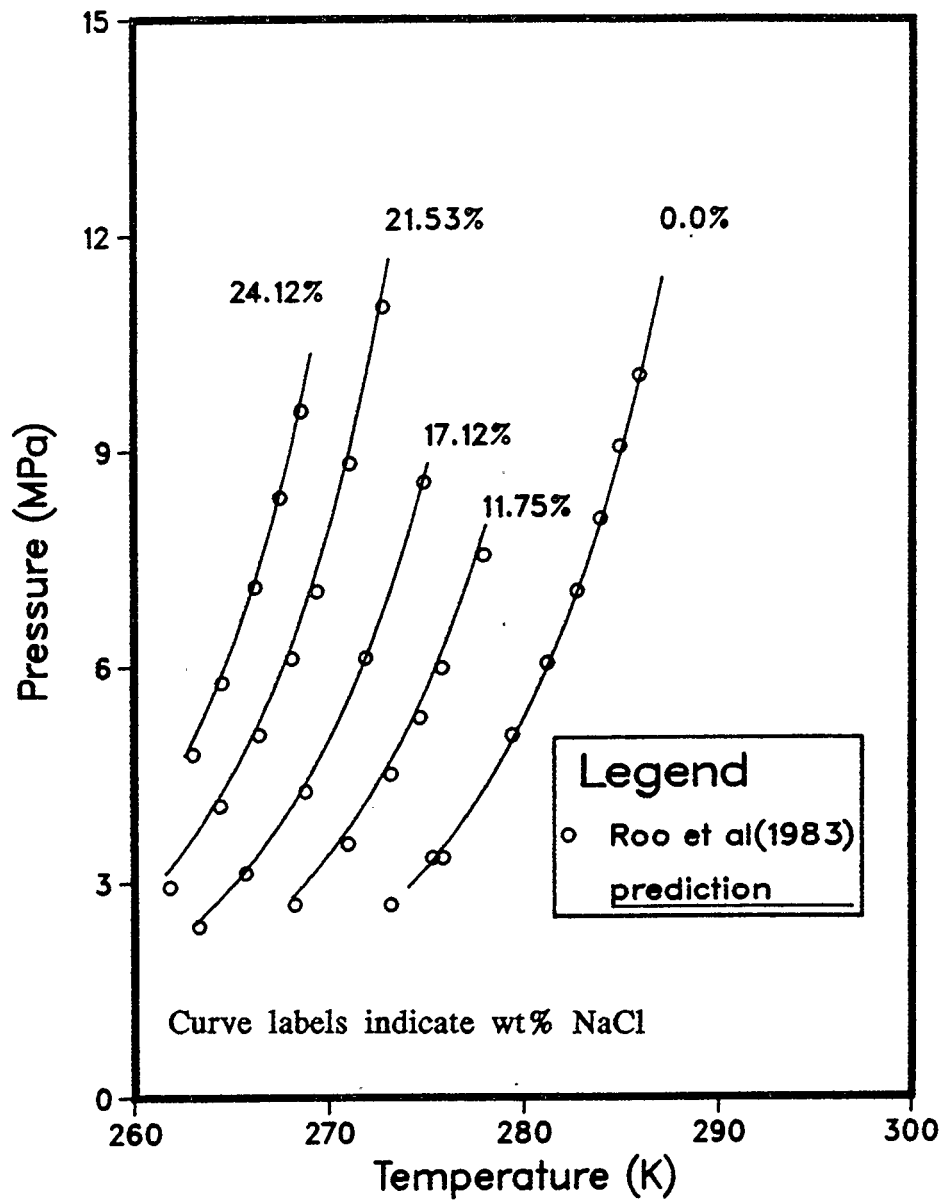
Figure 1: Experimental and predicted pressures for methane
hydrate formation in aqueous solutions containing
sodium chloride.

3. EXPERIMENTAL APPARATUS AND MATERIALS

3.1   Experimental equipment

The experimental equipment used for this work (Figure 2) is a part of the assembly used by Bishnoi et al (1985, 1986) for the study of kinetics of hydrate formation and decomposition. Only the following equipment from the assembly shown in Figure 2 were used in this study : The reactor, its bias cell R5, Heise gauge, differential pressure transmitter DP4, gas cylinder and the glycol bath with its related tubing. The rest of the equipment were isolated from the equipment in use. The following gives brief descriptions of the relevant units :

A 500 cm^3 capacity, high pressure, stainless steel "reactor" (Figure 3) fabricated out of stainless steel 316 bar stock was used for contacting methane and salt solutions. It was provided with a magnetic stir bar, baffles and two Plexiglas windows for observations. Agitation in the reactor was accomplished by coupling the magnetic stir bar with an external magnet mounted on the shaft of a motor. The speed of the motor was regulated by an RPM controller. The baffles broke the vortex formed and thus kept the liquid level high enough to be seen from the windows. The reactor was provided with 1/8" (3 mm) connections for charging the solution, introducing the gas and for pressure measurement. The reactor was immersed in an insulated tank in which glycol-water coolant was continuously circulated from a refrigerated and heated constant temperature bath supplied by Forma Scientific. A 1/8" (3 mm) tubing from
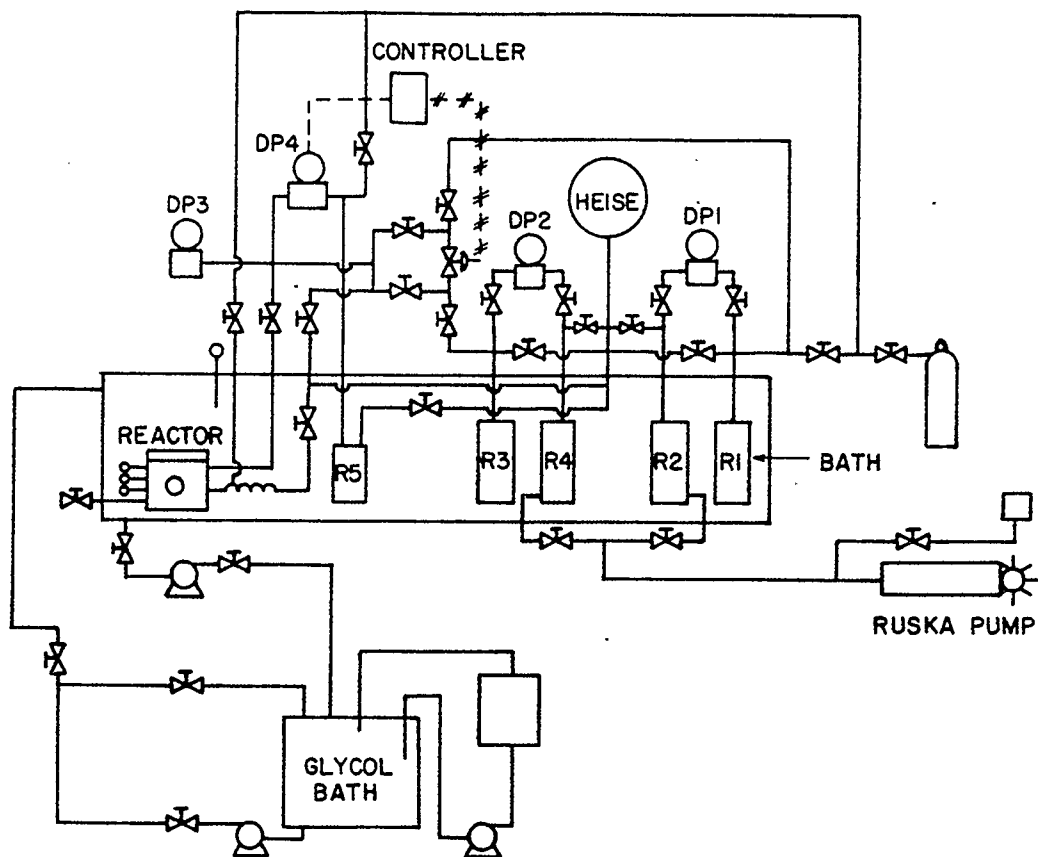
Figure 2: Schematic diagram of the experimental equipment.

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THERMOCOUPLE Ⓣᴳ
FOR BULK GAS

THERMOCOUPLE Ⓣᴵ
FOR INTERFACE

THERMOCOUPLE Ⓣᵂ
FOR WATER

WATER
INJECTION

TO HEISE GAUGE
GAS SUPPLY

FRONT VIEW

NEOPRENE O-RING

MARINE
TYPE WINDOWS

BAFFLE

MOUNTED
CERAMIC MAGNET

SECTION
SIDE VIEW

MAGNETIC
STIR BAR

BEARING

COUPLING

MOTOR
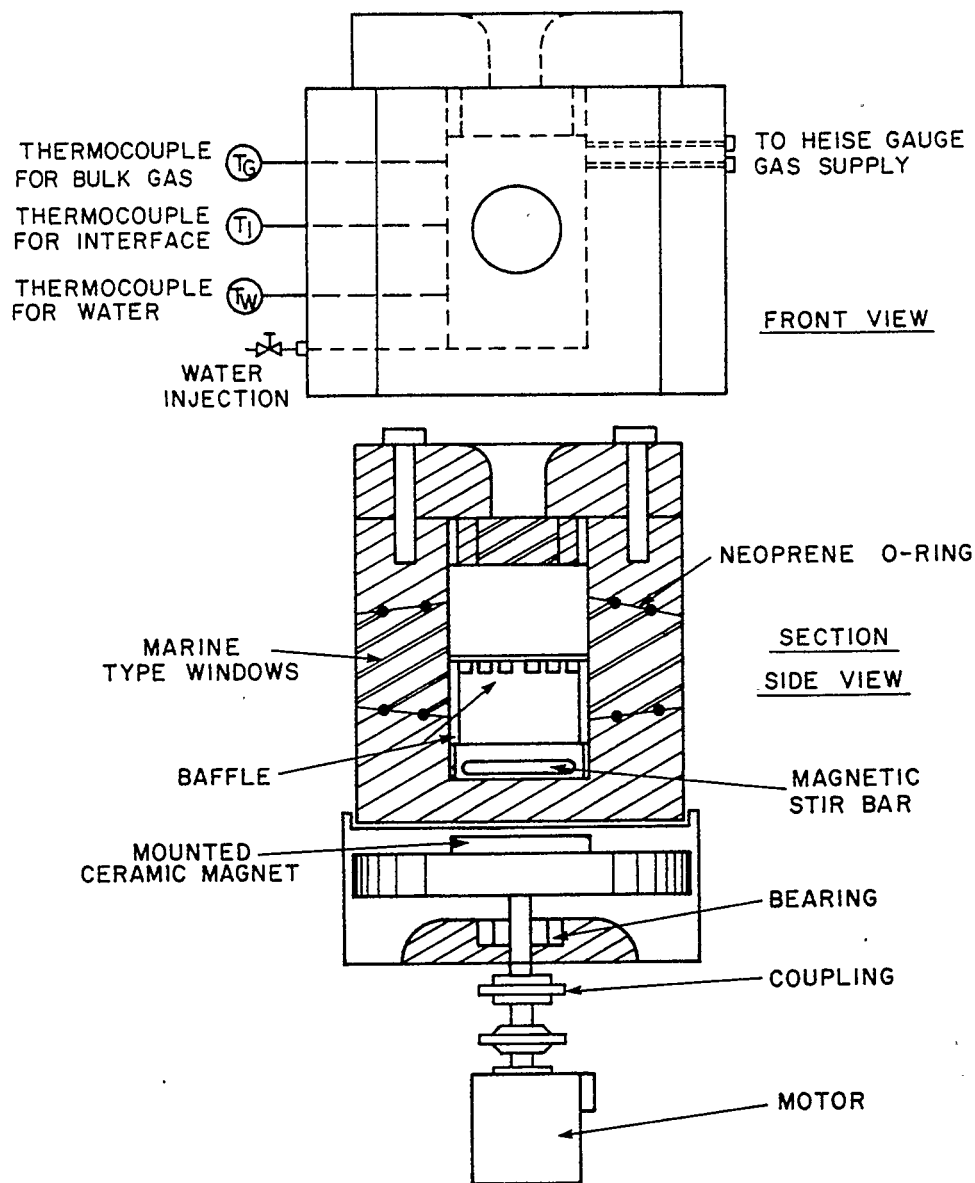
Figure 3: Schematic diagram of the reactor.

the reactor was connected, with a tee, to a 0 – 25 MPa, 16" (0.41 m) dial Bourdon tube Heise pressure gauge with a 660^0 of arc and to a Rosemount differential pressure transmitter, DP4, calibrated to a span of 0 – 0.5 MPa. Two Type T thermocouples, one immersed in the liquid phase and the other in the vapor phase, were used to measure the temperatures of the reactor contents. The thermocouples were calibrated with a mercury-in-glass long stem thermometer with graduations of 0.1 C.

A 1000 cm^3 stainless steel vessel, "bias cell", was also immersed in the glycol-water bath along with the reactor. It was provided with a Type T thermocouple and a 1/8" (3 mm) tubing which was connected to the low side of the DP transmitter DP4. The transmitter DP4 thus measured the differential pressure between the reactor and the bias cell.

The signals from pressure transmitter DP4 and the thermocouples were fed to a Digitrend 235 DORIC data acquisition system which displayed the differential pressure in percentage of the span of DP4 and temperature in degrees Celsius. The resolution of the temperature measurement was 0.1 C. The pressure and temperature values from DORIC were fed to a COMPAQ DESKPRO microcomputer through an RS-232 connection. An on-line software program was used to read the raw data transmitted by DORIC. The differential pressure value was converted into absolute units and the temperatures and the pressure of the system were displayed.

3.2   Measurement accuracies

3.2.1   Pressure

The reactor pressure was calculated as follows :

reactor pressure =   (% reading from DP4) *

(span of DP4 in MPa / 100)

+ Bias cell pressure (MPa)

+ Barometric pressure (MPa)

The bias cell pressure was set at the beginning of each experiment and was read off the Heise gauge. Barometric pressure was read off a mercury barometer.

The accuracy of the Heise gauge was checked against a dead weight tester. The inherent inaccuracy of the gauge was found to be within the manufacturer's allowable limit of 0.1% of the full scale of the gauge. Therefore,

accuracy of bias cell pressure = 0.1% of full scale of the

Heise   gauge

= $\pm$ 0.025 MPa

The differential pressure transmitter DP4 was calibrated to a span of 0.5 MPa by applying differential pressures from 0.0 to 0.5 MPa across the transmitter and recording the output from the data acquisition system. The output from the data acquisition system was in terms of percent of the span of the transmitter. The percent reading from the data acquisition system and the differential pressure applied were fitted to a

straight line. The average standard deviation of the fit was 0.00016 MPa which was within the accuracy of DP4 :

$$\text{accuracy of DP4} \qquad = \pm 0.25 \text{ \% of } 0.5 \text{ MPa}$$

$$= \pm 0.00125 \text{ MPa}$$

Since the accuracy of the transmitter DP4 was higher than the accuracy of the Heise gauge, the accuracy of pressure measurement was taken to be within $\pm$ 0.025 MPa.

3.2.2   Temperature

The thermocouple in the liquid phase in the reactor was calibrated by immersing it in a constant temperature bath. The thermocouple reading, as displayed by the data acquisition system, was recorded. At the same time, the bath temperature was measured with a mercury-in-glass thermometer graduated to 0.1 C. The accuracy of reading the thermometer was thus $\pm$ 0.05 C. The thermocouple and the thermometer readings in the range 0 – 12 C were fitted to a straight line. The average standard deviation of the fit was 0.035 C.   The accuracy of temperature measurement was thus taken to be $\pm$ 0.05 C.

3.3   Materials

The water used for the experiments was distilled and deionised. All electrolytes were of Certified ACS grade supplied by Fisher Scientific Company. Methane gas was Linde's Ultra High Purity grade.

4. EXPERIMENTAL PROCEDURE

4.1   Experimental techniques for hydrate equilibrium detection

The technique that has been used by a majority of researchers is by direct visual observation of hydrate formation and decomposition in a windowed equilibrium cell whose temperature is closely controlled. Agitation of the contents of the cell is brought about by a rocking or shaking mechanism.

Generally, two types of such visual methods are followed to determine the hydrate equilibrium conditions : the "temperature search" method and the "pressure search" method.

In a "temperature search" method the gas or the gas mixture and water are charged to an equilibrium cell and the temperature and pressure are adjusted to the desired equilibrium conditions. The hydrates are formed by lowering the temperature by several degrees. Once the hydrates are formed, the temperature is increased until almost all the hydrates decompose. The temperature is then lowered slightly so that hydrates start forming again. As soon as this happens, the temperature is increased slowly until the hydrates start decomposing. The temperature and pressure at which the hydrates start decomposing are taken to be the hydrate equilibrium conditions (Naoker et al. 1954; Otto and Robinson, 1960; Holder and Grigoriou, 1980). Unruh and Katz (1949) kept the system at constant temperature once the "search interval" was narrowed down

sufficiently and allowed it to reach a constant pressure. This pressure was taken to be the equilibrium pressure.

In a "pressure search" method, the temperature of the system is kept constant throughout the experiment. After charging the gas (or gas mixture) and water into the cell, the hydrates are formed by increasing the pressure beyond the expected equilibrium pressure. Bond and Russell (1949) reduced the pressure until a considerable amount of hydrates decomposed. On leaving the system at constant temperature, a constant pressure was reached. This pressure was taken as the equilibrium pressure. Falabella and Vanpee (1974) reduced the pressure in steps until an increase in pressure was observed, indicating hydrate decomposition. The procedure was repeated with progressively smaller decrements until a constant pressure was obtained.

Marshall et al. (1964) and Schroeter et al. (1983) followed a non-visual method. In this method, the gas and water are charged into a cell at the desired working pressure at a temperature above the equilibrium conditions. The system is cooled slowly and the changes in temperature and pressure are recorded. Once sufficient amounts of hydrates are formed (indicated by the drop in the pressure), the system is re-heated and the pressure-temperature changes are again recorded. The "P-T curves" for the heating and cooling processes are plotted and their point of intersection is taken to be the equilibrium point. The heating, cooling and data acquisition is automated.

In the present study, a "pressure search" type of visual process was followed. The degrees of freedom and the detection of equilibrium conditions are described next.

4.2 Degrees of freedom and detection of equilibrium

The degrees of freedom, F, for a system containing aqueous solution of n_s electrolytes and pure methane gas at the three phase equilibrium (aqueous liquid – gas – solid hydrate) is given by

$$F = (n_s+2) + 2 - 3 = n_s + 1$$

Since the electrolytes do not enter the hydrate or vapor phase, the amounts of the electrolytes in the aqueous liquid phase remain unchanged during an experiment. With the following assumptions :

1. the amount of water vapor present in the gas phase is negligible and

2. the amount of hydrates present at equilibrium is very small,

the amount of water present in the aqueous liquid phase also remains practically unchanged. Further, the solubility of methane in the aqueous liquid phase can be neglected. Therefore, it can be assumed that the *concentrations* of the electrolytes in the aqueous liquid phase remain unchanged during an experiment. With this assumption, the degrees of freedom reduce by n_s i.e. the degrees of freedom reduce to 1 (one).

For such a univariant system, specifying the temperature fixes

the equilibrium state completely. It also follows that a closed, well stirred univariant system at constant temperature and initially at a pressure higher than the three-phase equilibrium pressure, P_{EQ}, would ultimately attain the equilibrium pressure. This is also true for a system at a pressure lower than P_{EQ} where a sufficient amount of hydrates is present to raise the system pressure to P_{EQ} due to hydrate decomposition.

To detect the equilibrium pressure at a constant temperature the system pressure is manipulated such that it (the pressure) is in the vicinity of the equilibrium pressure, indicated by very slow changes in the system pressure. Further manipulations are stopped until a "hydrate point", P_H, or a "no-hydrate point", P_{NH}, is obtained. The hydrate point, P_H, is the constant pressure attained by the system (at the constant experimental temperature) *with a very small amount of hydrates present*. A "no-hydrate point" is the constant pressure attained by the system (at constant experimental temperature) *with no hydrates present*. If a "no-hydrate point" is obtained, hydrates are formed again and pressure manipulated as before. This is repeated until a "hydrate point" is obtained. Once a "hydrate point" is obtained, the system pressure is lowered by a small amount, ΔP_{CH}, to confirm that the hydrates decompose at this lower pressure. The "hydrate point", P_H, represents the equilibrium pressure P_{EQ} once such a confirmation is made.

4.3   Preparation of electrolyte solution

Appropriate quantities of each electrolyte were weighed on a

top-loading Mettler balance with a readability of 0.01 g (quantities smaller than 1 g were weighed on a Mettler balance with a readability of 0.0001 g) and added to a weighed quantity of distilled-and-deionised water. The mixture was stirred to dissolve all the electrolytes at room temperature. The reactor was rinsed twice with distilled-and-deionised water and then 250 cm^3 of the prepared solution was charged into the empty reactor. The vapor phase of the reactor was then purged with methane gas to drive away any air that may have entered the reactor during the charging process.

4.4   Experimental Procedure

For every salt mixture, a partial phase diagram in the region aqueous solution-hydrate-gas was computed using the methodology of Englezos and Bishnoi (1988). The partial phase diagram was then used to select four target temperatures at which the hydrate equilibrium pressures would be obtained. The temperatures selected were such that the equilibrium pressures would be well spaced in the range 0 - 10 MPa and also such that none of the salts were expected to precipitate out of the solution at that temperature. The approximate temperature at which one of the electrolytes would precipitate out of the solution were determined using published solubility product data. The minimum target temperature was kept at least 2 C above this temperature.

In order to start an experiment, one has to decide on P$_{SET}$, the initial pressure at which the system is left for observation. The equilibrium pressure calculated by the method of Englezos and Bishnoi

(1988) is the obvious choice. However, by observing the *rate* at which the system pressure changes during an experiment one can judge how far the equilibrium pressure is from P_{SET} : if the system pressure is very much higher than P_{EQ}, the system pressure would fall rapidly due to hydrate formation; if the system pressure is very much lower than the equilibrium pressure, the system pressure would rise rapidly due to hydrate decomposition; and if the system pressure is close to the equilibrium pressure (either higher or lower), the change in the system pressure would be slow.

The typical experimental procedure is now described.

Once the desired temperature is attained, the bias cell is pressurized with methane gas to about 0.3 MPa below the expected hydrate equilibrium pressure. The bias cell pressure is read off the Heise gage. The bias cell is then isolated from the Heise gage.The pressure in the reactor is then raised to 1.5 – 2.0 MPa above the expected equilibrium pressure to form hydrates. As soon as the hydrates are formed, the pressure is decreased rapidly at a controlled rate by venting out methane from the vapor phase, taking care that the contents do not cool down by more than 0.1 C from the experimental temperature. The pressure is set (P_{SET}) at the expected equilibrium pressure. It is important to make sure that the amount of hydrates present at this stage is very small. Depending on the relative values of P_{SET} and the true equilibrium value, P_{EQ}, four cases arise :

Case 1: $P_{EQ} = P_{SET}$

In this case there will be very little variation in the system pressure. If the system temperature and pressure remain steady for an extended period of time, typically 4 - 5 hours, with very little hydrates present, then a "hydrate point" P_H, which represents the equilibrium pressure at the experimental temperature, is said to have been obtained. If a "no-hydrate" point, P_{NH}, has already been determined such that $P_H - P_{NH} = \Delta P_{CH}$, a predetermined value, then the experiment is terminated. Otherwise, the system pressure is decreased by an amount ΔP_{CH} to verify that all the hydrates decompose at the new pressure and the experiment is terminated.

Case 2: $P_{SET} \gg P_{EQ}$

In this case the pressure of the reactor will start falling rapidly due to hydrate formation. The pressure is reduced suitably so that the changes taking place in the pressure are slow. Observations are continued until a "hydrate" point, P_H is obtained. The subsequent procedure is the same as that under Case 1 after a P_H is obtained.

Case 3: $P_{SET} \ll P_{EQ}$

In this case the pressure in the reactor will keep rising until all the hydrates decompose. A "no-hydrate" point, P_{NH}, is said to have been obtained. If a "hydrate point", P_H, has already been obtained, such that the difference between P_H and P_{NH} is equal to ΔP_{CH} then the experiment is terminated. Otherwise, hydrates are formed at 1.5 - 2.0 MPa above the expected equilibrium value and the procedure repeated. The new value of P_{SET} is selected based on the observed

rate of hydrate decomposition.

Case 4: P_{SET} close to P_{EQ}

In this case the pressure of the reactor will either fall or rise slowly until it becomes steady. A "hydrate-point", P_H, is said to have been obtained if hydrates are present. Further action to be taken is the same as that under Case 1. If the hydrates decompose, a "no-hydrate point" is said to have been obtained. Further action to be taken is then the same as that under Case 3.

The procedure is summarized in Figure 4. In this figure, ΔP is arbitrarily selected based on observed rate of hydrate formation or decomposition.

4.5   Variation of temperature during an experiment

As stated earlier, once a "hydrate point", P_H, is obtained, the system pressure is reduced by $ΔP_{CH}$ to confirm that the hydrates decompose at the lower pressure. In a number of runs, on reducing the pressure by 0.025 MPa the hydrates decomposed. However, due to changes in the room temperature, in many experiments the two points were obtained at two different temperatures typically 0.1 C apart. The following example illustrates the implications :

Assume that

1. a "hydrate point" of 3.0 MPa was obtained at 1.0 C.

2. Pressure in the system was brought down to

3.0 − .05 = 2.95 MPa
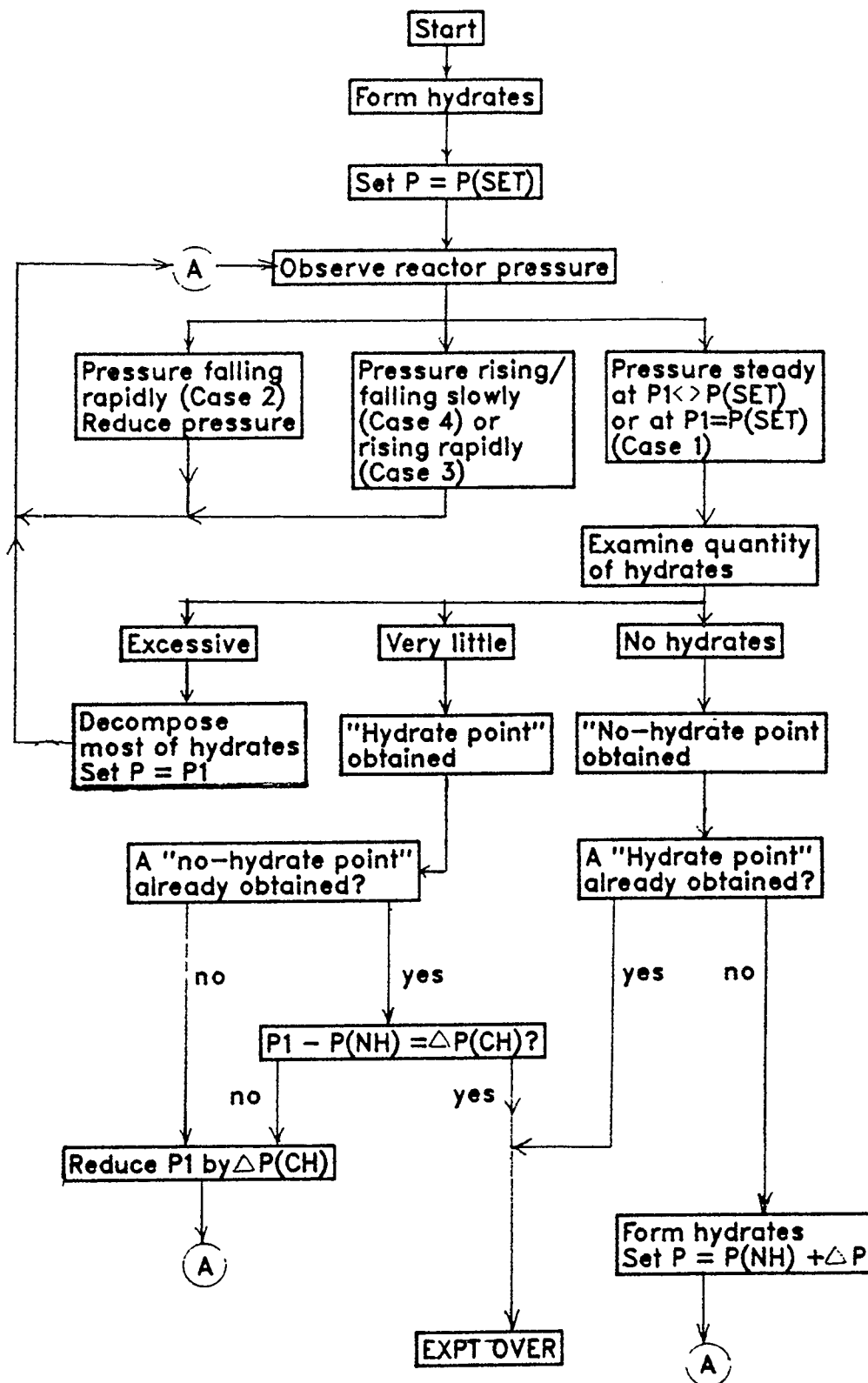
Figure 4: Summary of experimental procedure.

to confirm that hydrates decompose.

3. Hydrates decomposed at 2.95 MPa but temperature had changed to 0.9 C.

To check the consistency of the data ·obtained, the equilibrium pressure *at 0.9 C could be calculated from that obtained at 1.0 C (3.0 MPa)* by assuming the P-T curve to be linear in the small range around 1.0 C :

$$P_H - \left(\frac{\Delta P}{\Delta T} \right)_{at\ 1.0C} \times\ 0.1 = P_H^t$$

If the slope computed from the calculated pressure-temperature curve were to be 0.4 MPa per degree C,

$$P_H^t = 3.0 - 0.04 = 2.96\ MPa.$$

Thus at 0.9 C the difference between a "hydrate point" and a "no-hydrate point" would be 2.96 - 2.95 = 0.01 MPa.

In order to avoid such a situation, during the latter part of the experimental program the value of ΔP_{CH} was set, at the beginning of each experiment, at the sum of 0.05 MPa (twice the inaccuracy of pressure measurement) and the local slope of the equilibrium curve :

$$\Delta P_{CH} = 0.05 + \left(\frac{\Delta P}{\Delta T}\right) \times 0.1$$

In the example being considered, the new value of P_{SET}, after the "hydrate point" was obtained at 1.0 C would be :

$$P_{SET} = P_H - (0.05 + 0.04) = 3.0 - 0.09 = 2.91 \text{ MPa.}$$

One consequence of setting ΔP_{CH} larger than 0.05 MPa was that if the temperature did not change during an experiment, it would be larger than 0.05 MPa even when not required to be so. The largest value of ΔP_{CH} was 0.17 MPa thus giving a spread of 0.12 MPa in case the temperature did not change. This high value of ΔP_{CH} was used only in the steeper parts of the P-T curve, typically above 7.5 MPA. This was considered adequate.

5. Experimental Results and Discussion

5.1   Experimental results

Experiments were carried out with 5 mixtures of NaCl and KCl, 6 mixtures of NaCl and $CaCl_2$ and a synthetic sea water mixture. The compositions of the NaCl and KCl and NaCl and $CaCl_2$ binaries are given in Table 2 and that of the synthetic sea water in Table 3. The composition of synthetic sea water was taken from Leyendekkers (1976). The wt% in these tables are on wet basis.

The results of the experiments are given in Table 4. The results for the NaCl and KCl experiments are given in graphical form in Figure 5, those for $NaCl-CaCl_2$ experiments in Figure 6 and those for synthetic sea water are given in Figure 7 along with the predicted pressure curves. The predicted equilibrium pressures for pure water are also given for comparison. The inhibition effect of the electrolytes can be gaged by moving along a constant pressure line.

It can be seen in Figure 6 that the experimental data and the cacluated curves for the following two mixtures are very close :

3 wt% NaCl and 10 wt% $CaCl_2$

10 wt% NaCl and 3 wt% $CaCl_2$

A similar observation can be made for the following mixtures :

6 wt% NaCl and 10 wt% $CaCl_2$

10 wt% NaCl and 6 wt% $CaCl_2$

TABLE 2
Compositions of the aqueous solutions

Solution ID*	Composition wt% (wet basis)			molality		
	Nacl	KCl	CaCl$_2$	NaCl	KCl	CaCl$_2$
Na5K5	5.003	5.006	0.0	0.9514	0.7461	0.0
Na5K10	4.999	9.982	0.0	1.0050	1.5759	0.0
Na5K15	4.999	15.004	0.0	1.0684	2.5177	0.0
Na10K12	10.008	12.001	0.0	2.1936	2.0655	0.0
Na15K8	14.987	7.991	0.0	3.3262	1.3927	0.0
Na3Ca3	3.001	0.0	3.002	0.5458	0.0	0.2877
Na6Ca3	6.003	0.0	3.002	1.1277	0.0	0.2972
Na10Ca3	10.002	0.0	3.001	1.9653	0.0	0.3107
Na10Ca6	9.972	0.0	5.984	2.0284	0.0	0.6415
Na3Ca10	2.999	0.0	9.997	0.5891	0.0	1.0351
Na6Ca10	6.000	0.0	9.999	1.2210	0.0	1.0723

* Key to solution ID is given under "Nomenclature".

TABLE 3
Composition of synthetic sea water

Component	wt% (wet basis)	molality
NaCl	2.394	0.4244
Na$_2$SO$_4$	0.401	0.0293
NaF	0.009	0.0002
KCl	0.069	0.0095
KBr	0.011	0.0009
MgCl$_2$	0.508	0.0553
CaCl$_2$	0.115	0.0107
SrCl$_2$	0.002	0.0001

TABLE 4
Experimental Results

Label*	Temp. K	P_{exp} MPa	P_{pred} MPa	% prediction error
Na5K5-03	272.23±0.05	3.464	3.560±0.018	– 2.77
Na5K5-04	270.32±0.05	2.829	2.940±0.015	– 3.92
Na5K5-05	274.25±0.05	4.215	4.371±0.023	– 3.70
Na5K5-06	276.27±0.05	5.169	5.389±0.029	– 4.26
Na5K5-07	272.23±0.05	3.439	3.560±0.019	– 3.52
Na5K5-08	281.46±0.05	9.379	9.563±0.055	– 1.96
Na5K5-09	279.35±0.05	7.340	7.519±0.042	– 2.52
Na5K10-02	272.07±0.05	4.174	4.351±0.023	– 4.24
Na5K10-04	267.49±0.05	2.569	2.735±0.014	– 6.46
Na5K10-05	279.00±0.05	9.046	9.341±0.055	– 3.23
Na5K10-06	276.44±0.05	6.764	6.962±0.039	– 2.93
Na5K15-02	272.22±0.05	5.564	5.822±0.032	– 4.64
Na5K15-03	269.20±0.05	4.014	4.213±0.022	– 4.96
Na5K15-04	266.29±0.05	2.914	3.117±0.016	– 6.97
Na5K15-05	276.19±0.05	8.689	9.487±0.056	– 9.18
Na10K12-01	272.22±0.05	7.144	7.571±0.045	– 5.98
Na10K12-02	269.40±0.05	5.144	5.498±0.030	– 6.88
Na10K12-03	266.29±0.05	3.689	3.932±0.020	– 6.59
Na10K12-06	264.58±0.05	2.989	3.290±0.014	–10.07
Na10K12-07	274.23±0.05	8.819	9.638±0.060	– 9.29
Na15K8-01	270.21±0.05	7.049	7.503±0.045	– 6.44
Na15K8-02	266.29±0.05	4.400	4.813±0.026	– 8.30
Na15K8-03	264.38±0.05	3.614	3.920±0.021	– 8.47
Na15K8-04	272.12±0.05	8.839	9.468±0.060	– 7.12

TABLE 4 (contd.)
Experimental Results

Label*	Temp. K	P_{exp} MPa	P_{pred} MPa	% prediction error
Na3Ca3-01	274.13±0.05	3.584	3.646±0.018	− 1.73
Na3Ca3-02	277.14±0.05	4.874	4.951±0.026	− 1.58
Na3Ca3-03	281.76±0.05	8.159	8.119±0.045	0.49
Na3Ca3-04	270.41±0.05	2.504	2.526±0.013	− 0.88
Na6Ca3-01	274.13±0.05	4.189	4.263±0.021	− 1.77
Na6Ca3-02	277.04±0.05	5.679	5.775±0.030	− 1.69
Na6Ca3-03	280.06±0.05	7.839	8.027±0.045	− 2.40
Na6Ca3-04	271.31±0.05	3.134	3.210±0.016	− 2.43
Na10Ca3-01	274.33±0.05	5.399	5.621±0.031	− 4.11
Na10Ca3-02	272.22±0.05	4.339	4.497±0.024	− 3.64
Na10Ca3-03	269.40±0.05	3.214	3.370±0.017	− 4.85
Na10Ca3-04	277.34±0.05	7.444	7.842±0.045	− 5.35
Na10Ca6-01	274.23±0.05	6.779	7.037±0.040	− 3.81
Na10Ca6-02	266.02±0.05	2.819	2.958±0.015	− 4.93
Na10Ca6-03	269.30±0.05	3.939	4.137±0.022	− 5.03
Na10Ca6-04	274.33±0.05	6.899	7.117±0.040	− 3.16
Na3Ca10-01	276.99±0.05	7.159	7.329±0.041	− 2.37
Na3Ca10-02	279.70±0.05	9.664	10.019±0.060	− 3.67
Na3Ca10-03	274.23±0.05	5.189	5.427±0.029	− 4.59
Na3Ca10-04	268.80±0.05	3.019	3.110±0.016	− 3.01
Na6Ca10-01	274.13±0.05	6.739	6.977±0.039	− 3.53
Na6Ca10-02	277.14±0.05	9.514	9.909±0.061	− 4.15
Na6Ca10-03	270.81±0.05	4.699	4.865±0.026	− 3.53
Na6Ca10-04	268.60±0.05	3.689	3.864±0.020	− 4.74

TABLE 4 (contd.)
Experimental Results

Label*	Temp. K	P_{exp} MPa	P_{pred} MPa	% prediction error
SEA-01	277.04+0.05	4.364	4.425+0.022	– 1.40
SEA-02	279.04+0.05	5.424	5.433+0.028	– 1.66
SEA-03	281.16+0.05	6.659	6.799+0.037	– 2.10
SEA-04	283.88+0.05	9.064	9.173+0.047	– 1.20

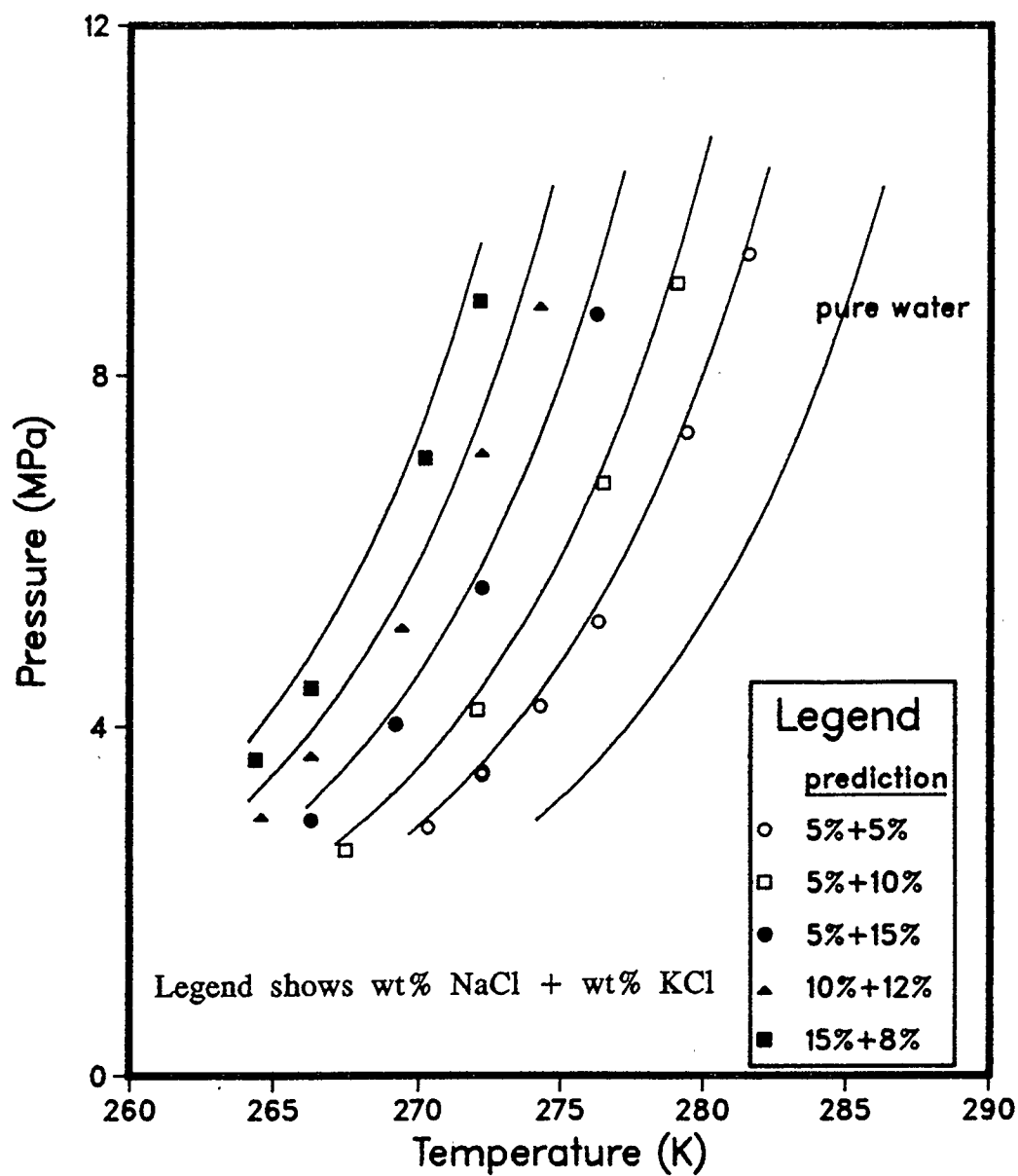* Key to Label is given under "Nomenclature".

Figure 5: Experimental and predicted pressures for methane hydrate formation in aqueous solutions containing mixtures of sodium and potassium chlorides.
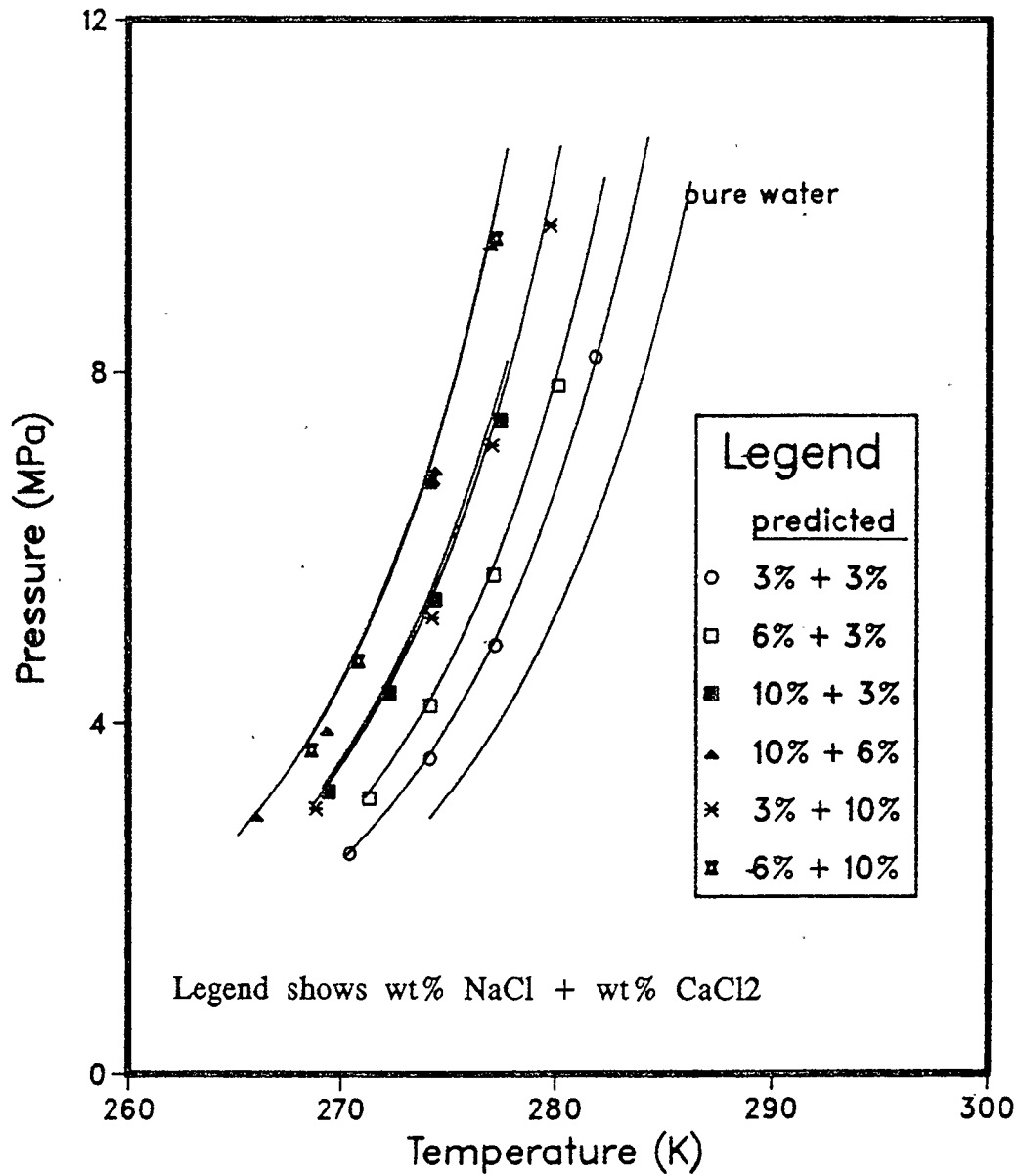
Figure 6: Experimental and predicted pressures for methane hydrate formation in aqueous solutions containing mixtures of sodium and calcium chlorides.
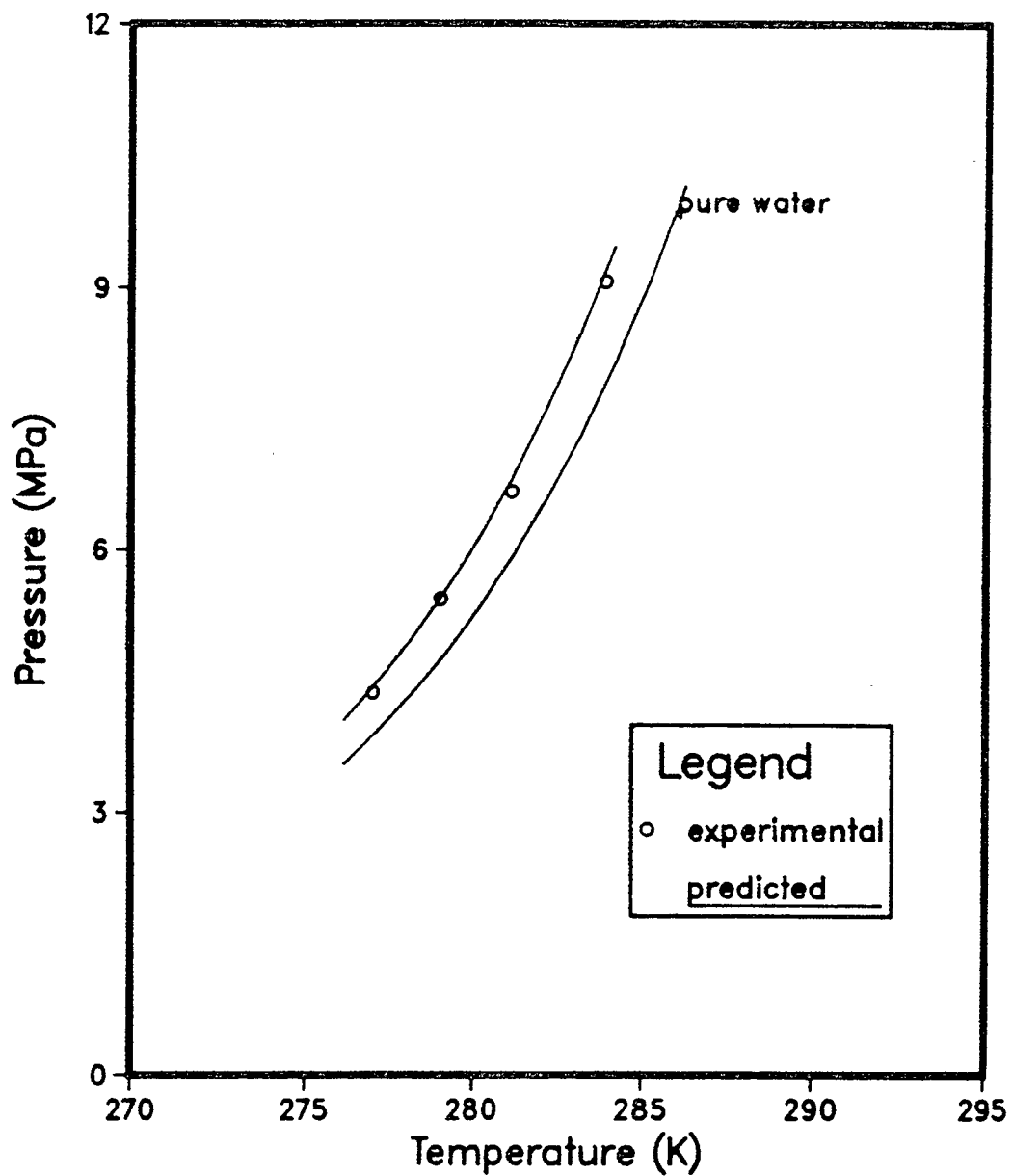
Figure 7: Experimental and predicted pressures for methane
hydrate formation in synthetic sea water.

An explanation for this behaviour is given later in section 5.2.

5.2   Discussion

Table 4 also gives the equilibrium pressures calculated with the method of Englezos and Bishnoi (1988) and the relative deviations for each data point. Table 5 gives the RMSD for NaCl and KCl, NaCl and $CaCl_2$ and sea water experiments. Table 6 gives the total ionic strength and RMSD for the *individual* mixtures.

Since the accuracy of pressure measurement was $\pm$ 0.025 MPa and that of temperature measurement $\pm$ 0.05 C, the actual equilibrium point for each data point reported would lie anywhere in the box *abcd* shown in Figure 8. The relative deviation is calculated between the reported pressure and the point *g* on the prediction curve, although the *maximum possible* deviation *could be* that represented by points *b* and *f* whereas the *minimum possible* deviation *could be* that represented by points *d* and *e*.

It is observed that the deviations increase with an increase in the ionic strength. Moreover, the deviations are higher for NaCl and KCl mixtures than for the NaCl and $CaCl_2$ mixtures.   Table 6 also gives the molality of the individual electrolytes, m_k^0, used to calculate the activity of water, $a_{w,k}^0$ in equation 15 (section 2.2). When these values are compared with the maximum molalities of the electrolytes permitted by the model of Pitzer (Table 7), it is evident that for NaCl and KCl mixtures, the molalities of KCl were close to the maximum. This could be

TABLE 5
Root Mean Squared Deviations (RMSD)

Electrolytes	RMSD
NaCl+KCl	6.06%
NaCl+CaCl$_2$	3.50%
Synthetic Sea Water	1.40%

TABLE 6
Total ionic strengths and RMSDs of the electrolytes solutions

| Mixture	Ionic str.	RMSD	m^o_k in equation 15 NaCl	KCl	CaCl$_2$
Na5K5	1.6975	3.33%	1.6975	1.6975	0.0
Na5K10	2.5809	4.44%	2.5809	2.5809	0.0
Na5K15	3.5860	6.69%	3.5860	3.5860	0.0
Na10K12	4.2591	7.93%	4.2591	4.2591	0.0
Na15K8	4.7189	7.63%	4.7189	4.7189	0.0
Na3Ca3	1.2651	1.27%	1.2651	0.0	0.5060
Na3Ca6	1.7221	2.10%	1.7221	0.0	0.6888
Na10Ca3	2.7422	4.54%	2.7422	0.0	1.0969
Na10Ca6	3.6321	4.30%	3.6321	0.0	1.4528
Na3Ca10	3.1770	3.51%	3.1770	0.0	1.2708
Na6Ca10	3.9019	4.02%	3.9019	0.0	1.5608
SEA	0.6295	1.40%			
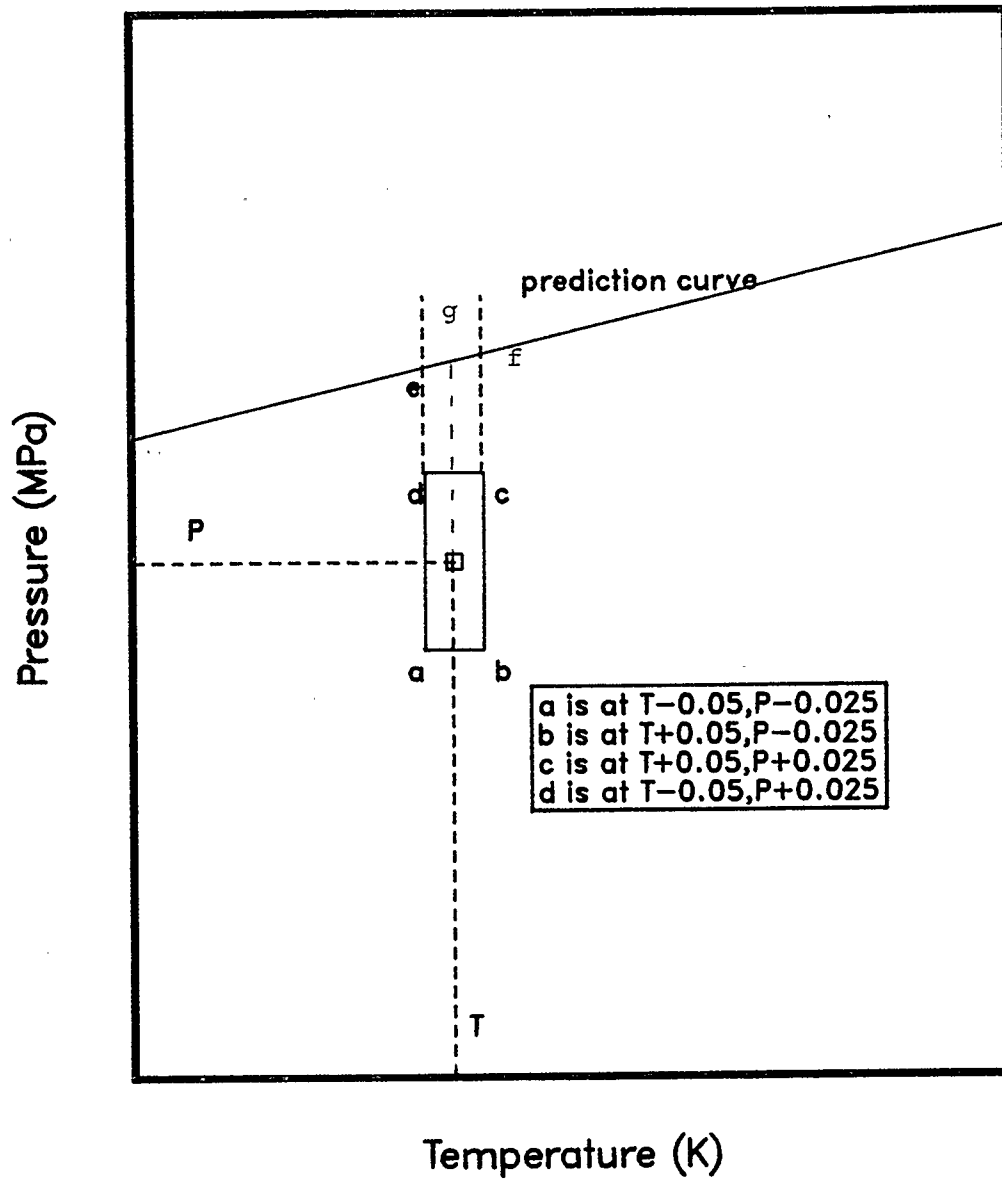
Figure 8: Error bounds of reported data.

TABLE 7
Maximum molalities permitted by activity model

Electrolyte	Molality
NaCl	6.0
KCl	4.8
$CaCl_2$	2.5

the reason for the higher deviation.

5.2.1 Sensitivity of predictions to hydrate model parameters

The deviations reported in this study are valid only for the hydrate parameters $\Delta\mu_w^0$, Δh_w^0, Δv_w and a and b (section 2.2) used because with different values for these parameters, the predictions change. Figure 9 shows the predictions with three different sets of parameters for pure water and a 5-5 wt% NaCl and KCl binary mixture. The set of parameters used by Englezos et al (1988) is that which gave them the least error with pure water and methanol solutions. The sets used by Parrish and Prausnitz (1972) and Holder et al (1980) were regressed using hydrate formation in pure water. In this study, the parameters suggested by Parrish and Prausnitz (1972) were used. It is evident that with different sets of parameters, the method of Englezos and Bishnoi (1988) would predict equilibrium data in electrolyte solutions with different deviations. This is not a short coming of the method of Englezos and Bishnoi (1988) but that of the implementation of the hydrate model of van der Waals and Platteeuw (1959).

5.2.2 Relative inhibiting strengths of the electrolytes on a weight-to-weight basis

In Figure 6 it can be observed that the experimental data *and* the calculated curves for the 10 wt% NaCl and 3 wt% $CaCl_2$ mixture and those for the 3 wt% NaCl and 10 wt% $CaCl_2$ mixture almost coincide. A similar behavior is also observed for the two mixtures : 6% by wt NaCl and 10 wt% $CaCl_2$ on the one hand and 10 wt% NaCl and 6 wt% $CaCl_2$ on the other. This leads one to suspect that the inhibiting strengths of the two
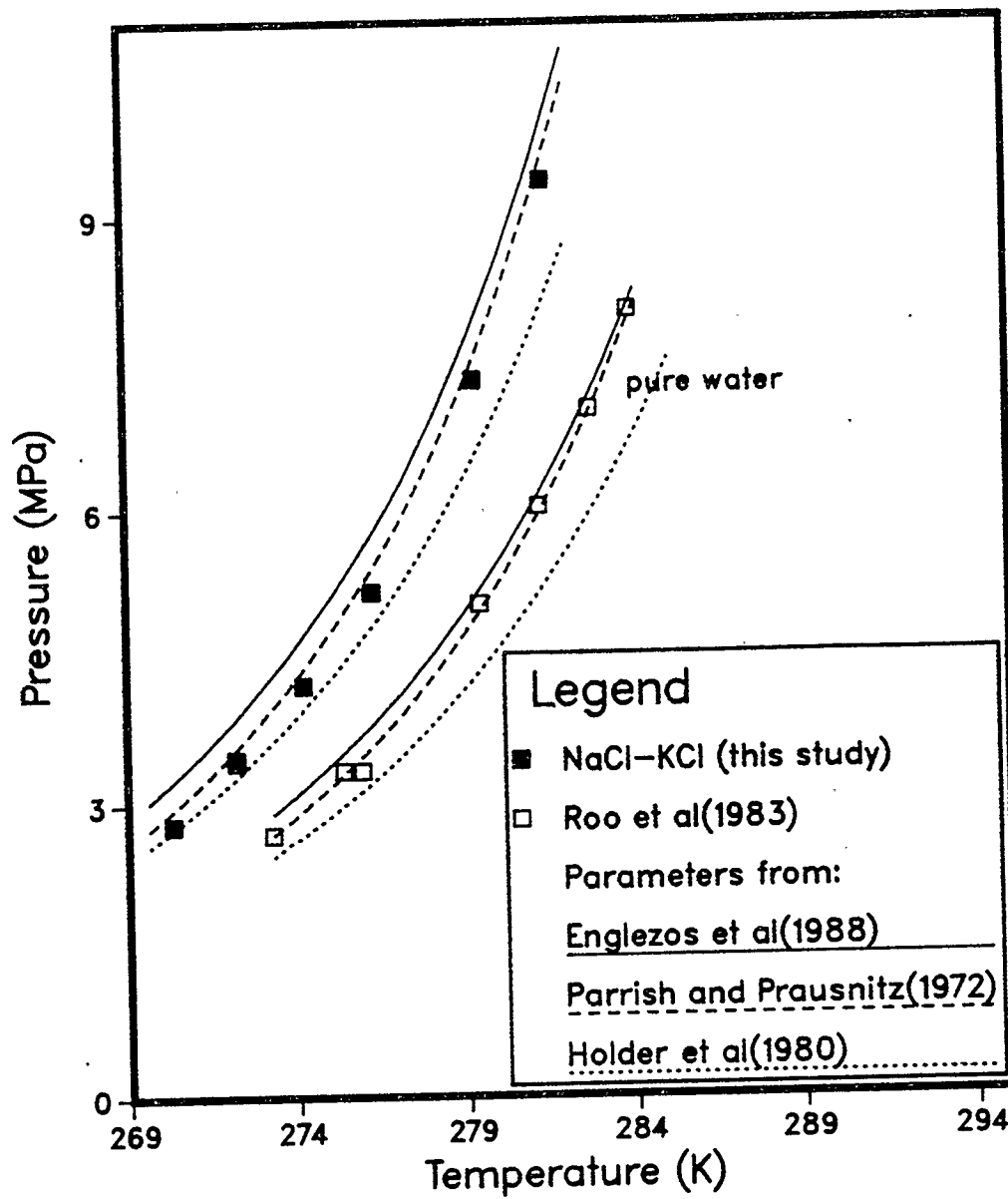
Figure 9: Predictions with different sets of hydrate model parameters for methane hydrate formation in pure water and in a 5-5 wt% mixture of sodium and potassium chlorides using the method of Englezos and Bishnoi (1988).

electrolytes, on a weight-to-weight basis, are close. Calculations with .13 wt% of *individual* electrolytes NaCl and $CaCl_2$ show this to be true. On Figure 10 are shown the calculated prediction curves for

13 wt% NaCl

13 wt% $CaCl_2$

4 wt% NaCl + 9 wt% $CaCl_2$

9 wt% NaCl + 4 wt% $CaCl_2$.

It can be seen that all the curves are very close to each other. On a weight-to-weight basis NaCl is only slightly stronger inhibitor than $CaCl_2$.

A similar analysis with NaCl and KCl showed that NaCl is a much stronger inhibitor than KCl on a weight-to-weight basis. On Figure 11 are shown the calculated curves for

15 wt% NaCl

15 wt% KCl

5 wt% NaCl + 10 wt% KCl and

10 wt% NaCl + 5 wt% NaCl.

It can be seen that the mixture containing higher wt% of NaCl inhibits the hydrate formation to a greater extent.
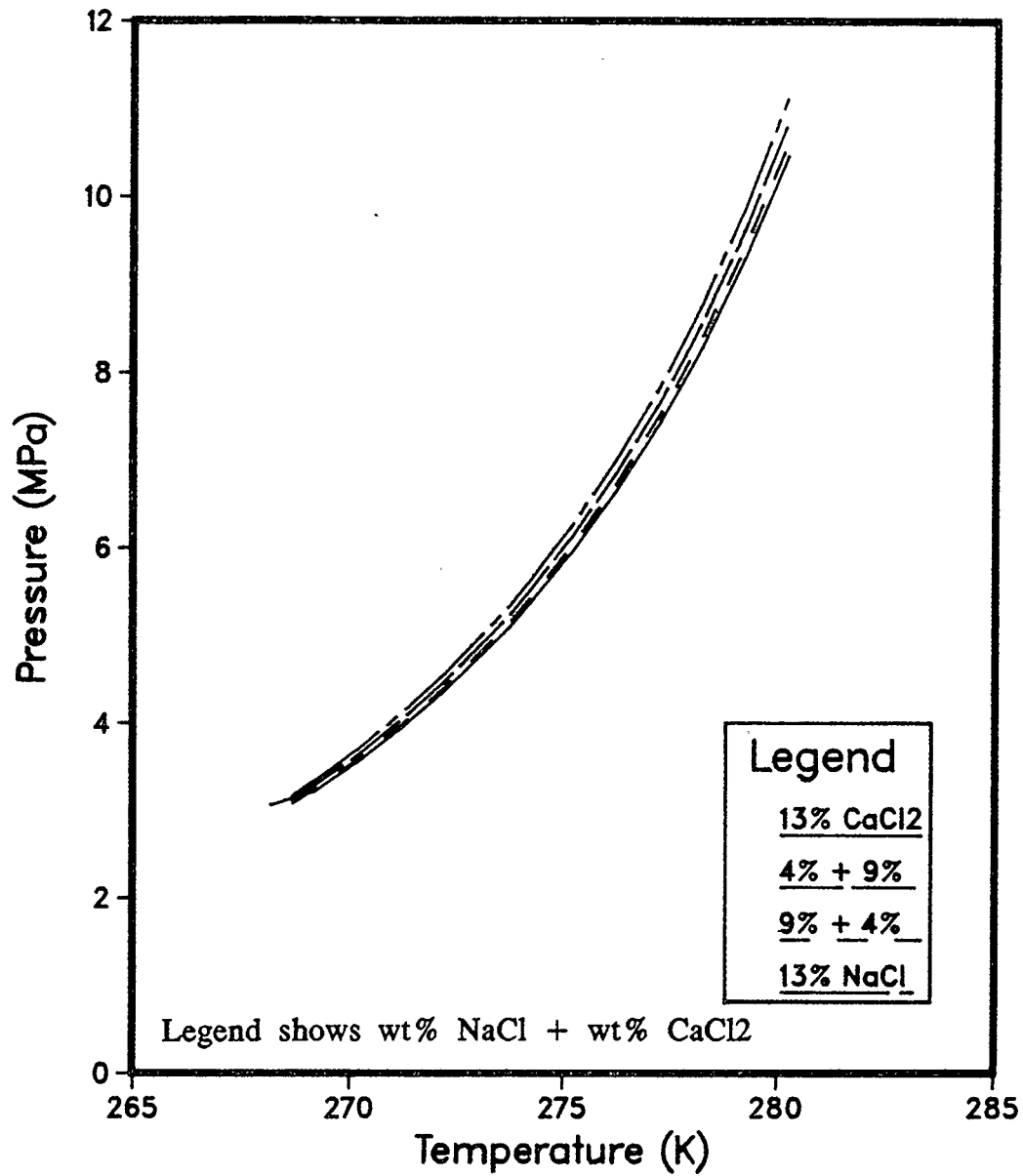
Figure 10: Calculated curves for sodium chloride, calcium chloride and their mixtures showing relative strengths on a weight-to-weight basis.
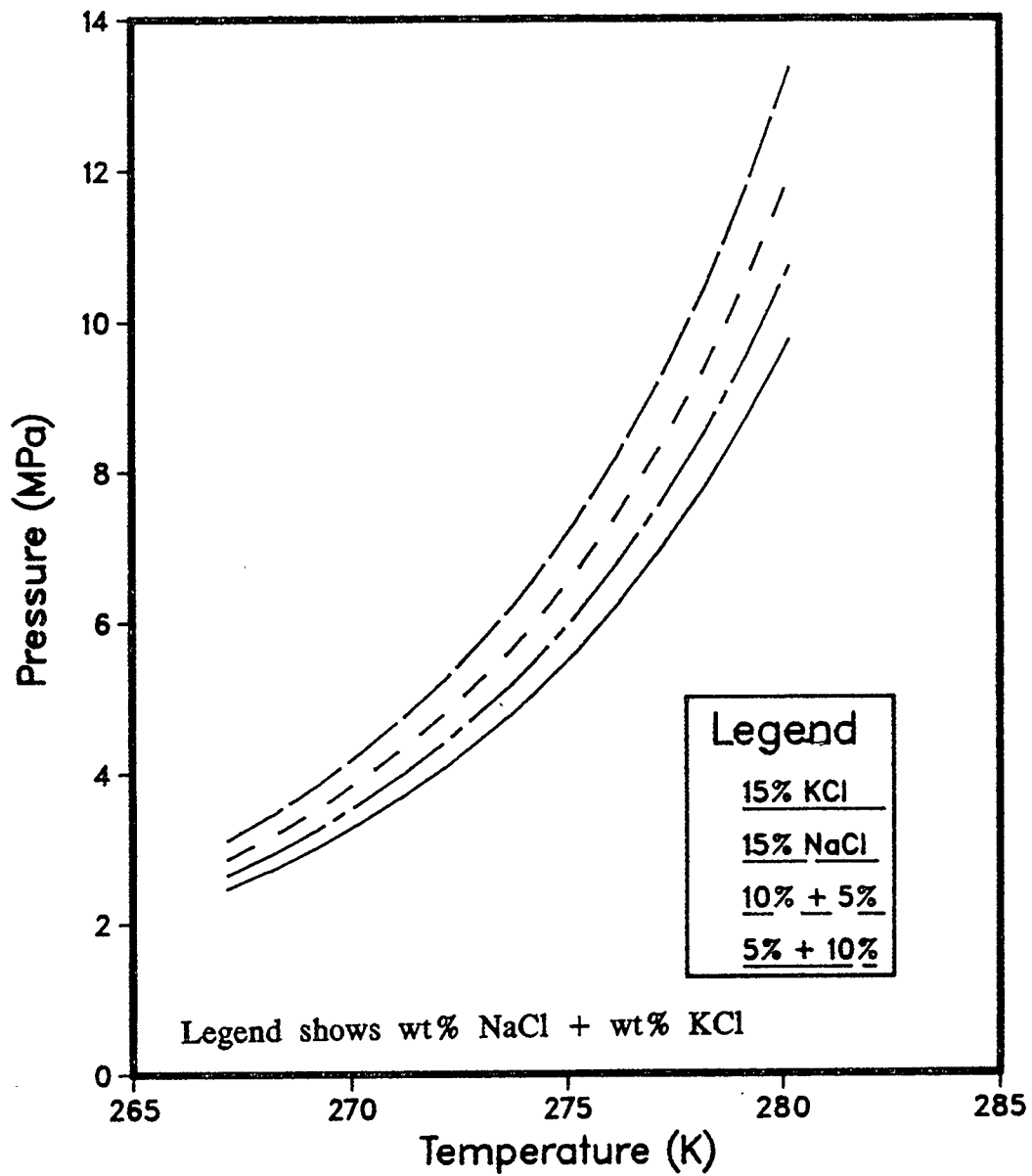
Figure 11: Calculated curves for sodium chloride and potassium chloride and their mixtures showing relative strengths on a weight-to-weight basis.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1   Conclusions

Experimental equilibrium data on incipient methane hydrate formation in aqueous solutions of NaCl and KCl and NaCl and $CaCl_2$ have been obtained. The maximum total ionic strength for the NaCl and KCl mixtures was 4.72 and that for the NaCl and $CaCl_2$ mixtures 3.90. Similar data were also obtained for a synthetic sea water consisting of eight electrolytes.

The experimental data were compared with predictions based on the method of Englezos and Bishnoi (1988). The method was able to predict the equilibrium pressures within 6.06% for the NaCl and KCl mixtures, 3.50% for the NaCl and $CaCl_2$ mixtures and 1.40% for synthetic sea water. The method generally over-estimated the equilibrium pressures. The hydrate predictions model (van der Waals and Platteeuw, 1959) is built into the method. Since various sets of fitted parameters are in use for the hydrate prediction model of van der Waals and Platteeuw (1959), the method of Englezos and Bishnoi (1988) would give different predictions with different sets of these parameters. This is not a short coming of the method, but that of the parameter values available for the van der Waals-Platteeuw model.

6.2   Recommendations

One of the assumptions made in the method of Englezos and Bishnoi (1988) is that the solubility of the hydrate forming gas in water is

negligible. It will thus be not applicable to highly soluble gases like carbon dioxide. It is recommended that experiments be carried out in the same equipment to obtain data for pure carbon dioxide. The prediction method should also be modified to be applicable to soluble gases.

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