Prediction of Gas Hydrate Formation Conditions in Aqueous Electrolyte Solutions

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Gas hydrates are solid clathrate compounds. They are formed by the enclosure of light nonpolar gases, such as natural gas components, in a lattice-like structure of water molecules. They have been extensively reviewed recently by Berecz and Balla-Achs (1983). Hydrates are known to occur naturally in vast quantities on ocean floors and in the permafrost regions of the world (Makogon, 1974, 1987). Majority of the thermodynamic studies on gas hydrates have focused on formation from pure water. The methods for predicting the formation conditions are based on the statistical thermodynamics model of van der Waals and Platteeuw (1959). An algorithm for the predictions was developed by Parrish and Prausnitz (1972), and subsequently improved by Ng and Robinson (1976), Holder et al. (1980), and John et al. (1985). When electrolytes or molecular species like methanol are present in the liquid water, the hydrate formation is inhibited. Inhibition of gas hydrate formation is of particular interest to the oil and gas industry. In the present work, only the studies on the effect of electrolytes are investigated. Makogon (1974) and Berecz and Balla-Achs (1983) discuss the inhibiting effects of various salts and classify them according to their inhibiting activities. Knox et al. (1961) investigated the seawater desalination process via propane hydrate formation. Recently Kubota et al. (1984) also studied the propane hydrate formation.

In both studies, data are reported on the formation from sodium chloride solutions. Roo et al. (1983) studied methane hydrate formation from NaCl solutions. Their experimental data were useful in examining the possibility of gas storage in the crust of the earth. Menten (1979) and Menten et al. (1981) reported experimental data on the cyclopropane hydrate formation conditions from water containing KCl or $CaCl_2$. In addition, they presented a predictive method for the calculation of the hydrate forming conditions in the single salt solutions. The method is based on calculating the activity of water by using freezing point depression data. This is the only available predictive method for the effect of single electrolytes on gas hydrate formation. In the present work, a computer implementable methodology is developed (Englezos, 1987) for the prediction of hydrate formation conditions in systems containing light hydrocarbon gases and aqueous solutions of single or mixed electrolytes. No adjustable parameters are needed in addition to those for the thermodynamic model for predictions from pure water and for the activity coefficient models for the salts in aqueous solutions, which are available from the literature.

Methodology

Equilibrium among the solid hydrate, the gas, and the liquid water solution may be represented by the following equation

$$\mu_w^H = \mu_w^{sl}. \tag{1}$$

In writing Eq. 1 the amount of water vapor present in the gas phase is considered negligible. In addition, it is assumed that the salts are present only in the liquid solution. Since the salts do not enter the hydrate lattice, the statistical thermodynamics model of van der Waals and Platteeuw (1959) is valid, and the chemical potential of water in the hydrate is given by the following equation

$$\mu_w^H = \mu_w^{MT} - RT\sum_1^2 \nu_i \ln\left(1 + \sum_1^{nc} c_{ij} f_j\right), \tag{2}$$

where c_{ij} are the Langmuir type constants, ν_i are the number of cavities of type i and f_j, are the fugacities of the various gas hydrate formers. The fugacities, f_j, are those calculated in the gas phase. Hence, the isofugacity criterion is implicitly incorporated. In the present work, the fugacities are calculated using the Trebble-Bishnoi equation of state (Trebble and Bishnoi, 1987). The chemical potential of water in the solution is given by

$$\mu_w^{sl} = \mu_w + RT\ln a_w, \tag{3}$$

where a_w is the activity of water. It is now assumed that the mole fractions of the dissolved light hydrocarbon gases are negligibly small, as is the case with methane, ethane and propane. The activity of water, a_w, is then calculated by using the activity of a dissolved salt and the Gibbs-Duhem equation as given later. The expression for the chemical potential of pure water, μ_w, is obtained from the correlation of Holder et al. (1980) and inserted in Eq. 3. The resulting expression and Eq. 2 are then substituted in Eq. 1 to obtain the following criterion for equilibrium

$$\frac{\Delta v_w}{R\,T}P + \phi(T) - \ln a_w - \sum_1^2 \nu_i \ln\left(1. + \sum_1^{nc} c_{ij} f_j\right) = 0. \qquad (4)$$

In the above equation, Δv_w is the volume difference between the empty hydrate and pure liquid water, and $\phi(T)$ is a temperature function obtained from the Holder's correlation. The constants, c_{ij}, are obtained from the correlation of Parrish and Prausnitz (1972).

Activity of Water, a_w

The activity of water in the liquid phase is calculated by assuming that it is influenced only by the presence of electrolytes. A number of models are available for calculating the activity of single salts in aqueous solutions, and recently an elegant method has been made available to account for the overall nonideal effects of salts in mixed salt solutions. The models have been used to develop (Zemaitis, 1986; Pitzer and Mayorga, 1973; Patwardhan and Kumar, 1986) expressions for the activity of water.

Single Electrolyte Solutions

For an aqueous solution of a single electrolyte by integrating the Gibbs-Duhem equation (Lewis and Randall, 1961) the following expression for the activity of water, a_w can be obtained

$$\ln a_w = -\frac{36\,I}{1{,}000\,z_+z_-} - \frac{36}{1{,}000\,z_+z_-}\int_1^{\gamma_\pm} I\,dln\gamma_\pm \qquad (5)$$

where I is the ionic strength and z_+, z_- are the changes of the ions. An alternate expression, given below, for a_w is obtained by expressing $\gamma_\pm$ in terms of the reduced activity coefficient Γ (Meissner and Kusik, 1972)

$$\ln a_w = -\frac{36\,I}{1{,}000\,z_+z_-} - \frac{36}{1{,}000}\int_1^{\Gamma} I\,dln\Gamma \qquad (6)$$

Equations 5 and 6 are general and can be used with any of the available activity coefficient models for electrolyte solutions. In the present work, Pitzer's and Meissner's models were used. When using Meissner's activity coefficient model, Eq. 6 is integrated numerically by the Simpson's composite rule (Burden et al., 1981). When the Pitzer's activity coefficient model is used, Eq. 5 takes the following form after integration

$$\ln a_w = -\frac{18\,\nu m}{1{,}000}(1 + z_+z_-\theta_1 + m\,\theta_2 + m^2\beta_2) \qquad (7)$$

where

$$\theta_1 = -\frac{A_\phi I^{0.5}}{1 + 1.2I^{0.5}} \qquad (8)$$

$$\theta_2 = \beta_o + \beta_1 \exp(-2I^{0.5}) \qquad (9)$$

A_ϕ is the Debye-Huckel coefficient, ν is the stoichiometric number of moles of ions in one mole of salt and β_o, β_1, β_2 are the adjustable parameters for Pitzer's activity coefficient model.

Mixed Electrolyte Solutions

Patwardhan and Kumar (1986) introduced the concept of overall reduced activity coefficient, Γ^*, for handling mixed electrolyte solutions, and derived the following predictive equation for the activity of water in such solutions,

$$\ln a_w = \sum_1^{ns}\left(\frac{m_k}{m_k^o}\right)\ln a^o_{w,k}. \qquad (10)$$

In Eq. 10, m_k is the modality of electrolyte k in the mixed solution, m_k^o is the molality of a solution containing only electrolyte k, which has the same ionic strength as that of the mixed solution and $a^o_{w,k}$ is the activity of water in the single salt solution. The equation does not contain any additional adjustable parameters. It is valid over the entire concentration region encountered in practice and has a predictive accuracy of 2%. In the present work, the activity of water in the liquid solution is calculated using Eq. 10. The activities of water in single salt solutions, $a^o_{w,k}$ required in the equation are calculated from Eq. 6 or 7.

Results and Discussion

At a given temperature, the incipient hydrate formation pressure is calculated by solving Eq. 4 which is nonlinear in pressure. The various parameters required in the equation are taken from Parrish and Prausnitz (1972). In Figures 1–3, predictions based on the above methodology are shown along with experimental data. The activity of water was calculated using Eq. 7 which is based on Pitzer's model. The calculations were also done with Eq. 6. It was, however, found that the calculations based on Pitzer's model gave overall smaller deviations from the experimental data.

Figure 1 shows the experimental and calculated inhibiting effects of sodium chloride on methane gas hydrate formation. As seen, the predictions are in excellent agreement with the experimental data. The maximum deviation of the predictions is 6.2% and the percent root mean square deviation (RMSD) is 3.3. The strong inhibiting effect of the electrolyte can be seen by comparing the hydrate formation pressures with those at zero salt concentration at any temperature. The pressures differ by almost 2 MPa at 273.3 K for the 2.2763 m solution. The profound effect of salts is seen mathematically from Eq. 4 where a nonlinear term, $RT\,ln\,a_w$, is added to the equation describing the formation from pure water. It was noticed during the calculations that the pressure predictions are very sensitive to the calculated values of the activities of water. Figure 2 shows the inhibiting effect of sodium chloride on another well studied clathrate, the propane hydrate. The maximum percent deviation between the predicted and the experimental values is 5.9 and the percent RMSD is 3.0. In addition, the method was used to predict the inhibiting effect of potassium chloride and calcium chloride on cyclopropane gas hydrate formation. The predicted values and the experimental data are in very good agreement and are shown in Figure 3. Cyclopropane forms structure II hydrates below 274.61 K and structure I above this temperature without the presence of the salts. This behavior can also be seen from the predictions at 0.0 M by the change in the slope of the curve. Menten also reported that structure II forms from 0.1 M calcium chloride solution at 273.71 K. The prediction at 273.71 K for the solution also gave the formation of structure II hydrate.

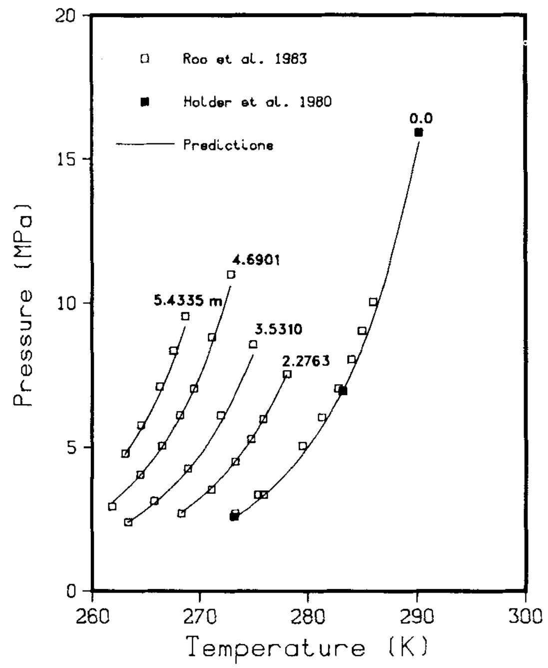

Figure 1. Experimental and predicted pressures for gas hydrate formation from CH_4 and aqueous sodium chloride solution.

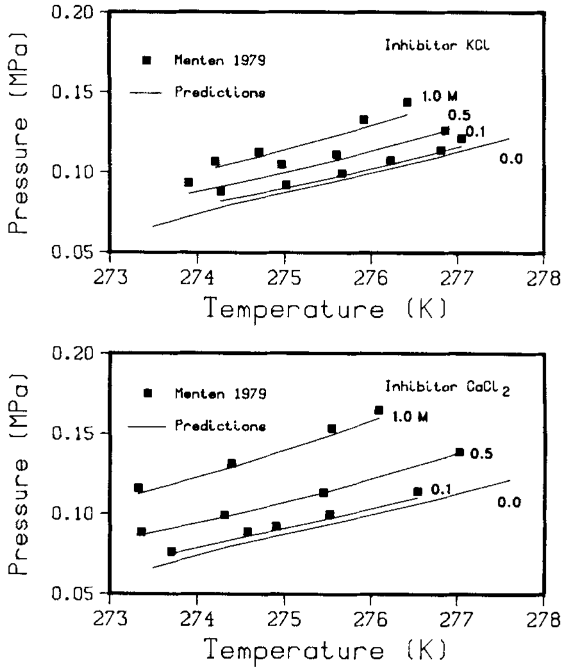

Figure 3. Experimental and predicted pressures for cyclopropane gas hydrate formation from aqueous solutions of potassium chloride and calcium chloride.

In Figure 3, the maximum percent deviations are 7.2 and 3.5 for the potassium chloride and the calcium chloride solutions respectively. In addition, the percent RMSD's are 4.1 and 2.4.

Finally, the proposed algorithm was used to predict the methane gas hydrate formation pressures from seawater and from aqueous mixed salt solutions of NaCl, KCl, $CaCl_2$ and NaOH. Seawater is treated as a multicomponent aqueous mixture of electrolytes. An artificial seawater recipe has been taken from Leyendekkers (1976). The activity of water was calculated from Eq. 10. The predictions are shown in Figure 4. The presence of the various salts in seawater affects the gas hydrate for-

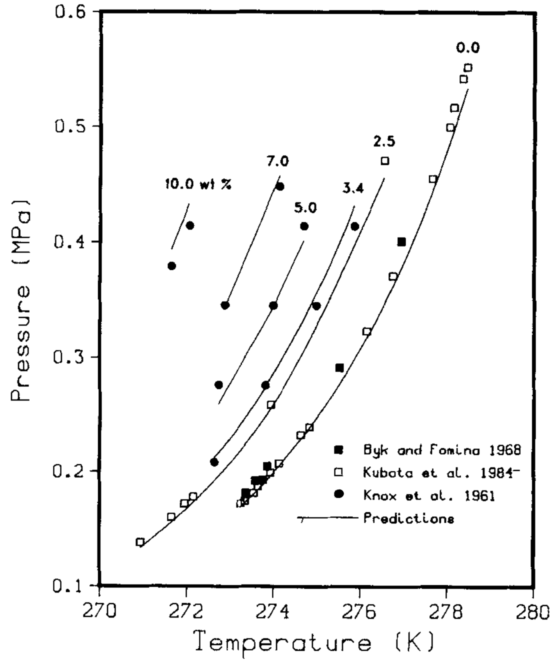

Figure 2. Experimental and predicted pressures for gas hydrate formation from C_3H_8 and aqueous sodium chloride solution.

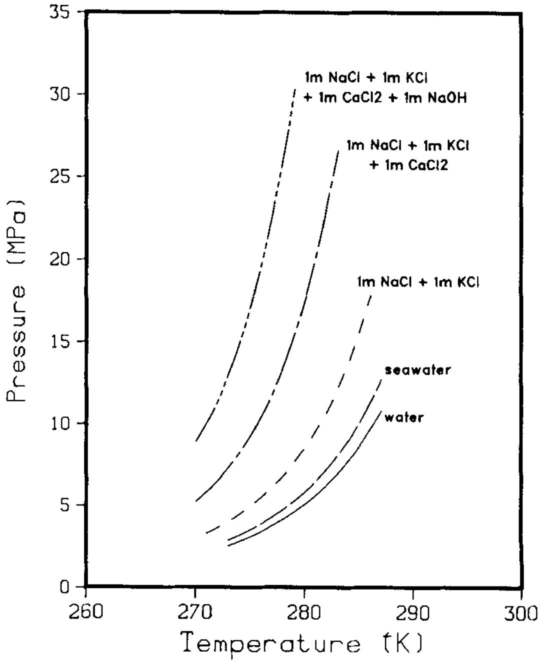

Figure 4. Predicted methane gas hydrate formation pressures from aqueous solutions of mixed electrolytes.

mation and in general the temperature depression at a given pressure is about 1 K. The strong inhibiting effect of $CaCl_2$ is also clearly seen from the figure. The addition of $1m$ $CaCl_2$ in a solution of $1m$ NaCl and $1m$ KCl doubles the depression of the hydrate formation temperatures. Makogon (1974) rated calcium chloride as one of the strongest inhibitors, but it is not used by the industry because of its strong corrosive action. Sodium hydroxide also has a strong inhibiting effect. No experimental data are available for hydrate formation in aqueous mixed electrolyte solutions. Hence, in order to test the reliability of the predictions, experimental data on such systems are needed.

Conclusions

From the above analysis, it is concluded that the proposed methodology provides a valuable tool for the investigation of the gas hydrate formation conditions in environments such as sea or ground water. In addition, it can facilitate feasibility studies for water desalination, gas storage via gas hydrate formation, and natural gas recovery. Finally, since the modeling of hydrate formation and decomposition kinetics require an accurate knowledge of the equilibrium formation conditions (Kim et al., 1987; Englezos et al., 1987a, b), the proposed methodology provides a valuable tool in that direction.

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Notation

a = activity
A_ϕ = Debye-Huckel coefficient
c = Langmuir constant, 1/Pa
f = fugacity, Pa
I = ionic strength
m = molality
M = molarity
nc = number of gas hydrate formers
ns = number of electrolytes in a mixed solution
P = pressure, Pa
R = universal gas constant, J/mol · K
T = temperature, K
v = molar volume, m^3/mol
z = ion charge

Greek letters

γ = ion activity coefficient
Γ = reduced activity coefficient
Γ^* = overall reduced activity coefficient
μ = chemical potential, J/mol
ν = stoichiometric number of ions in one mole of salt
ν_i = number of cavities of type i, $i = 1, 2$

Superscripts

H = hydrate
MT = empty hydrate
o = pure salt property at same I as that of mixture
sl = solution

Subscripts

k = electrolyte
w = water
wt = weight

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