

## **A Generalized Correlation for Predicting Methane Hydrate Equilibrium Data in Pure Water and Aqueous Solutions of Chloride Salts at pressure up to 500 MPa**

**Azeez G Aregbe<sup>1,2\*</sup>**

<sup>1</sup>Department of Petroleum and Gas Engineering, University of Lagos, Lagos, Nigeria

<sup>2</sup>College of Petroleum Engineering, China University of Petroleum (East China), China

---

### **ABSTRACT**

*A generalized empirical correlation for predicting methane hydrate equilibrium data in pure water and aqueous solutions of single sodium chloride, potassium chloride, calcium chloride and magnesium chloride salts is developed in this work. Contrary to the general thermodynamic approach which involves rigorous and complex computations, an easy-to-use prediction method is developed by regressing several experimental data for methane hydrate formation in pure water and aqueous salt solutions. The predictions from the generalized correlation show satisfactory agreements with all the experimental data reported in the literature and are more accurate than the results from the common hydrate prediction programs.*

**Keywords:** Methane hydrate, Equilibrium data, Chloride salts, Electrolytes, Pure water, High pressure, High salinity

---

### **INTRODUCTION**

Hydrates are crystalline compounds formed from water molecules and volatile compounds existing at high pressure and low temperature conditions. The water molecules form different types of cavities such as pentagonal dodecahedron ( $5^{12}$ ) and are linked together by hydrogen bonding. These cavities are usually occupied by guest compounds having molecular diameters that are smaller than those of the cavities. The guest compounds improve the stability of the hydrate crystal lattice. The common hydrate formers are methane, carbon dioxide, ethane, propane, n-butane, i-butane, nitrogen and hydrogen sulfide. Hydrates are mainly grouped into sI, sII and sH crystal structures. They are stable at temperatures above the freezing point of water to about 300 K and at pressures higher than 0.6 MPa [1,2]. The formation conditions of hydrate are influenced by the presence of heavier hydrocarbon, phase compositions and salinity of the system. Hydrate formation and dissociation can cause severe problems in oil and gas exploration, transportation and processing. Hydrate-related problems can lead to equipment blockage and affect the safety/integrity of deep water facilities. In order to solve these hydrate-related problems, techniques/methods such as dehydration, the use of electrolytes (salts) and inhibitors (methanol) are commonly employed [3,4]. The applications of these methods require accurate hydrate equilibrium data, i.e., temperature and pressure. Error and uncertainty in these data will affect the efficiency of any of the techniques. Therefore, it is vital to ensure that the hydrate equilibrium data are as accurate and precise as possible.

Reliable prediction techniques and accurate phase equilibrium data are important in the design of deep water hydrocarbon facilities due to the conditions of the environments. Mohammadi et al. [4] discovered that electrolytes such as sodium chloride can reduce hydrate equilibrium conditions due to the strong electrostatic forces that are created when salt dissolves in water. The ionization of salt in water distorts the hydrogen bonding that exists between the molecules of water and hydrate former. The presence of ions in the system inhibits the formation of hydrate. Thus, aqueous solutions of salts are used as electrolytes to suppress hydrate formation temperature [4,5]. The amount and type of salt dissolve in water affect the degree of temperature reduction at any given pressure. Hu et al. [6] stated that

there is uncertainty on how hydrate formation occurs in systems containing saturated salt solutions. Hydrate formation and salt precipitation will occur simultaneously in systems containing saturated salt solutions.

Therefore, it is important to extensively investigate salt precipitation and hydrate formation for these types of systems. Hydrate formation in salt solutions is important in the exploration and development deep water reserves such as the Gulf of Mexico. The salinity, temperature and pressure conditions of these environments significantly influence the formation of hydrates. In addition, aqueous solutions of salts are mixed with drilling fluid in most drilling processes. These salts are used to reduce the freezing point of water and control hydrate formation in the wellbore [7-9]. There are also few experimental data and correlations in the literature on hydrate formation conditions in high salinity systems and at extremely high pressure. This is because of the difficulties associated with conducting research under such severe conditions. Thus, reliable prediction techniques must be developed to estimate accurate values of hydrate equilibrium data in different salt solutions/high salinities and at very high pressure.

Experimental data and thermodynamic models for predicting hydrate equilibrium data in pure water and low to moderate salinity systems have been extensively determined. Englezos and Bishnoi [1] conducted experiments to determine ethane hydrate formation conditions in systems containing sodium chloride, potassium chloride, calcium chloride and potassium bromide salts. Their experimental results showed satisfactory agreement with the theoretical predictions. Dholabhai et al. [3] performed experiments to investigate the three-phase equilibrium data of carbon dioxide hydrate in the presence of electrolytes and methanol. They reported that in the presence of methanol, sodium chloride acts as a stronger inhibitor than calcium chloride in the same solvent. Holzammer et al. [10] conducted experiments to study carbon dioxide hydrate equilibrium properties in the presence of sodium chloride using Raman spectroscopy. They concluded that thermodynamic inhibitors do not only alter the hydrate equilibrium conditions but also decrease the amount of hydrate crystals formed in the system. Parrish and Prausnitz [11] combined van der Waals-Platteeuw solid theory and the Kihara spherical-core potential function to predict hydrate dissociation data. The Kihara parameters and thermodynamic properties of different hydrate formers. They also compared experimental results and predictions from their model. Good agreement was recorded for equilibrium data of hydrates formed by gas mixtures. Ng and Robinson [12] modified Parrish and Prausnitz model. They combined the improved model with the Clapeyron equation and Peng-Robinson Eos to predict fluid properties for gas mixtures (methane – propane and methane – isobutane). They used the calculated fluid properties to estimate hydrate equilibrium data for the systems and recorded minimal difference between predicted and experimental results. John et al. [13] modified the solid theory of van der Waals and Platteeuw by considering the effects of spherical asymmetric. They also calculated the deviation of Langmuir constants from ideality by using a corresponding states correlation. The Kihara parameters were also determined from hydrate equilibrium data and the results showed satisfactory agreement with those obtained from the viral coefficient data. The developed model can be used to predict hydrate equilibria of most gas mixtures except hydrogen rich gas mixtures. Chen and Guo [14] proposed a two-step hydrate formation mechanism which comprises hydrate formation by a quasi-chemical reaction process and linking of gas molecules in the hydrate cavities by adsorption process. The proposed mechanism was used to develop a prediction model for hydrate formation. The developed model was used to predict hydrate equilibrium data for different hydrate formers. They concluded that the proposed model is a good predictive tool for estimating the hydrate equilibrium data of pure gases and gas mixtures. Generally, the thermodynamic models are rigorous and complex. Different variables such as water activity, cell potential and Langmuir constant must be accurately estimated to ensure reasonable predictions from these models. The computation of these variables is tedious.

Another method for predicting hydrate equilibrium data is the use of empirical correlations and there are several correlations in the literature. The empirical correlations are used to estimate hydrate formation suppression temperature caused by the presence of inhibitors and/or electrolytes. The first empirical correlation was developed by Hammerschmidt [15] to estimate the suppression temperature of hydrate caused by aqueous solutions of inhibitors. The principle of freezing point depression was used to develop the correlation shown in equation 1. The variable  $\Delta T$  is the temperature depression ( $^{\circ}\text{C}$ ),  $M$  is the molar mass (g/mol),  $W$  is the concentration (wt %) of the inhibitor in the aqueous solution and  $K_H$  is a constant equivalent to 1297. The correlation can only be used for methanol/ethylene glycol concentrations less than 30 wt % and 20 wt % for other glycols.

$$\Delta T = \frac{K_H W}{M(100 - W)} \quad (1)$$

In deep water drilling processes, salts solutions are blended with the drilling mud to inhibit the formation of hydrate and reduce the freezing point of water. The most widely used salts are sodium, potassium, calcium and magnesium chlorides salts. Yousif and Young [16] developed a correlation for calculating the hydrate suppression temperature in

the presence of aqueous solutions of salts and glycerol. The correlation is shown in equation 2 and  $\Delta T$  is the hydrate temperature suppression ( $^{\circ}\text{F}$ ) and 'x' is the total mole fraction of the inhibitors in the aqueous solution, i.e., 0.2. The value of 'x' depends on the apparent molecular weight and degree of ionization of the inhibitors in the aqueous solution.

$$\Delta T = 112.3x + 2011.6x^2 - 6505.0x^3 \quad (2)$$

Mohammadi and Tohidi [17] proposed an improved Yousif and Young's [16] correlation as shown in equation 3. In the correlation,  $X_{\text{solute}}$  is the mole fraction of the inhibitor,  $W_i$  is the weight percent of the salt 'i' in aqueous solution, and a, b,  $c_1$ ,  $c_2$  and  $c_3$  are constants. But the proposed correlation ignores the effects of pressure on hydrate depression temperature which can lead to large error for high pressure systems.

$$\Delta T = -a \left[ \ln(1 - X_{\text{solute}}) + bX_{\text{solute}}^2 + \sum (c_{1,i} W_i + c_{2,i} W_i^2 + c_{3,i} W_i^3) \right] \quad (3)$$

Hu et al. [7] proposed an empirical correlation referred to as Hu-Lee-Sum correlation for hydrate suppression temperature in aqueous solutions of single salts. The proposed correlation is shown in equation 4 and  $\Delta T$  ( $^{\circ}\text{C}$ ) is the hydrate suppression temperature,  $T_0$  ( $^{\circ}\text{C}$ ) and  $T$  ( $^{\circ}\text{C}$ ) are the hydrate dissociation temperatures in fresh water and in aqueous solution of single salt respectively,  $a_w$  is the water activity,  $\beta$  is a constant which depends on the type of hydrate formers,  $x_i$  is the salt concentration and  $X$  is the effective mole fraction.

$$\frac{\Delta T}{T_0 T} = \beta \ln a_w(x_i, T) = C_1 X + C_2 X^2 + C_3 X^3 \quad (4)$$

Generally, the thermodynamic models are too complex and require rigorous computations. In addition, the correlations available in the literature are restricted to certain conditions and ignored the effects of pressure on hydrate formation condition. The predictions from the correlations will give large errors for high pressure systems. Therefore, it is vital to develop a simple and reliable method for accurate prediction of hydrate equilibrium data in aqueous solutions of electrolytes such as chloride salts. In this work, a generalized correlation is developed for prediction of methane hydrate equilibrium data in pure water and aqueous solutions of single NaCl, KCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> at pressure up to 500 MPa.

## METHODOLOGY

Thermodynamic models are commonly used to predict hydrate equilibrium data for different systems. In developing these models, several assumptions are made. It is usually assumed that the chemical potential of each component in a given system is uniform. And at constant temperature the fugacity of each component in the system will not be uniform [4,5,11]. These assumptions are used to develop thermodynamic models and combined with the specific equation of state selected for the given system. In contrast to the statistical thermodynamic approach, regression analysis is used to develop the empirical correlation for predicting methane hydrate equilibrium data. Regression analysis is a simple but reliable modeling technique for predicting the relationships that exist between two or more variables. In this work, a generalized correlation was developed for predicting methane hydrate equilibrium data in pure water, and aqueous solutions of single sodium chloride, potassium chloride, calcium chloride and magnesium chloride salts. Several experimental data in the literature were used to develop the correlation [1,3,7,18-21]. The concentration range of the electrolytes is 0.5 wt %-28 wt % for NaCl and CaCl<sub>2</sub>, 0.5 wt %-36 wt % for KCl and 0.5 wt %-26 wt % for MgCl<sub>2</sub>. The temperature range is 273 K-320.61 K and the pressure range is 1 MPa-500 MPa. The generalized correlation developed in this work is shown in equation 5.

$$P_{\text{eq}} = A_x [T_{\text{eq}}^5] + B_x [T_{\text{eq}}^4] + C_x [T_{\text{eq}}^3] + D_x [T_{\text{eq}}^2] + E_x [T_{\text{eq}}] + F_x \quad (5)$$

The parameters  $P_{\text{eq}}$  (MPa) and  $T_{\text{eq}}$  (K) are the hydrate equilibrium pressure and temperature respectively. The correlation variables are  $A_x$  (Mpa/K<sup>5</sup>),  $B_x$  (Mpa/K<sup>4</sup>),  $C_x$  (Mpa/k<sup>3</sup>),  $D_x$  (Mpa/k<sup>2</sup>),  $E_x$  (Mpa/k) and  $F_x$  (Mpa) for dimensional consistency. These variables were studied by considering the type/amount of salts in solution and specific trends were observed. For example,  $A_x$  has different values when 10 wt % and 20 wt % sodium chloride salt are dissolved separately in water. Also, the type of salts dissolved in solution affects the values of these constants. Based on the properties of these regression variables, the generalized correlation was simplified for pure water and aqueous solutions of the chloride salts considered in this work. They are affected by the amount and type of salts dissolved in water and these characteristics were used as bases to develop equations for these regression coefficients. The developed equations can be used to approximate their values for different type/amount of chloride salts. The values of the variable  $A_x$  (Mpa/K<sup>5</sup>)

can be approximated by using equation 6.

$$A_x = \sum_{n=0}^6 A_n x^n = A_0 + A_1 x + A_2 x^2 + A_3 x^3 + A_4 x^4 + A_5 x^5 + A_6 x^6 \quad (6)$$

The constants  $A_0, A_1, A_2, A_3, A_4, A_5$  and  $A_6$  depend on the type and amount of salts dissolved in water, and 'x' is the weight fraction of salt in solution. The constants  $A_0$ - $A_6$  have the same units as  $A_x$  (MPa/k<sup>5</sup>). Also, the variable  $B_x$  (MPa/K<sup>4</sup>) can be approximated by using equation 7.

$$B_x = \sum_{n=0}^6 B_n x^n \quad (7)$$

The constants  $B_0$ - $B_6$  have the same units as  $B_x$  (MPa/k<sup>4</sup>) and also depend on the amount/type of salt dissolved in water. Similarly, for  $C_x$  (MPa/k<sup>3</sup>),  $D_x$  (MPa/k<sup>2</sup>),  $E_x$  (MPa/k) and  $F_x$  (MPa), the expressions in equations 8-11 can be used to estimate their values.

$$C_x = \sum_{n=0}^6 C_n x^n \quad (8)$$

$$D_x = \sum_{n=0}^6 D_n x^n \quad (9)$$

$$F_x = \sum_{n=0}^6 F_n x^n \quad (10)$$

$$F_x = \sum_{n=0}^6 F_n x^n \quad (11)$$

The constants  $C_0$ - $C_6$  (MPa/k<sup>3</sup>),  $D_0$ - $D_6$  (MPa/K<sup>2</sup>),  $E_0$ - $E_6$  (MPa/K) and  $F_0$ - $F_6$  (MPa) in equations 8–11 have the same characteristics as those in equations 6 and 7.

## CORRELATIONS FORMULATION

### Methane hydrate equilibrium data in pure water

In the presence of pure water system, the generalized correlation in equation 5 was simplified by using several experimental data reported for methane hydrate formation in pure water [8,17,22-25]. The simplified correlation in equation 12 was derived for methane hydrate equilibrium data in pure water systems.

$$P_{eq} = A [T_{eq}^5] + B [T_{eq}^4] - C [T_{eq}^3] + D [T_{eq}^2] - E [T_{eq}] + F \quad (12)$$

The variables  $P_{eq}$  (MPa) and  $T_{eq}$  (K) are the methane hydrate equilibrium pressure and temperature in pure water respectively, and A, B, C, D, E, and F are constants with definite values. This is because in pure water system, there are no dissolved salts or ions in solution. As a result, these constants are definite and independent on any variable. The temperature and pressure ranges considered in this analysis are 273 K-320.61 K and 1 MPa-500 MPa, respectively.

### Methane hydrate equilibrium data in aqueous solutions of chloride salts

The correlation for methane hydrate formation conditions in aqueous solutions of sodium, potassium, calcium and magnesium chloride salts was developed by considering relevant experimental data published in the literature [2,3,5,9,18,19,21]. The generalized correlation in equation 5 was also simplified to derive the empirical correlation in equation 13.

$$P_{eq} = B_x [T_{eq}^4] - C_x [T_{eq}^3] + D_x [T_{eq}^2] - E_x [T_{eq}] + F_x \quad (13)$$

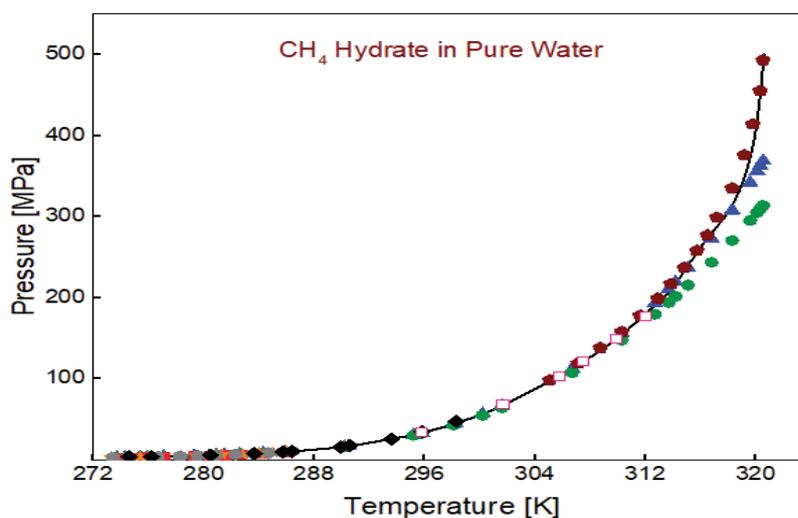
The variables  $P_{eq}$  (MPa) and  $T_{eq}$  (K) are the methane hydrate equilibrium pressure and temperature in pure water respectively, and the coefficients are  $A_x$  (Mpa/K<sup>5</sup>),  $B_x$  (MPa/K<sup>4</sup>),  $C_x$  (Mpa/k<sup>3</sup>),  $D_x$  (Mpa/k<sup>2</sup>),  $E_x$  (Mpa/k) and  $F_x$  (Mpa). The concentration ranges of NaCl and CaCl<sub>2</sub> salts considered are 0.5 wt %-28 wt %, KCl salt is 0.5 wt %-36 wt % and MgCl<sub>2</sub> salt is 0.5 wt %-26 wt %. The temperature and pressure ranges considered are 273 K-300 K and 1 MPa-200 MPa, respectively.

## RESULTS AND DISCUSSION

The developed correlations were validated using experimental data for methane hydrate equilibrium data in pure water and aqueous solutions of chloride salts. The experimental data used for validation are different from those used to develop the correlations [2,4,6,17,26-28]. The formation conditions of methane hydrate in pure water are shown in Figure 1 and those in aqueous solutions of the chloride salts are shown in Figures 2-5. In these figures, it is clearly shown that hydrate formation pressure is directly proportional to the formation temperature at any given condition, i.e., increase in temperature leads to a corresponding increase in pressure and vice versa. Also, the equilibrium conditions of hydrate are affected by the type/amount of salts dissolved in water. For example, hydrate equilibrium data in 12 wt % sodium chloride solution are higher than those in 5 wt % sodium chloride solution. In addition, hydrate equilibrium data in 10 wt % potassium chloride solution are different from that in 10 wt % calcium chloride or magnesium chloride solution. This is because the chloride salts have different degrees of ionization and chemical activities in water.

Methane hydrate equilibrium data in pure water system are shown in Figure 1. The predictions from the correlation developed in this work are compared with different experimental data and data from hydrate prediction programs (Multiflash and CSMGem). The correlation developed in this work gives a better prediction and also fits very well with the experimental data reported in the literature. At high temperatures, i.e.,  $\geq 300$  K and high pressures, i.e.,  $\geq 200$  MPa, the prediction errors of Multi flash and CSM Gem increase and their predicted results deviate from the available experimental data. This shows that the developed correlation is an excellent prediction tool for methane hydrate equilibrium data in pure water system at low, moderate and high-pressure systems. This is a simple but reliable alternative in situations/conditions where experimental data are not available or difficult to obtain (Figure 1).

The inhibitive power of sodium chloride salt on methane hydrate equilibrium data is shown in Figure 2. The results from the correlation developed in this work are compared with the methane hydrate experimental data reported in the literature: 5 wt% NaCl [4] and 12 & 23 wt% NaCl [6], and data from hydrate prediction programs: 5 & 12 wt% NaCl [29] and 12 & 23 wt% NaCl [30]. It is clearly shown that the predictions from this work fit with the experimental data and are better than those from the hydrate prediction programs. These prediction errors from these programs increase with increase in salt concentration, temperature and pressure of the system. The prediction error from CSM Gem [29] is more than that from Multi flash [30]. Methane hydrate equilibrium data in aqueous solutions of potassium chloride are shown in Figure 3. The predicted data from the correlation developed in this work are compared with experimental data: 5 wt% & 10 wt% KCl [4], and data from hydrate prediction programs: 10 wt% & 20 wt% KCl [30] and 5 wt%, 10 wt% & 20 wt% KCl [29]. There is a satisfactory agreement between the predictions from the correlation developed in this work and experimental data of methane hydrate equilibrium conditions in presence potassium chloride solution. The predicted results in this work are also more accurate than those from Multiflash [30] and CSMGem [29]. The prediction error of CSMGem increases with increase in the salt concentration and at salt concentration  $\geq 20$  wt%, CSM Gem gave the largest error when compared with Multi flash and the correlation developed in this work. Also,



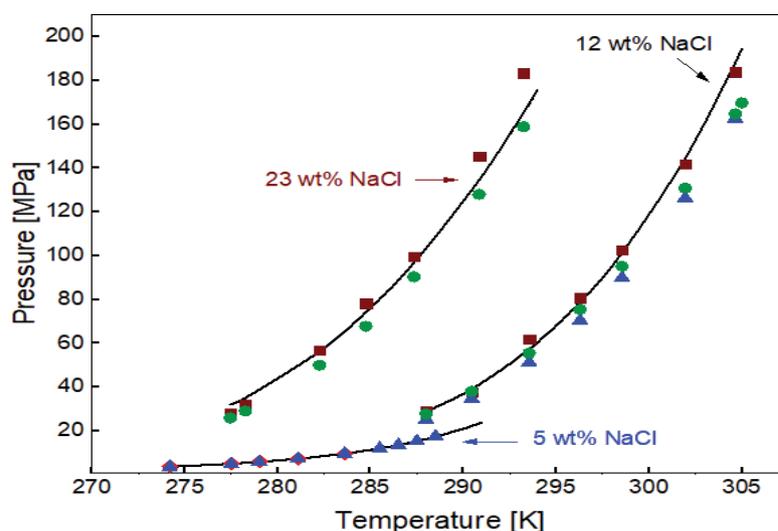
**Figure 1:** Methane hydrate equilibrium data in pure water system. Experimental data for CH<sub>4</sub> hydrate equilibrium data: rectangle – red [22], star – yellow [27], heptagon – ash [26], pentagon – brown [28], rectangle – white [8], rhombus – black [17], circle – green [30] and triangle – blue [29]. This work (curve - black)

for Multiflash, the prediction error increases more at salt concentrations  $\geq 20$  wt% but gave more accurate prediction than CSMGem. It can be inferred that the correlation developed in this work is also a good prediction tool for methane hydrate equilibrium data in aqueous solution of potassium chloride salts. Methane hydrate formation conditions in aqueous solution of calcium chloride are shown in Figure 4. The predictions in this work are compared with different experimental data: 5 wt%  $\text{CaCl}_2$  [4], 17.05 wt%  $\text{CaCl}_2$  [2] and 20 wt%  $\text{CaCl}_2$  [9], and data from hydrate prediction programs: 5 wt% & 17.05 wt%  $\text{CaCl}_2$  [29] and 17.05 wt% & 20 wt%  $\text{CaCl}_2$  [30] (Figures 2 and 3).

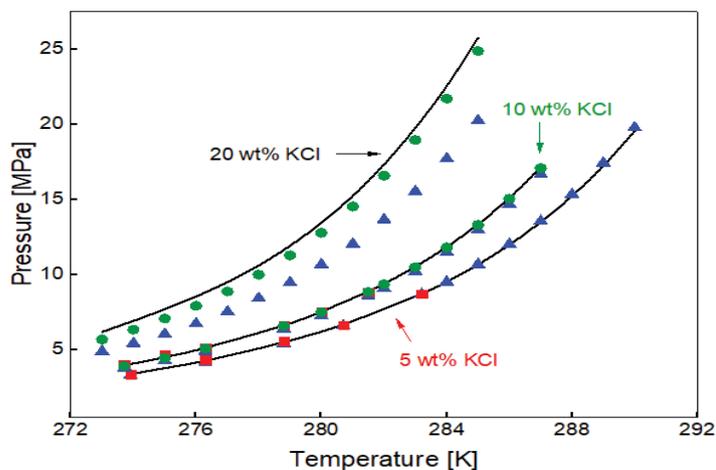
There was good agreement between the predictions in this work and experimental data in the literature. The predictions are better than those from the hydrate prediction program and also more accurate at higher salt concentrations and pressure. The prediction error from CSMGem is higher than that of Multiflash. Also, the predictions from these programs deviate from experimental data at high salt concentration and extremely high pressure. The equilibrium data of methane hydrate in aqueous solutions of magnesium chloride are plotted in Figure 5. The results from the correlation developed in this work are also compared with experimental data: 5 wt%, 10 wt% & 15 wt%  $\text{MgCl}_2$  [2] and 20 wt%  $\text{MgCl}_2$  [9] and predicted data from hydrate prediction programs: 5 wt%, 10 wt%, 15 wt% & 20 wt%  $\text{MgCl}_2$  [30]. CSM Gem cannot be used to predict hydrate formation conditions in the presence of magnesium chloride salts, therefore it was not considered in this analysis. The predicted data in this work are in excellent agreement with the experimental results and more accurate than the predictions from Multi flash at higher salt concentrations and pressure as high as 200 MPa. Prediction error from Multi flash increases with increase in salt concentration and pressure of the system. In general, the correlation developed in this work is a good prediction tool for methane hydrate equilibrium data in pure water and aqueous solutions of the chloride salts considered in this work. This is also reflected in the overall AADP (%) shown in Table 1. The overall AADP (%) for CSM Gem, Multi flash and the correlation developed in this work are 16.51 %, 7.44 % and 4.04%, respectively. The overall AADP (%) value of the predictions from the developed correlation is the lowest and the best among the three prediction tools Therefore, the developed correlation is a simple but accurate prediction tool for methane hydrate formation conditions in pure water and aqueous solutions of single sodium chloride, potassium chloride, calcium chloride and magnesium chloride salts (Figures 4 and 5) (Table 1).

The absolute average deviations of the hydrate equilibrium pressure (AADP). Percentage is calculated by using the formula in equation 14. In the equation,  $N_p$  is the number of data points,  $P_{\text{cal}}$  (MPa) is the equilibrium pressure calculated using either CSM Gem, Multi flash or the developed correlation and  $P_{\text{exp}}$  (MPa) is the equilibrium pressure determined experimentally as reported in the literature.

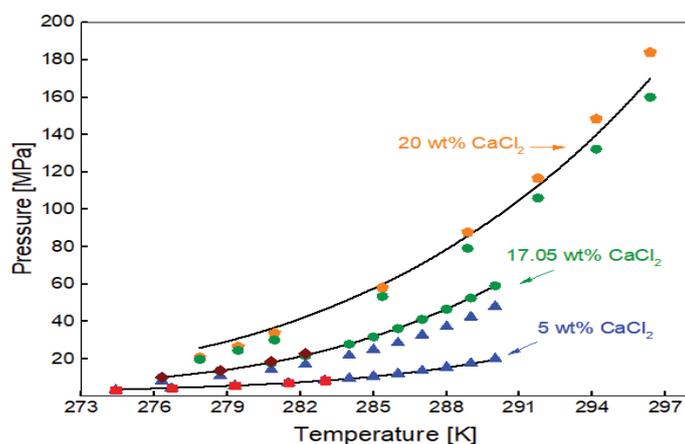
$$\text{AADP}(\%) = \frac{1}{N_p} \sum_{i=1}^{N_p} \left[ \left| \frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}} \right| \right] \times 100 \quad (14)$$



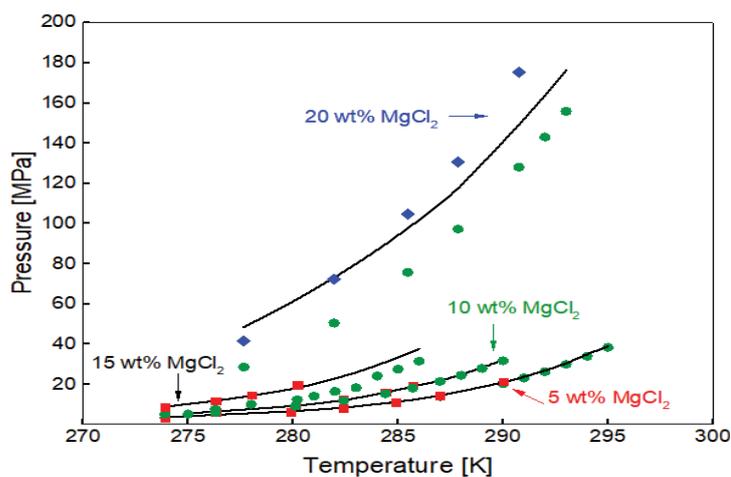
**Figure 2:** Methane hydrate equilibrium data in aqueous solutions of sodium chloride. Experimental data for  $\text{CH}_4$  hydrate equilibrium data: rectangle – brown [6] and rhombus – red [4]. Data from hydrate prediction programs: circle – green [30] and triangle - blue [29]. This work (curve - black)



**Figure 3:** Methane hydrate equilibrium data in aqueous solutions of potassium chloride. Experimental data for  $\text{CH}_4$  hydrate equilibrium data: rectangle – red [4]. Data from hydrate prediction programs: circle – green [30] and triangle - blue [29]. This work (curve - black)



**Figure 4:** Methane hydrate equilibrium data in aqueous solutions of calcium chloride. Experimental data for  $\text{CH}_4$  hydrate equilibrium data: rectangle – red [4], rhombus – brown [2], pentagon – yellow [9]. Data from hydrate prediction programs: circle – green [30] and triangle - blue [29]. This work (curve - black)



**Figure 5:** Methane hydrate equilibrium data in aqueous solutions of magnesium chloride. Experimental data for  $\text{CH}_4$  hydrate equilibrium data: rectangle – red [2], rhombus – blue [9]. Data from hydrate prediction program: circle – green [30]. This work (curve - black)

**Table 1:** Average deviations of the predicted methane hydrate equilibrium pressures (AADP%) in pure water and aqueous solutions of chloride salts

Solution/Salts concentration	Temperature range (K)	Pressure range (MPa)	Data points	Ref.	AADP (%)		
					CSMGem	Multiflash	This work
Pure water	273.70-285.90	2.77-9.78	12	[22]	0.65	1.38	1.10
	290.20-320.10	15.9-397.0	17	[23]	2.89	7.63	1.85
12 wt% NaCl	288.00-304.65	29.1-183.9	7	[6]	12.34	6.88	2.92
23 wt% NaCl	277.45-293.25	28.0-183.4	7	[6]	50.14	10.98	7.17
5 wt% KCl	273.90-283.20	3.35-8.69	5	[4]	1.92	1.14	0.72
10 wt% KCl	273.70-281.50	4.02-8.85	6	[4]	4.85	2.19	0.91
17.05 wt% CaCl <sub>2</sub>	276.30-282.20	10.15-22.93	4	[2]	21.99	1.97	1.71
20 wt% CaCl <sub>2</sub>	277.87-296.37	21.0-184.2	8	[9]	37.31	9.46	9.76
10 wt% MgCl <sub>2</sub>	276.30-285.70	6.24-19.42	5	[2]	-	4.70	3.62
20 wt% MgCl <sub>2</sub>	277.65-290.75	41.7-175.3	5	[9]	-	28.09	10.59
Overall			76		16.51	7.44	4.04

## CONCLUSION

A reliable correlation has been developed and successfully used to predict methane hydrate equilibrium data in pure water and aqueous solution of single chloride salts. The overall absolute average deviations of methane hydrate equilibrium pressure, AADP (%) for CSM Gem, Multiflash and the correlation developed in this work are 16.51%, 7.44% and 4.04%, respectively. The predicted data in this work are more accurate and closest to all experimental data reported in the literature than those from CSM Gem and Multi flash. Therefore, the generalized correlation is an excellent prediction tool for estimating methane hydrate formation conditions in pure water and aqueous solutions of single sodium, potassium, calcium and potassium chloride salts.

## ACKNOWLEDGEMENT

We are thankful to Central Pathology Laboratory Peshawar, Pakistan staff for their technical support

## REFERENCES

- [1] Englezos P, Bishnoi PR. Experimental study on the equilibrium ethane hydrate formation conditions in aqueous electrolyte solutions. *Ind Eng Chem Res*, **1991**, 30: 1655-1659.
- [2] Atik Z, Windmeier C, Oellrich LR. Experimental gas hydrate dissociation pressures for pure methane in aqueous solutions of MgCl<sub>2</sub> and CaCl<sub>2</sub> and for a (Methane+Ethane) gas mixture in an aqueous solution of (NaCl+MgCl<sub>2</sub>). *J Chem Eng Data*, **2006**, 51: 1862-1867.
- [3] Dholabhai PD, Parent JS, Bishnoi PR. Carbon dioxide hydrate equilibrium conditions in aqueous solutions containing electrolytes and methanol using a new apparatus. *Ind Eng Chem Res*, **1996**, 35: 819-823.
- [4] Mohammadi AM, Afzal W, Richon D. Gas hydrates of methane, ethane, propane and carbon dioxide in the presence of single NaCl, KCl and CaCl<sub>2</sub> aqueous solutions: Experimental measurements and predictions of dissociation conditions. *J Chem Thermodynamics*, **2008**, 40: 1693-1697.
- [5] Menten PD, Parrish WR, Sloan ED. Effect of inhibitors on hydrate formation. *Ind Eng Chem Process Des Dev*, **1981**, 20: 399-401.
- [6] Hu Y, Makogon TY, Karanjkar P, Lee KH, Lee BR, Sum AK. Gas hydrates phase equilibria and formation from high concentration NaCl brines up to 200 MPa. *J Chem Eng Data*, **2017**, 62: 1910-1918.
- [7] Hu Y, Lee BR, Sum AK. Universal correlation for gas hydrates suppression temperature of inhibited systems: I Single Salts. *AIChE J*, **2017**, 63: 5111-5124.
- [8] Hu Y, Lee BR, Sum AK. Insight into increased stability of methane hydrates at high pressure from phase equilibrium data and molecular structure. *Fluid Phase Equilibria*, **2017**, 450: 24-29.
- [9] Hu Y, Makogon TY, Karanjkar P, Lee KH, Lee BR, et al. Gas hydrates phase equilibria for structure I and II hydrates with chloride salts at high salt concentrations and up to 200 MPa. *J Chem Thermodynamics*, **2017**, 62: 1-6.

- 
- [10] Holzammer C, Schicks JM, Will S, Braeuer AS. Influence of sodium chloride on the formation and dissociation behavior of CO<sub>2</sub> gas hydrates. *J Phys Chem B*, **2017**, 121: 8330-8337.
- [11] Parrish WR, Prausnitz JM. Dissociation pressures of gas hydrates formed by gas mixtures. *Ind Eng Chem Process Des Dev*, **1972**, 11: 26-35.
- [12] Ng HJ, Robinson DB. The prediction of hydrate formation in condensed systems. *AIChE J*, **1977**, 23: 477-482.
- [13] John VT, Papadopoulos KD, Holder GD. A generalized model for predicting equilibrium conditions for gas hydrates. *AIChE J*, **1985**, 31: 252-259.
- [14] Chen GJ, Guo TM. A new approach to gas hydrate modeling. *Chem Eng J*, **1998**, 71: 145-151.
- [15] Hammerschmidt E. Gas hydrates formations: A further study on their prevention and elimination from natural gas pipe lines. *Gas*, **1939**, 15: 30-34.
- [16] Yousif M, Young D. A simple correlation to predict the hydrate point suppression in drilling fluids. Paper presented at: SPE/IADC Drilling Conference, Amsterdam, Netherlands. **1993**, 1-7.
- [17] Mohammadi AH, Tohidi B. A novel predictive technique for estimating the hydrate inhibition effects of single and mixed thermodynamic inhibitors. *Can J Chem Eng* **2005** 83:951-961.
- [18] Najibi H, Chapoy A, Haghghi H, Tohidi B. Experimental determination and prediction of methane hydrate stability in alcohols and electrolyte solutions. *Fluid Phase Equilibria*, **2009**, 275: 127-131.
- [19] Sloan ED. Clathrate hydrates of natural gases. In: Taylor & Francis Group, CRC Press, Boca Raton. **1998**.
- [20] Tohidi B, Danesh A, Todd AC, Burgass RW. Hydrate free zone for synthetic and real reservoir fluids in the presence of saline water. *Chem Eng Sci*, **1997**, 52: 3257-3263.
- [21] Kobayashi R, Withrow HJ, Williams GB, Katz DL. Gas hydrate formation with brine and ethanol solutions. *Proc NGAA*, **1951**, 27: 57-66.
- [22] Deaton WM Jnr, Frost EM. Gas hydrates and their relation to the operation of natural-gas pipe lines. *US Bureau of Mines Monograph*, **1946**, 8: 101-109.
- [23] Marshall DR, Saito S, Kobayashi R. Hydrates at high pressures: Methane-water, argon-water and nitrogen-water system (Part 1). *AIChE J*, **1964**, 10: 202-205.
- [24] Jhaveri J, Robinson DB. Hydrates in the methane and nitrogen system. *Can J Chem Eng*, **1965**, 43: 75-78.
- [25] Galloway TJ, Ruska W, Chappellear PS, Kobayashi R. Experimental measurement of hydrate numbers for methane and ethane and comparison with theoretical values. *Ind Eng Chem Fundam*, **1970**, 9: 237-243.
- [26] Adisasmito S, Frank RJ Jnr, Sloan ED. Hydrates of carbon dioxide and methane mixtures. *J Chem Eng Data*, **1991**, 36: 68-71.
- [27] de Roo JL, Peters CJ, Lichtenthaler RN, Diepen GAM. Occurrence of methane hydrates in saturated and unsaturated solutions of sodium chloride and water in dependence of temperature and pressure. *AIChE J*, **1983**, 29: 651-657.
- [28] Nakano S, Moritoki M, Ohgaki K. High-pressure phase equilibrium and Raman microprobe spectroscopic studies on the methane hydrate system. *J Chem Eng Data*, **1999**, 44: 254-257.
- [29] CSMGem hydrate prediction Program. Colorado School of Mines. **2001**.
- [30] Multiflash. Version 6.1.35: KBC advance technologies.