

Prediction of Gas and Refrigerant Hydrate Equilibrium Conditions With and Without Thermodynamic Inhibitors Using Simple Empirical Correlations

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Abstract

Clathrate hydrates (gas hydrates) are solid crystalline compounds formed from water molecules as host molecules and gas molecules as guest molecules. Due to the hydrogen bonds, water constructs a framework that entraps some small nonpolar molecules (typically gases) and in suitable conditions (i. e. low temperature and high pressure) gas hydrate forms. The objective of this research is to estimate the gas and refrigerant hydrate dissociation conditions with and without alcohols and sodium chloride aqueous solutions using simple empirical correlations. Generally, the empirical suggested correlations to estimate the equilibrium clathrate hydrate pressure of CH₄, C₂H₆, C₃H₈, CO₂, N₂, H₂S, R22, R23, R134a, R116, R125a, R152a, R141b, R410a, R407c, R507c, CH₄ + methanol, CH₄ + ethylene glycol, CH₄ + triethylene glycol, CH₄ + ethanol, CH₄ + sodium chloride, CO₂ + methanol, CO₂ + glycerol, CO₂ + sodium chloride, R134a + sodium chloride, R507c + sodium chloride and R410a + sodium chloride systems are a function of equilibrium hydrate temperature and concentration. A genetic algorithm was employed as an optimization method to determine correlation coefficients, and the mean squared error was selected as its fitness function. Due to the low values of the calculated absolute average deviations (between 0.00 and 7.65), except for H₂S + pure water with the highest amount of the absolute average deviation percent (AAD% equal to 11.51), these correlations are capable of predicting the studied hydrate dissociation conditions.

Keywords: Gas Hydrate, Refrigerant Hydrate, Inhibitor, Equilibrium Conditions, Empirical Correlation, Genetic Algorithm.

Introduction

Gas hydrates or clathrate hydrates are crystalline compounds with solid structures where water molecules form cages of hydrogen bonds and small guest molecules, typically light gases. In other words, gases are trapped inside the cages like crystal structures made up of water molecules in special conditions (i. e. low temperatures and high pressures). These hydrate forming conditions could be found in natural gas and oil production pipelines, which causes pipeline blockage. To prevent hydrate formation, there exist several chemicals such as alcohols (e.g. methanol, ethanol, ethylene glycol) and salts (e.g. sodium, magnesium and potassium chloride) injected into the oil and gas streams to avoid the gas hydrate formation [1]. However, scientists have found that hydrates can be applied as an important energy resource considerably. Moreover, hydrates could be a new way of gas storage and transformation [2-4], water desalination [5], carbon dioxide capture and sequestration [6], or even

refrigeration [7].

Furthermore, refrigeration and air-conditioning play an essential role in domestic and industrial applications [8, 9]. One of the alternative applications of refrigerants might be using them as a guest in clathrate hydrate [10-18]. Since empty hydrate lattice can store large amounts of refrigerants, refrigerant hydrate could be formed at lower temperatures (above the ice-point) and low pressures. Refrigerant hydrates have many advantages such as: appropriate phase change temperature (5-12 °C), high volumetric storage density (362-466Kj/Kg), high heat transfer coefficient. Therefore, they might be a favorite ingredient in energy storage and air conditioning systems. On the other side, they are considered a helpful agent in the desalination process to generate fresh-water from seawater and wastewater [13, 19]. Briefly, during the desalination process, when the refrigerant hydrate dissociates, pure

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water is produced, and the refrigerant is released. Finally, the refrigerant is then to be recycled [13].

Whether to enjoy the advantageous application of hydrates or to inhibit the hydrate formation, it is important to determine reliable experimental equilibrium data [20]. Researchers have conducted a great deal of work on measuring experimental gas and refrigerant hydrate equilibrium data during the past decades [1, 13, 16, 21, 22]. But the measurement of all data sets in the laboratory is not practical in terms of time and money. Hence, various beneficial tools are considered to do a correct estimation.

Several methods are proposed to predict clathrate hydrate equilibrium conditions, such as thermodynamic models, artificial neural networks, and empirical correlations [11-13, 21, 23-45]. The statistical thermodynamic approach is common for equilibrium hydrate condition prediction but this method is complex, involves rigorous computations, and is not user-friendly [46]. On the other side, among these methods, the empirical correlation seems to be a simple-to-use method. Indeed, it is an interpolation among experimental data, and ideally, it would be able to extrapolate beyond the data that is not interpolated [47]. Therefore, various empirical correlations have been presented to predict hydrate equilibrium conditions [34-45]. A correlation was presented by Hammerschmidt as the results of the experiments, which it could predict hydrate equilibrium temperature only as a function of pressure. This method causes considerable errors at temperatures greater than 60 °F and pressures more than 2000 psi [34]. A simple equation has been presented by Makogon, which it could estimate hydrate equilibrium pressure when the temperature and gas gravity are known [35]. An empirical equation which consists of fifteen coefficients has been developed by Kobayashi et al. This equation predicts the hydrate temperature at the given pressure and gas gravity. It must be mention that therein, the coefficients were computed by a regression method [36]. An empirical correlation has been developed by Sangtam and Majumder to estimate the hydrate equilibrium condition of methane, ethane, and propane in the presence of pure water and two inhibitors, methanol and ethylene glycol. In their correlation, hydrate equilibrium pressure was a function of temperature and concentration percentage with different coefficients [37]. Furthermore, a correlation was presented by Chavoshi et al. to predict methane, ethane, propane, isobutane, carbon dioxide, nitrogen, and hydrogen sulfide and their binary mixture and gas mixture similar to natural gas. Their correlation has three adjustable parameters, and it results in the equilibrium hydrate temperature as a function of equilibrium pressure and gas-specific gravity [38]. Later, a generalized empirical correlation was proposed by Aregbe to estimate hydrate equilibrium temperature and pressure of methane in pure water and the presence of some aqueous saline solutions. The equilibrium pressure was predicted by recording the temperature and concentration of the solution [39]. Moreover, a correlation for predicting sweet natural gas equilibrium hydrate condition has been proposed by Bahadori and Vuthaluru. Their correlation contains wide ranges of temperatures and pressures and molecular weights [40]. Finally, empirical modeling for predicting $\text{CH}_4 + \text{CO}_2$, $\text{N}_2 + \text{CO}_2$, $\text{H}_2 + \text{CO}_2$ in the presence of some promoters has been

studied by Sayyad Amin et al. Their proposed correlation quantifies the temperature as a function of pressure and concentration. In addition, by utilizing the genetic algorithm method, the constants of the correlation have been computed by them [41]. Some correlations presented in the literature are summarized in Table 1.

To develop a correlation, several experimental data must be taken into consideration alongside the regression method. To get better results, it is important that a suitable method to be used to optimize the proposed correlation. In this study, the genetic algorithm (GA) was chosen as the optimization solution. The GA is a kind of computational method inspired by Darwinian natural selection. It is a global optimization technique derived from evolution and natural selection to maximize or minimize a particular function. It works by searching in a population of solutions rather than a single point (like a traditional search algorithm). Therefore, it has a higher chance to get the best results based on the predetermined criteria [48-51].

This study's main objective is to develop a simple and reliable empirical correlation to predict equilibrium hydrate conditions of several gases and refrigerant hydrates in the presence of pure water and inhibitor aqueous solutions. The GA technique has been taken into account to compute all of the undetermined constant coefficients. Finally, a comparative study was presented based on the deviation between predicted and experimental data to examine the validity of the proposed correlations.

Materials and Methods

Data Acquisition

Various published experimental data have been extracted from several pieces of literature [1, 13, 16, 21, 22]. In Table 2, the studied equilibrium hydrate temperature, pressure ranges, and the concentration values of alcohols and sodium chloride are presented. All the studied systems have been investigated in the L_w -H-V phase.

Genetic Algorithm

With curve fitting, a function that is a good fit (typically a best fit) to the original data points is obtained. In linear problems with unspecified constants, the least squared method is usually considered as the most suitable approach of curve fitting. However, there are some limitations in applying the conventional least-squared method with nonlinear equations and equations with no derivative information. GA is an alternative method to overcome these problems. In the least squared curve fitting problems, the objective is to minimize the sum of the squared of the distances between a curve of a given form and the data points [49]. Here, the GA could be a beneficial method to seek an optimum solution. Indeed, in this problem, the least squared error is involved as the GA's fitness function. To do this, the populations of possible solutions would be generated first. Afterwards, the proposed solutions are compared based on their fitness function. Next, the better solutions are selected as parents that would create the next generation. This process is iterated until one of the obtained solutions is good enough [48, 50, 51]. The MATLAB Genetic Algorithm Toolbox aims to make GAs accessible to the users, and it is used in this study to do the regression.

Table 1 several published correlations with their limitations.

Reference	Empirical correlation*	Validity limitation
Hammes Schmidt (1934) [34]	$T = 8.9 \times P^{0.285}$	Methane hydrate, P in psi, T in °F
Makogon (1981) [35]	$\log P = \beta + 0.0497(t + kt^2) - 1$ $t = \sqrt{\frac{\log P + 1 - \beta}{0.0497k} + \frac{0.25}{k^2}} - k$ $k = -0.006 + 0.011\gamma + 0.011\gamma^2$ $\beta = 2.681 - 3.811\gamma + 1.679\gamma^2$	P in MPa, T in °C
Kobayashi et al. (1987) [36]	$t = 1/[a_1 + a_2 \ln(\gamma) + a_3 \ln(P) + a_4 \ln(\gamma^2) + a_5 \ln(\gamma) \ln(P) + a_6 \ln(P^2) + a_7 \ln(\gamma^3) + a_8 \ln(\gamma^2) \ln(P) + a_9 \ln(\gamma) \ln(P^2) + a_{10} \ln(P^3) + a_{11} \ln(\gamma^4) + a_{12} \ln(\gamma^3) \ln(P) + a_{13} \ln(\gamma^2) \ln(P^2) + a_{14} \ln(\gamma) \ln(P^3) + a_{15} \ln(P^4)]$	Temperature ranges of 34-60 °F, Pressure ranges of 65-1500 psi, P in psi, T in °F
Maekawa et al. (1995) [42]	$P = P_0 \exp\left(-926.815 + \frac{31979.3}{T} + 144.9 \ln(T)\right)$	Methane in pure water system with pressure up to 20 MPa, P in MPa, T in K
Jager and Sloan (2001) [43]	$P = \exp\left(-\frac{8375.06}{T} + 31.5775\right)$	Methane in pure water system with pressure up to 70MPa, P in MPa, T in K
Maekawa (2008) [44]	$P = \exp\left(60.821 - \left(\frac{17106.1}{T}\right)\right)$	Propane in pure water, methanol, and ethylene glycol system with pressure up to 0.527 MPa, P in MPa, T in K
Bahadori and Vuthaluru (2009) [40]	$\ln(T) = a + b\left(\frac{1}{P}\right) + c\left(\frac{1}{P}\right)^2 + d\left(\frac{1}{P}\right)^3 \quad \ln(P) = a + b\left(\frac{1}{T}\right) + c\left(\frac{1}{T}\right)^2 + d\left(\frac{1}{T}\right)^3$ $a = A_1 + B_1M + C_1M^2 + D_1M^3 \quad b = A_2 + B_2M + C_2M^2 + D_2M^3$ $c = A_3 + B_3M + C_3M^2 + D_3M^3 \quad d = A_4 + B_4M + C_4M^2 + D_4M^3$	Sweet natural gas Ranges of temperature: 265-298K pressure: 1200-4000 K P a molecular weight: 16-29, , P in MPa, T in K
Maekawa (2012) [45]	$P = \exp\left(-2726.64 + \frac{106675}{T} + 416.2985 \ln(T)\right)$	Ethane in pure water system pressure up to 3.12MPa, P in MPa, T in K
Chavoshi et al. (2018) [38]	$T = 242 \times \gamma^{0.02} \times P^{0.021}$	methane, ethane, propane, isobutan, carbon dioxide, nitrogen, and hydrogen sulfide and their binary mixture and gas mixture similar to natural gas, P in MPa, T in K
Aregbe (2018) [39]	$P = A \times T^5 + B \times T^4 + C \times T^3 + D \times T^2 + E \times T + F$ $A = A_4x^4 + A_3x^3 + A_2x^2 + A_1x^1 + A_0$ $B = B_4x^4 + B_3x^3 + B_2x^2 + B_1x^1 + B_0$ $C = C_4x^4 + C_3x^3 + C_2x^2 + C_1x^1 + C_0$ $D = D_4x^4 + D_3x^3 + D_2x^2 + D_1x^1 + D_0$	Methane in pure water and aqueous solutions of sodium chloride, potassium chloride, calcium chloride, and magnesium chloride, P in MPa, T in °C

* In all empirical correlations, T, P, γ , M, x, Ai, Bi, Ci, and Di represent temperature, pressure, specific gas gravity, concentration of inhibitor, and constant coefficients

Table 2 The ranges of equilibrium hydrate temperature, pressure, and concentration values of alcohols and sodium chloride with the number of data points [1, 13, 16, 21, 22].

Hydrate former (Data points)	Equilibrium hydrate temperature (K)		Equilibrium hydrate pressure (MPa)		Mass fraction/ molality
	min	max	min	max	
CH ₄ (37)	273.70	320.10	2.770	397.000	-
C ₂ H ₆ (7)	273.70	279.80	0.510	1.083	-
C ₃ H ₈ (10)	273.20	278.00	0.165	0.472	-
CO ₂ (36)	271.80	283.20	1.048	4.502	-
N ₂ (34)	272.00	291.00	14.480	95.860	-
H ₂ S (11)	277.60	302.10	0.157	2.068	-
CH ₄ + methanol	194.60	286.40	0.760	20.510	0.1, 0.2, 0.35, 0.5, 0.65, 0.737, 0.85*
CH ₄ + ethylene glycol	263.40	287.10	2.420	16.140	0.1, 0.3, 0.5*
CH ₄ + triethylene glycol	274.50	293.00	3.170	39.870	0.1, 0.202, 0.4*
CH ₄ + ethanol	273.30	284.70	3.380	13.670	0.15*
CH ₄ + sodium chloride	265.90	284.30	2.590	13.420	0.1, 0.2*
CO ₂ + methanol	232.60	274.90	0.379	3.480	0.1, 0.202, 0.35, 0.5*
CO ₂ + glycerol	270.10	279.30	1.391	3.556	0.1, 0.2, 0.25, 0.3*
CO ₂ + sodium chloride	263.20	276.10	1.517	3.227	0.1, 0.2*
R22 (11)	277.80	289.40	0.154	0.773	-
R23 (13)	275.40	292.00	0.450	3.440	-
R134a (6)	274.40	282.20	0.065	0.345	-
R152a (10)	273.65	287.35	0.065	0.399	-
R125a (14)	274.60	284.30	0.117	1.030	-
R507c (10)	277.70	283.70	0.221	0.874	-
R116 (6)	273.60	278.70	0.521	1.784	-
R410a (8)	277.00	292.50	0.178	1.365	-
R141b (6)	273.41	281.49	0.0078	0.040	-
R407c (11)	275.80	291.30	0.106	1.270	-
R134a + sodium chloride	268.10	280.60	0.086	0.383	0.900, 1.901, 3.020**
R507c + sodium chloride	273.90	281.00	0.304	0.802	1.901, 3.020**
R410a + sodium chloride	276.10	290.90	0.240	1.345	1.901, 3.020**

* mass fraction

** molality (mol/Kg)

The fitness function in the GA process is defined in the following equation:

$$FitnessFunction = \sum_{i=1}^N (K_{exp} - K_{predict})^2 \quad (1)$$

In Eq. (1), K_{exp} and $K_{predict}$ represent the experimental and predicted values. $K_{predict}$ is the target empirical correlation, and the proposed correlation is implemented in it.

Statistical Errors

To compute the deviation of predicted results of the developed correlations from the correspondent experimental data, the absolute average deviation percent (AAD%) was measured as a statistical error. The mathematical definition of the mentioned statistical error is calculated by the following expression:

$$AAD\% = \frac{1}{N} \sum_{i=1}^N \frac{|K_{exp} - K_{predict}|}{K_{exp}} \times 100 \quad (2)$$

where K_{exp} , $K_{predict}$, K_{mean} and, N are the experimental data,

predicted data, the average value of the experimental data, and total data, respectively.

Results and Discussion

Prediction of the Equilibrium Hydrate Conditions

This study attempts to develop reliable correlations for predicting equilibrium gas and refrigerant hydrate conditions with and without different alcohol and sodium chloride aqueous solutions by regression of several available experimental data. Two empirical correlations are proposed to predict (1) pure gas and (2) refrigerant hydrate dissociation conditions, which P are described (MPa) as a function of T (K) as bellow:

$$P = \exp\left(A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3}\right) \quad (3)$$

$$P = \exp\left(A + \frac{B}{T} + C \times \ln(T)\right) \quad (4)$$

A, B, C, and D are coefficients of correlations that should be

computed by fitting available experimental data. Eqs. (3) and (4) are the simple forms of Bahadori and Vuthaluru in 2009 and Maekawa et al. in 1995 respectively. The calculated

constant coefficients in Eqs (3) and (4) and AAD% are reported in Table 3. In this table, the respective correlation for each component is also presented in the first column.

Table 3 The constant coefficients of Equations (3) and (4) and AAD%.

Hydrate former (Correlation)	A	B	C	D	Equilibrium Temperature range (K)	AAD%
CH ₄ (3)	28.421	-7501.518	-247.114	-303.304	273.70-279.30	0.48
	34.696	-9261.509	-669.049	-356.184	280.40-288.90	1.00
	41.713	-11301.517	-816.955	-356.441	290.20-298.10	1.15
	35.637	-9483.384	-850.007	-316.838	300.20-306.70	0.26
	36.594	-9805.035	-297.444	-164.112	310.30-320.10	1.75
C ₂ H ₆ (3)	34.016	-9497.216	-240.563	-182.075	273.70-279.80	0.61
C ₃ H ₈ (3)	59.486	-16743.845	-305.167	-60.463	273.20-278.00	0.60
CO ₂ (3)	34.793	-9452.252	-787.09	-341.754	271.80-279.80	1.14
	42.566	-11630.651	-78.734	-165.722	280.10-283.20	0.97
N ₂ (3)	31.42	-7819.677	-712.854	-486.417	272.00-279.20	0.86
	31.467	-7825.635	-924.773	-469.094	280.20-291.00	0.39
H ₂ S (4)	-190.917	122.766	33.486	16.324	283.20-302.10	6.66
R22 (4)	-220.229	-139.056	38.893	-0.659	277.80-289.40	1.69
R23 (4)	-202.178	-5.575	35.836	14.027	275.40-292.00	2.24
R134a (4)	-365.496	-24.025	64.591	18.761	274.40-282.20	1.80
R152a (4)	-210.892	-62.316	37.130	29.492	273.39-288.15	0.88
R125a (4)	-306.063	13.944	54.121	2.816	274.60-279.60	3.24
	-410.527	29.297	72.643	31.081	280.2-284.3	2.03
R507c (4)	-368.110	-15.718	65.155	-4.232	277.70-283.70	3.26
R116 (4)	-386.407	85.420	68.668	-11.282	273.60-278.70	6.53
R410a (4)	-217.797	15.550	38.399	15.698	277.00-292.50	2.61
R141b (4)	-319.226	1.506	56.028	-13.943	273.41-281.49	0.13
R407c (4)	-255.986	-27.117	45.172	50.101	275.80-291.30	1.92

From Table 3, it could be understood that AAD% for H₂S is in the maximum amount, 6.66. However, the five other studied gases of CH₄, C₂H₆, C₃H₈, CO₂, and N₂ indicate low AAD% from 0.26 to 1.75. Thus, Eqs. (3) and (4) could be reliable correlations to estimate these studied gas hydrates' equilibrium conditions in studied temperature ranges. The minimum AAD% for refrigerant hydrates is for R141b (0.13) and the maximum AAD% is for R116 (6.53). Since the deviations between experimental data and estimated ones are small enough, it could be concluded that there is a good agreement between the actual values and predicted values by Eqs. (3) and (4).

The developed correlations for the prediction of investigated CH₄ and CO₂ hydrate equilibrium pressure with inhibitors are described as below:

$$P = \exp(A + B \times m + C \times m^2 + D \times m^3) \quad (5)$$

$$A = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} + \frac{a_4}{T^3} \quad (6)$$

$$B = b_1 + \frac{b_2}{T} + \frac{b_3}{T^2} + \frac{b_4}{T^3} \quad (7)$$

$$C = c_1 + \frac{c_2}{T} + \frac{c_3}{T^2} + \frac{c_4}{T^3} \quad (8)$$

$$D = d_1 + \frac{d_2}{T} + \frac{d_3}{T^2} + \frac{d_4}{T^3} \quad (9)$$

$$P = A + B \times T + C \times T^2 + D \times T^3 \quad (10)$$

$$A = a_1 + a_2 \times m + a_3 \times m^2 + a_4 \times m^3 \quad (11)$$

$$B = b_1 + b_2 \times m + b_3 \times m^2 + b_4 \times m^3 \quad (12)$$

$$C = c_1 + c_2 \times m + c_3 \times m^2 + c_4 \times m^3 \quad (13)$$

$$D = d_1 + d_2 \times m + d_3 \times m^2 + d_4 \times m^3 \quad (14)$$

where a_i , b_i , c_i and d_i are coefficients reporting in Table 4 and the variable m indicates the concentration of inhibitor, mass fraction. In the above correlations, P is obtained in MPa and T in Eqs. (6-9) is in K and in Eq. 10 is in °C. The amounts of AADs% are presented in Table 4.

As shown in Table 4, the maximum and minimum values of AAD% are reported for CH₄ + 0.65 (mass fraction) methanol, 18.48, and CO₂ + 0.1 sodium chloride, 0.00 respectively. Thus, the worst and the best equilibrium pressure prediction are for CH₄ + 0.65 methanol and CO₂ + 0.1 sodium chloride, respectively. Since other reported AADs% are from 0.10 to 7.69. Eqs. (5-14) are good enough to estimate the equilibrium pressure of studied gas hydrate with inhibitors, especially for systems with low concentrations of inhibitors.

Table 4 The constant coefficients of Equations (5-14) and statistical error calculation.

Hydrate former + inhibitor	CH ₄ + methanol						
	0.1 (10-14)	0.2 (10-14)	0.35 (5-9)	0.5 (5-9)	0.65 (5-9)	0.737 (5-9)	0.85 (5-9)
Mass fraction (correlation)							
Coefficient							
a1	5.587	4.843	41.483	15.807	16.003	25.847	79.544
a2	-23.637	8.771	-7104.411	-4837.949	-4080.214	-4444.446	-3140.393
a3	91.812	23.476	-1471.18	-1539.154	-1043.002	-1645.538	-1322.183
a4	64.229	34.721	-257.619	85.857	164.793	-299.059	-431.408
b1	7.619	1.393	4.091	28.242	49.92	35.295	-57.56
b2	-90.793	-1.968	-3118.072	-2774.966	-2700.737	-3274.418	-2682.115
b3	148.957	2.317	-1205.511	-1088.046	-1136.001	-1362.529	-1167.108
b4	329.455	-21.705	32.1	-58.677	-104.243	-338.464	-466.156
c1	1.264	0.450	-69.666	-27.057	-43.506	-0.929	14.222
c2	-4.04	-2.015	-1178.411	-1625.383	-2087.918	-2558.073	-2307.101
c3	-49.542	0.962	-383.236	-876.104	-834.711	-1421.315	-1184.152
c4	-340.487	-2.147	156.266	-30.075	-217.682	-224.036	-461.648
d1	-0.45	0.864	-62.968	29.94	-0.914	-29.355	3.015
d2	3.441	-5.115	-551.444	-730.63	-1403.72	-1701.073	-1953.809
d3	1.553	4.816	-240.371	-409.875	-586.107	-1201.586	-1314.416
d4	92.761	-3.891	-184.695	-175.352	-258.163	-126.156	-293.818
AAD%	2.67	2.38	7.69	4.07	18.48	4.81	6.10

Continued

Hydrate former + inhibitor	CH ₄ + ethylene glycol			CH ₄ + triethylene glycol		
	0.1 (10-14)	0.3 (5-9)	0.5 (5-9)	0.1 (10-14)	0.202 (5-9)	0.4 (10-14)
Mass fraction (correlation)						
Coefficient						
a1	-4.152	26.234	10.859	2.895	34.204	-6.605
a2	51.470	-7942.424	-7028.655	4.493	-9491.333	15.914
a3	214.863	-1363.411	-155.458	-44.706	-935.918	-6.478
a4	155.083	-190.114	-24.081	-161.594	-45.009	92.552
b1	4.376	18.988	39.153	-0.441	-31.695	5.947
b2	-47.242	-2793.671	-3496.81	7.946	-3003.36	-0.463
b3	49.767	-816.875	-83.155	-2.375	-380.523	-3.966
b4	140.261	-48.851	-31.548	25.358	40.069	-51.066
c1	0.469	-31.858	9.592	0.263	97.611	6.745
c2	4.828	-1393.259	-1702.767	-2.216	-1175.431	-15.456
c3	-85.569	-638.332	-69.733	-4.115	-205.686	-8.305
c4	-91.511	168.411	-82.183	-0.520	-91.217	11.757
d1	-1.068	121.389	20.232	0.772	514.974	0.205
d2	8.956	-538.635	-917.116	-6.562	-315.909	1.869
d3	9.900	-277.484	-18.849	-8.441	-164.54	-3.379
d4	76.522	59.832	-4.888	-29.506	4.614	-6.220
AAD%	2.46	3.72	1.87	2.61	3.08	1.52

Continued

Hydrate former + inhibitor	CH ₄ + ethanol	CH ₄ + sodium chloride		CO ₂ + methanol		
Mass fraction (correlation)	0.15 (10-14)	0.1 (10-14)	0.2 (10-14)	0.1 (10-14)	0.202 (5-9)	0.35 (5-9)
Coefficient						
a1	3.161	1.031	6.245	3.281	27.874	23.57
a2	-6.397	18.385	-10.984	-1.619	-7962.336	-6273.384
a3	44.494	57.244	75.741	-51.428	-584.546	-887.896
a4	30.614	-10.285	119.650	16.845	-43.599	-103.036
b1	1.802	2.055	-6.359	-1.951	1.752	-21.022
b2	-7.394	-18.193	33.373	22.761	-1593.925	-2359.243
b3	3.981	3.542	6.100	1.667	-281.242	-498.055
b4	-83.839	45.669	38.597	33.43	-89.97	-78.888
c1	-0.194	-0.035	-1.854	-0.326	28.96	68.076
c2	0.421	1.361	17.389	3.18	-364.802	-1061.159
c3	6.44	-8.857	-29.889	5.959	-97.028	-419.193
c4	-5.716	13.680	-48.327	1.249	-31.837	10.965
d1	0.205	0.286	-0.276	-0.172	31.109	49.708
d2	-1.908	-2.106	3.005	1.937	-38.793	-243.209
d3	4.153	-5.424	-6.685	-0.609	-63.799	-168.242
d4	-2.642	-19.247	-7.132	-8.577	44.66	135.917
AAD%	0.43	3.97	2.21	0.44	2.35	2.88

Continued

Hydrate former + inhibitor	CO ₂ + methanol	CO ₂ + glycerol			CO ₂ + sodium chloride	
Mass fraction (correlation)	0.5 (5-9)	0.1 (10-14)	0.2 (10-14)	0.3 (10-14)	0.1 (10-14)	0.2 (5-9)
Coefficient						
a1	25.421	0.821	-0.613	-3.359	0.921	31.994
a2	-4759.644	-3.596	8.877	-3.381	8.812	-9409.146
a3	-92.326	89.026	10.731	80.110	34.538	-204.404
a4	56.616	166.931	47.095	4.736	-59.695	2.262
b1	-0.652	-1.949	2.689	10.302	2.304	13.943
b2	-2442.627	11.956	-9.258	-19.964	-10.411	-1444.124
b3	-143.3	100.907	-9.707	-45.725	0.745	-30.864
b4	-27.054	-90.056	-28.255	4.935	-36.950	0.593
c1	-5.616	0.847	-1.396	0.968	-0.589	12.509
c2	-1198.051	4.267	3.563	-1.742	9.252	-331.735
c3	-82.267	-102.303	18.279	-1.395	9.957	-88.578
c4	10.922	-232.872	-2.214	-15.248	70.172	-0.382
d1	4.875	-0.760	2.021	2.110	-1.006	-39.665
d2	-584.495	5.919	-9.715	-7.384	7.519	-41.829
d3	-109.326	7.605	-0.320	1.592	0.043	12.7
d4	-54.395	92.902	-7.683	-2.289	-15.200	-16.588
AAD%	0.92	1.00	0.81	0.10	0.00	1.77

Since seawater and industrial wastewater consist of salts such as sodium chloride, to do the desalination by the refrigerant hydrate method and to measure dissociation condition, it seems economical to supply a simplified correlation instead of measuring that experimentally. The Eqs. (15-20) below express the equilibrium hydrate pressure predictions (MPa)

for R134a, R507c, and R410a depend on the temperature (K) and sodium chloride's molality.

$$P = \exp\left(A + \frac{B}{T^*} + C \times \ln(T^*) + D \times T^*\right) \quad (15)$$

$$A = a_1 + \frac{a_2}{m} + \frac{a_3}{m^2} + \frac{a_4}{m^3} \quad (16)$$

$$B = b_1 + \frac{b_2}{m} + \frac{b_3}{m^2} + \frac{b_4}{m^3} \tag{17}$$

$$C = c_1 + \frac{c_2}{m} + \frac{c_3}{m^2} + \frac{c_4}{m^3} \tag{18}$$

$$D = d_1 + \frac{d_2}{m} + \frac{d_3}{m^2} + \frac{d_4}{m^3} \tag{19}$$

$$T^* = \frac{T}{100} \tag{20}$$

The experimental refrigerant equilibrium hydrate data are

compared with those calculated by the correlations (15 -20). These comparisons are presented in Table 5.

In Table 5, it is indicated that the hydrate equilibrium conditions of studied systems estimated by correlations (15-20) have been the nearest to that of the experimental data because of the low amounts of AAD%. In Figs. 1-4, the values of equilibrium hydrate pressures that have been predicted by Eqs. (3-20) have been drawn compared to studied experimental data.

Table 5 The constant coefficients of Equations (15- 20) and statistical error calculation.

Hydrate former + inhibitor	R134a + sodium chloride			R507c + sodium chloride		R410a + sodium chloride	
Coefficient							
a1	-28.338			-31.860		-14.878	
a2	-23.629			-14.204		10.390	
a3	-0.936			2.214		-29.653	
a4	8.062			-1.687		4.187	
b1	-36.201			-25.370		-19.775	
b2	-7.792			-1.728		-31.527	
b3	4.382			3.658		21.987	
b4	7.651			-7.108		16.363	
c1	13.058			11.891		-3.038	
c2	-1.034			-3.689		3.920	
c3	-2.427			5.092		-14.203	
c4	-2.867			0.262		20.061	
d1	11.089			13.492		11.180	
d2	5.048			-0.167		0.134	
d3	6.243			-3.581		-6.009	
d4	-5.086			4.845		3.218	
Molality (mol/Kg)	0.900	1.901	3.020	0.900	1.901	0.900	1.901
AAD%	0.92	1.42	1.74	1.66	1.42	1.10	1.47

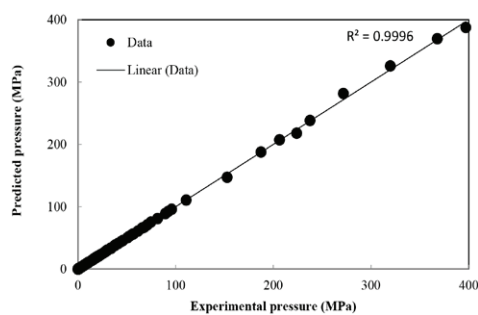


Fig. 1 Predicted versus experimental hydrate equilibrium pressure for gas/refrigerant + pure water systems.

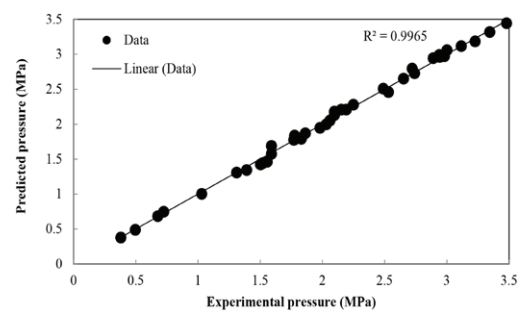


Fig. 3 Predicted versus experimental hydrate equilibrium pressure for CO₂ + water + inhibitor systems.

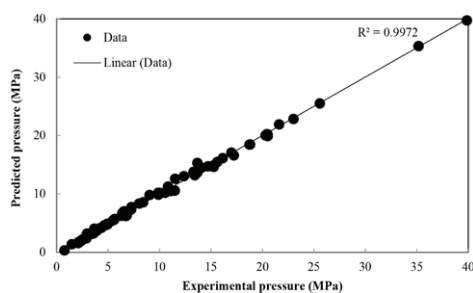


Fig. 2 Predicted versus experimental hydrate equilibrium pressure for CH₄ + water + inhibitor systems.

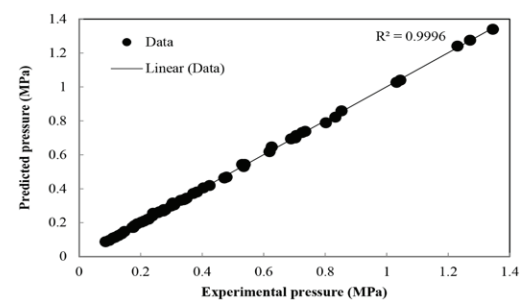


Fig. 4 Predicted versus experimental hydrate equilibrium pressure for refrigerant + water + sodium chloride systems.

As shown in Figs. 1-4, the amount of R^2 or squared correlation coefficient for all systems is greater than one. Therefore, proposed correlations are successfully able to estimate equilibrium hydrate pressure. Although using empirical correlation indicates some advantages such as (1) fast calculation, (2) good results, and (3) ignoring rigorous thermodynamic model computation, this approach indicates a major drawback. Empirical correlations are only effective for the specific systems and the studied temperature, pressure, and concentration ranges.

Validation of the Empirical Correlations

To check the accuracy of the proposed empirical correlations,

extrapolations of experimental data are investigated. In this study, the developed correlations were validated by using different sets of experimental data available in the literature for CH_4 , C_2H_6 , C_3H_8 , CO_2 , N_2 , H_2S , R22, R23, R152a, R116, R507c, R134a, R125a, R410a + pure water systems [1, 13, 16, 52-55]. Remained systems, which the data are not available as many as the earlier systems, some experimental data are trained in the previous section, and the rest are validated in this section. The corresponding results are presented in Table 6.

Table 6 New correlation accuracy in comparison with experimental data.

Hydrate former (Data points)	Solution	Equilibrium Temperature range (K)	AAD%	Reference
CH_4 (5)	Pure water	273.40-279.60	1.30	[1]
CH_4 (11)	Pure water	280.90-289.90	1.92	[1]
CH_4 (14)	Pure water	305.08-319.80	3.66	[1]
CH_4 (6)	methanol, ethylene glycol, triethylene glycol, ethanol, sodium chloride	264.60-283.00	6.21	[1]
C_2H_6 (3)	pure water	277.50-279.90	3.97	[1]
C_3H_8 (5)	pure water	273.70-277.10	0.75	[1]
CO_2 (7)	pure water	273.90-283.30	1.82	[1]
CO_2 (6)	methanol, glycerol, sodium chloride	252.40-277.70	2.19	[1]
N_2 (10)	pure water	273.20-290.00	1.39	[1]
H_2S (4)	pure water	283.20-302.70	11.51	[1]
R22 (4)	pure water	279.00-285.90	6.54	[52]
R23 (12)	pure water	275.15-291.75	2.91	[53]
R152a (11)	pure water	273.39-288.15	6.52	[22]
R116 (5)	pure water	277.40-279.30	4.70	[54]
R507c (9)	pure water	278.10-283.30	6.90	[16]
R134a (18)	pure water	278.92-283.17	7.65	[55]
R125a (19)	pure water	274.94-283.70	5.32	[55]
R410a (12)	pure water	277.50-293.00	2.00	[13]
R141b (2)	pure water	274.61 and 278.70	0.00	[22]
R407c (3)	pure water	281.60, 283.80, and 289.1	4.24	[16]
R134a, R507c, R410a (7)	sodium chloride	268.60-288.50	1.85	[13]

As given in Table 6, the deviation between experimental data and prediction results for systems CH_4 , C_2H_6 , C_3H_8 , CO_2 , N_2 , R23, R410a, R141b + pure water, and CO_2 + water + methanol/ glycerol/ sodium chloride, and R134a, R507c, R410a + water + sodium chloride is smaller than 4. It shows that for these systems, the correlations developed in this study are excellent prediction tools. The large amounts of AAD% belong to systems H_2S (11.51), R22 (6.54), R152a (6.52), R507c (6.90), R134a (7.65), R125a (5.53) + pure water, and CH_4 + water + methanol, ethylene glycol, triethylene glycol, ethanol, sodium chloride (6.21). An important reason for the high deviation is the different conditions of which hydrate formations in laboratories. The methodology, ambient temperature, and equipment cause experimental data would differ in various articles. On the other hand, in the previous

section, two systems of H_2S + pure water and CH_4 + water + 0.35, 0.5, 0.65, 0.737, and 0.85 methanol demonstrate high amounts of AAD%. Thus, it is usual that the proposed correlations could not predict the equilibrium pressure of these systems very well. To investigate deviations, in Fig. 5, the experimental equilibrium hydrate conditions are plotted against estimated ones.

Fig. 5 shows that for systems R22 (T higher than 279.6 K), R152a (T higher than 279.26K), R134a (T higher than 282.3 K), and R125a (T higher than 279K), the new correlations are more precise in high temperatures and show good results. However, for system R507c, the experimental data at moderate temperatures, T between 287.7 and 282.3 K, are in concordance with estimated ones. Therefore, in these ranges, the correlation could predict reliable points.

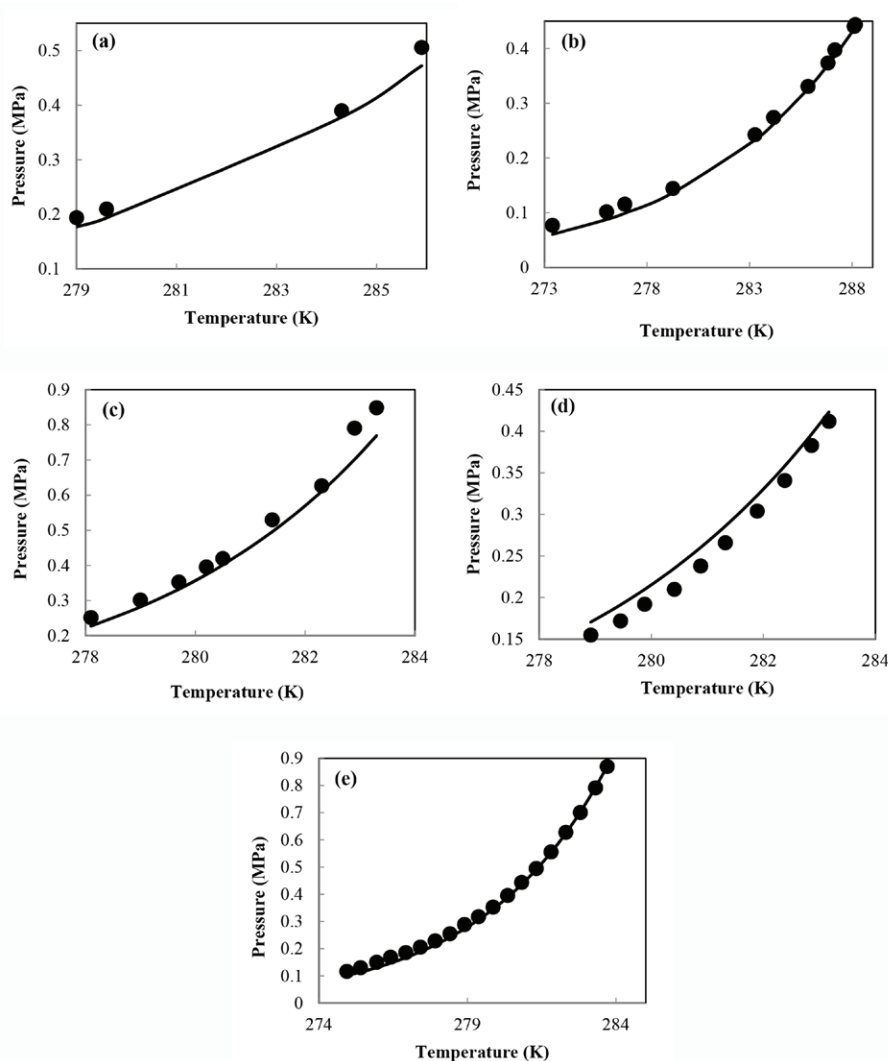


Fig. 5 Experimental and estimated hydrate equilibrium conditions in pure water. the symbol represents experimental data: a) R22. b) R152a. c) R507c. d) R134a. e) R125a. The line represents prediction results.

Conclusions

This study aimed to describe the CH_4 , C_2H_6 , C_3H_8 , CO_2 , N_2 , H_2S , R22, R23, R134a, R116, R125a, R152a, R141b, R410a, R407c, R507c, CH_4 + methanol, CH_4 + ethylene glycol, CH_4 + triethylene glycol, CH_4 + ethanol, CH_4 + sodium chloride, CO_2 + methanol, CO_2 + glycerol, CO_2 + sodium chloride, R134a + sodium chloride, R507c + sodium chloride and R410a + sodium chloride hydrate equilibrium conditions by new empirical correlations. The coefficients of the proposed correlation were computed by the GA method in MATLAB R2014b software. Furthermore, to ensure the reliability of the correlations, estimated results were compared with actual ones. Ultimately, it could be concluded that developed correlations can be regarded as an appropriate method especially for systems with low AAD%, CH_4 (1.30, 1.92, and 3.66), C_2H_6 (3.97), C_3H_8 (0.75), CO_2 (1.82, 2.19), N_2 (1.39), R23 (2.91), R410a (2.00), R141b (0.00), CO_2 + studied inhibitors (2.19), and R134a, R507c, R410a + sodium chloride (1.8). Among these systems, H_2S + pure water shows the largest amount of AAD%, and it can be inferred that the correlation could not successfully predict the experimental data for this system.

Nomenclatures

AAD: Absolute average deviation (%)

GA: Genetic algorithm

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