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Thermodynamic Model for the Prediction of Equilibrium Conditions of Clathrate Hydrates of Methane + Water-Soluble or -Insoluble Hydrate Former

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ABSTRACT: In this communication, equilibrium conditions of clathrate hydrates of cyclopentane, cyclohexane, acetone, or 1,4-dioxane + methane, which form structure II, and 1,1-dimethylcyclohexane, 2,2-dimethylpentane, methylcyclohexane, or *cis*-1,2-dimethylcyclohexane + methane, which form structure H, are modeled. The thermodynamic model is based on the van der Waals–Platteeuw solid solution theory combined with an equation of state and activity model. The Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) equations of state with random mixing rules are used to model the gas phase, while the UNIFAC method is used to model the liquid phase(s). It is shown that the use of the PR equation of state leads to better predictions of hydrate equilibrium conditions of the aforementioned water-insoluble heavy hydrocarbons, while the use of the SRK equation of state causes better predictions of hydrate equilibrium conditions of the latter water-soluble hydrate formers.

1. INTRODUCTION

Clathrate hydrates, or gas hydrates, are solid crystalline compounds consisting of water molecules forming special cages via a hydrogen-bonding network containing guest molecule(s).¹ Depending on the size and shape of the guest molecule(s), water molecules form different cages, which combine to form the hydrate of three typical crystallographic structures: I, II, and H.¹ Guest molecules can be gas or liquid.¹ In general, gas hydrates are stabilized by small (<9 Å diameter) molecules, like methane, ethane, carbon dioxide, nitrogen, cyclic ethers, etc.

Gas hydrates have been proposed as a potential medium for gas separation, storage, and transportation.^{1–6} However, the pressure required for hydrate formation is generally high.^{1–6} The addition of some organic compounds, called “water-soluble” or “water-insoluble” hydrate formers, lowers the hydrate equilibrium pressure at a given temperature or, stated differently, raises the hydrate equilibrium temperature at a given pressure.^{1–5,7–12} Economical, safety, and environmental aspects are important in selecting the aforementioned “water-soluble” or “water-insoluble” compounds.^{1,6}

Water-soluble organic hydrate formers could be some cyclic ethers and ketones like tetrahydrofuran, 1,4-dioxane, 1,3-dioxalane, acetone, etc.^{1,7–12} The latter chemicals generally form structure II of clathrate hydrates in the presence (or absence) of a gas.^{1,7–12} The addition of organic compounds in smaller concentrations than almost 6 mol % relative to water lowers the hydrate equilibrium pressure of some gases like methane at a given temperature significantly, while the addition of higher concentrations diminishes the pressure-reducing effect.^{8,9} There are also other water-soluble chemicals in addition to cyclic ethers and ketones that can form other types of hydrates. Examples are tetraalkylammonium halides, some alkylamines, etc. A good review of these compounds is given elsewhere.^{1,13}

Table 1. Kihara Potential Parameters Used in This Thermodynamic Model

hydrate former	<i>a</i> (Å)	<i>σ</i> (Å)	<i>ε</i> / <i>k</i> (K)
methane ^a	0.3834	3.1650	154.54
cyclohexane	1.0057	2.3459	423.66
cyclopentane	0.9293	2.7085	459.86
1,1-dimethylcyclohexane	1.1295	2.8975	483.61
2,2-dimethylpentane	1.3384	3.1198	360.50
methylcyclohexane	1.1473	3.1077	411.75
<i>cis</i> -1,2-dimethylcyclohexane	1.1038	3.5186	317.66
acetone	1.1093	3.2005	229.66
1,4-dioxane	0.9868	2.7398	279.43

^aTaken from ref 1.

Water-insoluble hydrate formers generally include some heavy hydrocarbons like cyclopentane, cyclohexane, methylcyclohexane, etc.^{1,5} Except for a few of them, i.e., cyclopentane and cyclohexane, which form structure II, most of the water-insoluble hydrate formers form structure H and therefore require the presence of a help gas like methane for stability.¹ The latter hydrate formers have been proposed as a means for gas storage partly because they form hydrates with high gas storage capacities.^{1,5} Indeed, sufficient experimental studies have been made on hydrates of water-soluble and -insoluble organic compounds.^{1–5,7–13} However, the theoretical efforts to model

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the equilibrium conditions of the aforementioned hydrate formers, particularly water-soluble hydrate formers, are limited.^{1,7–9}

Table 2. Reference Parameters Used in This Thermodynamic Model¹

parameter	unit	value
Structure I		
Δu_w^0	J/mol	1297
$\Delta h_w^0, T < T_0$	J/mol	1389
$\Delta h_w^0, T > T_0$	J/mol	−4620.5
$\Delta v_w, T < T_0$	cm ³ /mol	3
$\Delta v_w, T > T_0$	cm ³ /mol	4.601
ΔC_{pw}^0	J/mol·K	−38.12
\bar{a}	J/mol·K ²	0.141
Structure II		
Δu_w^0	J/mol	883.8
$\Delta h_w^0, T < T_0$	J/mol	1025
$\Delta h_w^0, T > T_0$	J/mol	−4984.5
$\Delta v_w, T < T_0$	cm ³ /mol	3.4
$\Delta v_w, T > T_0$	cm ³ /mol	5
ΔC_{pw}^0	J/mol·K	−38.12
\bar{a}	J/mol·K ²	0.141
Structure H		
Δu_w^0	J/mol	1187.5
$\Delta h_w^0, T < T_0$	J/mol	846.57
$\Delta h_w^0, T > T_0$	J/mol	−5162.93
$\Delta v_w, T < T_0$	cm ³ /mol	3.85
$\Delta v_w, T > T_0$	cm ³ /mol	5.451
ΔC_{pw}^0	J/mol·K	−38.12
\bar{a}	J/mol·K ²	0.141

Table 3. Critical Temperature (T_c /K), Critical Pressure (P_c /MPa), and Acentric Factor ($\bar{\omega}$) Values Used in This Thermodynamic Model^{4,19}

compound	T_c (K)	P_c (MPa)	$\bar{\omega}$
1,1-dimethylcyclohexane	590.9	2.965	0.238
cis-1,2-dimethylcyclohexane	605.9	2.965	0.236
methylcyclohexane	572.2	3.475	0.233
2,2-dimethylpentane	520.5	2.773	0.3
cyclohexane	280.1	4.053	0.2133
cyclopentane	238.5	4.509	0.192
methane	190.7	4.641	0.0115

^aAs for modeling of hydrate phase equilibria of water-soluble-containing systems, the gas phase is assumed as pure methane and the presence of a water-soluble compound in the gas phase is ignored; therefore, T_c , P_c , and $\bar{\omega}$ of acetone and 1,4-dioxane have not been used in the equation of state.

Table 4. Binary Interaction Parameter Values Used in This Thermodynamic Model¹⁹

	cyclohexane	cyclopentane	1,1-dimethylcyclohexane	2,2-dimethylpentane	methylcyclohexane	cis-1,2-dimethylcyclohexane
PR EoS ¹⁶						
methane	0.0392	0.01282	0.03093	0.02796	0.02345	0.0321
SRK EoS ¹⁷						
methane	0.0311	0.01281	0.03093	0.02796	0.02347	0.0321

The equilibrium pressure reduction effect by water-soluble hydrate formers differs from the pressure effect of other compounds by its concentration dependence.^{8,9} Water-insoluble hydrate formers like cyclohexane, cyclopentane, methylcyclohexane, etc., form an extra liquid phase in the system, which reduces by 1 the number of degrees of freedom according to the Gibbs phase rule.^{8,9} This results in the absence of a concentration dependence on the hydrate equilibrium pressure.^{8,9}

Systems containing water-soluble hydrate formers lose their concentration dependence if the solubility limit is reached.^{8,9} Examples of this phenomenon are the water + methane + tetrahydropyran system and the water + methane + 1,3-dioxolane + sodium chloride system.^{8,9} The solubility of tetrahydropyran in water is about 1.5 mol %.^{8,9,14} Systems exceeding this concentration form an additional liquid phase and lose the concentration dependence of the hydrate equilibrium conditions.^{8,9} The same phenomenon is observed in the water + methane + 1,3-dioxolane + sodium chloride system.^{8,9} 1,3-Dioxolane is completely miscible with water, but the solubility is reduced dramatically by the addition of sodium chloride.^{8,9} This again contributes to an extra liquid phase and loss of concentration dependence.^{8,9}

Few studies have been published on modeling systems containing water-soluble hydrate formers, as mentioned earlier. Mainusch et al.⁷ described hydrate formation using a hydrate inhibition model. Jager et al.⁸ and later de Deugd et al.⁹ used a model based on the statistical thermodynamic approach originally introduced by van der Waals and Platteeuw.¹⁵ In water-soluble hydrate former containing systems, the activity coefficients of the components in the aqueous phase deviate from one that is described by means of an activity coefficient model.^{8,9} The aqueous phase is generally considered a mixture of water and a water-soluble hydrate former with low concentrations of dissolved methane (or other gases), and the activity coefficients of water and water-soluble hydrate former are calculated from binary water + water-soluble hydrate former vapor–liquid equilibrium (VLE) data.^{8,9} The effect of the additive on the methane solubility is ignored.^{8,9}

This work aims at developing a thermodynamic model for predicting the equilibrium conditions of clathrate hydrates of cyclopentane, cyclohexane, acetone, or 1,4-dioxane + methane, which form structure II, and 1,1-dimethylcyclohexane, 2,2-dimethylpentane, methylcyclohexane, or cis-1,2-dimethylcyclohexane + methane, which form structure H. In the aforementioned clathrate hydrates, the heavy hydrate

Table 5. Antoine's Constants Used in This Thermodynamic Model²¹

compound	A	B	\bar{C}
acetone	7.63130	1566.69	273.419
1,4-dioxane	7.43155	1554.679	240.337

Table 6. Parameters of the UNIFAC Model Used in This Thermodynamic Model²⁶

main group		subgroup	k'	R'_k	Q_k
1	CH ₂	CH ₃	1	0.9011	0.848
		CH ₂	2	0.6744	0.540
		CH	3	0.4469	0.228
		C	4	0.2195	0.000
3	ACH	ACH	10	0.5313	0.400
4	ACCH ₂	ACCH ₃	12	1.2663	0.968
		ACCH ₂	13	1.0396	0.660
5	OH	OH	15	1.0000	1.200
7	H ₂ O	H ₂ O	17	0.9200	1.400
9	CH ₂ CO	CH ₃ CO	19	1.6724	1.488
		CH ₂ CO	20	1.4457	1.180
13	CH ₂ O	CH ₃ O	25	1.1450	1.088
		CH ₂ O	26	0.9183	0.780
		CHO	27	0.6908	0.468
15	CNH	CH ₃ NH	32	1.4337	1.244
		CH ₂ NH	33	1.2070	0.936
		CHNH	34	0.9795	0.624
19	CCN	CH ₃ CN	41	1.8701	1.724
		CH ₂ CN	42	1.6434	1.416

		1	3	4	5	7	9	13	15	19
1	CH ₂	0.00	61.13	76.50	986.50	1318.00	476.40	251.50	255.70	597.00
3	ACH	−11.12	0.00	167.00	636.10	903.80	25.77	32.14	122.80	212.50
4	ACCH ₂	−69.70	−146.80	0.00	803.20	5695.00	−52.10	213.10	−49.29	6096.00
5	OH	156.4	89.60	25.82	0.00	353.50	84.00	28.06	42.70	6.712
7	H ₂ O	300.00	362.30	377.60	−229.10	0.00	−195.40	540.50	168.00	112.60
9	CH ₂ CO	26.76	140.10	365.80	164.50	472.50	0.00	−103.60	−174.20	481.70
13	CH ₂ O	83.36	52.13	65.80	237.70	−314.70	191.10	0.00	251.50	−18.51
15	CNH	65.33	−22.31	223.00	−150.00	−448.20	394.60	−56.08	0.00	147.10
19	CCN	24.82	−22.97	−138.40	185.40	242.80	−287.50	38.81	−108.50	0.00

Table 7. Four-Phase (L_w – H – G – L_{HC}) Equilibria for the Methane + Cyclohexane + Water System

T (K)	P_{exp} (MPa) ²⁸	P_{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}		P_{model} /MPa, using the PR EoS ¹⁶ + UNIFAC ^{18,19}	
		AD (%) ^a	AD (%) ^a	AD (%) ^a	AD (%) ^a
273.97	0.684	0.661	3.4	0.676	1.2
274.68	0.713	0.699	2.0	0.703	1.4
276.06	0.983	0.921	6.3	0.962	2.1
279.14	1.463	1.412	3.5	1.433	2.1
282.02	2.212	2.134	3.5	2.198	0.6
285.03	3.436	3.154	8.2	3.338	2.9
287.47	4.961	4.46	10.1	4.722	4.8
289.82	7.282	6.231	14.4	6.811	6.5
290.63	8.021	6.809	15.1	7.441	7.2
291.58	9.486	7.722	18.6	8.869	6.5
AAD (%) ^b			8.5		3.5

^aAbsolute (relative) deviation. ^bAverage absolute deviation.

former occupies a large cavity, while the rest can be occupied by methane.¹

The proposed thermodynamic model uses the van der Waals and Platteuw solid solution theory¹⁵ to model the hydrate

Table 8. Four-Phase (L_w – H – G – L_{HC}) Equilibria for the Methane + Cyclopentane + Water System

T(K)	P_{exp} (MPa) ²⁸	P_{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}		P_{model} (MPa), using the PR EoS ¹⁶ + UNIFAC ^{18,19}	
		AD (%)	AD (%)	AD (%)	AD (%)
282.15	0.165	0.217	31.5	0.212	28.5
284.98	0.380	0.507	33.4	0.411	8.2
287.13	0.568	0.647	13.9	0.634	11.6
289.87	1.033	1.020	1.3	1.008	2.4
292.72	1.678	1.567	6.6	1.571	6.4
295.18	2.547	2.411	5.3	2.417	5.1
297.83	3.824	3.496	8.6	3.711	3.0
300.22	5.636	4.923	12.7	5.139	8.8
301.90	7.312	6.442	11.9	6.821	6.7
AAD (%)			13.9		9.0

phase. The Peng–Robinson (PR)¹⁶ and Soave–Redlich–Kwong (SRK)¹⁷ equations of state with random mixing rules^{16,17} are used to model the gas phase, while the hydrocarbon and aqueous phases are modeled by the UNIFAC method.^{18,19} Unlike the previous thermodynamic models, we assume that the aqueous phase is a ternary mixture of water, water-soluble

Table 9. Four-Phase ($L_w-H-G-L_{HC}$) Equilibria for the Methane + 1,1-Dimethylcyclohexane + Water System

T(K)	P_{exp} (MPa) ²⁹	P_{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}		P_{model} (MPa), using the PR EoS ¹⁶ + UNIFAC ^{18,19}	
		AD (%)	AD (%)	AD (%)	AD (%)
274.67	1.07	1.041	2.7	1.127	5.3
276.67	1.37	1.314	4.1	1.417	3.4
278.65	1.76	1.722	2.2	1.816	3.2
280.63	2.19	2.137	2.4	2.268	3.6
282.28	2.90	2.619	9.7	2.759	4.9
284.57	3.74	3.527	5.7	3.578	4.3
286.53	4.75	4.881	2.8	4.722	0.6
288.51	6.08	6.636	9.1	6.201	2.0
289.31	6.77	7.589	12.1	7.211	6.5
AAD (%)			5.6		3.8

Table 10. Four-Phase ($L_w-H-G-L_{HC}$) Equilibria for the Methane + *cis*-1,2-Dimethylcyclohexane + Water System

T(K)	P_{exp} (MPa) ³⁰	P_{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}		P_{model} (MPa), using the PR EoS ¹⁶ + UNIFAC ^{18,19}	
		AD (%)	AD (%)	AD (%)	AD (%)
274.18	1.57	1.497	4.6	1.602	2.0
274.65	1.67	1.614	3.4	1.655	0.9
275.25	1.80	1.722	4.3	1.816	0.9
276.22	2.03	2.025	0.2	2.078	2.4
277.18	2.29	2.244	2.0	2.263	1.2
278.14	2.57	2.498	2.8	2.504	2.6
279.10	2.89	2.762	4.4	2.835	1.9
280.10	3.28	3.119	4.9	3.201	2.4
281.58	3.93	3.687	6.2	3.911	0.5
283.04	4.71	4.401	6.6	4.655	1.2
284.53	5.66	5.2682	6.9	5.523	2.4
285.99	6.83	6.348	7.1	6.612	3.2
286.93	7.75	7.344	5.2	7.764	0.2
287.96	8.89	8.688	2.3	9.516	7.0
AAD (%)			4.4		2.1

hydrate former, and dissolved gas. Moreover, the use of the UNIFAC method^{18,19} eliminates any need for binary VLE data required to adjust the interaction parameters in the molecular activity models used in the previous thermodynamic models.^{7–9} Note that such VLE data are indeed rare and scarce. Because of the low fugacities of the water-soluble hydrate former in the systems, we assume that the gas phase consists of pure methane in the case where water-soluble hydrate former exists in the system.^{8,9}

2. THERMODYNAMIC MODEL

At equilibrium, the chemical potential of water in the hydrate phase is considered equal to the chemical potential of water in the aqueous phase:²⁰

$$\mu_w^H = \mu_w^L \quad (1)$$

where, μ_w^H and μ_w^L are chemical potentials of water in the filled hydrate and liquid phases, respectively. For

Table 11. Four-Phase ($L_w-H-G-L_{HC}$) Equilibria for the Methane + Methylcyclohexane + Water System

T (K)	P_{exp} (MPa) ³⁰	P_{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}		P_{model} (MPa), using the PR EoS ¹⁶ + UNIFAC ^{18,19}	
		AD (%)	AD (%)	AD (%)	AD (%)
274.09	1.42	1.581	11.3	1.439	1.3
274.78	1.54	1.622	5.3	1.512	1.8
275.28	1.66	1.649	0.7	1.587	4.4
275.79	1.75	1.692	3.3	1.692	3.3
276.26	1.87	1.883	0.7	1.789	4.3
276.79	1.99	1.933	2.9	1.913	3.9
277.26	2.11	2.021	4.2	2.031	3.7
277.80	2.25	2.199	2.3	2.162	3.9
278.30	2.39	2.361	1.2	2.314	3.2
279.25	2.70	2.589	4.1	2.642	2.1
280.26	3.05	2.891	5.2	2.994	1.8
281.27	3.45	3.223	6.6	3.362	2.6
282.28	3.90	3.654	6.3	3.845	1.4
283.29	4.43	4.077	8.0	4.454	0.5
284.30	5.03	4.556	9.4	5.201	3.4
285.29	5.72	5.135	10.2	6.009	5.1
286.28	6.50	5.727	11.9	6.889	6.0
287.25	7.42	6.424	13.4	7.857	5.9
288.29	8.48	7.111	16.1	8.968	5.8
AAD (%)			6.5		3.4

Table 12. Four-Phase ($L_w-H-G-L_{HC}$) Equilibria for the Methane + 2,2-Dimethylpentane + Water System

T(K)	P_{exp} (MPa) ²⁷	P_{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}		P_{model} (MPa), using the PR EoS ¹⁶ + UNIFAC ^{18,19}	
		AD (%)	AD (%)	AD (%)	AD (%)
273.7	2.430	2.260	7.0	2.307	5.1
274.2	2.592	2.330	10.1	2.391	7.8
274.9	2.811	2.476	11.9	2.568	8.6
275.5	3.040	2.640	13.2	2.790	8.2
276.0	3.248	2.813	13.4	3.005	7.5
276.5	3.434	3.028	11.8	3.289	4.2
277.1	3.697	3.400	8.0	3.700	0.1
277.7	3.991	3.918	1.8	4.240	6.2
278.1	4.202	4.371	4.0	4.670	11.1
AAD (%)			9.0		6.5

convenience, the chemical potential differences between a theoretical empty hydrate lattice and a liquid or hydrate lattice are compared:

$$\left. \begin{aligned} \Delta\mu_w^H &= \mu_w^\beta - \mu_w^H \\ \Delta\mu_w^L &= \mu_w^\beta - \mu_w^L \end{aligned} \right\} \rightarrow \Delta\mu_w^H = \Delta\mu_w^L \quad (2)$$

where μ_w^β is the chemical potential of water in the empty hydrate (β). The subscript w stands for water.

2.1. Water Chemical Potential in the Hydrate Phase. van der Waals and Platteeuw¹⁵ defined the chemical potential of water in the hydrate phase as a function of the fractional

Table 13. Three-Phase (L_w-H-G) Equilibria for the Methane + Acetone + Water System

T (K)	P_{exp} (MPa) ⁷	P_{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}	AD (%)	P_{model} (MPa), using the PR EoS ¹⁶ + UNIFAC ^{18,19}	AD (%)	P_{model} (MPa), literature model ⁷	AD (%)
Mole Fraction of Acetone in Aqueous Solution = 0.0167							
279.6	2.50	2.55	2.0	2.63	5.2	2.88	15.2
282.7	3.75	3.69	1.6	3.61	3.7	3.57	4.8
284.8	5.00	4.77	4.6	4.65	7.0	4.55	9.0
286.6	6.25	6.18	1.1	5.91	5.4	5.85	6.4
287.8	7.50	7.43	0.9	7.22	3.7	6.99	6.8
289	8.75	8.87	1.4	8.61	1.6	8.11	7.3
289.9	10.00	10.27	2.7	9.92	0.8	9.09	9.1
290.7	11.25	11.75	4.4	11.08	1.5	10.31	8.4
AAD (%)			2.3		3.6		8.4
Mole Fraction of Acetone in Aqueous Solution = 0.0333							
281.4	2.50	2.52	0.8	2.59	3.6	2.30	8.0
284.2	3.75	3.70	1.3	3.81	1.6	3.59	4.3
286.3	5.00	4.81	3.8	4.81	3.8	4.81	3.8
287.9	6.25	6.18	1.1	6.10	2.4	5.81	7.0
289.3	7.50	7.60	1.3	7.48	0.3	7.42	1.1
290.3	8.75	8.78	0.3	8.60	1.7	8.41	3.9
291.2	10.00	9.82	1.8	9.62	3.8	9.40	6.0
292.1	11.25	11.31	0.5	10.99	2.3	10.69	5.0
AAD (%)			1.4		2.4		4.9
Mole Fraction of Acetone in Aqueous Solution = 0.0528							
281.7	2.50	2.62	4.8	2.58	3.2	2.50	0.0
284.7	3.75	3.74	0.3	3.72	0.8	3.71	1.1
286.7	5.00	4.90	2.0	4.73	5.4	4.69	6.2
288.3	6.25	6.30	0.8	6.12	2.1	5.90	5.6
289.6	7.50	7.43	0.9	7.24	3.5	7.01	6.5
290.6	8.75	8.68	0.8	8.30	5.1	8.51	2.7
291.5	10.00	9.98	0.2	9.63	3.7	9.58	4.2
292.3	11.25	11.50	2.2	11.00	2.2	10.76	4.4
AAD (%)			1.5		3.3		3.8
Mole Fraction of Acetone in Aqueous Solution = 0.0721							
281.5	2.50	2.55	2.0	2.63	5.2	2.92	16.8
284.4	3.75	3.73	0.5	3.83	2.1	3.95	5.3
286.5	5.00	4.88	2.4	4.84	3.2	4.88	2.4
288.1	6.25	6.18	1.1	6.06	3.0	6.11	2.2
289.4	7.50	7.62	1.6	7.43	0.9	7.14	4.8
290.4	8.75	8.83	0.9	8.41	3.9	8.12	7.2
291.4	10.00	10.12	1.2	9.59	4.1	9.08	9.2
292.1	11.25	11.46	1.9	10.69	5.0	10.24	9.0
AAD (%)			1.5		3.4		7.1
Mole Fraction of Acetone in Aqueous Solution = 0.0936							
281.1	2.50	2.64	5.6	2.45	2.0	3.31	32.4
284.0	3.75	3.78	0.8	3.50	6.7	4.23	12.8
286.1	5.00	4.92	1.6	4.70	6.0	4.88	2.4
287.6	6.25	6.21	0.6	5.91	5.4	5.83	6.7
288.9	7.50	7.73	3.1	7.32	2.4	6.91	7.9
290.0	8.75	9.12	4.2	8.39	4.1	8.04	8.1
290.9	10.00	10.23	2.3	9.60	4.0	8.96	10.4
291.7	11.25	11.61	3.2	10.71	4.8	9.85	12.4
AAD (%)			2.7		4.4		11.6

Table 13. Continued

<i>T</i> (K)	<i>P</i> _{exp} (MPa) ⁷	<i>P</i> _{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}	AD (%)	<i>P</i> _{model} (MPa), using the PR EoS ¹⁶ + UNIFAC ^{18,19}	AD (%)	<i>P</i> _{model} (MPa), literature model ⁷	AD (%)
Mole Fraction of Acetone in Aqueous Solution = 0.1437							
279.5	2.50	2.60	4.0	2.49	0.4	2.81	12.4
282.5	3.75	3.69	1.6	3.67	2.1	3.54	5.6
284.6	5.00	4.87	2.6	4.70	6.0	4.48	10.4
286.1	6.25	6.50	4.0	6.20	0.8	5.60	10.4
287.5	7.50	7.58	1.1	7.20	4.0	6.80	9.3
288.6	8.75	8.63	1.4	8.28	5.4	7.87	10.1
289.5	10.00	9.83	1.7	9.51	4.9	9.02	9.8
290.3	11.25	11.61	3.2	11.03	2.0	10.16	9.7
AAD (%)			2.4		3.2		9.7
Mole Fraction of Acetone in Aqueous Solution = 0.2755							
275.6	2.50	2.39	4.4	2.49	0.4	2.76	10.4
278.8	3.75	3.75	0.0	3.39	9.6	3.72	0.8
280.9	5.00	4.94	1.2	4.61	7.8	4.74	5.2
282.6	6.25	6.40	2.4	5.89	5.8	5.80	7.2
284.1	7.50	7.85	4.7	7.20	4.0	6.87	8.4
285.2	8.75	9.00	2.9	8.19	6.4	7.74	11.5
286.2	10.00	10.33	3.3	9.24	7.6	8.66	13.4
287.1	11.25	11.59	3.0	10.59	5.9	9.55	15.1
AAD (%)			2.7		5.9		9.0
Mole Fraction of Acetone in Aqueous Solution = 0.4769							
274.2	3.75	3.80	1.3	3.85	2.7	3.42	8.8
276.6	5.00	4.89	2.2	4.61	7.8	4.24	15.2
278.6	6.25	5.70	8.8	5.41	13.4	5.09	18.6
280.2	7.50	7.26	3.2	6.93	7.6	6.17	17.7
281.5	8.75	8.21	6.2	7.83	10.5	7.12	18.6
282.6	10.00	9.35	6.5	8.68	13.2	8.27	17.3
283.7	11.25	10.53	6.4	9.82	12.7	9.30	17.3
AAD (%)			4.9		9.7		16.2

occupancy of cavities as follows:¹

$$\mu_w^\beta - \mu_w^H = \Delta\mu_w^H = -RT \sum_i v_i \ln(1 - \sum_k \theta_{ki}) \quad (3)$$

R and *T* represent the universal gas constant and temperature, respectively. *v_i* is the number of cavities per water molecule in the unit cell.¹ The parameter θ_{ki} is defined as¹

$$\theta_{ki} = \frac{C_{ki} f_k}{1 + \sum_j C_{ji} f_j} \quad (4)$$

f represents the fugacity, which is calculated as described in the next section. *C_{ki}* is the Langmuir constant and is defined as¹

$$C_{ki} = \frac{4\pi}{kT} \int_0^{\bar{R}-a} \exp\left(\frac{-\omega(r)}{kT}\right) r^2 dr \quad (5)$$

where *k* stands for Boltzmann's constant. For calculation of the Langmuir constant, the potential function, $\omega(r)$, is

calculated as follows:¹

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

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

In the above equations, *z*, \bar{R} , and *r* are the coordination number, the radius of the cavity, and the distance of the guest molecule from the cavity center, respectively. *N* is an integer. Table 1 reports the Kihara potential parameters, *a*, σ , and ϵ , used in this thermodynamic model.¹

2.2. Chemical Potential of Water in the Liquid Phase. Holder et al.²⁰ presented a method to find the chemical potential of water in the aqueous phase:

$$\frac{\Delta\mu_w^L}{RT} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^T \frac{\Delta h_w}{RT^2} dT + \int_{P_0}^P \frac{\Delta v_w}{RT} dP - \ln(\gamma_w x_w) \quad (8)$$

where $\Delta\mu_w^L = \mu_w^\beta - \mu_w^L$, μ_w^L is the chemical potential of water in the aqueous phase. $\Delta\mu_w^0$ is the chemical potential difference between the empty hydrate lattice and ice at the ice point and zero pressure, Δv_w represents the molar volume difference between the empty hydrate

Table 14. Three-Phase (L_w-H-G) Equilibria for the Methane + 1,4-Dioxane + Water System

T (K)	P_{exp} (MPa) ⁸	P_{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}	AD (%)	P_{model} (MPa), using the PR EoS ¹⁶ + UNIFAC ^{18,19}	AD (%)	P_{model} (MPa), literature model ⁸	AD (%)
Mole Fraction of 1,4-Dioxane in Aqueous Solution = 0.01							
279.82	2.06	1.97	4.4	2.11	2.4	2.10	1.9
283.84	3.55	3.46	2.5	3.67	3.4	3.65	2.8
286.58	5.05	4.98	1.4	5.30	5.0	5.25	4.0
288.48	6.55	6.40	2.3	6.46	1.4	6.75	3.1
289.92	8.05	7.94	1.4	8.12	0.9	8.17	1.5
291.17	9.55	9.48	0.7	9.72	1.8	9.64	0.9
292.18	11.05	10.73	2.9	11.51	4.2	11.03	0.2
293.06	12.55	12.33	1.8	13.12	4.5	12.42	1.0
293.80	14.05	14.11	2.2	14.70	2.9	13.71	1.9
AAD (%)			2.2		2.9		1.9
Mole Fraction of 1,4-Dioxane in Aqueous Solution = 0.02							
282.16	2.06	1.92	6.8	1.86	9.7	2.17	5.3
286.13	3.56	3.55	0.3	3.49	2.0	3.81	7.0
288.53	5.05	5.00	1.0	5.15	2.0	5.30	5.0
290.44	6.55	6.51	0.6	6.41	2.1	6.87	4.9
291.76	8.05	7.83	2.7	7.84	2.6	8.22	2.1
293.06	9.55	9.39	1.7	9.91	3.8	9.82	2.8
294.04	11.05	10.89	1.4	11.43	3.4	11.23	1.6
294.83	12.55	12.58	0.2	13.11	4.5	12.52	0.2
295.63	14.05	14.53	1.8	15.30	3.8	13.97	3.6
AAD (%)			1.8		3.8		3.6
Mole Fraction of 1,4-Dioxane in Aqueous Solution = 0.05							
278.30	1.06	1.03	2.8	0.92	13.2	0.93	12.3
284.71	2.56	2.62	2.3	2.65	3.5	2.53	1.2
287.88	4.06	4.14	2.0	4.26	4.9	3.99	1.7
289.36	5.05	5.18	2.6	5.19	2.8	4.92	2.6
291.73	7.05	7.00	0.7	7.13	1.1	6.85	2.8
292.68	8.05	7.92	1.6	8.05	0.0	7.82	2.9
293.47	9.05	9.11	0.7	9.21	1.8	8.37	7.5
294.21	10.05	10.22	1.7	10.09	0.4	9.68	3.7
294.87	11.05	11.34	2.6	11.45	3.6	10.61	4.0
295.50	12.05	12.29	2.0	12.56	4.2	11.59	3.8
295.96	13.05	13.30	1.9	13.65	4.6	12.36	5.3
296.48	14.05	14.34	2.1	14.99	6.7	13.28	5.5
AAD (%)			1.9		3.9		4.4
Mole Fraction of 1,4-Dioxane in Aqueous Solution = 0.07							
282.66	2.06	2.12	2.9	2.12	2.9	1.90	7.8
286.81	3.56	3.71	4.2	3.44	3.4	3.50	1.7
289.29	5.06	5.03	0.6	4.99	1.4	4.97	1.8
291.18	6.55	6.48	1.1	6.40	2.3	6.48	1.1
292.82	8.05	7.95	1.2	8.31	3.2	8.16	1.4
294.02	9.55	9.57	0.2	9.76	2.2	9.66	1.2
294.91	11.05	10.91	1.3	11.26	1.9	10.94	1.0
295.75	12.55	12.55	0.0	12.63	0.6	12.31	1.9
296.52	14.05	13.89	1.1	14.51	3.3	13.71	2.4
AAD (%)			1.4		2.4		2.2
Mole Fraction of 1,4-Dioxane in Aqueous Solution = 0.10							
281.87	2.06	2.07	0.5	2.07	0.5	1.90	7.8
285.92	3.56	3.47	2.5	3.61	1.4	3.44	3.4
288.54	5.06	4.88	3.6	5.07	0.2	4.99	1.4

Table 14. Continued

T (K)	P_{exp} (MPa) ⁸	P_{model} (MPa), using the SRK EoS ¹⁷ + UNIFAC ^{18,19}	AD (%)	P_{model} (MPa), using the PR EoS ¹⁶ + UNIFAC ^{18,19}	AD (%)	P_{model} (MPa), literature model ⁸	AD (%)
290.49	6.56	6.52	0.6	6.45	1.7	6.56	0.0
291.91	8.06	7.86	2.5	8.08	0.2	8.01	0.6
293.16	9.56	9.44	1.3	9.78	2.3	9.55	0.1
294.06	11.05	10.81	2.2	11.24	1.7	10.85	1.8
294.96	12.55	12.36	1.5	12.97	3.3	12.31	1.9
295.7	14.05	14.11	0.4	14.91	6.1	13.66	2.8
AAD (%)			1.7		1.9		2.2
Mole Fraction of 1,4-Dioxane in Aqueous Solution = 0.20							
278.21	2.06	2.09	1.5	2.35	14.1	2.02	1.9
282.21	3.55	3.55	0.0	3.57	0.6	3.56	0.3
284.94	5.05	5.02	0.6	4.75	5.9	5.2	3.0
287.1	6.55	6.32	3.5	6.33	3.4	7.01	7.0
288.44	8.05	7.65	5.0	7.70	4.3	8.44	4.8
289.64	9.55	9.35	2.1	9.34	2.2	9.98	4.5
290.64	11.05	11.00	0.5	11.51	4.2	11.48	3.9
291.59	12.55	12.53	0.2	13.09	4.3	13.11	4.5
292.34	14.05	13.80	1.8	14.34	2.1	14.55	3.6
AAD (%)			1.7		4.6		3.7
Mole Fraction of 1,4-Dioxane in Aqueous Solution = 0.30							
275.83	2.06	2.39	16.0	2.28	10.7	2.64	28.2
280.03	3.56	3.83	7.6	3.75	5.3	4.62	29.8
282.64	5.06	4.80	5.1	4.60	9.1	6.56	29.6
284.58	6.56	6.30	4.0	6.21	5.3	8.53	30.0
286.28	8.06	7.61	5.6	7.75	3.8	10.76	33.5
287.36	9.55	9.14	4.3	9.39	1.7	12.47	30.6
288.59	11.05	11.11	0.5	11.95	8.1	14.76	33.6
289.43	12.55	13.07	4.1	13.98	11.4	16.54	31.8
290.09	14.05	14.61	4.0	15.85	12.8	18.06	28.5
AAD (%)			5.7		7.6		30.6

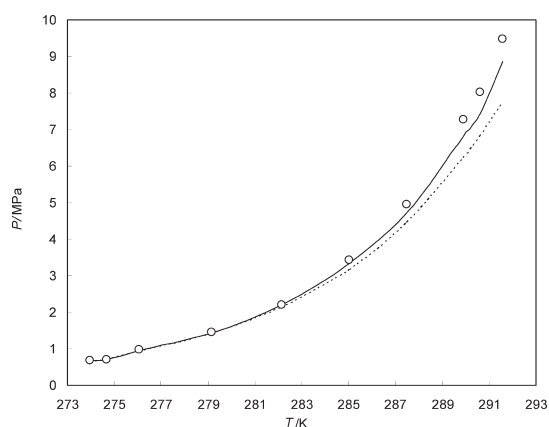


Figure 1. L_w –H–G– L_{HC} equilibria for the methane + cyclohexane + water system. Symbols represent experimental data.²⁸ Solid curve: Prediction of the model using the PR¹⁶ EoS for modeling of the gas phase. Dashed curve: Prediction of the model using the SRK¹⁷ EoS for modeling of the gas phase.

lattice and ice/liquid water, Δh_w is the enthalpy difference between the empty hydrate lattice and ice/liquid water, T_0 stands for the ice point, P_0 is zero pressure, γ_w is the activity coefficient of water, P represents

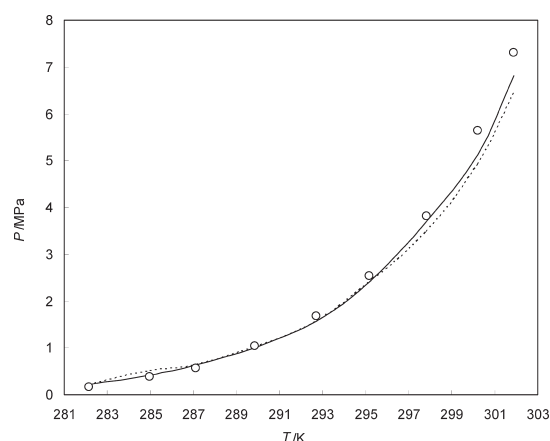


Figure 2. L_w –H–G– L_{HC} equilibria for the methane + cyclopentane + water system. Symbols represent experimental data.²⁸ Solid curve: Prediction of the model using the PR¹⁶ EoS for modeling of the gas phase. Dashed curve: Prediction of the model using the SRK¹⁷ EoS for modeling of the gas phase.

the pressure, and x_w represents the mole fraction of water in the aqueous phase.

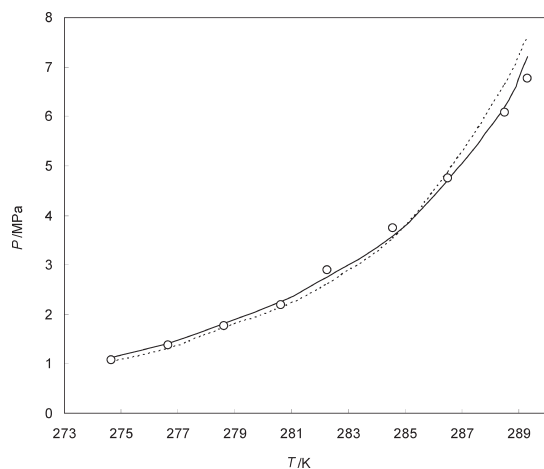


Figure 3. $L_w-H-G-L_{HC}$ equilibria for the methane + 1,1-dimethylcyclohexane + water system. Symbols represent experimental data.²⁹ Solid curve: Prediction of the model using the PR¹⁶ EoS for modeling of the gas phase. Dashed curve: Prediction of the model using the SRK¹⁷ EoS for modeling of the gas phase.

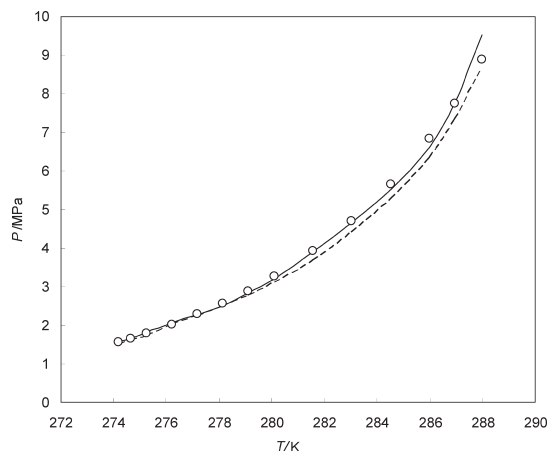


Figure 4. $L_w-H-G-L_{HC}$ equilibria for the methane + *cis*-1,2-dimethylcyclohexane + water system. Symbols represent experimental data.³⁰ Solid curve: Prediction of the model using the PR¹⁶ EoS for modeling of the gas phase. Dashed curve: Prediction of the model using the SRK¹⁷ EoS for modeling of the gas phase.

Δh_w is given by eq 9:²⁰

$$\Delta h_w(T) = \Delta h_w^0 + \int_{T_0}^T [\Delta C_{pw}^0 + \bar{a}(T - 273.15)] dT \quad (9)$$

where Δh_w^0 is the enthalpy difference between the empty hydrate lattice and ice at the ice point and zero pressure and ΔC_{pw}^0 represents the reference heat capacity difference between the empty hydrate lattice and liquid water at 273.15 K.

The parameters that were used for calculation of the water chemical potential in the aqueous phase are given in Table 2.²⁰

2.3. Gas-Phase Fugacity. As mentioned earlier, the PR¹⁶ and SRK¹⁷ equations of state with random mixing rules^{16,17} are used for calculating the gas-phase fugacity. Because of the low fugacities of the water-soluble hydrate former in the systems, it is assumed that the gas phase consists of pure methane in the case where a water-soluble hydrate former exists in the system.^{8,9} However, the model takes into

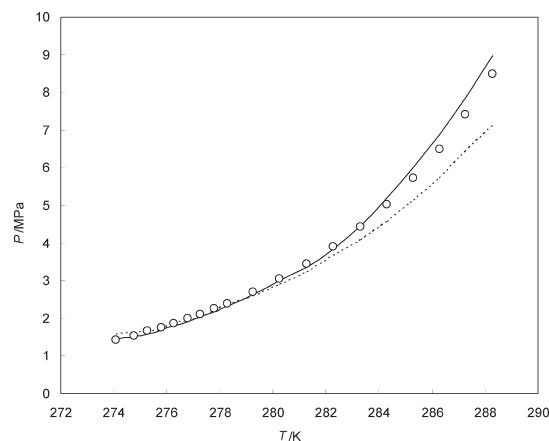


Figure 5. $L_w-H-G-L_{HC}$ equilibria for the methane + methylcyclohexane + water system. Symbols represent experimental data.³⁰ Solid curve: Prediction of the model using the PR¹⁶ EoS for modeling of the gas phase. Dashed curve: Prediction of the model using the SRK¹⁷ EoS for modeling of the gas phase.

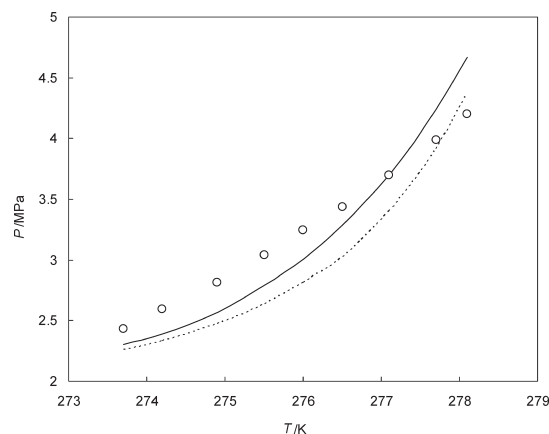


Figure 6. $L_w-H-G-L_{HC}$ equilibria for the methane + 2,2-dimethylpentane + water system. Symbols represent experimental data.²⁷ Solid curve: Prediction of the model using the PR¹⁶ EoS for modeling of the gas phase. Dashed curve: Prediction of the model using the SRK¹⁷ EoS for modeling of the gas phase.

account the distribution of the water-insoluble hydrate former in various phases including the gas phase. Tables 3 and 4 report the critical properties and acentric factors as well as the binary interaction parameters used in this thermodynamic model, respectively.

2.4. Aqueous/Liquid-Phase Fugacity. The fugacity of the component, f_k , in the liquid phase is calculated as follows:^{8,9}

$$f_k = x_k \gamma_k \phi_k^{\text{sat}} P_k^{\text{sat}} \exp\left(\frac{V_k^L(P - P_k^{\text{sat}})}{RT}\right) \quad (10)$$

In this equation, x_k , V_k^L , and γ_k are the mole fraction of component k , the molar volume of component k , and the activity coefficient of this component, respectively. ϕ_k^{sat} is the fugacity coefficient of component k at saturation condition which is assumed to be equal to unity. V_k^L is calculated by following the method of Poling et al.:¹⁹

$$V^L = 7(N'_H + N'_C + N'_O + N'_N + N'_{DB} + N'_{TB}) + 31.5N'_{Br} + 24.5N'_{Cl} + 10.5N'_F + 38.5N'_I + 21N'_S - 7^* \quad (11)$$

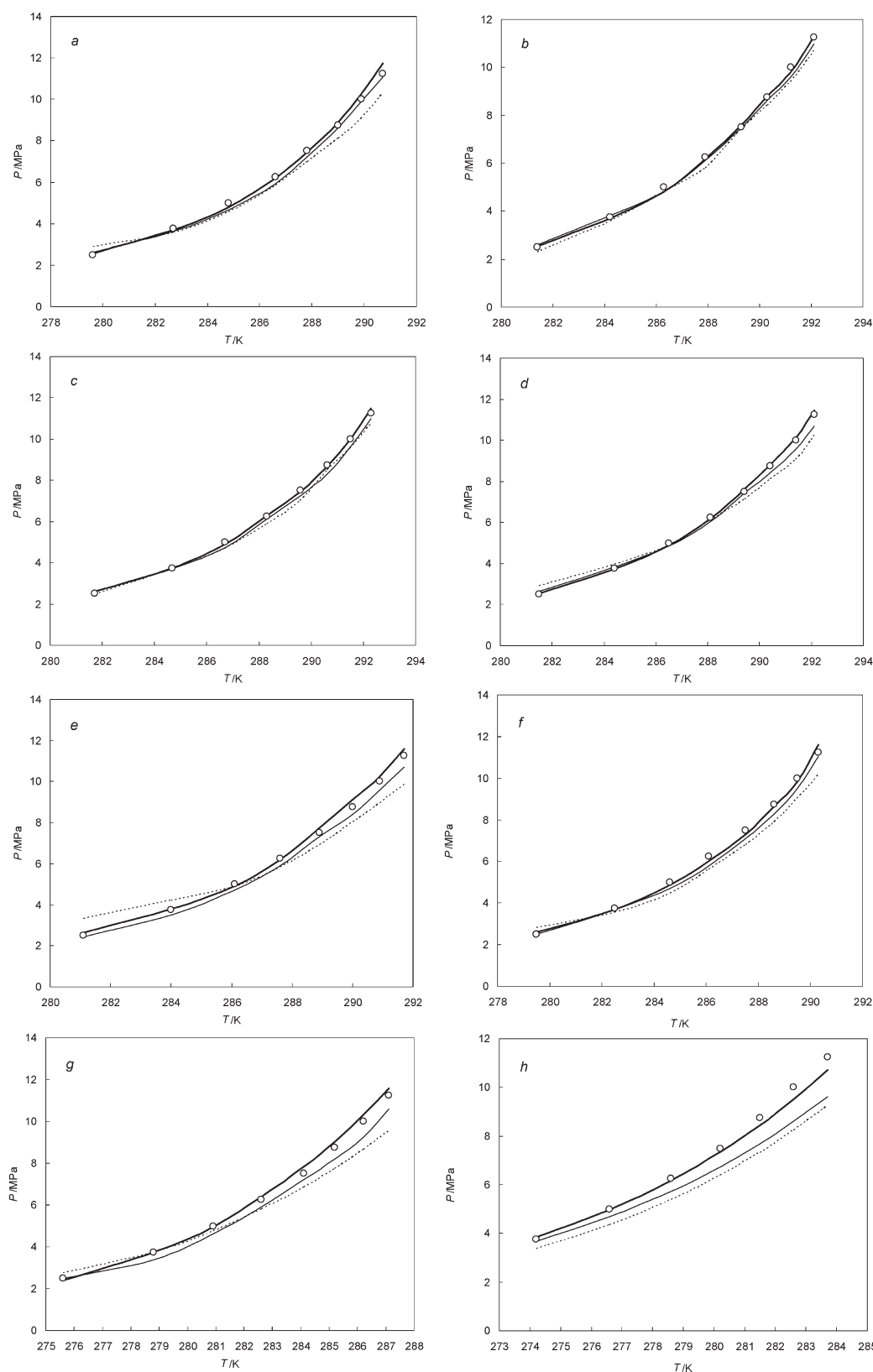


Figure 7. L_w-H-G equilibria for the methane + acetone + water system. Symbols represent experimental data.⁷ Solid curve: Prediction of the model using the PR^{16} EoS for modeling of the gas phase. Bold solid curve: Prediction of the model using the SRK^{17} EoS for modeling of the gas phase. Dashed curve: Prediction of literature model⁷ (in parts f and h, the smoothed predicted results are shown). Mole fraction of acetone in aqueous solution: (a) 0.0167; (b) 0.0333; (c) 0.0528; (d) 0.0721; (e) 0.0936; (f) 0.1437; (g) 0.2755; (h) 0.4769.

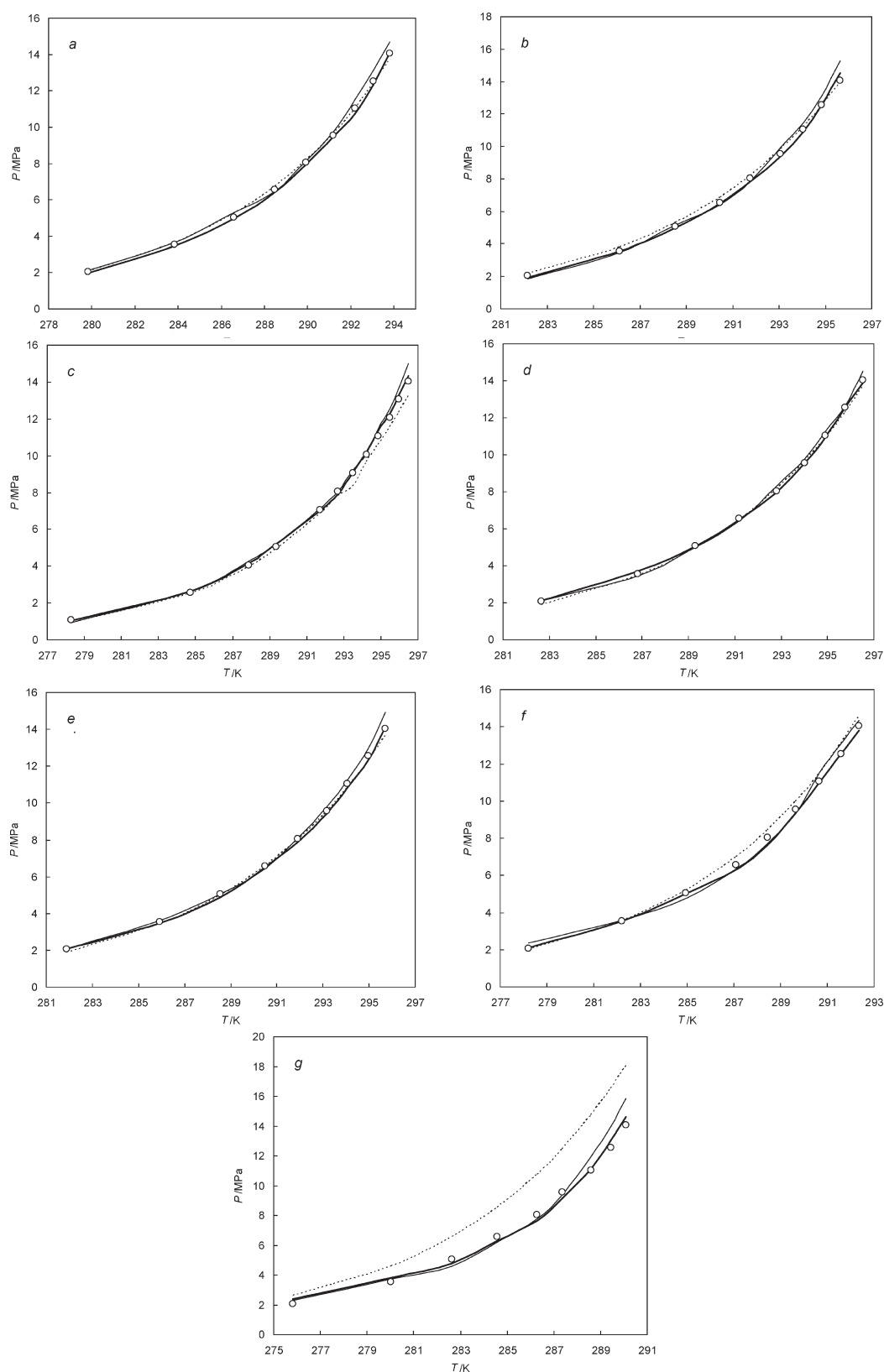


Figure 8. L_w –H–G equilibria for the methane + 1,4-dioxane + water system. Symbols represent experimental data.⁷ Solid curve: Prediction of the model using the PR¹⁶ EoS for modeling of the gas phase. Bold solid curve: Prediction of the model using the SRK¹⁷ EoS for modeling of the gas phase. Dashed curve: Prediction of the literature model.⁸ Mole fraction of 1,4-dioxane in aqueous solution: (a) 0.01; (b) 0.02; (c) 0.05; (d) 0.07; (e) 0.10; (f) 0.20; (g) 0.30.

where N shows the number of bonds and V^L has the unit of cm^3/mol . The subscripts in eq 11 are given in the Nomenclature.

Antoine's equation with constants $A-\overline{C}$, reported in Table 5, is used to calculate P_k^{sat} , the vapor pressure of pure compound:

$$\log(P_k^{\text{sat}}) = \left(A - \frac{B}{T + \overline{C}} \right) \quad (12)$$

In the above equation, P_k^{sat} and T are in mmHg and $^{\circ}\text{C}$, respectively.

2.4.1. Activity Coefficient Calculation for the Aqueous Phase. As mentioned earlier, the previous models assume that the aqueous phase contains water and a water-soluble hydrate former^{8,9} and the activity coefficients are calculated using the van Laar^{22–24} or Wilson²⁵ model. However, when the concentration of the water-soluble hydrate former increases, the solubility of methane in the aqueous phase deviates from that in pure water.^{8,9} This affects the concentration of water in the aqueous phase and the accuracy of the assumption that activity coefficients of water and a water-soluble hydrate former can be calculated from binary VLE data.^{8,9} Therefore, ternary VLE data for the system water + methane + water-soluble hydrate former should be used.^{8,9} To the best of our knowledge, such data are rare in the literature.

Calculation of the activity coefficients by the UNIFAC model^{18,19} is therefore more accurate than that of other models like van Laar^{22–24} or Wilson²⁵ which have been used in the literature. The UNIFAC model^{18,19} considers the presence of all components, including dissolved gas, in the aqueous phase. Table 6 reports the parameters and subgroups of the UNIFAC model^{18,19} used in our work.

3. RESULTS AND DISCUSSION

Tables 7–14 and Figures 1–8 compare the model results with some selected experimental data from the literature. It should be mentioned that the uncertainty of the literature data reported in these tables and shown in the figures is expected to be less than 0.5 K for the dissociation temperatures and not higher than 0.3 MPa for the dissociation pressures. The Kihara potential parameters were tuned using the experimental data reported in Tables 7–14 and shown in Figures 1–8. These parameters are given in Table 1, as mentioned earlier. Note that the Kihara potential parameters of methane were set to those reported in ref 1 because it has been shown that when the latter parameters are used, good predictions are obtained for equilibrium conditions of methane hydrates.¹

Four-phase equilibria ($L_w-G-L_{\text{HC}}-H$) of the cyclohexane, cyclopentane, 1,1-dimethylcyclohexane, *cis*-1,2-dimethylcyclohexane, methylcyclohexane, or 2,2-dimethylpentane + methane + water systems were first studied. The model results are reported in Tables 7–12 and illustrated in Figure 1–6, respectively. As mentioned earlier, it has been assumed that large cavities of sII/sH are occupied by heavy hydrate former molecules, while the rest are occupied by methane molecules. As can be observed in these tables and figures, the use of the PR equation of state (EoS)¹⁶ in the thermodynamic model yields better results than the SRK EoS.¹⁷

The results for modeling of three-phase equilibria (L_w-G-H) of methane–water–acetone are reported in Table 13 and are shown in Figure 7. Note that Mainusch et al.'s model,⁷ which is based on hydrate formation enthalpy, can predict the equilibrium conditions of this system. The experimental results were applied for fitting of the enthalpy function which seem to be questionable. As can be seen, the results of our thermodynamic model are in better agreement with the

experimental data. In our model, the use of the SRK¹⁷ EoS yields better results than the PR¹⁶ EoS.

Table 14 and Figure 8 compare the experimental L_w-G-H equilibrium data of methane–water–1,4-dioxane with the results of our model and the model of Jager et al.⁸ Note that Jager et al.⁸ assumed that the aqueous solution in equilibrium with hydrate and gas phases is a binary mixture of water and 1,4-dioxane, ignoring the presence of dissolved methane in the liquid phase. They computed the activity coefficient of water using the van Laar model.^{22–24} It is clear that the results of our thermodynamic model are in better agreement with the experimental data. Again, the use of the SRK¹⁷ EoS in our model yields better results than the PR¹⁶ EoS.

Overall, our model shows better predictions in comparison with the predictions of the literature models,^{7–9} particularly at high concentrations of acetone or 1,4-dioxane in aqueous solutions. This is partly because the use of the UNIFAC model^{18,19} for the latter aqueous solutions is more appropriate.

4. CONCLUSIONS

In this work, $L_w-G-L_{\text{HC}}-H$ phase equilibria of the cyclohexane, cyclopentane, 1,1-dimethylcyclohexane, *cis*-1,2-dimethylcyclohexane, methylcyclohexane, or 2,2-dimethylpentane + methane + water and L_w-G-H phase equilibria of the acetone or 1,4-dioxane + methane + water systems were modeled. The model uses either the SRK¹⁷ or PR¹⁶ EoS with random mixing rules for modeling of the gas phase, ignoring the presence of water and a water-soluble hydrate former. The hydrate phase is modeled using the van der Waals and Platteeuw solid solution model.¹⁵ The aqueous phase is modeled using the UNIFAC^{18,19} activity model. Note that, in the previous modeling studies, the aqueous phase was considered as a binary mixture consisting of water and a water-soluble hydrate former and the water activity was modeled using the van Laar^{22–24} or Wilson²⁵ activity model. In our model, the presence of a gas component (dissolved gas) is taken into account along with water and a hydrate former in the aqueous phase. The model results are in acceptable agreement with the experimental data. The use of the PR¹⁶ EoS in the systems containing water-insoluble hydrate formers yielded better results. In the systems containing acetone and 1,4-dioxane, the results of the SRK¹⁷ EoS were in better agreement with experimental data. In comparison with the predictions of literature models,^{7–9} the results of our model were in better agreement with the existing experimental data.

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■ NOMENCLATURE

A	parameter in eq 12
ΔD	absolute deviation
\bar{a}	heat capacity temperature dependency
a	Kihara potential parameter (spherical potential hard-core radius)
B	parameter in eq 12
\overline{C}	Langmuir constant
\overline{C}	parameter in eq 12
ΔC_p	heat capacity difference

EoS	equation of state
f	fugacity
G	gas
H	hydrate
Δh	enthalpy difference
k	Boltzmann's constant
k'	parameter of the UNIFAC activity model
L	liquid
N	an integer in eq 7
N'	number of bonds
V_L	molar volume
P	pressure
PR	Peng–Robinson
Q	parameter of the UNIFAC activity model
r	distance to the hydrate cavity center
R	universal gas constant
\bar{R}	radius of the hydrate cavity
R'	parameter of the UNIFAC activity model
SRK	Soave–Redlich–Kwong
T	temperature
VLE	vapor–liquid equilibria
ν	number of cavities per water molecule in a unit hydrate cell
$\Delta \nu$	volume difference
x	aqueous/liquid-phase mole fraction
z	coordination number

Greek Symbols

γ	activity coefficient
μ	chemical potential
ε	Kihara potential parameter
θ	fractional occupancy
$\Delta \mu$	chemical potential difference
σ	Kihara potential parameter (collision diameter)
φ	fugacity coefficient
ω	cell potential function
$\bar{\omega}$	acentric factor
β	empty hydrate lattice
δ	parameter of the cell potential function

Subscripts

Br	bromine
C	carbon
c	critical property
Cl	chlorine
DB	double bond
exp	experimental
F	fluorine
H	hydrogen
HC	hydrocarbon
I	iodine
i	type of cavity
j	type of molecule
k	type of molecule
N	nitrogen
O	oxygen
S	sulfur
TB	triple bond
W	water
0	reference property

Superscripts

H	hydrate phase
L	liquid phase
sat	saturated state
β	empty hydrate lattice
0	difference property between the specified state and the empty hydrate lattice

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