

Modelling of hydrate dissociation curves with a modified Cubic-Plus-Association equation of state.

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Abstract

A modified Cubic-Plus-Association equation of state (CPA EoS) has been presented in recent works that enforces the representation of the pure component critical point, is based on an extended Mathias-Copeman alpha function and uses a volume shift to improve liquid densities. In this work, this same version of the CPA model is applied together with the hydrate van der Waals and Platteeuw model for the description of hydrate dissociation curves. The model is applied to the description of both single and mixed guest hydrates, the results being compared with the available experimental data, and the predictions obtained using the commercial hydrates models from the Multiflash software. This analysis shows that, for most cases, this approach is accurate, with results similar to those of Multiflash. The accuracy of the model for describing the three phase compositions in hydrate + liquid + gas systems is also discussed.

Keywords: CPA, Equation of state, Gas hydrates, van der Waals-Platteeuw

Introduction

Gas hydrates can be a hazard, an energy resource, and a raw material for industrial applications. The first case is mainly observed in the oil and gas industry, where their occurrence leads to decreases in production, or in more extreme cases, the blockage of pipelines, which present dramatic effects, especially in deep sea drilling. ¹ However, the use of hydrates is also a promising approach for the capture of CO₂ ² and storage of gases such as methane ³ or hydrogen, ⁴ while the natural gas hydrates present in the ocean and permafrost are being considered as an alternative energy resource. ⁵

Gas hydrates are obtained when water molecules in the presence of a gas at high pressure and low temperature form crystalline structures, encasing the said gas molecules. Depending on the gas the structure of these hydrates may vary, existing three different hydrate structures denominated sI, sII and sH. ⁶

The modelling of hydrate phases requires a dedicated model, the most commonly applied models being based on the work of van der Waals and Platteeuw (vdWP). ⁷ From the modifications proposed to this model, the one from Parrish and Prausnitz, ⁸ is still one of the most widely applied.

While these models are applicable for hydrate phases, to describe the presence of other phases it is necessary to use a second model in tandem with those. Generally, for industrial applications, these fall into two categories: Equations of state or activity coefficient models. The former tends to be more frequently applied due to the high dissociation pressures of gas hydrates.⁹

While most process simulators use cubic equations of state, activity coefficient models or CPA¹⁰ to describe the fluid phases, some recent studies have also considered some SAFT variants. For the representation of non-inhibited hydrates of light gases and hydrocarbons some of these studies include those of Fouad *et al.*¹¹ and el Meragawi *et al.*¹² with PC-SAFT and that of Waseem and Alsaifi¹³ with the SAFT-VR Mie. These equations, as well as CPA, have the advantage of explicitly accounting for association, which tends to improve the description of the interactions between water and the hydrate formers in both the liquid and gas phases.

The goal of this study is to evaluate the performance of a recently modified CPA model, when coupled with the vdWP theory for the description of uninhibited hydrates. Throughout this work, a comparison between this approach and the hydrates model present on the Multiflash software¹⁴ (which also uses a version of CPA) is studied. Such a comparison is of high relevance as Multiflash is one of the most applied software packages for the study of hydrate dissociation and inhibition. For most compounds, the binary interaction parameters of the modified CPA model have been introduced on a previous work¹⁵ while studying gas solubility in water/water solubility in gas. Comparisons are also presented with the results by Waseem and Alsaifi¹³ and El Meragawi *et al.*¹²

Models

In what follows, for modelling the hydrate phase the Multiflash thermodynamics package model¹⁴ is used, where the modification proposed by Parrish and Prausnitz² to the van der Waals and Platteeuw theory¹ is applied. This model has been coupled with diverse equations of state, presenting a good accuracy for the description of hydrate phases, despite some known issues and limitations of the model, as is the case of the model assuming a spherical symmetry.

The modified CPA model, detailed below, was used for the fluid phases.^{16,17}

Modified CPA

The modified CPA EoS shares most of its structure with the simplified CPA.¹⁸ One of its distinctive differences concern the forcing of the correct representation of the pure compound critical temperatures and pressures, as presented in the equations below:

$$P_{CPA}(T_c^{exp}, v_c^{calc}) = P_c^{exp} \quad (1)$$

$$\left(\frac{\partial P}{\partial v}\right)_T \Big|_{T=T_c, v=v_c^{calc}} = 0 \quad (2)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T \Big|_{T=T_c, v=v_c^{calc}} = 0 \quad (3)$$

where T is temperature, P is pressure and v is the molar volume. Subscript c stands for critical.

Beside this change, the modified CPA also considers a different alpha function from the one used on the simplified CPA, as well as adds a volume shift to fit the saturated liquid density at $T = 0.7 T_c$, instead of fitting this property directly:

$$a(T) = a_c \left(1 + T' \times c_1 + T'^2 \times c_2 + T'^3 \times c_3 + T'^4 \times c_4 + T'^5 \times c_5 \right)^2 \quad (4)$$

with $T' = (1 - \sqrt{T_r})$, $T_r = T/T_c$

$$v_t = v_0 - c_{vs} \quad (5)$$

v_t is the volume after translation, v_0 is the volume before translation and c_{vs} is the volume shift.

As it is well known that higher order polynomial alpha functions tend to behave erratically when extrapolated above the critical point, a continuous interpolation procedure is used between T_c and $1.1 \times T_c$ after which the model considers the API alpha function for the compound.¹⁹

More details about this modified CPA model and its applications can be found in previous works.²⁰⁻²⁴ Table 1 presents the pure component parameters applied in this study.

Table 1 – Pure compound parameters applied in this work for the modified CPA.

Compound	a_c ($\text{Pa.m}^6.\text{mol}^{-2}$)	$b. 10^5$ ($\text{m}^3.\text{mol}^{-1}$)	$c1$	$c2$	$c3$	$c4$	$c5$	$\beta.10^2$	ε (J.mol^{-1})
water	0.43	2.39	0.56	-2.54	-2.01	1.46	8.63	0.483	22013
benzene	1.91	8.27	0.91	-1.94	13.14	-41.13	50.75		
THF	1.66	7.50	1.00	-2.55	13.41	-30.16	24.75		
methane	0.23	2.98	0.59	-1.47	9.02	-27.39	31.55		
ethane	0.57	4.51	0.71	-1.17	7.00	-20.37	22.42		
propane	0.95	6.27	0.82	-1.63	9.36	-24.39	23.68		
isobutane	1.35	8.07	0.89	-1.94	11.12	-29.03	28.57		
n-butane	1.41	8.07	0.88	-1.39	7.72	-20.51	21.48		
n-pentane	1.94	10.05	1.00	-2.08	12.24	-32.87	32.84		
N ₂	0.14	2.68	0.63	-1.45	9.42	-29.74	36.21		
O ₂	0.14	2.21	0.66	-2.05	10.83	-25.44	21.76		
CO ₂	0.37	2.97	0.90	-1.35	5.61	0.00	0.00		
H ₂ S	0.46	2.99	0.72	-1.07	4.82	-8.86	5.24		
Xe	0.42	3.57	0.56	-0.51	1.60	-5.49	7.49		

Results and discussion

This work addresses the study of the performance of the modified CPA for the description of uninhibited mixtures of water + hydrate formers. To evaluate the quality of these modelling results, all Figures (up to Figure 17) present results using both this version of CPA, and the CPA-Infochem model available in the thermodynamics package Multiflash.¹⁴ In Table 4 a comparison is presented for other equations of state and simulators reported by Waseem and Alsaifi¹³ and by El Meragawi *et al.*¹²

Most of the binary interaction parameters applied in this work for water + gases, using the modified CPA, were obtained from literature.¹⁵ For mixtures containing THF, no binary interaction parameter was applied between THF and the gases. However, between THF and water, binary interaction parameters were applied ($k_{ij} = -0.018$ and $\beta_{ij} = 0.0283$), while between

water and isobutane a k_{ij} of 0.2 (fitted to LLE data ²⁵) was applied. The pure compound parameters, as well as the binary interaction parameters used in this work are presented in Tables 2 and 3.

Table 2 – Binary interaction parameters for gas mixtures, using the modified CPA. xenon and oxygen were only analysed as single hydrate formers.

k_{ij}	methane	ethane	propane	<i>i</i> -butane	<i>n</i> -butane	<i>n</i> -pentane	N ₂	CO ₂	H ₂ S
methane		0.015	0.020	0.025	0.025	0.029	0.028	0.093	0.081
ethane	0.015		0.000	0.024	0.024	0.028	0.058	0.113	0.077
propane	0.020	0.000		0.000	0.000	0.027	0.072	0.112	0.071
<i>i</i> -butane	0.025	0.024	0.000		0.000	0.000	0.089	0.111	0.064
<i>n</i> -butane	0.025	0.024	0.000	0.000		0.000	0.086	0.111	0.065
<i>n</i> -pentane	0.029	0.028	0.027	0.000	0.000		0.100	0.110	0.059
N ₂	0.028	0.058	0.072	0.089	0.086	0.100		-0.032	0.152
CO ₂	0.093	0.113	0.112	0.111	0.111	0.110	-0.032		0.099
H ₂ S	0.081	0.077	0.071	0.064	0.065	0.059	0.152	0.099	

Table 3 – Binary interaction parameters between water/benzene/THF and the remaining compounds in study.

k_{ij}	water	benzene	THF
methane	-0.210 + 0.00185 T	0.030	0.000
ethane	0.000 + 0.00010 T	0.030	0.000
propane	-0.010 + 0.00089 T	0.029	0.000
<i>i</i> -butane	0.240	0.000	0.000
<i>n</i> -butane	0.200	0.000	0.000
<i>n</i> -pentane	0.210	0.000	0.000
N ₂	-0.600 + 0.00330 T	0.088	0.000
CO ₂	-0.070 + 0.00072 T	0.111	0.000
H ₂ S	0.170 - 0.00010 T	0.064	0.000
O ₂	0.540	0.000	0.000
Xe	0.000	0.000	0.000
benzene	0.170	-	0.000
THF	-0.018	0.000	-

To start this analysis, it is important to look at mixtures containing gaseous hydrocarbons. Figures 1 to 9 present results for pure and mixed hydrate formers of this family, with water, water + tetrahydrofuran, or water + benzene with gaseous. In Figure 1 the results for water + methane are presented.

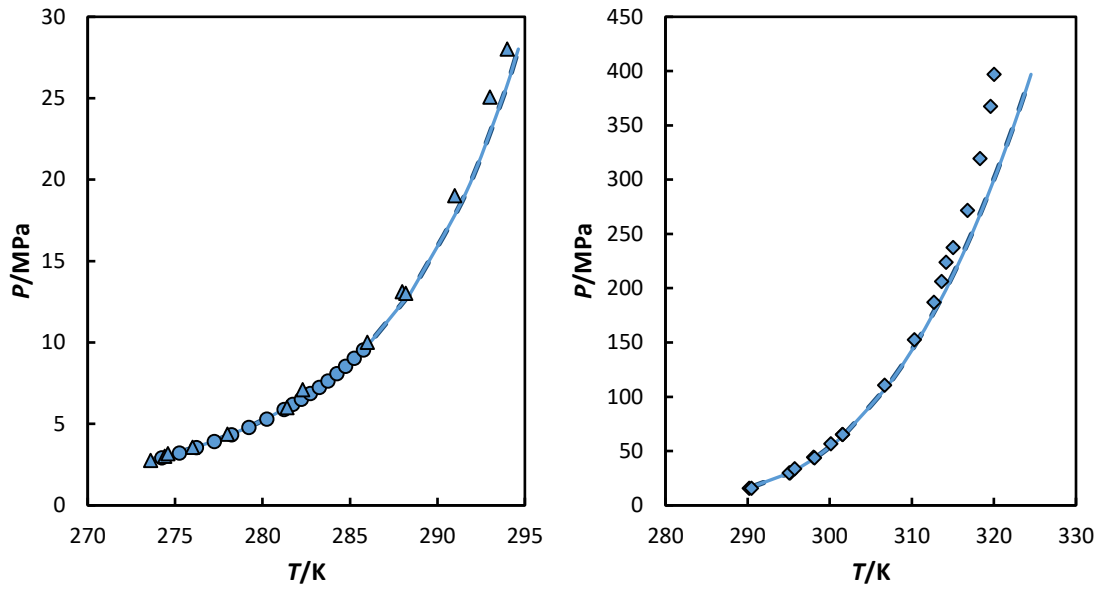


Figure 1 – Hydrate dissociation curve for water + methane. Full lines – This work; Dashed lines – Multiflash results. Data from Nakamura *et al.*²⁶ (o), Ross and Toczylkin²⁷ (Δ) and Marshall *et al.*²⁸ (\diamond).

The results for water + methane are very similar when considering the modified CPA and the CPA-Infochem model present on the Multiflash package. Both approaches are capable of accurate descriptions of the dissociation curve even at high pressure conditions. However, when tetrahydrofuran is added the difference between these approaches is more pronounced, as can be seen in Figure 2.

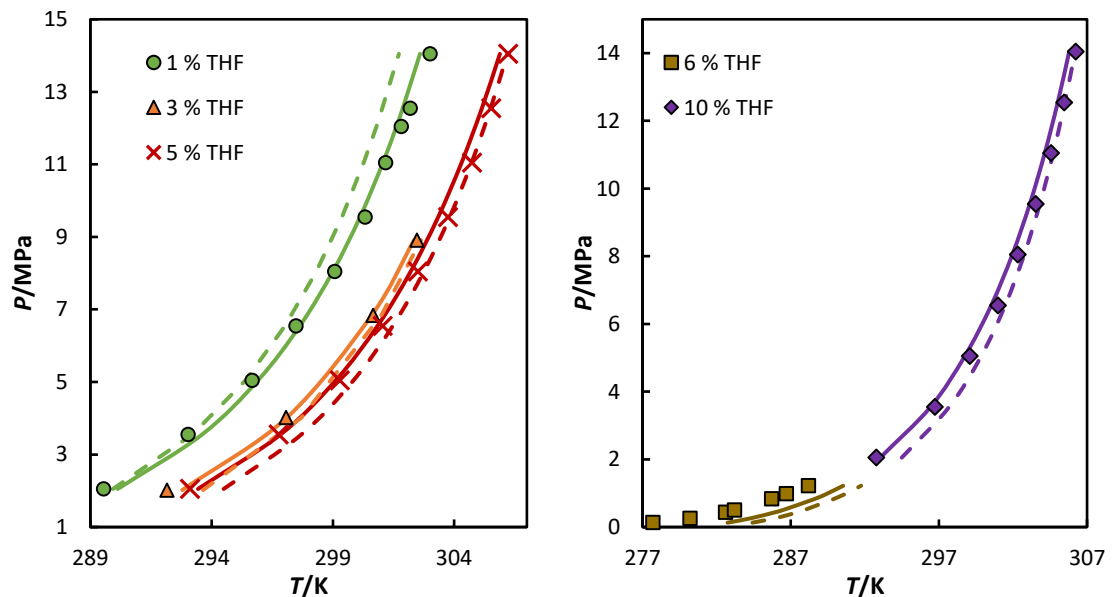


Figure 2 – Hydrate dissociation curve for water + methane + THF. Percentages are referent to the mole amount of THF on the liquid phase. Full lines – This work; Dashed lines – Multiflash results. Data from Seo *et al.*²⁹ (Δ), de Deugd *et al.*³⁰ (o, \diamond , X) and Zhang *et al.*³¹ (\square).

The present model tends to be slightly more accurate for these curves, while using a smaller number of interaction parameters. This might be due to the approach used on the fitting of the parameters. While the binary interaction parameters for water + THF, in the modified CPA, were

fitted to VLE data between 0.4 and 1 bar (view Table 1 on a previous work ²⁴), the parameters from Multiflash were fitted to other conditions and/or other types of data.

For benzene, the binary interaction parameters were fitted from LLE, as presented in a previous work. ²² Figure 3 presents results the hydrate dissociation curve for mixtures of water + methane + benzene.

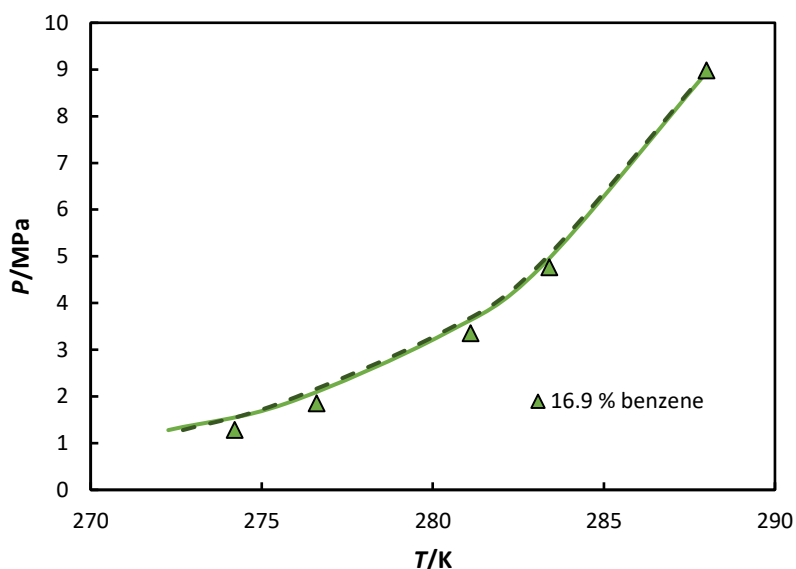


Figure 3 – Hydrate dissociation curve for water + methane + benzene. Percentages are referent to the total mole amount of benzene on the liquid phases. Full line – This work; Dashed line – Multiflash results. Data from Mohammadi *et al.* (Δ). ³²

Very similar results are obtained with both versions of the CPA model. Such results could be expected since both approaches use a version of CPA. However, the binary interaction parameters between water and benzene are rather different, with the present approach considering solvation and describing the LLE for this mixture, while the parameters from CPA-Infochem in Multiflash do not consider solvation and are fitted to a different type of data. It is important to note that the introduction of benzene changes the hydrate on the presented conditions from type from sI to sII, and that this change is observed by both models.

After looking at the description of hydrates containing methane, in Figure 4 the hydrates of ethane, propane and their mixtures are analysed.

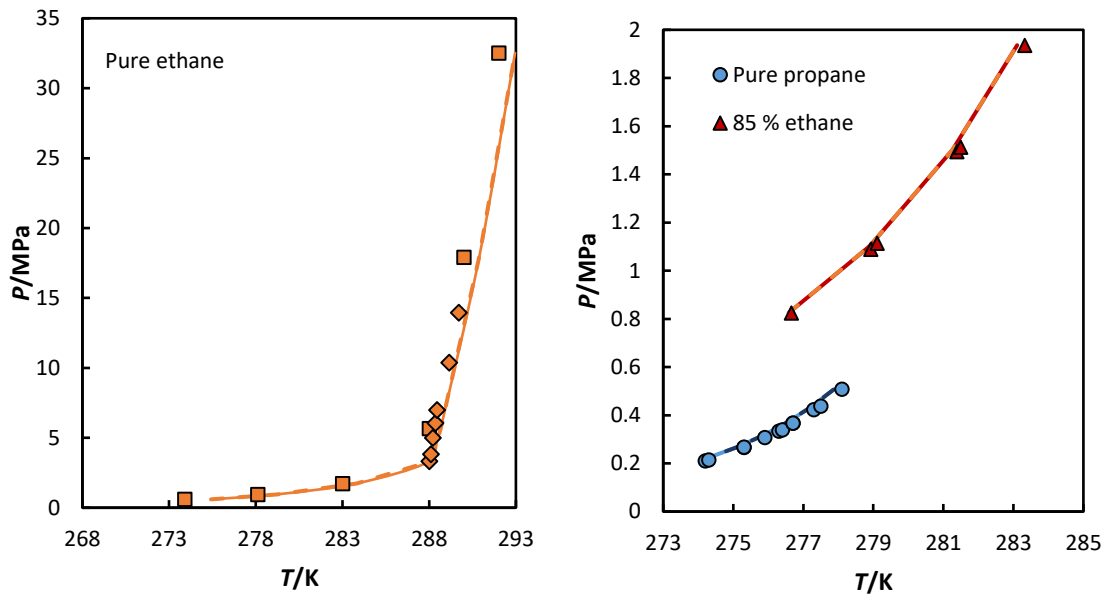


Figure 4 – Hydrate dissociation curve for mixtures of water with ethane and/or propane. Percentages are for the gas on a mole basis. Full lines – this work; Dashed lines – Multiflash results. Data from Maekawa ³³ (o), Nixdorf and Oellrich ³⁴ (Δ) Ross and Toczylkin ²⁷ (□) and Ng and Robinson ³⁵ (◊).

As in the case of methane hydrates, the results using the two CPA versions are very similar. It is important to note, that in spite of the differences in the liquid phase models and their parameter sets, both modelling results used the same solid “hydrate” phase parameterization. Both approaches are successful in the description of the hydrate dissociation curve of propane and of the mixture containing 85 mol % of ethane. The ethane hydrate dissociation curve is also obtained within a margin of 1.6 K from the experimental data.

To conclude the analysis of water + pure alkanes, Figure 5 presents the results for water + isobutane.

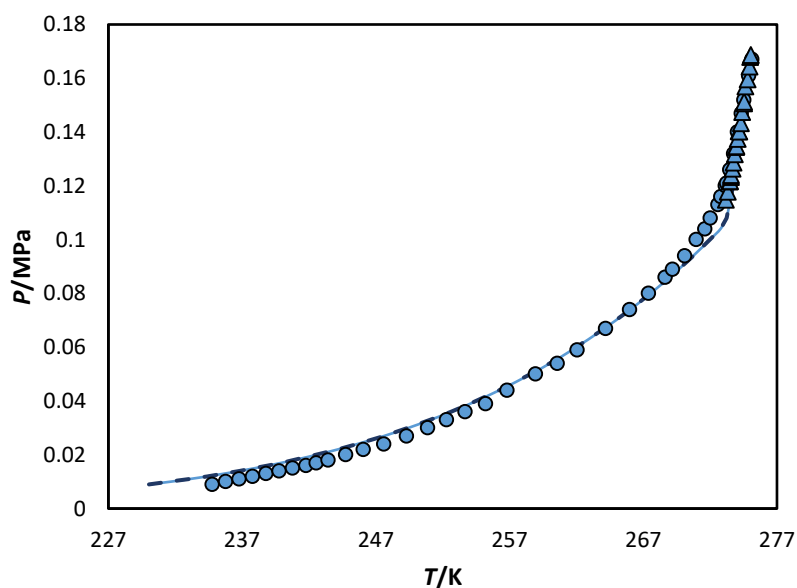


Figure 5 – Hydrate dissociation curves for mixtures of water + isobutane. Full line – This work; Dashed line – Multiflash results. Data from Buleiko *et al.* ³⁶ (o) and Rouher and Barduhn ³⁷ (Δ).

Both models describe this dissociation curve, above 250 K, within 2 K. For harsher temperature conditions, below 250 K, the deviations increase, but are always below 5 K. It is also important to note that above 265 K both models tend to over predict the dissociation temperatures, leading to more conservative estimates for flow assurance problems. El Meragawi *et al.*¹² have studied hydrates of pure isobutane, analyzing the data from Rouher and Bardhun between 273 and 275 K. Within this interval El Meragawi *et al.* results present great accuracy, while the CPA-based approaches predict a results that is intermediate between the two sets of available data.

In Figure 6 the hydrates formed from mixtures of methane with ethane or propane are studied.

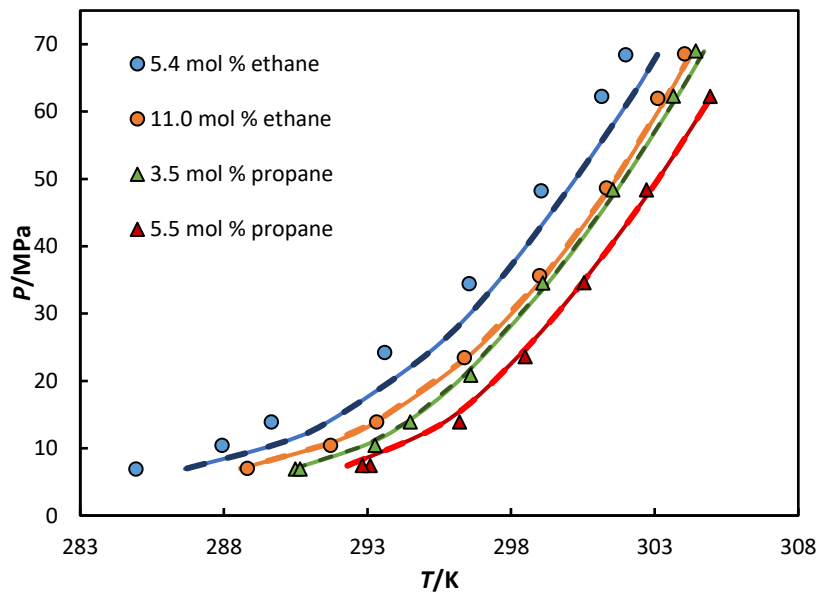


Figure 6 – Hydrate dissociation curves for water + methane + ethane or propane. Percentages are for the gas on a mole basis. Full lines – This work; Dashed lines – Multiflash results. Data from McLeod and Campbell.³⁸

As in previous results both models describe very well the experimental data. With the exception of the mixture with 5.4 mol % of ethane, the results are within 1 K of the experimental data. Nevertheless, even for that mixture, the results are obtained with a difference below 2 K from the experimental data.

Figure 7 presents results for hydrates of methane + isobutane.

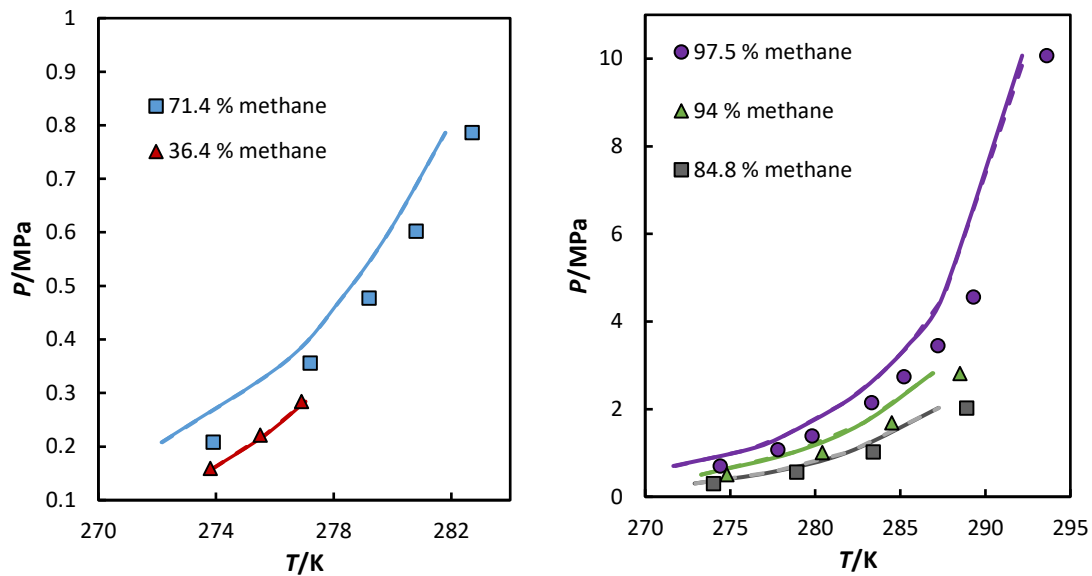


Figure 7 – Hydrate dissociation curves for water + methane + isobutane. Percentages are mole amounts on the gas phase. Full lines – This work; Dashed line – Multiflash results. Data from Wu *et al.*³⁹

For these mixtures, both models present results within a 2 K margin from the experimental data. In most cases, there is an underestimation of the dissociation temperature. El Meragawi *et al.*¹² studied hydrates of mixtures of isobutane and methane, with both the PC-SAFT and Peng Robinson equations of state. In their studies they analyzed a re-parameterization of both the original Kihara parameters by Sloan and Koh (S&K)⁴⁰ and the parameters of Parish and Prausnitz (P&P).^{8,41} Large differences were observed with both sets and a second set of parameters, using PC-SAFT presented the best results. Both the CPA-Infochem and modified CPA dissociation curves from this study use the same set of Kihara parameters from Multiflash. The average deviations on pressure for this mixture are smaller than those considering the S&K parameters, but present higher deviations than the best set with PC-SAFT. This comparison is presented on Table 4.

Figure 8 presents the results for ternary mixtures of methane, ethane and propane.

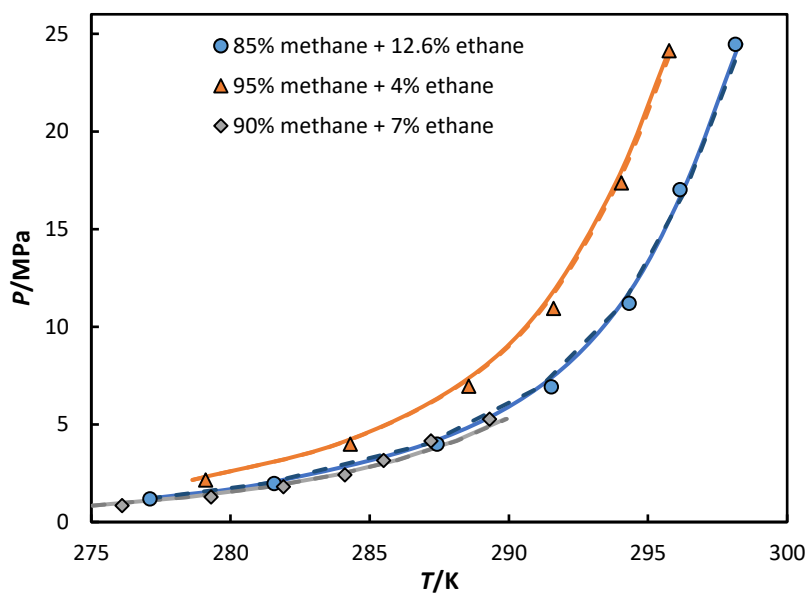


Figure 8 – Hydrate dissociation curves for mixtures of water + methane + ethane + propane. Percentages are the gas compositions in mole basis. Full lines – This work; Dashed lines – Multiflash results. Data from Nixdorf and Oellrich³⁴ (○, △) and Lee *et al.*⁴² (◇).

As before, both CPA versions combined with the Multiflash hydrates model present similar results for these hydrate dissociation curves. It is important to note that, as presented by Ballard and Sloan⁴³, there are ranges of concentration and temperature, where the structure of the hydrate is changed for these mixtures (between type sI and type sII). In this case both models present a change from sII to sI at the higher temperature for the mixture with higher content of methane. This is in agreement with the diagrams presented by Ballard and Sloan.⁴³

Before looking at other gases, that promote hydrate formation, it is interesting to look at the performance of both CPA models to cope with the addition of THF to ternary mixtures similar to those of Figure 8. These results are presented in Figure 9.

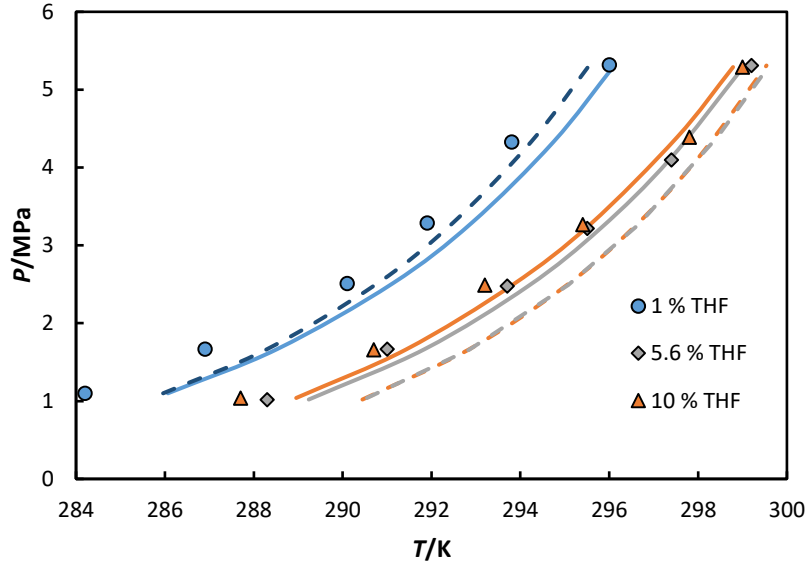


Figure 9 – Hydrate dissociation curve for water + methane (90 mol %) + ethane (7 mol %) + propane (3 mol %) + tetrahydrofuran. THF percentages are in mole basis in the liquid. Full lines – This work; Dashed lines – Multiflash results. Data from Lee *et al.*⁴²

Both CPA models are able to describe the dissociation curves, within a 3 K margin (Average of 0.69 K for the present model and of 1.06 K for the one on the Multiflash Package). The modified CPA model is slightly superior for the higher concentrations of THF, in the analyzed pressure range, while being slightly less accurate for the lower concentration data, similarly to what was observed previously for methane hydrates in Figure 2.

Having looked at hydrates containing hydrocarbons it is now important to look at other hydrate forming gases such as N₂, O₂, CO₂ and H₂S. Figure 10 presents the results for water + nitrogen and oxygen.

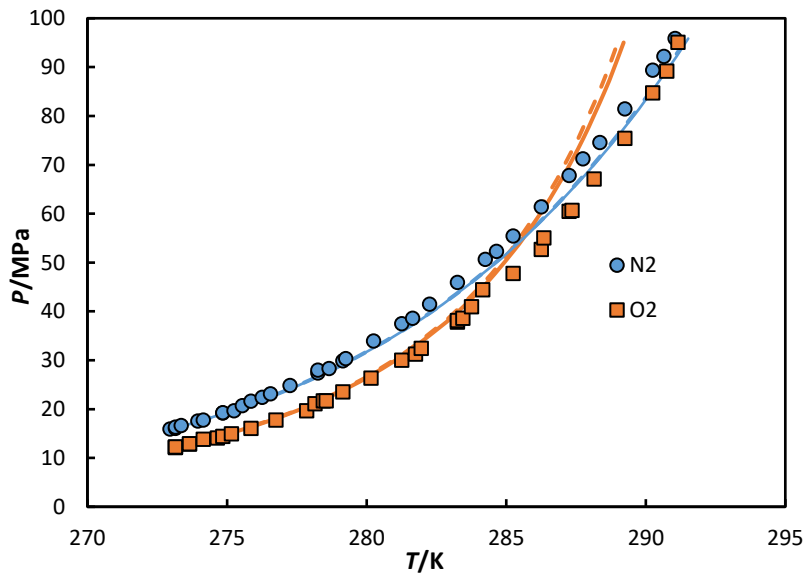


Figure 10 – Hydrate dissociation curves for water + oxygen or nitrogen. Full lines – This work; Dashed lines – Multiflash results. Data from van Cleef and Diepen.⁴⁴

Both variants of the CPA model provide an accurate description of nitrogen hydrates, while for the description of oxygen hydrates, both are able to accurately describe the dissociation curve up to around 285 K, but then overestimate the dissociation pressure.

Figure 11 presents the results for CO₂-hydrates.

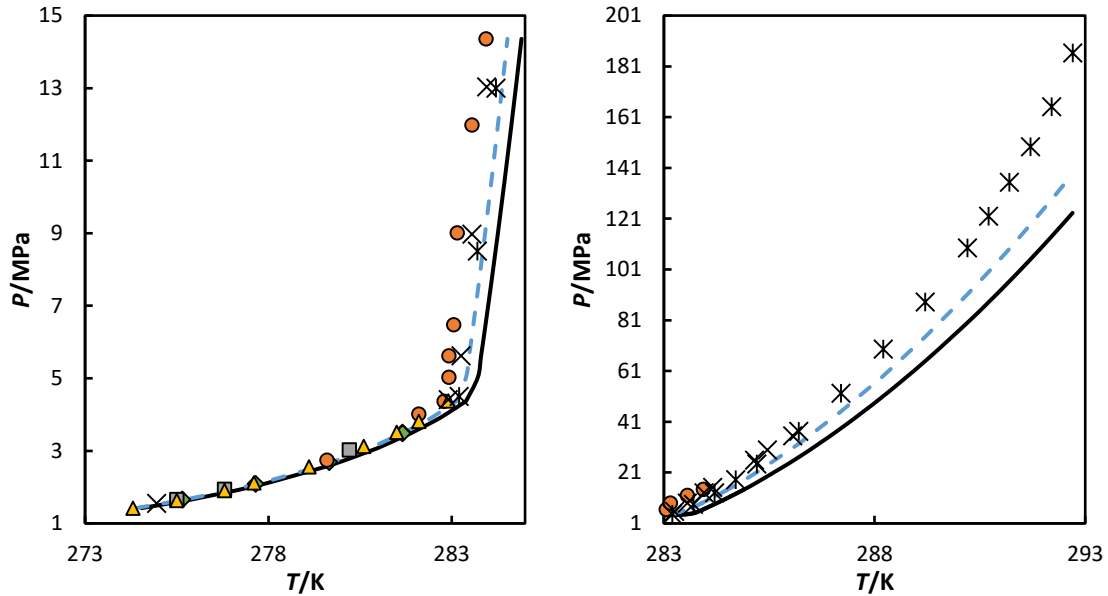


Figure 11 – Hydrate dissociation curve for water + CO₂. Full lines – This work; Dashed lines – Multiflash results. Data from Ferrari *et al.*⁴⁵ (\diamond), Ng and Robinson³⁵ (o), Breland and Englezos⁴⁶ (\square) Adisamito *et al.*⁴⁷ (Δ), Takenouchi and Kennedy⁴⁸ (*) and Chapoy *et al.*⁴⁹ (X)

The hydrate dissociation curve of CO₂, as for the mixtures containing THF presented before, show relevant differences between the two CPA models. Here, the performance of the Multiflash CPA-Infochem model is superior in the whole range of temperatures, being more noticeable in the hydrate-liquid phase boundary. As in previous cases, the fitting of the binary interaction parameters is different in the two approaches, with the modified CPA binary interaction parameters, being fitted to CO₂ solubility data in liquid water.¹⁵ In the portion of the diagram detailing water-liquid-hydrate, there are relevant differences between the experimental data. The present set of Kihara parameters are correct for the data of Takenouchi and Kennedy⁴⁸ and Chapoy *et al.*⁴⁹, when considering the Multiflash model. Thus, we opted to keep this set of parameters.

For mixtures containing CO₂ and benzene, the results are presented in Figure 12.

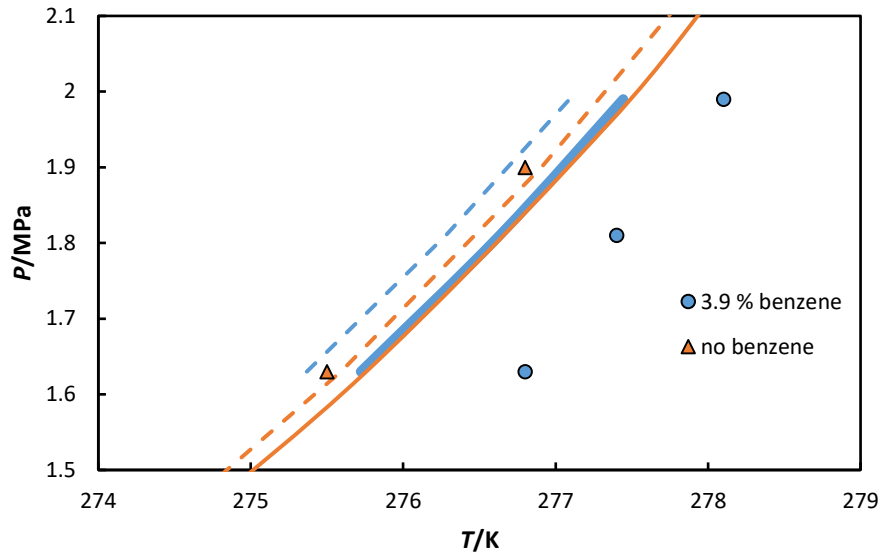


Figure 12 – Hydrate dissociation curve for water + CO₂ + benzene. Percentages are referent to the total amount in mole of benzene on the liquid phases. Full line – This work; Dashed line – Multiflash results. Data from Tavasoli and Feyzi⁵³ (o) and Adisamito *et al.*⁴⁷ (Δ).

The introduction of benzene in this mixture leads to a stabilization of the hydrate structure of type I. The models tend to present the opposite effect and fail in this increase in temperature due to the presence of benzene and thus, the present version, which already overestimated the dissociation temperatures for water + CO₂ and presents a smaller change when compared to the pure CO₂ hydrate, presents more accurate results.

Figures 13 and 14 present results for pure H₂S and H₂S containing mixtures.

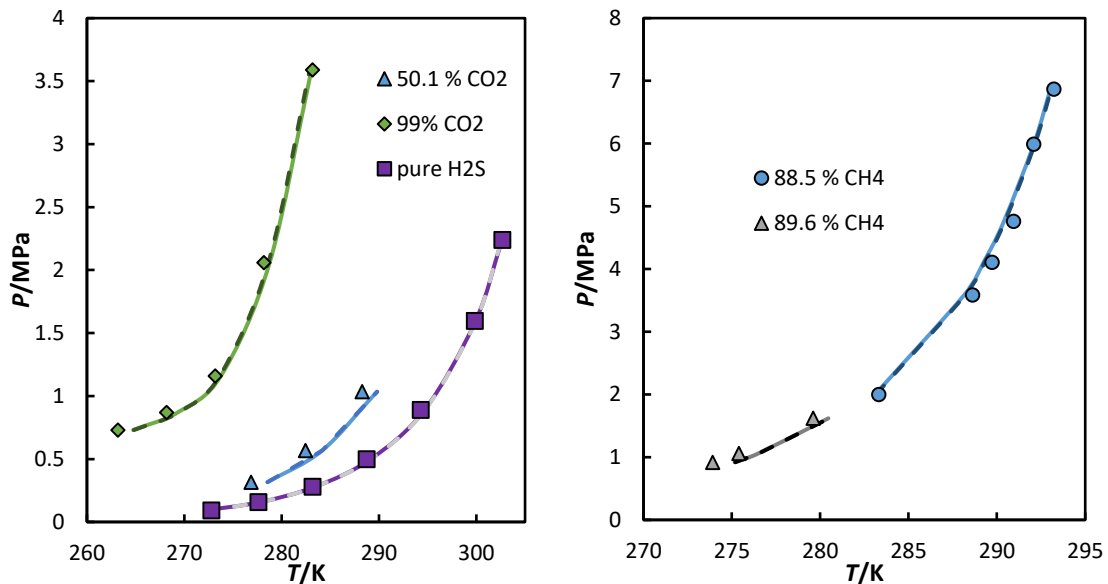


Figure 13 – Hydrate dissociation curves for mixtures of water, H₂S and methane or CO₂. Percentages are mole amounts in the gas. Full lines – This work; Dashed lines – Multiflash. Data from Selleck *et al.*⁵⁴ (□), Mohammadi and Richon⁵⁵ (Δ), Ward *et al.*⁵⁶ (o) and Chen *et al.*⁵⁷ (◇).

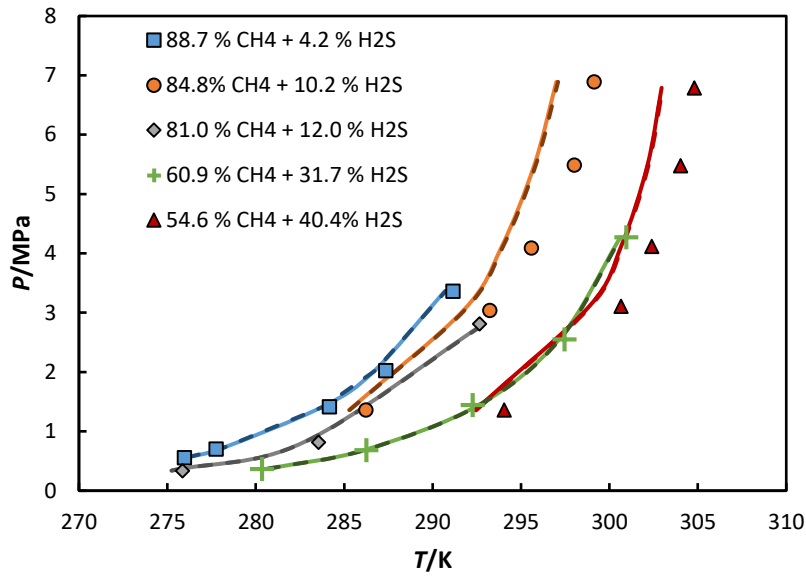


Figure 14 – Hydrate dissociation curves for water + H₂S + methane + propane. Percentages are mole amounts in the gas. Full lines – This work; Dashed lines – Multiflash. Data from Ward *et al.*⁵⁶ (O, Δ) and Schroeter *et al.*⁵⁸ (□, ◇, +).

For these mixtures, the model results are quite accurate, even when CO₂ is present. However, somewhat higher deviations are obtained for the data by Ward *et al.*⁵⁶. The mole fraction of propane, in these mixtures, is smaller than that of the other three mixtures (approximately 5 mole %, whereas for the other sets of data the mole fraction is approximately 7%).

The last pure hydrate former in this study is xenon, which is presented in Figure 15.

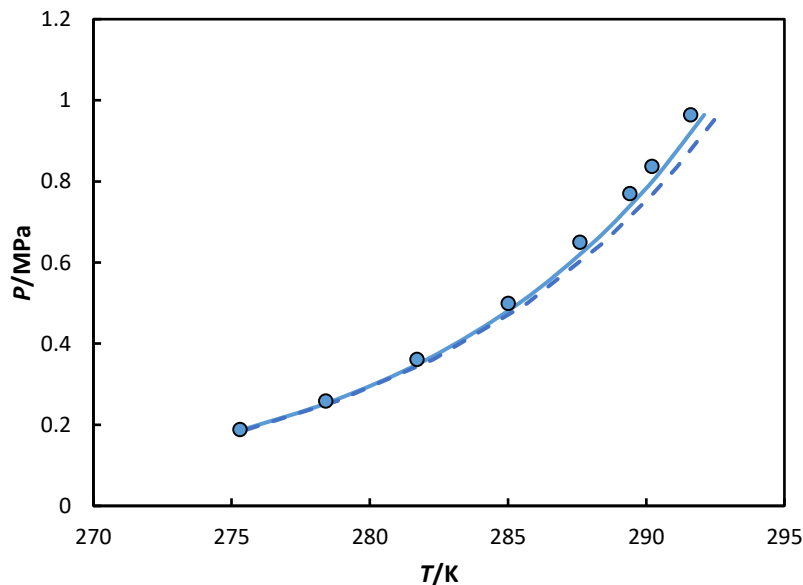


Figure 15 – Hydrate dissociation curves for water + xenon. Full line – This work; Dashed line – Multiflash. Data from Maekawa⁵⁹ (o).

The xenon hydrate dissociation temperatures were predicted within 1 K with both CPA models. The modified CPA model here used is slightly more accurate at higher temperatures and reduces

the max ΔT to half of its value. Both approaches are purely predictive, with no binary interaction parameters being used.

After analyzing binary and ternary mixtures containing CH_4 , CO_2 , H_2S and nitrogen, it is important to look at sour gases containing all four compounds. Figure 16 presents results for the hydrate dissociation curves of three sour gases determined experimentally by Liu *et al.*⁶⁰

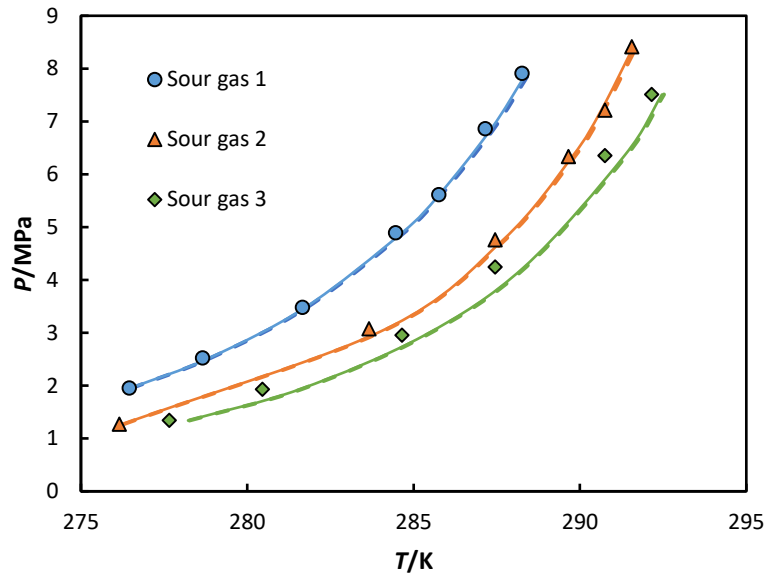


Figure 16 – Hydrate dissociation curves for water + Sour Gas (CH_4 , N_2 , CO_2 and H_2S). Compositions of the sour gases are presented on Table A1 of the supporting information. Full lines – This work; Dashed lines – Multiflash. Data from Liu *et al.*⁶⁰ (o, Δ , \diamond)

As in the case of the binary and ternary gases containing these compounds, the results are accurate with both approaches predicting the experimental dissociation curved within 1.2 K.

To conclude the study seven other mixtures are studied, including three synthetic natural gas mixtures.^{61–63} The results are presented on Figure 17.

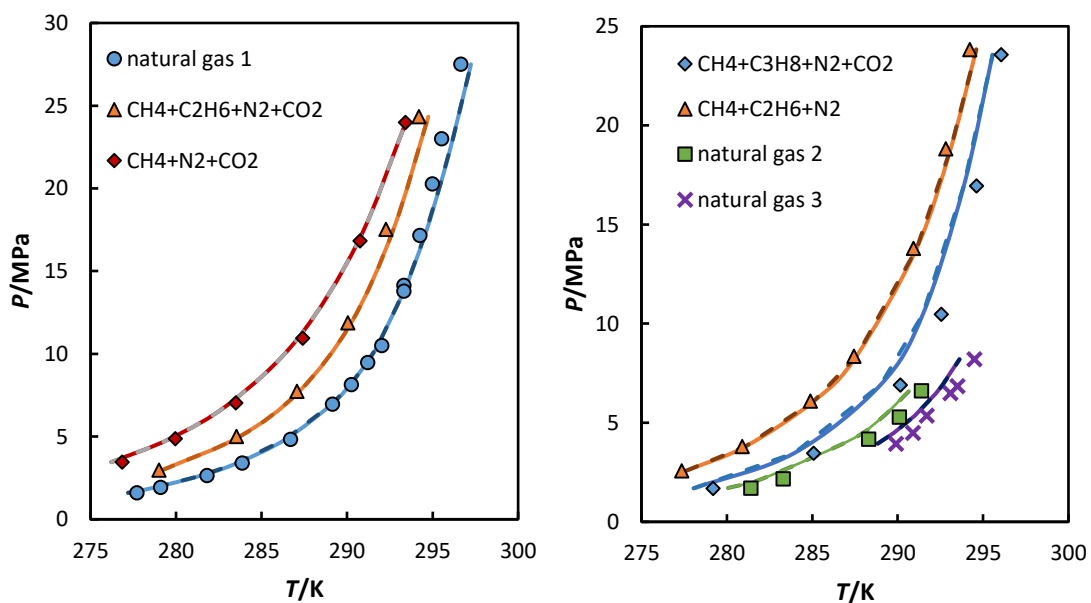


Figure 17 – Hydrate dissociation curves for multicomponent gas mixtures. Compositions of the gases are presented on Table A1 of the supporting information. Full lines – This work; Dashed lines – Multiflash results. Data from Wilcox *et al.*⁶¹ (o), Nixdorf and Oellrich³⁴ (◊, Δ), Lee and Kang⁶² (□) and Saberi *et al.*⁶³

The results here shown reveal again a similar performance of the two CPA-based approaches.

Despite having compared the results with those of Multiflash, which also uses a CPA model, it is also important to compare these results with those of other approaches. Table 4 shows deviations, on dissociation pressures, obtained for twelve of the systems analyzed in this work. Results with the modified CPA and Multiflash CPA-Infochem are compared to those by Waseem and Alsaifi¹³ with SAFT-VR Mie-LJ, and those by El Meragawi *et al.*¹² using PC-SAFT and PR, with two different sets of Kihara parameters, as well as with those obtained from the CSMGem simulator also by El Meragawi *et al.*¹².

Table 4 – Comparison of deviations (%AAD for dissociation *P*) between the modified CPA (this work), Multiflash CPA-Infochem and the results presented by Waseem and Alsaifi¹³ and by El Meragawi *et al.*,¹² for some of the mixtures studied in this work.

	T range (K)	This work	SAFT-VR Mie-LJ	PC-SAFT ^{e)}		PR ^{e)}		CSMGem	Multiflash
				P&P	S&K	P&P	S&K		
Natural gas 1 ⁶¹	279.1-296.7	4.5	12.8	-	-	-	-	-	4.4
CH ₄ /C ₂ H ₆ /N ₂ /CO ₂ ³⁴	279.0-294.2	3.9	13.9	17.4	18.5	8.3	11.4	9.7	3.9
CH ₄ /C ₃ H ₈ /N ₂ /CO ₂ ³⁴	279.2-296.1	16.6	16.6	22.2	0.5	27.0	4.5	10.2	16.7
CH ₄ /N ₂ /CO ₂ ³⁴	276.9-293.4	3.0	5.5	0.8	1.5	13.2	3.8	11.5	3.1
CH ₄ /C ₂ H ₆ /N ₂ ³⁴	277.4-294.2	2.6	18.9	20.3	21.9	20.8	15.4	-	2.7
CH ₄ /C ₂ H ₆ /C ₃ H ₈ ³⁴	277.1-298.1	4.2	20.0 ^{a)}	43.0	13.6	26.2	6.5	3.1	4.0
CH ₄ /C ₂ H ₆ ³⁸	284.9-299.0	18.4	2.5	-	-	-	-	-	18.4
CH ₄ /iC ₄ H ₁₀ ³⁹	273.8-276.9	2.4 ^{b)} /18.9 ^{c)}	1.7 ^{b)}	21.5	7.9	22.3	- ^{d)}	8.7	2.4 ^{b)} /18.9 ^{c)}
H ₂ S ⁵⁴	277.6-299.8	2.9	3.8	-	-	-	-	-	3.2
O ₂ ⁴⁴	273.2-284.2	2.3	1.8	16.5	-	13.9	-	-	2.9
CO ₂ ⁴⁷	274.3-282.9	4.8	1.9	-	-	-	-	-	2.3
CH ₄ ²⁶	274.3-285.8	0.7	2.7	-	-	-	-	-	0.7

- The number of data points analyzed with SAFT-VR Mie-LJ for this mixture is smaller than with the remaining models.
- Only considers the composition of 36.4 mol % methane.
- Results considering 23 data points
- No convergence.
- PR = Peng-Robinson; P&P = Parish and Prausnitz; S&K = Sloan and Koh, CSMGem = Colorado School of Mines CSMGem software.

The results from the modified CPA compare well with those of other approaches, being in most cases within the three best approaches of those analyzed.

To complete this study an analysis on the capacity of the model to describe the influence of water content on the dissociation curves, as well as on the predictions of the hydrate phase concentration of specific hydrate formers, is conducted. The presented results are only for the modified CPA and not for the Multiflash model. However the results are very similar between the two approaches. This section is based on the data from Belandria *et al.*⁶⁴ for mixed hydrates

constituted of CO₂ + methane, as well as on the data by Ng.⁶⁵ Table A2 in the Supporting Information and Table 5 present the deviations on the compositions for these mixtures. Figure 18 shows the results for dissociation curves depending on water composition, at three different gas phase compositions, while Figure 19 presents the results for the composition of CO₂ on the hydrate phase at three different temperatures. The results for this section are very similar with both approaches, thus only the approach proposed in this paper is presented.

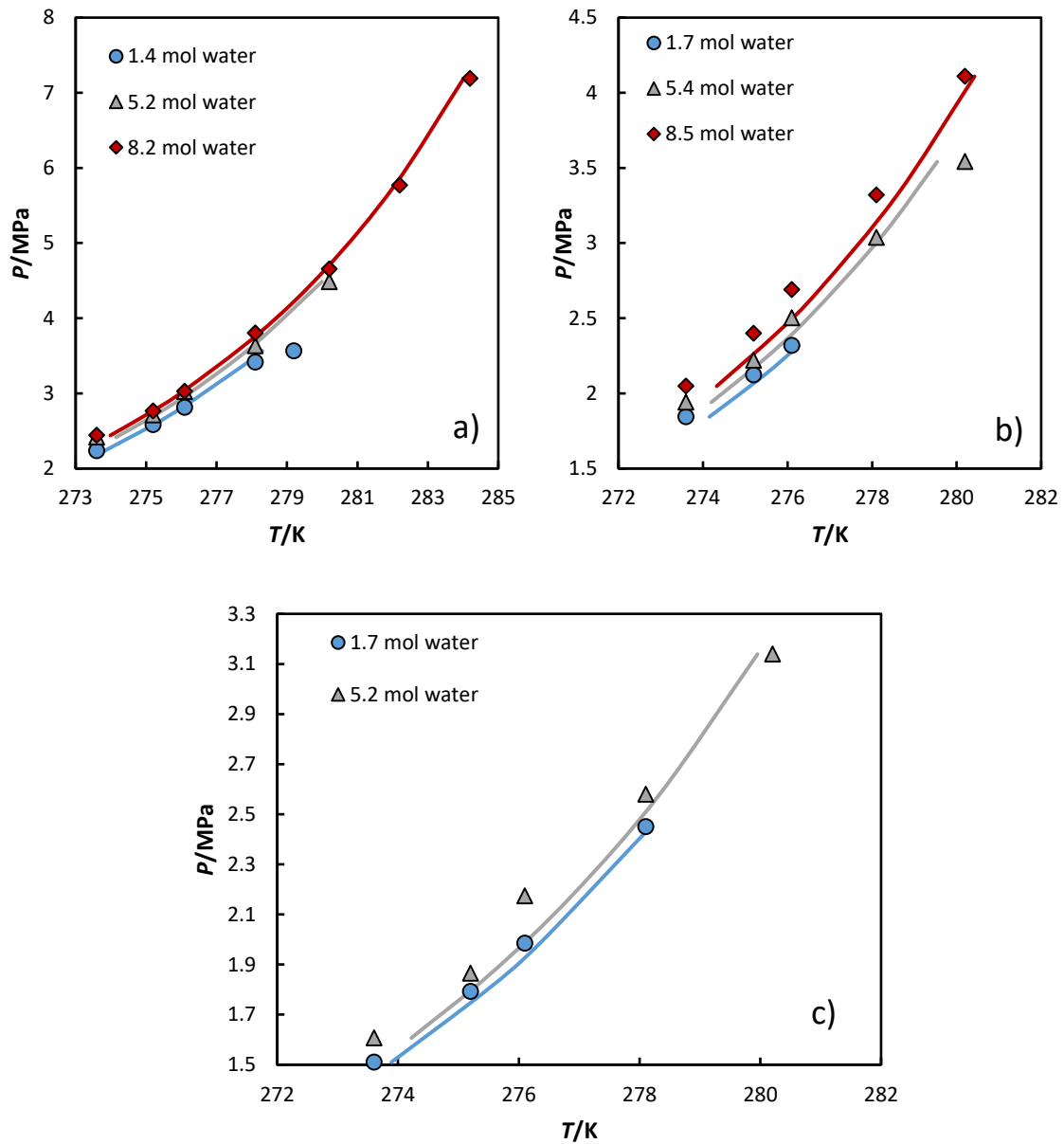


Figure 18 – Hydrate dissociation curves for H₂O + CO₂ + CH₄ at different water and gas compositions. a) $n_{\text{CO}_2} = 0.048$ moles $n_{\text{methane}} = 0.165$ moles; b) $n_{\text{CO}_2} = 0.116$ moles $n_{\text{methane}} = 0.115$ moles; c) $n_{\text{CO}_2} = 0.181$ moles $n_{\text{methane}} = 0.057$ moles. Data from Belandria *et al.*⁶⁴

Accurate results are obtained for the dissociation curves of these mixtures, with less than 1 K deviations between experimental data and the model results.

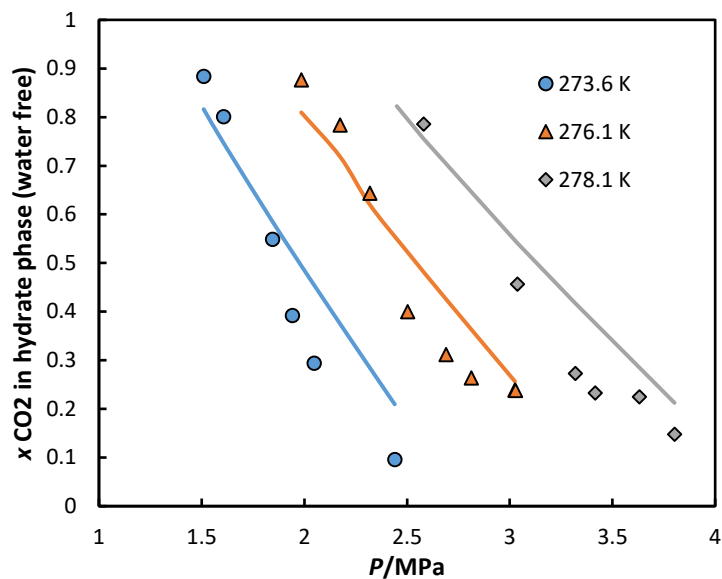


Figure 19 – CO₂ composition on the hydrate phase for mixtures of H₂O + CO₂ + CH₄ at three different temperatures. Data from Belandria *et al.*⁶⁴

The results for the composition of CO₂ in the hydrate phase are reasonably accurate for the lower and higher concentrations of this compound. However, there is an increase in the deviations for the intermediary compositions. This effect is observed for the three temperatures studied, where it seems that the model tends to predict a quasi-linear behavior of the CO₂ composition as a function of pressure, while the available data presents a more complex, non-linear, behavior.

Table 5 presents the results of the model when compared to the data by Ng.⁶⁵ It is important to note that the three equilibrium phases (gas-liquid-hydrate) were not found for all the data points with the model, while doing a P,T flash calculation at the set conditions. In these cases, a fixed phase fraction calculation was carried out, so that three phases were found. The calculated temperature was thus, in some cases, slightly different from that of the reported data, but, except for one case, this ΔT was less than 1 K. This is specified in Table A 3 of the supporting information.

Table 5 – Compositional results for the hydrate phase on mixtures containing water + gas alkanes and CO₂. Data from Ng.⁶⁵

P/MPa	T _{exp} /K	Feed	exp. hydrate composition mole%						calc. hydrate composition mole%					
			C1	C2	C3	iC4	nC4	CO ₂	C1	C2	C3	iC4	nC4	CO ₂
2.07	284.55	1	58.6	-	41.4	-	-	-	59.7	-	40.3	-	-	-
6.89	293.25	1	65.7	-	34.3	-	-	-	64.9	-	35.1	-	-	-
2.07	276.85	2	72.6	-	27.4	-	-	-	67.4	-	32.6	-	-	-
6.89	286.35	2	77.1	-	22.9	-	-	-	74.5	-	25.5	-	-	-
2.07	284.05	3	60.6	8.7	18.2	12.4	-	-	59.4	8.2	18.3	14.1	-	-
6.89	292.55	3	59	8.7	20	12.3	-	-	64.6	9.9	15.5	10.0	-	-
2.07	286.05	4	60	-	29.7	9.2	-	1.02	59.0	-	29.2	11.3	-	0.47
6.89	294.75	4	63	-	28.9	7.8	-	1.04	64.1	-	26.7	8.9	-	0.29
2.07	284.45	5	58.1	7.4	20.6	10.7	3.1	-	58.8	7.1	19.5	12.0	2.6	-
6.89	292.75	5	61.7	8.9	18.1	8.7	2.7	-	64.2	8.5	16.8	8.6	2.0	-
2.07	282.95	6	58.4	7.6	26.5	4.4	1.8	1.1	60.2	6.9	26.1	5.1	1.5	0.2
6.89	291.85	6	62.1	7.7	23.8	3.9	1.1	1	65.3	7.6	22.2	3.7	1.1	0.1
%AAD									3.5	6.6	7.4	12.8	15.6	74.1

The results obtained show a pressure dependency similar to that of the experimental data, and for most compounds present a reasonable composition estimation. However, for CO₂, which is a minor component, the obtained deviations are high. As discussed by Maghsoodloo Babakhani *et al.*⁶⁶ the relevant deviations obtained for some of these compounds, might be related to specific aspects of the experimental methodology and/or to kinetic effects on the crystallization process, which the model does not take into account.

Conclusions

A modified CPA EoS was applied for gas-liquid-hydrate equilibria of diverse hydrate formers. The results for pure guest hydrate formers are accurate and compare favorably with the standard Multiflash hydrate model and other models applied in the literature. For the pure gas hydrates the only relevant disadvantage in using the modified CPA model is for the case of CO₂ hydrates.

For the analyzed cases, both the modified CPA model and Multiflash's hydrate model tend to be within the most accurate for the description of multicomponent hydrate dissociation curves. The modified CPA model is also able to correctly describe the dissociation curves for differing limiting water compositions, while also being able to describe the compositions of gaseous components (including CO₂) in the hydrate phase.

For mixtures containing gas alkanes and CO₂ the compositional analysis reveals that the model is able to accurately describe the amounts of the smaller alkanes, but presents somewhat high deviations in the case of CO₂.

Supporting information

Composition of multicomponent gases, binary interaction parameters not presented in previous studies and deviations on the compositions obtained for mixtures of water + methane + carbon dioxide. VLE results for water + THF.

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Nomenclature

Abbreviations

$$\%AAD = \text{Percentage of average absolute deviation} : \%AAD = \sum_i^{n \text{ data points}} \left| \frac{a^{i,exp} - a^{i,calc}}{a^{i,exp}} \right| \times 100$$

CPA EoS = Cubic Plus Association Equation of State

c_{vs} = volume shift

LJ = Lennard-Jones

P = Pressure

PC-SAFT = Perturbed Chain SAFT

P&P = Parish and Prausnitz

SAFT = Statistical Associating Fluid Theory

SAFT-VR = SAFT Variable Range

S&K = Sloan and Koh

T = temperature

T_r = reduced temperature $T_r = \frac{T}{T_c}$

$$T' = (1 - \sqrt{T_r}), T_r = T/T_c$$

v = molar volume

v_0 = molar volume before translation

v_t = molar volume after translation

Subscripts and superscripts

c = critical

exp = experimental

calc = calculated

Chemical Formulas

CH₄ = methane

C₂H₆ = ethane

C₃H₈ = propane

iC₄H₁₀ = iso-butane

CO₂ = carbon dioxide

H₂O = water

H₂S = hydrogen sulfide

N₂ = nitrogen

THF = tetrahydrofuran

References

- (1) Kelland, M. A. History of the Development of Low Dosage Hydrate Inhibitors. *Energy & Fuels* **2006**, *20* (3), 825–847. <https://doi.org/10.1021/ef050427x>.
- (2) Yang, M.; Song, Y.; Jiang, L.; Zhao, Y.; Ruan, X.; Zhang, Y.; Wang, S. Hydrate-Based Technology for CO₂ Capture from Fossil Fuel Power Plants. *Appl. Energy* **2014**, *116*, 26–40. <https://doi.org/10.1016/J.APENERGY.2013.11.031>.
- (3) Thomas, S.; Dawe, R. A. Review of Ways to Transport Natural Gas Energy from Countries Which Do Not Need the Gas for Domestic Use. *Energy* **2003**, *28* (14), 1461–1477. [https://doi.org/10.1016/S0360-5442\(03\)00124-5](https://doi.org/10.1016/S0360-5442(03)00124-5).
- (4) Struzhkin, V. V.; Militzer, B.; Mao, W. L.; Mao, H. K.; Hemley, R. J. Hydrogen Storage in Molecular Clathrates. *Chem. Rev.* **2007**, *107* (10), 4133–4151. <https://doi.org/10.1021/cr050183d>.
- (5) Walsh, M. R.; Hancock, S. H.; Wilson, S. J.; Patil, S. L.; Moridis, G. J.; Boswell, R.; Collett, T. S.; Koh, C. A.; Sloan, E. D. Preliminary Report on the Commercial Viability of Gas Production from Natural Gas Hydrates. *Energy Econ.* **2009**, *31* (5), 815–823. <https://doi.org/10.1016/J.ENERGY.2009.03.006>.
- (6) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, Third ed.; Press, C., Ed.; Taylor & Francis Group: Boca Raton, 2008.
- (7) Platteeuw, J. C.; van der Waals, J. H. Thermodynamic Properties of Gas Hydrates. *Mol. Phys. An Int. J. Interface Between Chem. Phys.* **1958**, No. June 2013, 91–96. <https://doi.org/10.1080/00268976.2013.804960>.
- (8) Parrish, W. R.; Prausnitz, J. M. Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures. *Ind. Eng. Chem. Process Des. Dev.* **1972**, *11* (1), 26–35. <https://doi.org/10.1021/i260041a006>.
- (9) Dadmohammadi, Y.; Gebreyohannes, S.; Abudour, A. M.; Neely, B. J.; Gasem, K. A. M. Representation and Prediction of Vapor-Liquid Equilibrium Using the Peng-Robinson Equation of State and UNIQUAC Activity Coefficient Model. *Ind. Eng. Chem. Res.* **2016**, *55* (4), 1088–1101. <https://doi.org/10.1021/acs.iecr.5b03475>.
- (10) Kontogeorgis, G. M.; Folas, G. K. *Thermodynamic Models for Industrial Applications*; John Wiley & Sons, Ltd: Chichester, UK, 2010. <https://doi.org/10.1002/9780470747537>.
- (11) Fouad, W. A.; Song, K. Y.; Chapman, W. G. Experimental Measurements and Molecular Modeling of the Hydrate Equilibrium as a Function of Water Content for Pressures up to

- 40 MPa. *Ind. Eng. Chem. Res.* **2015**, *54* (39), 9637–9644.
<https://doi.org/10.1021/acs.iecr.5b02240>.
- (12) El Meragawi, S.; Diamantonis, N. I.; Tsimpanogiannis, I. N.; Economou, I. G. Hydrate - Fluid Phase Equilibria Modeling Using PC-SAFT and Peng-Robinson Equations of State. *Fluid Phase Equilib.* **2016**, *413*, 209–219. <https://doi.org/10.1016/j.fluid.2015.12.003>.
- (13) Waseem, M. S.; Alsaifi, N. M. Prediction of Vapor-Liquid-Hydrate Equilibrium Conditions for Single and Mixed Guest Hydrates with the SAFT-VR Mie EOS. *J. Chem. Thermodyn.* **2018**, *117*, 223–235. <https://doi.org/10.1016/j.jct.2017.09.032>.
- (14) MULTIFLASH Version 6.1, KBC Process Technology, London, United Kingdom.
- (15) Palma, A. M.; Queimada, A. J.; Coutinho, J. A. P. Improved Prediction of Water Properties and Phase Equilibria with a Modified CPA EoS. *Ind. Eng. Chem. Res.* **2017**, *56*, 15163–15176. <https://doi.org/10.1021/acs.iecr.7b03522>.
- (16) Hendriks, E. M.; Edmonds, B.; Moorwood, R. A. S.; Szczepanski, R. Hydrate Structure Stability in Simple and Mixed Hydrates. *Fluid Phase Equilib.* **1996**, *117* (1–2), 193–200. [https://doi.org/10.1016/0378-3812\(95\)02953-2](https://doi.org/10.1016/0378-3812(95)02953-2).
- (17) Pedrosa, N.; Szczepanski, R.; Zhang, X. Integrated Equation of State Modelling for Flow Assurance. *Fluid Phase Equilib.* **2013**, *359*, 24–37. <https://doi.org/10.1016/j.fluid.2013.07.019>.
- (18) Kontogeorgis, G. M.; Yakoumis, I. V.; Meijer, H.; Hendriks, E.; Moorwood, T. Multicomponent Phase Equilibrium Calculations for Water–methanol–alkane Mixtures. *Fluid Phase Equilib.* **1999**, *160*, 201–209. [https://doi.org/10.1016/S0378-3812\(99\)00060-6](https://doi.org/10.1016/S0378-3812(99)00060-6).
- (19) Graboski, M. S.; Daubert, T. E. A Modified Soave Equation of State for Phase Equilibrium Calculations. 1. Hydrocarbon Systems. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17* (4), 443–448. <https://doi.org/10.1021/i260068a009>.
- (20) Palma, A. M.; Queimada, A. J.; Coutinho, J. A. P. Modeling of the Mixture Critical Locus with a Modified Cubic Plus Association Equation of State: Water, Alkanols, Amines, and Alkanes. *Ind. Eng. Chem. Res.* **2018**, *57* (31), 10649–10662. <https://doi.org/10.1021/acs.iecr.8b01960>.
- (21) Palma, A. M.; Oliveira, M. B.; Queimada, A. J.; Coutinho, J. A. P. Evaluating Cubic Plus Association Equation of State Predictive Capacities: A Study on the Transferability of the Hydroxyl Group Associative Parameters. *Ind. Eng. Chem. Res.* **2017**, *56* (24), 7086–7099. <https://doi.org/10.1021/acs.iecr.7b00760>.
- (22) Palma, A. M.; Queimada, A. J.; Coutinho, J. A. P. Improved Prediction of Water Properties and Phase Equilibria with a Modified Cubic Plus Association Equation of State. *Ind. Eng. Chem. Res.* **2017**, *56* (51), 15163–15176. <https://doi.org/10.1021/acs.iecr.7b03522>.
- (23) Palma, A. M.; Oliveira, M. B.; Queimada, A. J.; Coutinho, J. A. P. Re-Evaluating the CPA EoS for Improving Critical Points and Derivative Properties Description. *Fluid Phase Equilib.* **2017**, *436*, 85–97. <https://doi.org/10.1016/j.fluid.2017.01.002>.
- (24) Palma, A. M.; Queimada, A. J.; Coutinho, J. A. P. Modeling of the Mixture Critical Locus with a Modified Cubic Plus Association (CPA) EoS: Aromatics, Ketones, Ethers, Diethyl Carbonate, and THF. *Ind. Eng. Chem. Res.* **2018**, *57* (46), 15857–15868. <https://doi.org/10.1021/acs.iecr.8b03657>.

- (25) Mokraoui, S.; Coquelet, C.; Valtz, A.; Hegel, P. E.; Richon, D. New Solubility Data of Hydrocarbons in Water and Modeling Concerning Vapor-Liquid-Liquid Binary Systems. *Ind. Eng. Chem. Res.* **2007**, *46* (26), 9257–9262. <https://doi.org/10.1021/ie070858y>.
- (26) Nakamura, T.; Makino, T.; Sugahara, T.; Ohgaki, K. Stability Boundaries of Gas Hydrates Helped by Methane - Structure-H Hydrates of Methylcyclohexane and Cis-1,2-Dimethylcyclohexane. *Chem. Eng. Sci.* **2003**, *58* (2), 269–273. [https://doi.org/10.1016/S0009-2509\(02\)00518-3](https://doi.org/10.1016/S0009-2509(02)00518-3).
- (27) Ross, M. J.; Toczylkin, L. S. Hydrate Dissociation Pressures for Methane or Ethane in the Presence of Aqueous Solutions of Triethylene Glycol. *J. Chem. Eng. Data* **1992**, *37* (4), 488–491. <https://doi.org/10.1021/je00008a026>.
- (28) Marshall, D. R.; Saito, S.; Kobayashi, R. Hydrates at High Pressures: Part I. Methane-water, Argon-water, and Nitrogen-water Systems. *AIChE J.* **1964**, *10* (2), 202–205. <https://doi.org/10.1002/aic.690100214>.
- (29) Seo, Y. T.; Kang, S. P.; Lee, H. Experimental Determination and Thermodynamic Modeling of Methane and Nitrogen Hydrates in the Presence of THF, Propylene Oxide, 1,4-Dioxane and Acetone. *Fluid Phase Equilib.* **2001**, *189* (1–2), 99–110. [https://doi.org/10.1016/S0378-3812\(01\)00580-5](https://doi.org/10.1016/S0378-3812(01)00580-5).
- (30) de Deugd, R. M.; Jager, M. D.; de Swaan Arons, J. Mixed Hydrates of Methane and Water-Soluble Hydrocarbons Modeling of Empirical Results. *AIChE J.* **2001**, *47* (3), 693–704. <https://doi.org/10.1002/aic.690470316>.
- (31) Zhang, Q.; Chen, G.-J.; Huang, Q.; Sun, C.-Y.; Guo, X.-Q.; Ma, Q.-L. Hydrate Formation Conditions of a Hydrogen + Methane Gas Mixture in Tetrahydrofuran + Water. *J. Chem. & Eng. Data* **2005**, *50* (1), 234–236. <https://doi.org/10.1021/je0497146>.
- (32) Mohammadi, A. H.; Belandria, V.; Richon, D. Can Toluene or Xylene Form Clathrate Hydrates? *Ind. Eng. Chem. Res.* **2009**, *48* (12), 5916–5918. <https://doi.org/10.1021/ie900362v>.
- (33) Maekawa, T. Equilibrium Conditions of Propane Hydrates in Aqueous Solutions of Alcohols, Glycols, and Glycerol. *J. Chem. Eng. Data* **2008**, *53* (12), 2838–2843. <https://doi.org/10.1021/je800572q>.
- (34) Nixdorf, J.; Oellrich, L. R. Experimental Determination of Hydrate Equilibrium Conditions for Pure Gases, Binary and Ternary Mixtures and Natural Gases. *Fluid Phase Equilib.* **1997**, *139* (1–2), 325–333. [https://doi.org/10.1016/S0378-3812\(97\)00141-6](https://doi.org/10.1016/S0378-3812(97)00141-6).
- (35) Ng, H.-J.; Robinson, D. B. Hydrate Formation in Systems Containing Methane, Ethane, Propane, Carbon Dioxide or Hydrogen Sulfide in the Presence of Methanol. *Fluid Phase Equilib.* **1985**, *21* (1–2), 145–155. [https://doi.org/10.1016/0378-3812\(85\)90065-2](https://doi.org/10.1016/0378-3812(85)90065-2).
- (36) Buleiko, V. M.; Grigoriev, B. A.; Mendoza, J. Calorimetric Investigation of Hydrates of Pure Isobutane and Iso- and Normal Butane Mixtures. *Fluid Phase Equilib.* **2018**, *462*, 14–24. <https://doi.org/10.1016/j.fluid.2018.01.012>.
- (37) Rouher, O. S.; Barduhn, A. J. Hydrates of Iso- and Normal Butane and Their Mixtures. *Desalination* **1969**, *6* (1), 57–73. [https://doi.org/10.1016/S0011-9164\(00\)80011-9](https://doi.org/10.1016/S0011-9164(00)80011-9).
- (38) McLeod, H. O.; Campbell, J. M. Natural Gas Hydrates at Pressures to 10,000 Psia. *J. Pet. Technol.* **1961**, *13* (06), 590–594. <https://doi.org/10.2118/1566-G-PA>.
- (39) Wu, B. J.; Robinson, D. B.; Ng, H. J. Three- and Four-Phase Hydrate Forming Conditions

- in Methane + Isobutane + Water. *J. Chem. Thermodyn.* **1976**, *8* (5), 461–469.
[https://doi.org/10.1016/0021-9614\(76\)90067-7](https://doi.org/10.1016/0021-9614(76)90067-7).
- (40) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, Third edit.; CRC Press: Boca Raton, 2007.
- (41) Parrish, W.; Prausnitz, J. Correction- Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures. *Ind. Eng. Chem. Process Des. Dev.* **1972**, *11* (3), 462–462.
<https://doi.org/10.1021/i260043a025>.
- (42) Lee, S.; Lee, Y.; Park, S.; Kim, Y.; Cha, I.; Seo, Y. Stability Conditions and Guest Distribution of the Methane + Ethane + Propane Hydrates or Semiclathrates in the Presence of Tetrahydrofuran or Quaternary Ammonium Salts. *J. Chem. Thermodyn.* **2013**, *65*, 113–119. <https://doi.org/10.1016/j.jct.2013.05.042>.
- (43) Ballard, A. L.; Sloan, E. D. Structural Transitions in Methane+ethane Gas Hydrates - Part II: Modeling beyond Incipient Conditions. *Chem. Eng. Sci.* **2000**, *55* (23), 5773–5782.
[https://doi.org/10.1016/S0009-2509\(00\)00163-9](https://doi.org/10.1016/S0009-2509(00)00163-9).
- (44) van Cleeff, A.; Diepen, G. A. M. Gas Hydrates of Nitrogen and Oxygen. II. *Recl. des Trav. Chim. des Pays-Bas* **1965**, *84* (8), 1085–1093.
<https://doi.org/10.1002/recl.19650840815>.
- (45) Ferrari, P. F.; Guembaroski, A. Z.; Marcelino Neto, M. A.; Morales, R. E. M.; Sum, A. K. Experimental Measurements and Modelling of Carbon Dioxide Hydrate Phase Equilibrium with and without Ethanol. *Fluid Phase Equilib.* **2016**, *413*, 176–183.
<https://doi.org/10.1016/j.fluid.2015.10.008>.
- (46) Breland, E.; Englezos, P. Equilibrium Hydrate Formation Data for Carbon Dioxide in Aqueous Glycerol Solutions. *J. Chem. Eng. Data* **1996**, *41* (1), 11–13.
<https://doi.org/10.1021/je950181y>.
- (47) Adisasmito, S.; Frank, R. J.; Sloan, E. D. J. Hydrates of Carbon-Dioxide and Methane Mixtures. *J. Chem. Eng. Data* **1991**, *36* (1), 68–71.
<https://doi.org/10.1021/je00001a020>.
- (48) Takenouchi, S.; Kennedy, G. C. Dissociation Pressures of the Phase $\text{CO}_2 \cdot 5\frac{3}{4} \text{H}_2\text{O}$. *J. Geol.* **1965**, *73* (2), 383–390. <https://doi.org/10.1086/627068>.
- (49) Chapoy, A.; Burgass, R.; Tohidi, B.; Austell, J. M.; Eickhoff, C. Effect of Common Impurities on the Phase Behavior of Carbon-Dioxide-Rich Systems: Minimizing the Risk of Hydrate Formation and Two-Phase Flow. *SPE J.* **2011**, *16* (04), 921–930.
<https://doi.org/10.2118/123778-PA>.
- (50) Mohammadi, A. H.; Richon, D. Phase Equilibria of Hydrogen Sulfide and Carbon Dioxide Simple Hydrates in the Presence of Methanol, (Methanol + NaCl) and (Ethylene Glycol + NaCl) Aqueous Solutions. *J. Chem. Thermodyn.* **2012**, *44* (1), 26–30.
<https://doi.org/10.1016/j.jct.2011.08.001>.
- (51) Maekawa, T. Equilibrium Conditions for Carbon Dioxide Hydrates in the Presence of Aqueous Solutions of Alcohols, Glycols, and Glycerol. *J. Chem. Eng. Data* **2010**, *55* (3), 1280–1284. <https://doi.org/10.1021/je900626y>.
- (52) Robinson, D. B.; Ng, H. J. Hydrate Formation and Inhibition in Gas or Gas Condensate Streams. *J. Can. Pet. Technol.* **1986**, *25* (4), 26–30.
- (53) Tavasoli, H.; Feyzi, F. Four Phase Hydrate Equilibria of Methane and Carbon Dioxide

with Heavy Hydrate Former Compounds: Experimental Measurements and Thermodynamic Modeling. *Korean J. Chem. Eng.* **2016**, *33* (8), 2426–2438. <https://doi.org/10.1007/s11814-016-0110-x>.

- (54) Selleck, F. T.; Carmichael, L. T.; Sage, B. H. Phase Behavior in the Hydrogen Sulfide-Water System. *Ind. Eng. Chem.* **1952**, *44* (9), 2219–2226. <https://doi.org/10.1021/ie50513a064>.
- (55) Mohammadi, A. H.; Richon, D. Hydrate Phase Equilibria of Gaseous Mixtures of Methane + Carbon Dioxide + Hydrogen Sulfide. *Chem. Eng. Commun.* **2015**, *202* (5), 629–633. <https://doi.org/10.1080/00986445.2013.858322>.
- (56) Ward, Z. T.; Marriott, R. A.; Sum, A. K.; Sloan, E. D.; Koh, C. A. Equilibrium Data of Gas Hydrates Containing Methane, Propane, and Hydrogen Sulfide. *J. Chem. Eng. Data* **2015**, *60* (2), 424–428. <https://doi.org/10.1021/je5007423>.
- (57) Chen, L.; Lu, H.; Ripmeester, J. A. Dissociation Conditions and Raman Spectra of CO₂ + SO₂ and CO₂ + H₂S Hydrates. *Ind. Eng. Chem. Res.* **2015**, *54* (21), 5543–5549. <https://doi.org/10.1021/acs.iecr.5b00350>.
- (58) Schroeter, J. P.; Kobayashi, R.; Hildebrand, M. A. Hydrate Decomposition Conditions in the System H₂S-Methane-Propane. *Ind. Eng. Chem. Fundam.* **1983**, *22* (4), 361–364. <https://doi.org/10.1021/i100012a001>.
- (59) Maekawa, T. Equilibrium Conditions of Clathrate Hydrates Formed from Xenon and Aqueous Solutions of Acetone, 1,4-Dioxane and 1,3-Dioxolane. *Fluid Phase Equilib.* **2013**, *339*, 15–19. <https://doi.org/10.1016/j.fluid.2012.11.034>.
- (60) Liu, H.; Guo, P.; Du, J.; Wang, Z.; Chen, G.; Li, Y. Experiments and Modeling of Hydrate Phase Equilibrium of CH₄/CO₂/H₂S/N₂ Quaternary Sour Gases in Distilled Water and Methanol-Water Solutions. *Fluid Phase Equilib.* **2017**, *432*, 10–17. <https://doi.org/10.1016/j.fluid.2016.10.019>.
- (61) Wilcox, W. I.; Carson, D. B.; Katz, D. L. Natural Gas Hydrates. *Ind. Eng. Chem.* **1941**, *33* (5), 662–665. <https://doi.org/10.1021/ie50377a027>.
- (62) Lee, J. W.; Kang, S. P. Phase Equilibria of Natural Gas Hydrates in the Presence of Methanol, Ethylene Glycol, and NaCl Aqueous Solutions. *Ind. Eng. Chem. Res.* **2011**, *50* (14), 8750–8755. <https://doi.org/10.1021/ie2001814>.
- (63) Saberi, A.; Alamdari, A.; Shariati, A.; Mohammadi, A. H. Experimental Measurement and Thermodynamic Modeling of Equilibrium Condition for Natural Gas Hydrate in MEG Aqueous Solution. *Fluid Phase Equilib.* **2018**, *459*, 110–118. <https://doi.org/10.1016/j.fluid.2017.11.034>.
- (64) Belandria, V.; Eslamimanesh, A.; Mohammadi, A. H.; Théveneau, P.; Legendre, H.; Richon, D. Compositional Analysis and Hydrate Dissociation Conditions Measurements for Carbon Dioxide + Methane + Water System. *Ind. Eng. Chem. Res.* **2011**, *50* (9), 5783–5794. <https://doi.org/10.1021/ie101959t>.
- (65) NG, H.-J. Hydrate Phase Composition for Multicomponent Gas Mixtures. *Ann. N. Y. Acad. Sci.* **2006**, *912* (1), 1034–1039. <https://doi.org/10.1111/j.1749-6632.2000.tb06858.x>.
- (66) Maghsoodloo Babakhani, S.; Bouillot, B.; Ho-Van, S.; Douzet, J.; Herri, J. M. A Review on Hydrate Composition and Capability of Thermodynamic Modeling to Predict Hydrate Pressure and Composition. *Fluid Phase Equilib.* **2018**, *472*, 22–38.

<https://doi.org/10.1016/j.fluid.2018.05.007>.