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A Comparative Performance Evaluation of Cubic Equations of State for Predicting the Compositional Distribution of Hydrate Inhibitors in Reservoir Fluid Systems

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Abstract

This study presents a comparative computational examination of different cubic equations of state (EoS) on hydrate inhibition fluid systems involving real reservoir fluids. Two gas hydrate inhibitors (Monoethylene glycol – MEG and methanol) were considered alongside 4 cubic EoS namely; Cubic-Plus-Association (CPA) EoS coupled with Infochem mixing rules, Soave-Redlich-Kwong (SRK) EoS coupled with the Huron-Vidal (HV) mixing rule, Peng Robinson EoS coupled with the HV mixing rule and the Predictive-Soave-Redlich-Kwong EoS with the PSRK-type mixing rule. Pressure-Temperature (PT) – flash calculations were carried out using Multiflash™ software (version 6.1) and the obtained results were compared with experimental data from various literature. The tested Cubic EoS successfully modelled the distribution of water, a hydrate inhibitor and hydrocarbons in the complex mixtures at different conditions with the CPA performing best. The PSRK EoS produced results farthest from experimental data.

Keywords: Hydrates, Equation of State, Cubic-Plus-Association, Huron-Vidal, Soave-Redlich-Kwong, Peng-Robinson

1. Introduction

The movement of fluids from oil and gas fields to processing facilities (in wellbores and pipelines) presents complex multiphase flow challenges, which are regularly described as flow assurance problems. These may occur in forms such as gas hydrates, wax, asphaltenes, scales, and sand-erosion. Gas hydrates, the focus of this paper, are crystal-like solids that result from a physical combination of hydrocarbon gases and water, in which cages of water molecules trap the gas molecules (Gbaruko, et al., 2007; Epelle et al., 2020). Gas hydrates are usually formed under low temperature and high pressure and their deposition result in problems such as flow restriction (or even total blockage in pipelines), interference with valve operations and instrumentation, increased surface roughness of the pipe wall, increased pressure drop and corrosion problems (Sloan, 2010; Qasim et al., 2019). Hence, they must be inhibited for safe and economic production (Gbaruko, et al., 2007; Epelle et al., 2020).

Various methods exist for the prevention of gas hydrate formation; some of which include the removal of free water from the system, ensuring that the operating temperature and pressure of the system are outside the hydrate formation region and the injection of gas hydrate inhibitors into the system (Pedersen et al., 2014). A crucial part of onshore and offshore development processes is the injection of glycols and methanol into unrefined well streams. Hence, the accurate prediction of the physical properties for the mixtures of glycols/methanol, water and hydrocarbons is inevitable (Epelle et al., 2020). If the distribution of these hydrate inhibitors in the different phases that evolve during the transportation of reservoir fluids can be accurately predicted, the estimation of the inhibitor concentrations necessary for practical operations can be facilitated. This would minimize operating cost and enhance field profitability.

Cubic equations of state (EoS) are widely used in the petroleum industry for equilibrium calculations of oil and gas phase behaviour. However, for fluid mixtures relevant to hydrate inhibition, the usage of traditional EoS alongside standard mixing rules (such as van der Waals) has been proven to be inadequate (Yan et al., 2009). This is further complicated by the presence of water and the wide temperature and pressure range involved in these processes. To accurately model the phase behaviour of such systems, it is pertinent to understand the strengths and shortcomings of traditional EoS and the mixing rules associated with them (Epelle et al., 2020). When mixtures of water, non-polar and polar compounds exist, the representation of the phase behaviour using a cubic EoS and the van der Waal mixing becomes difficult (Folas et al., 2006). To deal with this shortcoming, other mixing rules such as Michelsen (1990), Wong and Sandler (1992) and Huron and Vidal (1979) have been proposed.

A considerable amount of literature has been published on the prediction of hydrate equilibrium behaviour by equations of state (EoS) and the experimental measurement of its phase equilibrium properties (Peng et al., 2010; Chen et al., 2009; Rasoolzadeh et al., 2016). Kondori et al. (2018) successfully applied the perturbed chain statistical association fluid theory (PC-SAFT) EoS together with the van der Waals and Platteuw model to predict the hydrate formation temperature for gases such as methane, ethane, propane, isobutane, carbon dioxide, and hydrogen sulfide. Esmailzadeh et al. (2020) provided a comprehensive review of previous studies related to the application of EoS for the thermodynamic modelling of gas hydrate formation. They compared the performance of three EoS available in literature (van der Waals–Platteuw (vdW–P) model, Chen–Guo model, and Klauda–Sandler model coupled with CPA and SAFT EoSs) with that of the cubic EoS. CPA and SAFT EoS were found to be very accurate especially for hydrate prediction systems given their ability to account for the association interactions. Mu and Cui (2019) applied the pressure searching method to measure the phase equilibrium data of two synthetic natural gas mixtures together with hydrogen sulphides in various systems. The experimental measurements were compared with predicted values using three commercial programs (CSMGem™, PVTsim™, and Multiflash™) and two semiempirical formulae (Hammerschmidt and Najibi). Their results show that the semiempirical formulae have reasonable agreement with systems containing low MeOH. On the other hand, the PVTsim calculations are favourable for measurements with NaCl solutions containing MeOH. The study of Chen et al. (2015) showed that Multiflash™ is more accurate when compared with CSMGem for hydrate modelling; hence its usage in this study.

Dehaghani (2017) applied 3 equations of state to model hydrate equilibria conditions of a real natural gas sample. They utilized the Peng–Robinson, Soave–Redlich–Kwong and Valderrama–Patel–Teja EoS coupled with general non-quadratic, van der Waals and Avlonitis non-density dependent mixing rules for this purpose. A good agreement was observed between the experimental and equilibrium prediction data. Furthermore, the Peng–Robinson equation coupled with Avlonitis non-density dependent proved to be the most accurate EOS with a deviation of 0.166%. The work of Dehaghani (2017) represents the most similar attempt in the literature to the one presented in this work, in terms of the comparative evaluation of different EoS. While Dehaghani (2017) focused on hydrate formation, we focus on hydrate inhibition.

It is important to note that despite the ample amount of information available on the prediction of hydrate formation conditions and the modelling of hydrate phase equilibria, few studies have provided a comprehensive evaluation of the performance of different EoS. In this study, the

mutual solubility and phase behaviour data of hydrate inhibitors and hydrocarbon-water systems from literature are predicted with 4 different EoS namely; the Cubic-Plus-Association (CPA) with Infochem mixing rules, Peng-Robinson (PR) with Huron-Vidal-type mixing rule, Redlich-Kwong-Soave (RKS) with Huron-Vidal-type mixing rules and the Predictive-Soave-Redlich-Kwong (PSRK) with the PSRK-type mixing rule. The gas hydrate inhibitors considered were MEG and methanol as these are conventionally used in the industry. The data applied herein are of industrial standard and are obtained from published Vapour-Liquid Equilibrium (VLE) and Liquid-Liquid Equilibrium (LLE) experiments. This study represents the first comparative assessment of different EoS on the prediction accuracy of the compositional distribution of 2 hydrate inhibitors in real reservoir fluid (condensates, gas and oil) mixtures. Further to this, an evaluation of the particular phase (aqueous, HC liquid, HC vapour) for which EoS predictions of the compositional distribution of the mixture's constituents are most accurate, is performed. We also probe the dependency of the performance of the EoS and the associating mixing rules on operating conditions of the multi-component systems studied. We consider these, strong elements of novelty since our results are expected to guide the selection of EoS, for hydrate-inhibition modelling studies in the future.

2. Theoretical Background

In this investigation, the four EoS were considered are widely used in the oil and gas industry. Expressed in Sections 2.1 – 2.5, are their respective mathematical equations. We refer the interested reader to the Multiflash™ user guide for an extensive description of these EoS.

2.1 The Cubic-Plus-Association (CPA) EoS

The CPA EoS was proposed by Kontogeorgis et al. (1996) and can be expressed for mixtures in terms of pressure, P as:

$$P = \frac{RT}{v_m - b} - \frac{a(T)}{v_m(v_m + b)} - \frac{1}{2} \frac{RT}{v_m} \left(1 + \rho \frac{\partial \ln g}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{Ai}) \quad (1)$$

X_{Ai} represents the fraction of sites A on molecule i that do not form bonds with other active sites ('site monomer fraction') and x_i is the mole fraction of component i . X_{Ai} denotes the association strength Δ^{AiBj} between two sites belonging to two different molecules; molecule i and site B on molecule j ; it is given by:

$$X_{Ai} = \frac{1}{1 + \sum_j x_j \sum_{B_j} X_{Bj} \Delta^{AiBj}} \quad (2)$$

Where Δ^{AiBj} is the associated strength and is given by:

$$\Delta^{A_i B_j} = g(\rho) \left[\exp \left(\frac{\varepsilon^{A_i B_j}}{RT} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (3)$$

With the radial distribution function:

$$g(\rho) = \frac{1}{1-1.9\eta} \text{ and } \eta = \frac{1}{4} b \rho \text{ while } b_{ij} = \frac{b_i + b_j}{2} \quad (4)$$

2.2 The Peng-Robinson EoS

As proposed by Peng and Robinson (1976), the EoS is given by;

$$\left(P + \frac{\alpha a}{v^2 + 2bv - a} \right) (v - b) = RT \quad (5)$$

Or, explicitly in pressure as:

$$P = \frac{RT}{v-b} - \frac{\alpha a}{v^2 + 2bv - a} \quad (6)$$

$$\alpha = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T_r}) \right]^2 \quad (7)$$

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (8)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (9)$$

The Peng Robinson cubic expression for Z becomes:

$$Z^3 - (1 - B)Z^2 + (A + 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \quad (10)$$

$$A = \frac{\alpha a P}{R^2 T^2} \quad (11)$$

$$B = \frac{b P}{RT} \quad (12)$$

2.3 Soave-Redlich-Kwong EoS

This is a modification of the original Redlich-Kwong equation of state by Giorgio Soave (1972)

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (13)$$

$$a(T) = a_c a(T) \quad (14)$$

$$a_c = \frac{0.42747 R^2}{P_c} \quad (15)$$

$$b = \frac{0.08664 RT_c}{P_c} \quad (16)$$

The compressibility factor is given as:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (17)$$

$$A = \frac{\alpha a P}{R^2 T^2} \quad (18)$$

$$B = \frac{b P}{RT} \quad (19)$$

2.4 The Predictive-Soave-Redlich-Kwong (PSRK) EoS

The PSRK model was developed by Holderbaum and Gmehling (1991) by combining the UNIFAC group contribution model with the SRK EoS, the ability to manage mixtures containing gases is its major advantage. The PSRK type mixing rules are given by;

$$N = \sum_i n_i \quad (20)$$

$$b = \sum_i b_i n_i \quad (21)$$

$$a = b \left[-\frac{G^E}{S_1} + \frac{RT}{S_1} \sum_i n_i \ln \left(\frac{b}{b_i} \right) + \sum_i n_i \left(\frac{a_i}{b_i} \right) \right] \quad (22)$$

$$S_1 = -0.64663 \quad (23)$$

2.5 Mixing Rules

In this study, 3 mixing rules were considered; the Huron-Vidal (HV) type mixing rules the Infochem mixing rules and the PSRK type mixing rules; these were selected as they have shown to be reliable in handling systems containing polar and non-polar compounds (Infochem, 2016).

2.5.1 The HV Mixing Rules

$$N = \sum_i n_i \quad (24)$$

$$b = \sum_i b_i n_i \quad (25)$$

$$a = b \left(-\frac{G^E}{S_1} + \sum_i n_i \left(\frac{a_i}{b_i} \right) \right) \quad (26)$$

$$S_1 = \ln 2 \text{ For the SRK EoS; } \quad (27)$$

$$S_1 = \frac{1}{2\sqrt{2}} \ln \left(\frac{2+\sqrt{2}}{2-\sqrt{2}} \right) = 0.623225 \text{ For the PR EoS; } \quad (28)$$

G^E is based on the NRTL models and is given as follows:

$$\frac{G^E}{RT} = \sum_{i=1}^N n_i \frac{\sum_{j=1}^N \tau_{ji} b_j n_j \exp(-\alpha_{ji} \tau_{ji})}{\sum_{k=1}^N b_k n_k \exp(-\alpha_{ki} \tau_{ki})} \quad (29)$$

The n_i is the mole fraction of component i , while α_{ji} is defined as a non-randomness parameter (Renon and Prausnitz, 1968). The parameter τ_{ji} is defined as:

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \equiv \frac{\gamma_{ji}}{T} \quad (30)$$

where g_{ji} is an energy parameter characteristic of the j - i interaction. In essence τ_{ji} represents the deviation between the energy interactions between a j and an i molecule and the energy interaction between two dissimilar molecules. When $i = j$ (like-like molecular interaction), α_{ji} and τ_{ji} are 0.

2.5.2 Infochem Mixing Rules

These are closely related to the HV mixing rules and are given by:

$$N = \sum_i n_i \quad (31)$$

$$b = \sum_i b_i n_i \quad (32)$$

$$a = b \sum_i n_i \frac{\sum_j n_j b_j \xi_{ji} G_{ji}}{\sum_j n_j b_j G_{ji}} \quad (33)$$

Where:

$$\xi_{ji} = \frac{2\sqrt{a_i a_j}(1-k_{ji})}{b_i + b_j} \quad (34)$$

and:

$$G_{ji} = \exp\left(\frac{\alpha_{ji}(\xi_{ji} - \xi_{ii})}{RT}\right) \quad (35)$$

G_{ji} represents the deviation between the energy interactions between a j and an i molecule and the energy interaction between two dissimilar molecules.

2.5.3 PSRK Type Mixing Rules

$$N = \sum_i n_i \quad (36)$$

$$b = \sum_i b_i n_i \quad (37)$$

$$a = b \left(-\frac{G^E}{S_1} + \frac{RT}{S_1} \sum_i n_i \ln\left(\frac{b}{b_i}\right) + \sum_i n_i \ln\left(\frac{a_i}{b_i}\right) \right) \quad (38)$$

where $S_1 = -0.64663$

3. Methodology

3.1 Data Collection

This section describes the various steps involved in the ranking of the selected EoS used in this work; the selected EoS being the CPA-Infochem EoS, PR-HV, RKS-HV and PSRK EoS. Firstly, several experimental solubility and phase equilibria datasets of systems containing real reservoir fluids, water and gas hydrate inhibitors (MEG and methanol), and their pure component properties (Table 1) were gathered from multiple published data (Kristensen et al., 1993; Pedersen et al., 1996; 2014; Dandekar et al., 2005; Haghghi, 2009; Frost et al., 2014). Although several other studies exist, which have experimentally studied the mutual solubility of MEG and methanol in hydrocarbons and water, these studies were not included, as our aim was to ensure the application of actual reservoir fluids obtained from the wellbores of industrial operators around the world.

Table 1: Critical properties of the pure components in this study.

Component	Tc (K)	Pc (bar)	ω (-)	Vc (m ³ /mol)
MeOH	512.64	80.92	0.5530	0.000118
MEG	719.70	77.00	0.4868	0.000191
H2O	647.30	221.20	0.3440	0.000056
N2	126.19	33.96	0.0372	0.000089
CO2	304.13	73.77	0.2230	0.000094
C1	190.56	45.99	0.0104	0.000099
C2	305.33	48.72	0.0991	0.000146
C3	369.85	42.48	0.1520	0.000200
2-Methylpropane	407.85	36.40	0.1844	0.000259
iC4	407.85	36.40	0.1844	0.000259
nC4	425.16	37.96	0.1985	0.000255
2,2-Dimethylpropane	433.75	31.94	0.1950	0.000303
2-Methylbutane	460.45	33.77	0.2270	0.000306
Neo-C5	433.75	31.94	0.1950	0.000303
iC5	460.45	33.77	0.2270	0.000306
nC5	469.70	33.67	0.2513	0.000311
C6	507.82	30.18	0.2979	0.000370
C7	540.13	27.27	0.3498	0.000432
C8	569.32	24.97	0.3960	0.000486
C9	594.60	22.88	0.4450	0.000548

3.2 PT-Flash Calculations

Following the collection of data, flash calculations, with the selected EoS, were performed to predict the respective values of the solubility of components in each dataset considered, using Multiflash™ (version 6.1) software (Infochem, 2016). Multiflash™ is an advanced thermodynamics and fluid property engine that is significantly applied in pipeline simulation in the petroleum industry. The comprehensive, physical property package it possesses, allows for the rigorous modelling of the PVT (pressure, volume, temperature) phase behaviour of complex hydrocarbon mixtures and pure substances. Schlumberger's PIPESIM® software was used to access the embedded Multiflash™ package for compositional simulations. The system's pressure, temperature and composition were the supplied inputs, after which an EoS is selected and PT-flash calculations performed. This procedure is repeated for each of the 4 EoS and the respective datasets used in this study. C7⁺ components are modelled by adding a new petroleum fraction and

supplying the molecular weight and specific gravity (provided by the data) into the Multiflash™ software.

3.3 Ranking the EoS

The ranking procedure firstly involves determining the Absolute Percentage Error (AbPE) between the predicted compositions and the experimental datasets for each system. Thereafter, these values (for each component) are averaged over each dataset to yield the Mean Absolute Percentage Error (MAbPE), as given by Eq. 32.

$$MAbPE(\%) = \frac{1}{N_{ds}} \left| \frac{X_{calc} - X_{exp}}{X_{exp}} \right| \times 100 \quad (39)$$

Where X_{calc} is the calculated composition, X_{exp} is the experimental composition value, and N_{ds} is the number of points/observations in the dataset. Furthermore, these MAbPEs are subsequently averaged again to yield the overall performance over the entire datasets applied. A comparative assessment of the EoS is also performed by plotting the Percentage Errors (PE) for the respective EoS and datasets (Eq. 33). These plots indicated the level of over-/under-prediction by the EoS, which is an important measure in assessing their performance.

$$PE(\%) = \left(\frac{X_{calc} - X_{exp}}{X_{exp}} \right) \times 100 \quad (40)$$

4. Results and Discussion

4.1 Methanol as the Hydrate Inhibitor

Table 2 shows typical calculations performed per dataset, whereas Table 3 shows the MAbPEs of the calculated compositions using the four EoS using experimental data of reservoir fluid systems involving methanol as a hydrate inhibitor. for the different datasets tested, it is observed (in Table 3), that the CPA EoS is the best performing EoS with average values of the MAbPEs as 12, 22 and 7% for the hydrocarbon vapour, hydrocarbon liquid and polar phases respectively. PR(HV) and RKS(HV) have similar performances, except in the polar phase where RKS(HV) is twice as accurate.

Table 2: Calculations performed for each dataset (data obtained from Kristensen et al., 1993; 10 °C and 75.8 bar – methanol as hydrate inhibitor).

Comp.	Feed	H.C Vapour Phase Composition					PE (%)			
		Exp.	CPA	RKS (HV)	PR (HV)	PSRK	CPA	RKS (HV)	PR (HV)	PSRK
Methanol	7.500	0.051	0.042	0.047	0.055	0.077	-18.394	-8.291	7.720	50.605
Water	40.090	0.034	0.019	0.016	0.025	0.060	-43.058	-52.869	-25.061	76.294
HC	52.410	99.915	99.939	99.937	99.920	99.863	0.024	0.022	0.005	-0.052
	Feed	H.C Liquid Phase Composition					PE (%)			
		Exp.	CPA	RKS (HV)	PR (HV)	PSRK	CPA	RKS (HV)	PR (HV)	PSRK
Methanol	7.500	0.482	0.187	0.052	0.048	0.832	-61.196	-89.203	-90.107	72.647
Water	40.090	1.195	0.031	0.017	0.021	1.110	-97.426	-98.554	-98.220	-7.116
H.C	52.410	98.323	99.782	99.931	99.931	98.058	1.484	1.635	1.635	-0.270
	Feed	Polar Phase Composition (ppm)					PE (%)			
		Exp.	CPA	RKS (HV)	PR (HV)	PSRK	CPA	RKS (HV)	PR (HV)	PSRK
Methanol	7.500	15.700	15.638	15.670	15.641	15.373	-0.392	-0.192	-0.374	-2.084
Water	40.090	84.300	84.018	84.025	83.892	83.423	-0.334	-0.327	-0.485	-1.040
H.C	52.410	0.000	0.343	0.306	0.467	1.204	–	–	–	–

Comp.: Component; *H.C*: Hydrocarbon; *PE*s: Percentage Errors; *Exp*: Experiments

The PSRK EoS is the worst performing with very large MAbPEs particularly noticed with the datasets from Pedersen et al. (1996). As observed in Table 3, the compositional distribution in the hydrocarbon liquid phase was the most difficult to predict (with significantly higher MAbPEs) compared to the hydrocarbon vapour and polar phases respectively. However, the aqueous phase (where hydrate inhibition occurs) has been reasonably represented in a majority of the datasets. It is also worth mentioning that the lack of data describing the experimental uncertainty (in all published literature data used in this work) poses extra difficulty in rigorously evaluating the models' performance.

The superior performance of the CPA EoS earlier outlined may be attributed to the inclusion of an association term from Wertheim theory (as implemented in the Statistical Associating Fluid Theory – SAFT) together with the modelling capabilities of the SRK EoS. The SRK model only accounts for the physical interactions between the molecules of the fluid mixture; whereas, the associating term accounts for the specific site these interactions take place. Thus, these specific interactions due to hydrogen bonding (in polar compounds) between like molecules (self-association) and unlike molecules (cross-association) can be accurately described. The results show that this approach is more effective than the application of mixing rules of the Huron-Vidal type for the description of hydrocarbon-polar compound interactions. Furthermore, according to Kontogeorgis et al. (2007), it is possible to gain better accuracy with the CPA EoS (with a single

interaction parameter), than the HV-type mixing rules in which 3 binary interaction parameters are usually applied. This further demonstrates the robustness of the CPA EoS.

Fig. 1 shows the Percentage Errors/Deviations (PEs) of calculated results (using the 4 EoS) from the experimental data of the hydrocarbon-methanol systems. The aim of doing this was to ascertain the existence of any trend in the percentage deviations as a function of temperature, pressure or composition of the mixture components. Furthermore (beyond analysing the absolute average deviations), it was desired to evaluate which EoS was mainly over-/under-predicting the compositional distributions after a PT-Flash.

However, on plotting the PEs against the system's properties (temperature, pressure or composition) for the entire datasets, no particular trend was observed. It is evident in Fig. 1a-c that PSRV mainly over-predicted the compositional distributions of the mixture components, whereas, PR(HV) and RKS(HV) mostly under-predicted the observed experimental data. The PEs of the CPA Eos are somewhat evenly distributed in the positive and negative regions respectively. In all 3 phases, it can be seen that a good number of the error values are concentrated around the zero line, implying that the errors were minimal at these points. To ensure comparability between all plots, it is also worth mentioning that the PEs $> 200\%$ were not displayed on the graph (particularly for the hydrocarbon liquid phase, where a few number of such large discrepancy points existed).

Table 3: Predictions of the compositional distribution of different reservoir fluid systems involving Methanol as the hydrate inhibitor.

Reference	Dataset	T-range (K)	P-range (bar)	MAbPEs Hydrocarbon Vapour Phase (%)				MAbPEs Hydrocarbon Liquid Phase (%)				MAbPEs Polar Phase (%)			
				CPA	RKS(HV)	PR(HV)	PSRK	CPA	RKS(HV)	PR(HV)	PSRK	CPA	RKS(HV)	PR(HV)	PSRK
Kristensen et al. (1993)	Dataset 1	283.15	75.8	20	20	11	42	53	63	63	27	0	0	0	1
	Dataset 2	323.15	75.8	9	11	2	34	18	48	48	102	0	1	0	1
Pedersen et al. (1996)	Dataset 3	279.65	120	-	-	-	-	8	25	26	766	1	0	0	2
	Dataset 4	281.05	200	-	-	-	-	9	26	26	101	1	0	0	2
Pedersen et al. (1996)	Dataset 5	276.75	60.3	10	9	17	26	42	24	25	167	21	22	22	19
	Dataset 6	280.85	149.9	9	3	6	515	7	25	25	168	1	1	1	2
Dandekar et al. (2005)	Dataset 7	273.75	14	21	26	15	20	-	-	-	-	3	6	5	15
	Dataset 8	288.85	167.1	29	20	39	335	-	-	-	-	1	4	8	23
	Dataset 9	269.25	21.1	28	33	23	26	-	-	-	-	2	8	3	29
	Dataset 10	282.55	16.78	37	29	24	290	-	-	-	-	2	7	5	37
Pedersen et al. (1996)	Dataset 11	263.15	69.15	0	5	2	17	26	40	74	3155	4	5	23	95
	Dataset 12	263.15	69.22	5	14	9	20	23	2052	2009	1617	7	56	49	61
	Dataset 13	293.15	69	4	0	5	22	12	17	39	1250	6	4	21	91
	Dataset 14	293.15	69.2	8	8	4	23	24	839	829	798	2	52	46	57
	Dataset 15	323.15	70.7	4	5	2	10	15	20	18	347	1	5	9	61
	Dataset 16	323.15	70.4	2	1	7	10	31	22	383	288	25	23	36	53
Haghighi (2009)	Dataset 17	263.15	69	8	23	3	39	-	-	-	-	19	50	164	508
	Dataset 18	277.15	69	7	8	10	59	-	-	-	-	26	14	96	318
	Dataset 19	293.15	69	12	1	14	65	-	-	-	-	9	16	94	290
	Dataset 20	323.15	69	8	11	4	33	-	-	-	-	17	22	24	137
	Dataset 21	263.15	69	4	46	36	31	-	-	-	-	-	-	-	-
	Dataset 22	277.15	69	0	0	0	0	-	-	-	-	-	-	-	-
	Dataset 23	293.15	69	26	15	7	70	-	-	-	-	-	-	-	-
	Dataset 24	323.15	69	7	22	21	27	-	-	-	-	-	-	-	-
Average MAPEs (%)				12	14	12	78	22	267	297	732	7	15	30	90

Figure 1: PEs for the different EoS used in the hydrocarbon-methanol systems.

Furthermore, as shown in Fig. 2 (for the selected datasets), the inhibitor composition in the aqueous phase was more accurately predicted by the EoS compared to the hydrocarbon vapour phase. This inaccuracy observed was higher at very low molar fractions as shown in Fig. 2c.

Figure 2: Performance of the CPA and RKS EoS relative to experimental data (with Methanol as the hydrate inhibitor).

4.2 MEG as the Hydrate Inhibitor

All datasets used here were obtained from Frost (2014); thus, demonstrating the scarcity of experimental studies, which examine the phase behaviour of MEG, water, and a real reservoir fluid. This data scarcity was greater with other inhibitors, such as Diethylene glycol (DEG) and Triethylene glycol (TEG); thus they did not feature in this study. As shown in Table 4, at atmospheric pressure and 303K, there is no formation of a hydrocarbon vapour phase for the reservoir fluids considered. Relative to these PT-flash conditions, the significantly higher boiling point of MEG (197°C) compared to the Methanol (64.7°C) is the reason for this observation in comparison to the methanol systems where a vapour phase forms. As with the methanol systems, Table 4 shows that the CPA EoS again outperforms the other EoS, with an average MAbPE of 21 and 16% for the polar and hydrocarbon phases, respectively.

Furthermore, PSRK also produced the farthest results from experimental data with average MAbPEs of 95 and 42% for the polar and hydrocarbon phases respectively. In addition, no convincing trend was observed with temperature, and thus it had no effect on the performance of

the cubic EoS considered. Predictions of the compositional distributions in the polar phase were superior with the CPA, RKS(HV) and PR(HV) EoS, compared to the hydrocarbon liquid phase. Conversely, PSRK showed better performance in the hydrocarbon-liquid phase compared to the polar phase. The PSRK EoS also showed a considerably better performance with the hydrocarbon liquid phase of the MEG systems (Table 4) compared to that of the methanol systems (Table 3). A likely explanation for this is the significant differences in pressure between the MEG and methanol datasets. This may be further verified with experimental data of MEG systems at higher pressures, which are currently scarce. Moreover, liquid-liquid equilibrium conditions may be more favourable for the PSRK equation compared to vapour-liquid equilibrium; again, further experimentation is required for full verification of its most suitable performance envelope.

Fig. 3 shows the PEs of the calculated compositions for the hydrocarbon-MEG-water systems. As previously observed, PSRK mainly over-predicts the compositional distribution. In Fig. 3b, there is a linear trend indicating that the increase in water composition in the feed decreases the accuracy of the PSRK EoS. It is also observed in both Figures 3a and b, that the cluster of points representing the RKS(HV) and PR(HV) at regions close to (-100%) increases as the water composition increases. Thus, it may be further pointed out that there is a slight deterioration in the performance of the EoS, as the water composition increases for the MEG-water-reservoir fluid mixtures.

Table 4: Predictions of the compositional distribution of different reservoir fluid systems involving MEG as the hydrate inhibitor.

All datasets obtained from Frost (2014)				MAbPEs Polar Phase (%)				MAbPEs Hydrocarbon Phase (%)			
	Dataset	T-range (K)	P-range (bar)	CPA	RKS(HV)	PR(HV)	PSRK	CPA	RKS(HV)	PR(HV)	PSRK
Condensate-1	Dataset 1	303.15	1.01325	6	33	33	90	15	40	37	28
	Dataset 2	303.15	1.01325	6	32	32	362	15	42	39	29
	Dataset 3	303.15	1.01325	11	30	27	347	35	41	38	72
	Dataset 4	323.15	1.01325	11	33	33	19	3	30	33	30
	Dataset 5	323.15	1.01325	11	33	33	105	9	32	30	24
	Dataset 6	323.15	1.01325	10	29	26	332	18	30	28	29
Condensate-2	Dataset 7	303.15	1.01325	24	33	33	70	13	40	36	49
	Dataset 8	303.15	1.01325	28	33	33	113	21	43	40	48
	Dataset 9	303.15	1.01325	29	33	32	176	21	45	41	46
	Dataset 10	323.15	1.01325	27	33	33	21	13	35	32	42
	Dataset 11	323.15	1.01325	28	33	33	80	7	34	31	47
	Dataset 12	323.15	1.01325	27	32	31	170	5	34	31	50
Condensate-3	Dataset 13	313.15	1.01325	11	33	33	81	7	31	34	59
	Dataset 14	313.15	1.01325	8	33	32	239	3	31	32	64
	Dataset 15	313.15	1.01325	5	29	26	483	6	32	30	66
Light Oil-1	Dataset 16	313.15	1.01325	3	33	33	37	17	47	46	39
	Dataset 17	313.15	1.01325	16	31	31	46	24	44	43	51
	Dataset 18	323.15	1.01325	3	33	32	36	14	44	43	38
	Dataset 19	323.15	1.01325	12	31	31	52	15	45	45	39
Light Oil-2	Dataset 20	313.15	1.01325	1	33	33	101	22	44	42	33
	Dataset 21	323.15	1.01325	4	33	33	66	20	40	39	38
	Dataset 22	323.15	1.01325	13	32	32	118	26	42	40	41
	Dataset 23	323.15	1.01325	18	30	28	160	26	44	43	39

Fluid-1	Dataset 24	303.15	1.01325	27	33	33	3	16	42	41	44
	Dataset 25	303.15	1.01325	27	33	33	25	17	43	42	50
	Dataset 26	303.15	1.01325	29	33	32	28	7	45	43	67
	Dataset 27	313.15	1.01325	26	33	33	7	29	35	34	45
	Dataset 28	313.15	1.01325	27	33	33	31	23	37	36	38
	Dataset 29	313.15	1.01325	29	33	32	36	17	40	39	36
	Dataset 30	323.15	1.01325	24	33	33	4	26	33	32	37
	Dataset 31	323.15	1.01325	26	33	33	32	21	36	35	32
	Dataset 32	323.15	1.01325	21	31	29	143	14	42	42	24
Fluid-2	Dataset 33	303.15	1.01325	33	33	33	31	21	53	52	35
	Dataset 34	303.15	1.01325	33	33	33	32	12	52	51	41
	Dataset 35	303.15	1.01325	33	33	33	32	7	51	50	43
	Dataset 36	313.15	1.01325	33	33	33	31	10	50	49	33
	Dataset 37	313.15	1.01325	33	33	33	31	5	49	48	39
	Dataset 38	313.15	1.01325	33	33	33	32	8	47	46	44
	Dataset 39	323.15	1.01325	33	33	33	31	9	46	46	34
	Dataset 40	323.15	1.01325	33	33	33	32	22	41	41	43
	Dataset 41	323.15	1.01325	33	33	33	32	33	41	40	44
Average MAbPEs (%)				21	33	32	95	16	41	39	42

Figure 3: PEs for the different EoS used in the hydrocarbon-MEG systems.

A similar representation to Fig. 2 is shown in Fig.4 for selected reservoir fluids which utilise MEG as the hydrate inhibitor. Similar to Fig. 2, a complete overlap between the experimental data and EoS predictions of MEG in the aqueous phase is observed; however, the compositions of MEG in the hydrocarbon vapour phase were difficult to replicate. CPA is clearly observed to perform significantly better than RKS-HV in the presented plots.

Figure 4: Performance of the CPA and RKS EoS relative to experimental data (with MEG as the hydrate inhibitor).

5. Conclusions

This study has presented a comparative evaluation of the performance of Cubic EoS for modelling the distribution of water, a hydrate inhibitor and hydrocarbons in complex mixtures observed in the oil and gas industry. The following conclusions can be derived from the observations made herein.

- Our review of existing experimental contributions in this field demonstrates the scarcity of published works that consider the phase behaviour of MEG in a real reservoir fluid (containing water) compared to methanol.
- The accuracy of a Cubic EoS in modelling the distribution of water, a hydrate inhibitor and hydrocarbons in complex reservoir fluid mixtures depends on the mixing rules adopted.

- For most of the considered systems, the CPA-Infochem and RKS-HV EoS showed better performance in predicting the inhibitor compositions in the aqueous phase than in the hydrocarbon phases.
- The CPA EoS (with Infochem mixing rules) performed most accurately, compared to the other EoS and is the recommended model for studying systems involving hydrocarbon + water + hydrate inhibitor.
- The PSRK EoS produced results farthest from experimental data.
- The over-/under-prediction of the compositional distribution showed no convincing dependence on temperature or pressure.
- In the MEG systems, the performance of all EoS used herein (except CPA) deteriorated with the increase in the molar composition of water in the feed.

Unlike EoS/ G^E models, which perform poorly with the classical van der Waals mixing rules (vdW1f) in the presence of polar compounds (Kontogeorgis and Coutsikos, 2012; Epelle et al., 2020); the use of the CPA EoS with the vdW1f mixing rules has shown satisfactory performance as demonstrated by Karamoddin and Varaminian (2012), in a mixture of water and hydrocarbons. Although we have not considered the performance of the CPA with vdW1f mixing rules in this study, we do not expect the findings of Karamoddin and Varaminian (2012) to be significantly different for the systems considered herein. However, such endeavour (with compiled vdW1f BIPs for all components and datasets employed) including the applications of other EoS are subjects of future investigations.

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7. Declaration of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

8. Credit Author Statement

Emmanuel I. Epelle: Conceptualization, Methodology, Software, Data Curation, Supervision, Writing Original Draft, Writing Review Draft.

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9. Nomenclature

Symbols

$\mathcal{A}$	Constant defined by Eq. 11
a, b	Parameters in the Soave-Redlich-Kwong EoS
B	Constant defined by Eq. 12
b	van der Waals co-volume in the Peng-Robinson EoS
$a(T)$	Parameter in Eq. 14
b_{ij}	Binary interaction parameter
G	Gibbs energy (J)
G^E	Excess Gibbs energy (J)
$g(\rho)$	Radial distribution function
n_i	Mole fraction of component i
N	Number of components
N_{ds}	Number of points/observations in the dataset
P	Pressure (Pa)
R	Gas constant
S_l	EoS-dependent numerical constant
T	Temperature (K)
v	Specific volume (m^3/kg)
V_c	Critical volume (m^3/mol)
x	Mole fraction
X_{calc}	Calculated composition
X_{exp}	Experimental composition value
Z	Compressibility factor

Greek Letters

α	Non-randomness parameter
$\propto$	Scaling factor defined by Eq. 7
β	Association volume parameter

Δ	Association strength
ε	Association energy parameter
ξ_{ji}	Energy parameter characteristic of the j - i interaction
η	Reduced density
ρ	Molar density
ω	Acentric factor
τ	Huron and Vidal interaction parameter
γ_1, γ_2	Huron and Vidal interaction coefficients

Subscripts and Superscripts

c	Critical property
E	Excess
i	Component index
j	Component index
k	Component index
r	Reduced property

Acronyms

AbPE	Absolute Percentage Error (%)
BIP	Binary interaction parameter
CPA	Cubic-Plus-Association
EoS	Equation of State
HV	Huron-Vidal
MABPE	Mean Absolute Percentage Error (%)
MEG	Monoethylene Glycol
PE	Percentage Error (%)
PR	Peng-Robinson
PSRK	Predictive-Soave-Redlich-Kwong
RKS	Redlich-Kwong-Soave
SRK	Soave-Redlich-Kwong
vdW1f	van der Waals one-fluid mixing rules

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