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Modelling of phase equilibrium of natural gas mixtures containing associating compounds

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A B S T R A C T

The effect of mixing rules and the incorporation of an association term in a cubic equation of state (EoS), on the modelling of phase equilibria of natural gas mixtures in the presence of hydrogen bonding compounds, is investigated. To this purpose, the Peng-Robinson equation of state coupled with the van der Waals one-fluid mixing rules, the UMR-PRU group contribution EoS and the CPA-PR EoS, are evaluated in the prediction of phase equilibrium in ternary and multicomponent mixtures containing natural gas components, water and methanol or monoethylene glycol. It is concluded that UMR-PRU and CPA-PR give significantly improved results over the classical Peng-Robinson EoS, indicating that the use of advanced mixing rules and the explicit implementation of an association term in a cubic EoS is important for modelling the phase equilibrium of natural gas mixtures containing associating compounds.

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1. Introduction

Natural gas (NG) consists mostly from hydrocarbons, but is saturated with water at reservoir conditions or during underground storage. The presence of water in natural gas may lead to corrosive effects, especially in the presence of sour gases, while at low temperature and high pressure conditions, such as those that occur in subsea transportation pipelines, hydrates may form, jeopardizing the equipment as well as the product quality. To prevent hydrate formation, a certain amount of hydrate inhibitor, such as methanol or monoethylene glycol (MEG), is injected into the flow in order to shift the hydrate formation curve outside the pipeline operating conditions. Additionally, a dehydration process typically precedes the further processing of natural gas and its distribution in onshore pipelines. In the majority of plants, physical absorption in glycols is sufficient to reach the water content specification of the natural gas. Thus, the availability of a sufficient thermodynamic framework that will be able to accurately predict the phase equilibria of mixtures containing hydrocarbons and polar compounds, such as water, methanol and MEG, is vital for the simulation of such operations in order to ensure product quality, safe and economic production and transportation, as well as to comply with the environmental legislation [1].

Cubic Equations of State (CEoS) are widely used for the calculation of thermodynamic properties and, especially, phase equilibrium, of pure components and mixtures both in industry and academia. However, it is well known that CEoS combined with the classic van der Waals one fluid (vdW1f) mixing rules are insufficient when strongly polar or associating compounds such as water, alcohols or glycols are present along with the hydrocarbons [2]. Accurate description of phase equilibrium of such mixtures requires the use of more sophisticated approaches. An easy way to extend the applicability of a CEoS to polar mixtures, while keeping its cubic character, is to use advanced mixing rules. Such an elegant approach is based on the idea of Huron and Vidal [3] to match the excess Gibbs free energy (G^E) of the mixture as calculated by the EoS with the one calculated by a Gibbs free energy (or equivalently activity coefficient) model at a reference pressure. These so-called EoS/G^E mixing rules allow the incorporation of an expression for the activity coefficient inside the EoS, permitting thus a CEoS to be applicable to polar compounds at high pressures as well. A number of EoS/G^E mixing rules have been proposed to extend the

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applicability of equations of state to highly non-ideal mixtures with varying degrees of success [4–9].

A more sophisticated approach, which violates the cubic character of the EoS, is the development of an EoS that accounts explicitly for strongly polar and hydrogen bonding interactions. A variety of models has been proposed in the literature for the modelling of associating components, but those based on the perturbation theory, such as the statistical associating fluid theory (SAFT) [10,11], the perturbed chain SAFT (PC-SAFT) [12,13] and the cubic plus association (CPA) [14], are most appealing nowadays and some of their versions are included in commercial simulators.

Recently, an increasing number of studies concerning the phase equilibrium of common natural gas components with alcohols or glycols and water have been published in the literature, involving new measurements or evaluation of existing ones. Frost et al. [15] evaluated some of the existing vapor-liquid equilibrium (VLE) data of the methane/water/methanol ternary mixture and its respective binaries and conducted new experimental measurements. Folas et al. [1] measured new experimental data for the binary methane/MEG and the ternary methane/MEG/water with emphasis to the water solubility measurements in the vapor phase. They used CPA and Soave-Redlich-Kwong (SRK), combined with both the conventional vdw1f mixing rules [16] and the Huron Vidal [3] ones, and concluded that both models, the latter with Huron − Vidal mixing rules (SRK-HV), perform satisfactorily for the prediction of MEG and water solubility in the vapor phase. According to the authors, CPA has an advantage over the other models. In another communication, Folas et al. [17] applied the CPA and the SRK-HV to predict the multiphase equilibria of ternary, MEG/water/ aromatic hydrocarbons, and quaternary mixtures, water/methane/ toluene/MEG. Chapoy et al. [18,19] focused on the hydrate forming conditions of natural gas mixtures; to that end, they evaluated the existing phase equilibrium data and measured the solubility of methane and water near hydrate forming conditions. Li and Englezos [20] employed the SAFT EoS to predict the phase equilibria of nine hydrocarbon/water/alcohol ternary systems, among them the methane/water/methanol and methane/water/MEG mixtures, using binary interaction parameters fitted to the respective binary mixtures. Overall, a satisfactory agreement between the model predictions and experimental data was found, except for the methane/water/methanol mixture.

Unfortunately, only very few experimental data are available in the open literature concerning phase equilibrium of natural gas mixtures with water, methanol/MEG and, consequently, the performance of thermodynamic models is ambiguous. In a series of publications, Avila et al. [21–24] and Jarne et al. [25] measured dew points of synthetic natural gas (SNG) mixtures with water and methanol and modelled them with a model based on the excess function equation of state. Also, Yan et al. [26] modelled, among others the dew points of two SNGs mixtures measured by Jarne et al. [25] with the CPA EoS.

In this work, the effect of advanced mixing rules and explicit accounting for the association on a cubic equation of state is examined. To this purpose, the Peng−Robinson (PR) is selected and is coupled with: (a) the conventional van der Waals one fluid mixing rules [27], (b) the universal mixing rules leading to the so-called UMR-PRU [28] model, and (c) the associating term of Wertheim [29,30] leading to CPA-PR EoS [31]. Initially, the VLE of two ternary systems, methane/water/methanol and methane/water/ MEG is examined, while next, the dew point curves of SNG mixtures with water and methanol are investigated. In order to ensure a fair comparison between the models, their interaction parameters are fitted to the same database of binary phase equilibrium experimental data.

2. Thermodynamic models

The three models examined in this work, PR, UMR-PRU and CPA-PR, have been extensively presented in the literature, and, consequently, only their basic equations are presented in the Appendix.

When available, the pure component parameters for all models have been taken from the literature. In all other cases, they were determined in this work by fitting experimental pure component vapor pressure and/or liquid density data taken from DIPPR compilation [32].

The pure component parameters of PR EoS, which are also used in UMR-PRU, are presented in Table 1. The UNIFAC group-volume, R, and area, Q, parameters, used in UMR-PRU are presented in Table 2. Pure component parameters for the CPA-PR are presented in Table 3.

The 2B associating scheme, i.e. one electron donor and one

Table 2
van der Waals volume (R) and area (Q) parameters.

	CO_2	N_2	CH_4	C_2H_6	CH_3	CH_2	H_2O	CH_3OH	MEG
R	1.296	0.934	1.129	1.8022	0.9011	0.6744	0.9200	1.4311	2.4088
Q	1.261	0.985	1.124	1.6960	0.848	0.5400	1.4000	1.4320	2.2480

Table 1
Pure component parameters for PR EoS.

Component	Ref.	T_r range	T_c (K)	P_c (bar)	ω	c_1	c_2	c_3	% AAD[a] in P^s	% AAD[a] in V_l
Nitrogen	[32]	0.53−0.99	126.10	33.944	0.0403	–	–	–	0.74	8.60
CO_2	[32]	0.72−0.98	304.19	73.815	0.2276	–	–	–	0.99	3.86
Methane	[32]	0.53−0.99	190.56	45.99	0.0115	–	–	–	0.79	8.02
Ethane	[32]	0.41−0.99	305.32	48.72	0.0995	–	–	–	1.28	6.47
Propane	[32]	0.33−0.98	369.83	42.48	0.1523	–	–	–	4.73	4.90
Isobutane	[32]	0.45−0.99	408.14	36.48	0.1770	–	–	–	2.71	5.34
n-butane	[32]	0.32−0.99	425.12	37.96	0.2002	–	–	–	5.75	4.31
Isopentane	[32]	0.45−0.99	460.43	33.812	0.2275	–	–	–	1.13	4.63
n-pentane	[32]	0.40−0.99	469.70	33.70	0.2515	–	–	–	2.47	3.47
n-hexane	[32]	0.40−0.99	507.60	30.25	0.3013	–	–	–	5.19	2.94
n-heptane	[32]	0.51−0.95	540.20	27.40	0.3495	–	–	–	1.14	2.62
H_2O	[4]	0.55−0.90	647.13	220.55	0.3449	0.92366	−0.37937	0.44243	0.10	34.40
MeOH	[4]	0.55−0.90	512.64	80.97	0.5640	1.22400	−0.27350	−0.39823	0.10	18.72
MEG	This work	0.45−0.96	720.00	82.00	0.5068	0.91003	1.34996	−1.89002	3.63	12.52

[a] $\%AAD = \frac{100}{NDP}\sum_{i=1}^{NDP}\frac{abs(X_i^{exp}-X_i^{calc})}{X_i^{exp}}$, where X: P^s or V_l.