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Published in:
Fluid Phase Equilibria

Link to article, DOI:
10.1016/j.fluid.2020.112884

Publication date:
2021

Document Version
Peer reviewed version

Density Modeling of High-Pressure Mixtures using Cubic and Non-Cubic EoS and an Excess Volume Method

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Abstract

A central issue in the equation of state (EoS) development is to describe accurately fluid density and thus other thermodynamic properties based on it. This study attempts to investigate the density modeling of high-pressure mixtures, particularly related to reservoir fluids, by cubic and non-cubic EoS. A large density database of binary mixtures related to petroleum fluids was established and used to compare some typical cubic and non-cubic EoS, including SRK, PR, PC-SAFT, Soave-BWR, and GERG-2008. For the first four EoS, their volume translated versions were also evaluated. The evaluation results suggest that the EoS form three groups in order of accuracy: GERG-2008 as the first group, Soave-BWR and PC-SAFT in the second, and PR and SRK in the last. Volume translation is more effective for the last group but it does not change the order. A model-to-model comparison was made between SRK and PC-SAFT, and between SRK and PR for 500 binary pairs over a wide range of conditions, showing that the differences in the excess volume are usually small between different models. This observation motivated the introduction of an excess volume method, which combines two EoS in estimating the final thermodynamic properties. The evaluation of this method using the binary density database shows that it can deliver reasonable density estimates using a simple model like SRK. Its limitations were analyzed and its potential application for estimating high-pressure reservoir fluid densities was discussed.

Keywords: cubic and non-cubic EoS, density, excess volume, reservoir fluids, high pressure

1. Introduction

Thermodynamic equations of state (EoS) are a powerful tool to calculate fluid phase equilibria and equilibrium phase properties. Among various thermodynamic properties, density is the most basic one. In a simple view, the two central issues in any EoS development are accurate description of phase equilibrium and fluid density although other thermodynamic properties, noticeably enthalpy and entropy, are also important to capture. Since most modern EoS use temperature, molar volume and composition as independent variables, the other thermodynamic properties are generated using density as input for these EoS.

In a review [1] thirty-five years ago, Tsonopolous and Heideman claimed "the cubic EoS is 'here to stay.'" The statement is largely valid today despite the dramatic advances in other types of EoS, particularly association models in recent years. In the cubic EoS family, the Redlich-Kwong (RK) EoS [2] represents a leap ahead of the van der Waals model in density and gas phase fugacity. Soave's modification [3] of the RK EoS is mainly on the phase equilibrium part and Peng and Robinson's subsequent improvement [4] over SRK is mainly on density. Another branch in the EoS family is the virial-type EoS, including the Bennedict-Webb-Rubin (BWR) EoS [5] and its modified version by Starling and Han [6]. Two more recent modifications of BWR were proposed by Soave [7],[8], with the latter version [8] being simpler and more accurate. We call this version Soave-BWR (further abbreviated to SBWR in tables or equations) here. These virial-type non-cubic EoS put more emphasis on the density accuracy. Modern reference EoS for various pure components also belong to this family, and provide the highest accuracy for thermodynamic properties of pure components. As an extension of these reference models, GERG-2008 [9] represents an attempt to generalize these reference EoS to natural gas related mixtures. In contrast to the virial-type non-cubic models that often bear a strong empirical nature, many modern non-cubic EoS, such as the most noteworthy examples of the SAFT (Statistical Association Fluid Theory) family EoS [10]-[17], are developed on a more theoretical basis. Characterized by using an association term from the Wertheim theory, the SAFT family EoS are better in describing the phase equilibria for systems with associating compounds. In addition, most models in this family use more rigorous repulsive and attractive terms. As a result, these models generally give a superior description of density and other thermodynamic properties than the cubic ones.

Density is a thermodynamic property of wide relevance and fundamental importance to science and industry. It is used for characterizing chemical compounds, understanding intermolecular interactions, and determining important derivative properties such as isothermal compressibility and isobaric thermal expansion coefficients. It is often needed in the experimental determination of other fluid properties such as viscosity, heat capacity, or interfacial tension. Density is also needed in the calculation of different dimensionless modules, such as the Reynolds

number, critical to analysis of transport phenomena. For chemical and many other industrial processes, the property is an integral part of their design and analysis, such as equipment sizing, through material and energy balances. Density is particularly important for oil and gas production. In addition to its general significance as a property associated with any process calculation, it is critical in the estimation of the oil and gas in place and the response of the reservoir to a pressure change. The increase in production from deeper reservoirs with high pressures requires knowledge on accurate fluid density over a larger pressure and temperature range, which requires not just expensive experimental measurement but also adequate modeling in order to predict at the conditions not covered in the experiment.

Most of the studies on EoS development involve some density modeling but usually those studies [9], [18]-[20] on non-cubic virial-type EoS comprise a more extensive density evaluation. For the oil industry or underground high-pressure processes, there have been efforts to modify existing cubic models to improve their density performance [21]-[23], usually through volume translation [24], and attempts to evaluate comprehensively the differences between cubic and non-cubic models [25]-[27]. High-pressure high-temperature reservoirs, as a new frontier for oil exploration and development, have motivated studies on the performance of EoS at the extreme conditions [23], [26], [28], [29]. Although it is generally known that the non-cubic models are more accurate in density than the cubic ones, especially for pure components, it is still worthwhile to quantify the differences for a specific type of system, such as systems related to reservoir fluids. The magnitudes of the differences are an important factor determining whether these non-cubic models can replace the cubic ones in relevant applications, and if yes, which ones and to what extent. The application of non-cubic models also has its challenges in the algorithmic aspect, mainly the concerns over their robustness and efficiency. These challenges were somewhat addressed in a simulation context, [30][31] bringing non-cubic models closer to reservoir engineering applications provided that their advantages are clearly shown for a specific scenario.

In this study, we investigate the density modeling of high-pressure binary mixtures by cubic and non-cubic EoS. Our discussion is restricted to hydrocarbon mixtures mainly related to petroleum reservoir fluids but the findings are also useful to the modeling of other mixtures. Since nitrogen, carbon dioxide and hydrogen sulfide are commonly present in reservoir fluids, the "hydrocarbon" mixtures discussed here also include these components although our main focus is still hydrocarbons. For the EoS models, we select SRK, PR, Perturbed Chain SAFT (PC-SAFT) [15][32], Soave-BWR and their volume translated versions in a comparison using a large density database for binary mixtures. When possible, GERG-2008 is also included in the comparison. Since we cannot expect that the literature density data cover all the binary pairs and all the temperature, pressure and composition conditions of interest, we propose here to carry out a model-to-model

comparison in the excess volume calculation without using experimental data. The model-to-model comparison does not provide the accuracy but can reveal the difference between two models in the description of a certain thermodynamic property. Moreover, the evaluation is no longer limited by the availability of experimental data. SRK is compared with PC-SAFT and PR in the excess volume and molar volume calculation for 500 binary pairs between 41 components. Based on the comparison results, we propose an excess volume method that utilizes the excess volumes from a simple EoS to estimate the high-pressure mixture densities. The approach can potentially be used to reduce the amount of work required for the costly high-pressure density measurement of reservoir fluids or other similar mixtures.

2. EoS models and volume translation

This study involves two cubic EoS (SRK and PR) and three non-cubic ones (PC-SAFT, Soave-BWR and GERG-2008). The non-cubic ones are briefly described below. Volume translation is often used to improve the density calculation for a cubic EoS. The same technique can be formally applied to a non-cubic model. We present below the correlations for volume translation parameters for SRK and PR, and discuss how to generate similar correlations for PC-SAFT and Soave-BWR.

2.1. PC-SAFT EoS

The PC-SAFT EoS proposed by Gross and Sadowski [15], [16] assumes the following form in reduced Helmholtz energy $\tilde{a}$:

$$\tilde{a} \equiv \frac{A}{NkT} = \tilde{a}^{id} + \tilde{a}^{hc} + \tilde{a}^{disp} + \tilde{a}^{assoc} \tag{1}$$

where $\tilde{a}^{id}$ is the ideal gas contribution, $\tilde{a}^{hc}$ is the contribution of the hard-sphere chain reference system, $\tilde{a}^{disp}$ is the dispersion contribution arising from the square well attractive potential and $\tilde{a}^{assoc}$ is the association contribution based on Wertheim's theory. This study only handles non-associating components and the $\tilde{a}^{assoc}$ term disappears. The remaining three terms still give a non-cubic form with three model parameters: the chain length m, the segment diameter σ and the segment energy ε. Designed for long-chain molecules, this model gives superior behavior for long chain alkanes and polymers. We here use the simplified version of PC-SAFT proposed by von Solms et al. [32]. The simplified version involves a small modification that improves the computation efficiency but does not affect the equilibrium calculation much. Indeed, it gives exactly the same results as the original PC-SAFT for pure components, and very similar results in describing mixture phase behavior. Here we just denote this version by PC-SAFT or its more abbreviated version SAFT in tables. All the pure component model parameters are taken from [15], [26] and the binary interation parameters (one per pair) from [26]. The interaction parameters for SRK and PR are also taken from [26].

2.2. Soave-BWR EoS

The Soave-BWR EoS proposed by Soave [8] is a simplified and generalized form of the BWR EoS. It assumes the following form:

$$z = \frac{P}{RT\rho} = 1 + B\rho + D\rho^4 + E\rho^2(1 + F\rho^2)\exp(-F\rho^2) \tag{2}$$

where ρ is the density. The four model coefficients B, D, E, and F are all generalized functions of the three model parameters, T_c, P_c, and ω, for each pure component. In addition, there is one interaction parameter per binary pair. Compared with PC-SAFT, Soave-BWR gives the correct critical point and a better phase behavior description close to the pure component critical point. All the interaction parameters for Soave-BWR are taken from [26].

2.4. GERG-2008 EoS

GERG-2008 is a wide-range EoS developed for 21 components of natural gases and their mixtures that meets the requirements of standard and advanced natural gas applications [9]. It is explicit in the Helmholtz free energy as a function of density ρ, temperature T and composition x. It is valid over the temperature range from 60 K to 700 K and up to 700 bar [1]. The EoS in the dimensionless reduced form is as follows:

$$\alpha(\delta,\tau,\bar{\boldsymbol{x}}) = \alpha^0(\rho,T,\bar{\boldsymbol{x}}) + \sum_{i=1}^{n} x_i \alpha_{0i}^r(\delta,\tau) + \Delta\alpha^r(\delta,\tau,\bar{\boldsymbol{x}}) \tag{3}$$

where δ is the reduced mixture density and τ is the inverse reduced mixture temperature. $\alpha(\delta,\tau,\bar{\boldsymbol{x}})$ is the dimensionless form of the reduced Helmholtz free energy, and $\alpha^0(\rho,T,\bar{\boldsymbol{x}})$ is the dimensionless form of the Helmholtz free energy for the ideal-gas mixture. The last two terms on the right hand side of Eq. (3) provide the residual contribution: $\alpha_{0i}^r(\delta,\tau)$ is the residual part of the reduced Helmholtz free energy of component i, and $\Delta\alpha^r(\delta,\tau,\bar{\boldsymbol{x}})$ is the so-called "departure function." [9] $\alpha^0(\rho,T,\bar{\boldsymbol{x}})$ and $\alpha_{0i}^r(\delta,\tau)$ contain a large number of component-specific coefficients for the 21 components, and $\Delta\alpha^r(\delta,\tau,\bar{\boldsymbol{x}})$ involves relatively complex mixing rules with four binary parameters for each pair. Here we use GERG-2008 in the model comparison only when the components are in the GERG-2008 component list.

2.5. Volume translation

Volume translation is a classical method used to improve the density results from an EoS without modification of the model. It is attractive because the phase equilibrium calculation is not affected if the same volume translation is applied to all the equilibrium phases. It is primarily

applied to cubic EoS, e.g., the Peneloux volume translation [24] applied to SRK. However, the method is essentially general and applicable to any EoS. The method can be summarized by the following two equations:

$$v = v^{EoS} - c \tag{4}$$

$$c = \sum_i x_i c_i \tag{5}$$

The volume translation parameter c is subtracted from the molar volume calculated by an EoS, v^{EoS}, to obtain the improved molar volume v. The mixture parameter c is calculated from the pure component parameters c_i with a linear mixing rule. In the Peneloux volume translation for SRK, the correlation for c_i is developed using the first ten n-alkanes. The Rackett compressibility factor Z_{RA} is used in the final expression:

$$c_{SRK} = 0.40768(RT_c / P_c)(0.29441 - Z_{RA}) \tag{6}$$

$$Z_{RA} = 0.29056 - 0.08775\omega_i \tag{7}$$

The above c_{SRK} correlations are supposed to reproduce the saturated liquid densities calculated using Z_{RA} at reduced temperature T_r=0.7 for the SRK model. There are several correlations for the volume translation parameter c_{PR} for PR and we use the following one recommended by Pedersen et al. [33]:

$$c_{PR} = 0.50033(RT_c / P_c)(0.25969 - Z_{RA}) \tag{8}$$

Similar correlations can also be developed for PC-SAFT and Soave-BWR following the Peneloux procedure. By matching the saturated liquid densities created using Z_{RA}, we obtain

$$c_{SAFT} = 0.0931184196(RT_c / P_c)(0.278176670 - Z_{RA}) \tag{9}$$

$$c_{SBWR} = 0.0689065477(RT_c / P_c)(0.275234626 - Z_{RA}) \tag{10}$$

The above two correlations are proposed in a way consistent with the Peneluox procedure. If we use the saturated densities from NIST instead of those calculated by Z_{RA}, the coefficients in the correlations will change:

$$c_{SAFT} = 0.0255159055(RT_c / P_c)(0.283523766 - Z_{RA}) \tag{11}$$

$$c_{SBWR} = 0.00130403359(RT_c / P_c)(0.22734036 - Z_{RA}) \tag{12}$$

corresponding to much smaller correction parameters, especially for Soave-BWR. In fact, the corrections are trivial for PC-SAFT and Soave-BWR if the latter two correlations are used.

We do not expect a dramatic change in the density calculation results for PC-SAFT and Soave-BWR after implementing the above volume translation because both non-cubic models have included density in their model development. We include here the volume translation for the two

non-cubic models mainly to keep the treatments similar in the comparison. It should be noted that the correlations for volume translation parameters are empirical and they may not represent the best way to perform volume translation. Actually, one can also select different translation parameters to get the best description for the density in a specific range. Here we restrict our discussion to the common translation correlations for SRK and PR, and those correlations for PC-SAFT and Soave-BWR in a way comparable to the Peneloux translation.

3. Density database for binary mixtures

A density database for binary mixtures related to petroleum fluids was established. It covers most n-alkanes up to C_{30} (we drop "n" in front of the symbols for n-alkanes in this paper for simplicity), iso-alkanes iC_4 and iC_5, and common non-hydrocarbon components N_2, CO_2, and H_2S. Aromatic hydrocarbons are also important constituents in petroleum fluids. They are not included in the current database but will be considered in the future. Table 1 presents the overview of the 88 pairs in this density database, and Table 2 gives the detailed information for each pair, including the data sources, the number of data points (N_p), and the range of conditions. There are 40688 data points in total with 98% of them at elevated pressures. In Table 1, the 22 pairs with only atmospheric data are marked in green and the remaining 66 pairs with high-pressure data in blue or yellow. Actually, most of the atmospheric data are in those green pairs, with the remaining few in some blue pairs whose components are heavier than C_5. The atmospheric data cover quite many heavy pairs although their total number of data points are just a small percentage. In contrast, the first four columns in Table 1, especially the pairs with N_2, CO_2, and C_1, account for nearly 1/3 of the pairs and 57% of the data points.

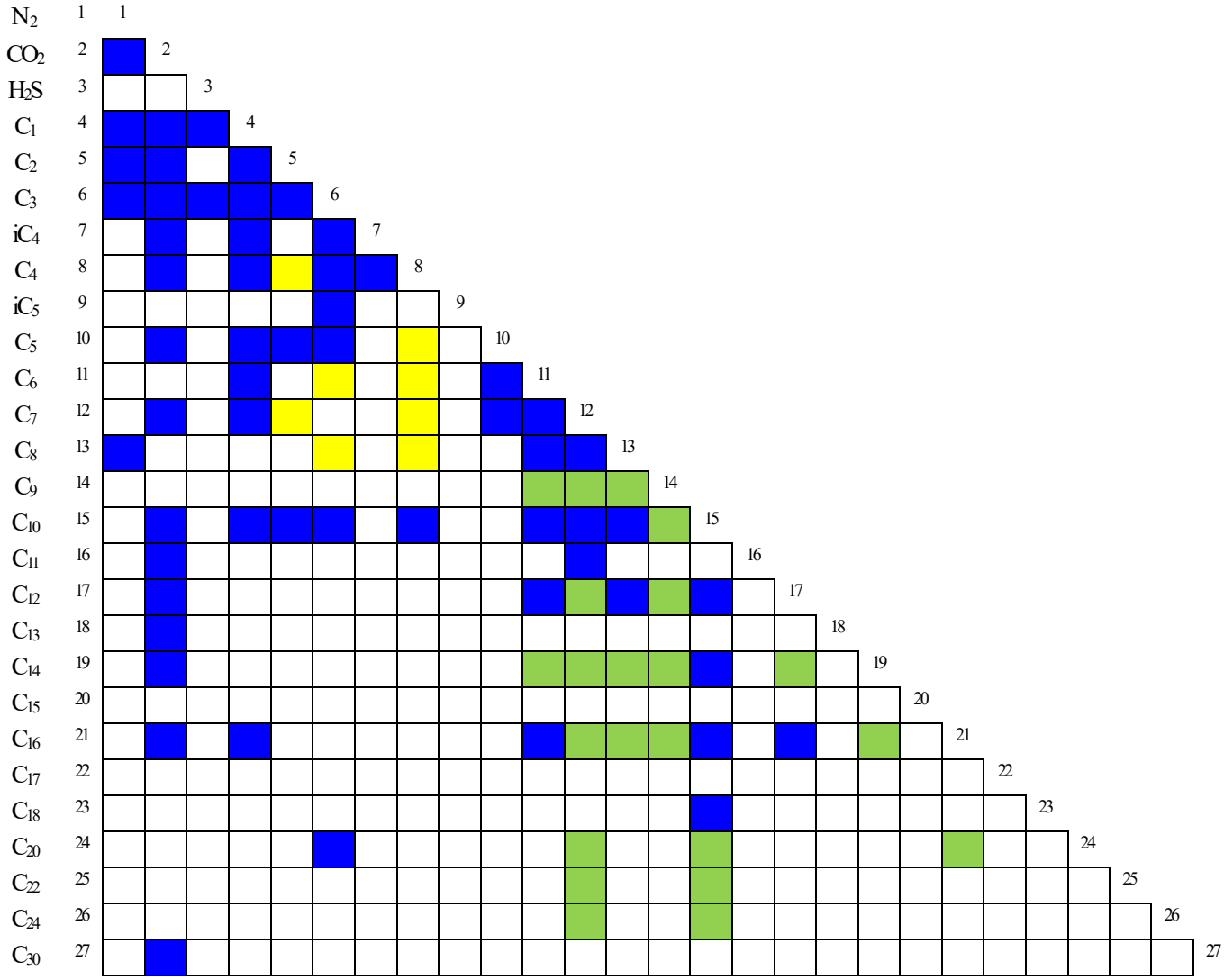
The high-pressure mixture densities in the literature include single-phase densities for a fixed composition and saturated densities measured at vapor-liquid equilibrium. Density measurement at saturation conditions require adequate equilibration and sometimes determination of the phase compositions. It generally involves larger uncertainty and the saturated densities are often less accurate than single-phase densities. In terms of the measurement of saturated densities, either a synthetic method or an analytical method is used in determining the corresponding compositions. For the former method, the phase boundary and saturated densities for a mixture with known composition are measured together. For the latter one, the coexisting phase compositions and densities are measured simultaneously. Since the latter tends to give larger errors in composition, the corresponding density calculated with the obtained composition will be more affected.

Most high-pressure densities in our database are single-phase ones at fixed compositions, with the majority measured as isotherms and some as isochores [76], [123], [136]. The pairs having

these high-pressure single-phase densities are marked in blue in Table 1. Kay and other researchers [124],[126], [133], [135], [140], [141], [144], [145] have reported saturated densities measured at the phase envelope boundaries using the synthetic method. They cover some important pairs where other types of data are not available. We have included these datasets in the database. The pairs with data only from these datasets of saturated densities are marked in yellow in Table 1, with one exception for C_2C_7, which has a few points from an additional isothermal isobaric dataset.[127] Only two sets [52], [103] in the database are saturated densities measured using the analytical method. We have excluded the pairs with only this type of saturated densities since we have noticed that the deviations in calculated densities are often higher for these densities probably due to the errors in measured phase compositions.

Table 2 presents the ranges of temperature T, pressure P and composition (mole fraction of component 1, x_1) for each pair. In addition, the table also presents the ranges of the reduced temperature (T_r) and the reduced pressure (P_r). In order to obtain the reduced temperature and reduced pressure at each density point, the pseudo critical temperature and pseudo critical pressure were calculated by Kay's rule at each point to scale the corresponding temperature and pressure. These pseudo critical properties do not correspond to the true critical points for a mixture but they are good scaling parameters in the two-parameter corresponding states principle, thus more suitable to generate the T_r and P_r ranges. The reason for introducing these two particular ranges is to make the data comparison between different systems easier.

Table 1. Binary pairs in the density database*



* The blue and yellow blocks are the systems with high-pressure data and the green blocks the systems with only atmospheric data. The yellow blocks are the systems only having saturated densities measured by the synthetic method, with one exception for C_2C_7 that has one additional isothermal isobaric dataset.

Table 2. Overview of the binary density database: sources, number of data points, and measurement conditions

System	Source	N_p	T range (K)	P range (bar)	x_1 range	T_r range	P_r range
N_2CO_2	Brygge et al. (1989) [34]	236	299-320	1-106	0.09-1.00	1.04-2.54	0.03-3.05
	Ely et al. (1989) [35]	79	250-330	23-331	0.02-0.02	0.83-1.10	0.31-4.52
	Esper et al. (1989) [36]	152	209-320	0.9-484	0.55-0.55	1.01-1.56	0.02-9.35
	Hacura et al. (1988) [37]	255	323-348	490-2737	0.25-0.75	1.25-2.03	8.85-50.5
	Haney and Bliss (1944) [38]	150	298-398	30-507	0.50-0.75	1.38-2.33	0.56-11.5
	Jiang et al. (1990) [39]	63	293-293	6-70	0.00-1.00	0.96-2.32	0.08-2.06
	Mondejar et al. (2012) [40]	209	250-400	5-200	0.50-0.80	1.28-2.47	0.12-4.76
	Seitz et al. (1996) [41]	192	323-573	99-999	0.10-0.90	1.13-3.98	1.42-26.3
	Seitz and Blencoe (1996) [42]	51	673-673	199-999	0.10-0.90	2.35-4.67	2.85-26.3
N_2C_1	Abadio et al. (2001) [43]	83	308-333	6-120	0.22-0.49	1.75-2.09	0.15-2.99
	Achtermann et al. (1986) [44]	400	323-323	10-335	0.00-1.00	1.70-2.56	0.22-9.40
	Blake et al. (1965) [45]	78	299-299	304-5066	0.00-1.00	1.57-2.37	6.61-149.0
	Bloomer and Parent (1953) [46]	28	166-273	52-237	0.30-0.74	1.04-1.91	1.31-6.38
	Chamorro et al. (2006) [47]	237	240-400	9-201	0.10-0.20	1.30-2.25	0.20-4.48
	Gomez-Osorio et al. (2016) [48]	133	304-470	100-1379	0.25-0.75	1.74-3.30	2.32-37.2
	Haynes and McCarty (1983) [49]	85	140-320	10-164	0.29-0.68	0.87-2.18	0.25-4.33
	Hiza et al. (1977) [50]	21	95-140	1-21	0.05-0.49	0.56-0.82	0.03-0.53
	Janisch et al. (2007) [52]	27	171-270	1-16	0.10-0.10	0.93-1.47	0.03-0.36
	Jensen and Kurata (1969) [53]	19	130-180	15-51	0.02-0.59	0.76-1.01	0.36-1.16
	Li et al. (2013) [54]	15	98-118	0.7-3	0.03-0.10	0.52-0.63	0.02-0.06
	Liu and Miller (1972) [55]	7	91-115	3-12	0.51-0.51	0.58-0.73	0.07-0.30
	Nunes da Ponte et al. (1978) [56]	369	110-120	10-1379	0.00-1.00	0.58-0.95	0.22-40.5
	Pan et al. (1975) [57]	7	91-115	1-11	0.14-0.50	0.50-0.73	0.03-0.27
	Rodosevich and Miller (1973) [58]	8	91-115	0.4-5	0.05-0.16	0.49-0.64	0.01-0.10
	Roe (1972) [59]	90	156-291	2-96	0.28-0.52	0.90-1.85	0.06-2.42
	Seitz et al. (1996) [41]	190	323-573	99-999	0.10-0.90	1.76-4.32	2.22-28.4
	Seitz and Blencoe (1996) [42]	43	673-673	299-999	0.10-0.90	3.66-5.08	6.68-28.4
	Straly and Diller (1980) [60]	461	82-320	9-356	0.29-0.68	0.52-2.11	0.22-9.18
N_2C_2	Achtermann et al. (1991) [61]	479	270-350	2-287	0.25-0.75	1.04-2.05	0.05-7.62
	Eakin et al. (1955) [62]	122	216-316	22-307	0.05-0.70	0.90-1.70	0.58-7.48
	Hiza et al. (1977) [50]	4	105-120	4-6	0.06-0.06	0.36-0.41	0.08-0.13
	Janisch et al. (2007) [52]	14	150-270	10-100	0.02-0.36	0.51-1.12	0.21-2.30
	Reamer et al. (1952) [63]	535	278-511	14-690	0.27-0.73	1.08-2.93	0.31-18.2
N_2C_3	Hiza et al. (1977) [50]	6	100-115	4-9	0.02-0.07	0.28-0.32	0.08-0.21
N_2C_8	Daridon et al. (1994) [51]	144	293-373	250-1000	0.21-0.21	0.61-0.78	9.33-37.3
CO_2C_1	Brygge et al. (1989) [34]	155	300-320	2-98	0.10-0.90	1.02-1.58	0.03-1.89
	Esper et al. (1989) [36]	119	206-320	0.8-483	0.48-0.48	0.84-1.31	0.01-8.15
	Hwang et al. (1997) [64]	218	225-350	18-695	0.10-0.90	0.77-1.74	0.33-14.3
	Liu et al. (2018) [65]	163	313-353	30-180	0.10-0.90	1.07-1.75	0.48-3.69
	Magee and Ely (1988) [66]	91	225-400	21-358	0.98-0.98	0.75-1.32	0.28-4.89
	Mondejar et al. (2012) [67]	314	250-400	10-200	0.20-0.60	1.16-1.88	0.16-3.87
	Reamer et al. (1944) [68]	700	311-511	14-689	0.15-1.00	1.02-2.46	0.19-13.7
	Seitz et al. (1996) [41]	194	323-573	99-999	0.10-0.90	1.10-2.84	1.46-20.5
	Seitz and Blencoe (1996) [42]	44	673-673	199-999	0.10-0.90	2.30-3.33	2.92-20.5
CO_2C_2	Brygge et al. (1989) [34]	206	300-320	1-68	0.10-0.90	0.98-1.05	0.02-1.12
	Gil et al. (2008) [69]	82	308-308	1-200	0.50-0.50	1.01-1.01	0.02-3.26
	Lau et al. (1997) [70]	280	240-350	11-346	0.00-1.00	0.79-1.15	0.22-7.04
	McElroy et al. (1990) [71]	176	303-333	5-62	0.00-0.77	0.99-1.09	0.10-0.97
	Reamer et al. (1945) [72]	805	311-511	1-690	0.17-0.82	1.02-1.68	0.01-13.0
	Sherman et al. (1989) [73]	94	245-400	28-348	0.99-0.99	0.81-1.31	0.38-4.73
	Weber (1992) [74]	153	290-320	53-122	0.25-0.74	0.95-1.05	0.91-1.81
CO_2C_3	de la Cruz de Dios et al. (2013) [75]	559	294-344	0.8-706	0.46-0.93	0.90-1.03	0.01-12.4
	Feng et al. (2010) [76]	225	320-400	2-78	0.52-0.80	0.95-1.26	0.02-1.33
	Galicia-Luna et al. (1994) [77]	233	323-398	25-395	0.00-0.31	0.87-1.14	0.59-9.30
	Miyamoto (2014) [78]	137	280-440	100-2000	0.58-0.77	0.84-1.38	1.50-32.9
	Reamer et al. (1951) [79]	692	278-511	14-689	0.20-0.79	0.78-1.61	0.20-14.2
CO_2iC_4	Tsuji et al. (1998) [80]	78	311-311	10-97	0.95-0.97	1.00-1.01	0.14-1.33
	Tsuji et al. (2004) [81]	46	360-360	11-105	0.80-0.90	1.11-1.15	0.16-1.53
CO_2C_4	Tsuji et al. (1998) [80]	67	311-311	12-98	0.95-0.97	1.00-1.01	0.17-1.35
	Tsuji et al. (2004) [81]	58	360-360	11-106	0.80-0.90	1.10-1.14	0.15-1.50
	Sugiyama et al. (2011) [82]	278	280-440	30-2000	0.23-0.71	0.71-1.30	0.65-43.2

CO_2C_5	Chen et al. (2003) [83]	339	312-328	2-149	0.21-0.96	0.74-1.03	0.05-3.08
	Kiran et al. (1996) [84]	473	323-423	81-650	0.00-1.00	0.73-1.39	1.35-19.2
CO_2C_7	Fenghour et al. (2001) [85]	27	302-459	35-555	0.29-0.43	0.69-0.97	0.73-12.2
	Medina-Bermudez et al. (2013) [86]	540	312-362	20-250	0.02-0.95	0.59-1.15	0.71-8.77
	Sanchez-Vicente et al. (2018) [87]	694	283-473	10-680	0.00-1.00	0.52-1.56	0.36-24.8
CO_2C_{10}	Bessieres et al. (2001) [88]	147	308-368	200-400	0.00-0.84	0.50-1.04	3.06-19.0
	Song et al. (2012) [89]	169	303-363	80-191	0.24-0.87	0.56-1.02	1.19-5.67
	Zambrano et al. (2016) [90]	299	283-393	100-1000	0.30-0.95	0.54-1.23	1.40-27.0
	Zuniga-Moreno et al. (2005) [91]	538	313-363	20-251	0.06-0.97	0.52-1.15	0.83-10.4
CO_2C_{11}	Zhang et al. (2016) [92]	150	313-354	80-191	0.25-0.89	0.56-1.03	1.42-5.76
CO_2C_{12}	Bazile et al. (2019) [93]	126	303-313	100-700	0.00-1.00	0.46-1.03	1.35-38.5
	Zambrano et al. (2016) [90]	319	283-393	100-1000	0.10-0.60	0.46-0.88	1.93-41.9
CO_2C_{13}	Medina-Bermudez et al. (2013) [86]	459	313-363	80-250	0.10-0.90	0.49-1.06	1.32-11.2
CO_2C_{14}	Zhang et al. (2015) [94]	136	313-354	100-191	0.25-0.88	0.52-1.00	1.49-6.34
CO_2C_{16}	Mohammed et al. (2017) [95]	82	298-473	104-1209	0.07-0.73	0.43-1.13	2.12-56.0
CO_2C_{30}	Zambrano et al. (2016) [90]	158	283-393	100-1000	0.10-0.20	0.36-0.53	4.71-68.5
H_2SC_1	Gonzalez-Perez et al. (2016) [96]	460	253-293	2-305	0.13-0.29	1.04-1.37	0.04-5.89
	Reamer et al. (1951) [97]	1127	278-444	14-689	0.10-0.90	0.78-2.13	0.16-13.7
H_2SC_3	Jarne et al. (2011) [98]	248	263-363	2-419	0.22-0.27	0.71-0.98	0.03-7.91
C_1C_2	Blanke and Weiss (1995) [99]	129	274-333	20-71	0.75-0.95	1.25-1.70	0.44-1.54
	Haynes et al. (1985) [100]	414	100-320	17-359	0.35-0.69	0.38-1.41	0.36-7.50
	Hiza et al. (1977) [50]	20	105-140	0.3-4	0.35-0.68	0.40-0.57	0.01-0.07
	Hou et al. (1996) [101]	219	300-320	1.0-103	0.00-1.00	0.98-1.68	0.02-2.23
	Janisch et al. (2007) [52]	15	140-270	4-66	0.05-0.94	0.56-1.05	0.08-1.40
	McElroy and Fang (1994) [102]	94	303-323	7-108	0.27-0.62	1.12-1.38	0.15-2.31
	Pan et al. (1975) [57]	8	91-115	0.2-1	0.51-0.70	0.37-0.51	0.01-0.03
	Rodosevich and Miller (1973) [58]	19	91-116	0.2-1	0.69-0.95	0.40-0.59	0.00-0.03
	Shana'a and Canfield (1968) [103]	5	108-108	0.2-0.7	0.19-0.87	0.38-0.53	0.00-0.01
C_1C_3	Arai and Kobayashi (1980) [104]	426	152-327	19-654	0.95-0.95	0.76-1.64	0.42-14.3
	Blanke et al. (1996) [105]	90	273-323	20-63	0.95-0.99	1.37-1.68	0.44-1.37
	Hiza et al. (1977) [50]	20	105-130	0.3-3	0.30-0.86	0.33-0.60	0.01-0.07
	Huang et al. (1967) [106]	140	123-311	34-345	0.22-0.75	0.46-1.32	0.76-7.97
	Karimi et al. (2016) [107]	80	256-422	220-350	0.89-0.95	1.22-2.11	4.80-7.67
	May et al. (2001) [108]	57	278-313	9-100	0.79-0.93	1.25-1.55	0.20-2.22
	Pan et al. (1975) [57]	8	91-115	0.3-1	0.83-0.90	0.41-0.55	0.01-0.03
	Richter and McLinden (2014) [109]	148	248-373	1-60	0.51-0.75	0.89-1.59	0.03-1.34
	Rodosevich and Miller (1973) [58]	12	91-115	0.3-1	0.90-0.97	0.44-0.59	0.01-0.03
	Shana'a and Canfield (1968) [103]	5	108-108	0.3-0.7	0.26-0.85	0.33-0.50	0.01-0.02
C_1iC_4	Haynes (1983) [110]	13	110-140	0.8-6	0.78-0.92	0.46-0.67	0.02-0.13
	Hiza et al. (1977) [50]	4	110-125	0.6-2	0.49-0.49	0.36-0.41	0.02-0.05
	Olds (1942) [111]	552	311-511	14-345	0.16-0.71	0.83-2.01	0.32-9.07
	Rodosevich and Miller (1973) [58]	7	95-115	0.4-1	0.92-0.95	0.45-0.57	0.01-0.03
C_1C_4	Beattie et al. (1941) [112]	302	348-573	30-357	0.25-0.75	1.09-2.30	0.73-8.50
	Fenghour et al. (1999) [113]	71	316-479	88-481	0.35-0.53	1.03-1.59	2.14-11.6
	Haynes (1983) [110]	19	115-140	1-6	0.78-0.93	0.47-0.67	0.03-0.13
	Hiza et al. (1977) [50]	4	120-130	2-3	0.59-0.59	0.42-0.45	0.04-0.07
	Pan et al. (1975) [57]	2	108-115	1-2	0.95-0.95	0.53-0.57	0.02-0.03
	Reamer et al. (1947) [114]	508	311-511	14-690	0.19-0.80	0.82-2.15	0.31-17.5
C_1C_5	Sage et al. (1936) [115]	59	311-378	59-207	0.26-0.63	0.78-1.28	1.60-5.61
	Sage et al. [115] [116]	776	311-511	14-345	0.13-0.98	0.72-2.61	0.30-9.78
C_1C_6	Sage et al. (1936) [115]	55	311-378	45-207	0.19-0.56	0.70-1.14	1.36-6.22
C_1C_7	Bazile et al. (2020) [117]	58	303-303	100-700	0.00-1.00	0.56-1.59	2.17-25.5
	Reamer et al. (1956) [118]	423	278-511	21-698	0.10-0.75	0.55-1.85	0.72-23.9
C_1C_{10}	Audonnet and Padua (2004) [119]	144	303-393	1-762	0.00-0.80	0.49-1.42	0.05-36.1
	Canet et al. (2002) [120]	375	293-373	200-1400	0.31-0.96	0.61-1.79	6.93-48.5
	Regueira et al. (2016) [121]	307	278-463	1-1400	0.00-0.85	0.45-1.82	0.05-66.4
C_1C_{16}	Mohammed et al. (2017) [95]	91	298-474	100-804	0.10-0.40	0.45-0.93	4.89-46.5
C_2C_3	Magee (1995) [122]	333	204-400	15-346	0.35-0.65	0.59-1.22	0.32-7.75
	Parrish (1984) [123]	315	283-322	28-97	0.30-0.95	0.81-1.04	0.57-2.18
C_2C_4	Kay (1940) [124]	257	269-414	5-58	0.17-0.95	0.69-1.06	0.11-1.29
C_2C_5	Reamer et al. (1960) [125]	1363	278-511	14-689	0.10-0.90	0.61-1.59	0.33-19.6
C_2C_7	Kay (1938) [126]	188	275-521	3-86	0.29-0.97	0.60-1.25	0.07-1.99
	Wu and Ehrlich (1973) [127]	24	353-353	75-75	0.83-0.98	1.02-1.14	1.56-1.67
C_2C_{10}	Reamer and Sage (1962) [128]	1366	278-511	14-689	0.10-0.90	0.47-1.52	0.40-28.9
	Saryazdi et al. (2013) [129]	38	288-448	100-400	0.23-0.40	0.53-0.91	3.10-14.5
C_3iC_4	Duarte-Garza and Magee (1999) [130]	340	200-400	12-354	0.30-0.70	0.50-1.05	0.32-9.25
	Kahre (1973) [131]	10	289-328	3-17	0.14-0.85	0.72-0.87	0.09-0.40

	Miyamoto et al. (2007) [132]	318	280-440	10-2000	0.28-0.75	0.70-1.16	0.24-52.4
C_3C_4	Kay (1970) [133]	126	343-419	16-43	0.15-0.93	0.88-1.01	0.40-1.05
	Kahre (1973) [131]	10	289-328	3-16	0.15-0.84	0.69-0.87	0.07-0.39
	Magee (1995) [122]	129	244-400	18-349	0.61-0.61	0.74-1.21	0.39-7.54
	Miyamoto and Uematsu (2008) [134]	292	280-440	10-2000	0.27-0.73	0.68-1.14	0.24-51.0
	Nysewander et al. (1940) [135]	42	311-411	6-42	0.20-0.85	0.75-1.01	0.14-1.06
	Parrish (1986) [136]	513	283-333	3-97	0.10-0.75	0.67-0.87	0.07-2.51
C_3iC_5	Vaughan and Collins (1942) [137]	597	298-573	5-81	0.10-0.90	0.78-1.51	0.12-2.34
C_3C_5	Kay (1970) [133]	79	321-460	10-45	0.15-0.88	0.79-1.03	0.26-1.15
	Sage and Lacey (1940) [138]	134	344-444	1-34	0.14-0.85	0.77-1.03	0.03-0.84
C_3C_6	Chun et al. (1993) [139]	146	348-497	1-50	0.14-0.92	0.71-1.07	0.05-1.28
	Kay (1971) [140]	82	325-491	14-50	0.22-0.92	0.80-1.07	0.34-1.29
C_3C_8	Kay et al. (1974) [141]	147	329-550	7-59	0.21-0.96	0.71-1.16	0.24-1.57
C_3C_{10}	Bamgbade et al. (2015) [142]	233	344-513	35-2625	0.16-0.82	0.63-1.10	1.16-106.4
	Reamer and Sage (1966) [143]	1485	278-511	14-689	0.10-0.90	0.47-1.29	0.34-29.7
	Saryazdi et al. (2013) [129]	60	291-448	100-400	0.17-0.52	0.51-0.92	3.11-16.2
C_3C_{20}	Bamgbade et al. (2015) [142]	177	319-525	50-2644	0.30-0.93	0.50-1.32	1.24-126.3
iC_4C_4	Kahre (1973) [131]	8	289-328	2-7	0.21-0.80	0.68-0.80	0.05-0.19
	Miyamoto et al. (2008) [146]	262	280-440	10-2000	0.26-0.75	0.67-1.07	0.27-54.2
C_4C_5	Kay et al. (1975) [144]	69	358-464	10-37	0.14-0.87	0.83-1.00	0.28-1.02
C_4C_6	Kay et al. (1975) [144]	156	375-502	6-39	0.10-0.90	0.80-1.02	0.20-1.08
C_4C_7	Kay (1941) [145]	202	329-528	3-30	0.16-0.94	0.68-1.02	0.08-1.04
C_4C_8	Kay et al. (1974) [141]	90	339-555	7-43	0.18-0.95	0.75-1.06	0.19-1.26
C_4C_{10}	Reamer et al. (1946) [147]	597	311-511	14-689	0.18-0.84	0.53-1.12	0.39-28.6
	Saryazdi et al. (2013) [129]	60	292-448	100-400	0.14-0.45	0.49-0.84	3.49-17.1
C_5C_6	Chen and Zwolinski (1974) [148]	8	298-298	1-1	0.06-0.96	0.59-0.63	0.03-0.03
	Pecar and Dolecek (2003) [149]	210	298-348	1-400	0.12-0.87	0.59-0.73	0.03-13.0
	Ramos-Estrada et al. (2006) [150]	100	273-333	1-2	0.10-0.90	0.54-0.68	0.03-0.06
C_5C_7	Pecar and Dolecek (2003) [149]	207	298-348	1-400	0.12-0.88	0.56-0.73	0.03-14.2
	Ramos-Estrada et al. (2006) [150]	107	273-343	1-2	0.10-0.90	0.51-0.67	0.03-0.06
C_6C_7	Chevaller et al.(1990) [151]	9	298-298	1-1	0.13-0.90	0.56-0.58	0.03-0.04
	Cooper and Asfour(1991) [152]	11	293-293	1-1	0.00-1.00	0.54-0.58	0.03-0.04
	Ramos-Estrada et al. (2006) [150]	149	273-363	1-2	0.10-0.90	0.51-0.69	0.03-0.07
	Pecar and Dolecek (2003) [149]	210	298-348	1-400	0.12-0.87	0.56-0.68	0.03-14.4
C_6C_8	Chevaller et al. (1990) [151]	9	298-298	1-1	0.10-0.90	0.53-0.58	0.03-0.04
	Cooper and Asfour (1991) [152]	11	293-293	1-1	0.00-1.00	0.52-0.58	0.03-0.04
	Quevedo-Nolasco et al. (2011) [153]	750	313-363	10-250	0.17-0.93	0.56-0.71	0.33-9.70
C_6C_9	Chevaller et al. (1990) [151]	9	298-298	1-1	0.11-0.90	0.51-0.58	0.03-0.04
C_6C_{10}	Chevaller et al. (1990) [151]	9	298-298	1-1	0.14-0.89	0.49-0.57	0.03-0.05
	Cooper and Asfour(1991) [152]	11	293-293	1-1	0.00-1.00	0.47-0.58	0.03-0.05
	Quevedo-Nolasco et al. (2011) [153]	21	298-298	1-1000	0.00-1.00	0.48-0.59	0.03-47.4
	Takagi and Teranishi (1985) [154]	750	313-363	10-250	0.05-0.90	0.51-0.70	0.34-11.6
C_6C_{12}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.47-0.55	0.04-0.05
	Dymond et al. (1981) [155]	24	298-373	1-4551	0.50-0.50	0.51-0.64	0.04-187.8
	Dymond et al. (1982) [156]	14	298-348	1-4360	0.50-0.50	0.51-0.60	0.04-180.0
C_6C_{14}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.66	0.45-0.52	0.04-0.05
C_6C_{16}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.44-0.54	0.04-0.06
	Dymond et al. (1979) [157]	171	298-373	1-5640	0.00-1.00	0.41-0.74	0.03-321.8
C_7C_8	Abdulagatov and Azizov (2006) [158]	141	293-557	1-108	0.28-0.79	0.52-1.02	0.04-4.21
	Chevaller et al. (1990) [151]	9	298-298	1-1	0.10-0.90	0.53-0.55	0.04-0.04
	Cooper and Asfour (1991) [152]	11	293-293	1-1	0.00-1.00	0.52-0.54	0.04-0.04
C_7C_9	Chevaller et al. (1990) [151]	9	298-298	1-1	0.10-0.90	0.51-0.55	0.04-0.04
C_7C_{10}	Chevaller et al. (1990) [151]	9	298-298	1-1	0.12-0.89	0.49-0.54	0.04-0.05
	Cooper and Asfour (1991) [152]	11	293-293	1-1	0.00-1.00	0.47-0.54	0.04-0.05
	Quevedo-Nolasco et al. (2012) [159]	963	313-376	10-250	0.00-1.00	0.51-0.67	0.36-11.8
C_7C_{11}	Elizande-Solis et al. (2013) [160]	894	313-363	10-251	0.00-0.95	0.49-0.67	0.37-12.8
C_7C_{12}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.47-0.53	0.04-0.05
	Cooper and Asfour (1991) [152]	11	293-293	1-1	0.00-1.00	0.45-0.54	0.04-0.06
	Dzida and Cempa (2008) [161]	84	293-318	1-1	0.00-1.00	0.45-0.59	0.04-0.06
C_7C_{14}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.45-0.52	0.04-0.06
	Cooper and Asfour (1991) [152]	11	293-293	1-1	0.00-1.00	0.42-0.54	0.04-0.06
C_7C_{16}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.43-0.52	0.04-0.06
C_7C_{20}	Queimada et al. (2003) [162]	34	293-343	1-1	0.00-1.00	0.41-0.64	0.04-0.09
C_7C_{22}	Queimada et al. (2003) [162]	34	293-343	1-1	0.00-1.00	0.40-0.64	0.04-0.10
C_7C_{24}	Queimada et al. (2003) [162]	21	313-343	1-1	0.00-1.00	0.41-0.64	0.04-0.10
C_8C_9	Chevaller et al. (1990) [162]	9	298-298	1-1	0.11-0.89	0.50-0.52	0.04-0.04
C_8C_{10}	Chevaller et al. (1990) [151]	9	298-298	1-1	0.14-0.89	0.49-0.52	0.04-0.05

	Cooper and Asfour (1991) [152]	11	293-293	1-1	0.00-1.00	0.47-0.52	0.04-0.05
	Quevedo-Nolasco et al. (2012) [159]	750	313-363	10-250	0.06-0.96	0.51-0.64	0.40-11.7
C_8C_{12}	Dymond et al. (1981) [155]	38	273-348	1-5055	0.50-0.50	0.45-0.57	0.05-234.5
	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.47-0.51	0.04-0.05
	Dymond et al. (1982) [156]	26	298-348	1-4126	0.50-0.50	0.49-0.57	0.05-191.5
	Takagi and Teranishi (1985) [154]	21	298-298	1-1000	0.00-1.00	0.45-0.52	0.04-54.9
C_8C_{14}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.82	0.45-0.50	0.04-0.06
	Cooper and Asfour(1991) [152]	11	293-293	1-1	0.00-1.00	0.42-0.52	0.04-0.06
C_8C_{16}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.43-0.50	0.04-0.06
C_9C_{10}	Chevaller et al. (1990) [151]	9	298-298	1-1	0.12-0.90	0.48-0.50	0.04-0.05
C_9C_{12}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.46-0.49	0.05-0.05
C_9C_{14}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.44-0.49	0.05-0.06
C_9C_{16}	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.43-0.48	0.05-0.06
$C_{10}C_{12}$	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.46-0.48	0.05-0.05
	Jia et al. (2018) [163]	594	283-363	1-1000	0.00-1.00	0.43-0.59	0.05-54.9
$C_{10}C_{14}$	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.44-0.47	0.05-0.06
	Kariznovi et al. (2012) [164]	30	295-296	10-100	0.25-0.75	0.44-0.46	0.51-5.87
	Snyder et al. (1974) [165]	104	298-358	1-4301	0.50-0.50	0.45-0.55	0.05-233.8
	Takagi and Teranishi (1985) [154]	20	298-298	1-1000	0.00-1.00	0.43-0.48	0.05-59.6
$C_{10}C_{16}$	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.42-0.47	0.05-0.07
	Dymond et al. (1982) [156]	22	348-373	1-4228	0.50-0.50	0.52-0.56	0.06-240.9
	Khasanshin et al. (2010) [166]	129	298-433	1-1000	0.25-0.75	0.43-0.67	0.05-63.4
$C_{10}C_{18}$	Nourozeih et al. (2013) [167]	55	323-323	1-100	0.00-1.00	0.43-0.52	0.05-7.87
$C_{10}C_{20}$	Queimada et al. (2005) [168]	24	293-343	1-1	0.20-0.80	0.42-0.53	0.05-0.08
$C_{10}C_{22}$	Queimada et al. (2005) [168]	20	303-343	1-1	0.20-0.80	0.43-0.53	0.05-0.08
$C_{10}C_{24}$	Queimada et al. (2005) [168]	16	313-343	1-1	0.20-0.80	0.42-0.52	0.05-0.08
$C_{12}C_{14}$	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.80	0.43-0.45	0.06-0.06
$C_{12}C_{16}$	Snyder et al. (1974) [165]	84	298-358	1-3313	0.50-0.50	0.43-0.52	0.06-205.8
$C_{14}C_{16}$	Chevaller et al. (1990) [151]	3	298-298	1-1	0.20-0.79	0.42-0.43	0.07-0.07
	Cooper and Asfour (1991) [152]	11	293-293	1-1	0.00-1.00	0.41-0.42	0.06-0.07
$C_{16}C_{20}$	Queimada et al. (2005) [168]	35	293-343	1-1	0.00-1.00	0.40-0.47	0.07-0.09

4. Comparison of cubic and non-cubic EoS using the binary density database

The selected cubic and non-cubic EoS are evaluated for their density description using the binary density database described in Section 3. These EoS include GERG-2008, SRK, PR, PC-SAFT, Soave-BWR, and the volume translated versions for the last four EoS. The results are presented in Tables 3 and 4 in terms of AAD%. Since most systems have multiple data sources, the reported AAD% for each system is a weighted average. In Tables 3 and 4, we use the number of data points as the weighting factors to calculate the average. This simple weighting approach is commonly used and it favors the data source with more data points. Although the approach somewhat reflects the coverage of temperature, pressure and composition conditions if the data point spacing is comparable between different sources, this is not always the case. To avoid the potential bias, we also tried another set of weighting factors based on the range of reduced temperature T_r, the range of reduced pressure P_r, and the number of points N_P. The results calculated using this weighting approach are provided in the **supplementary information** for reference. Although the final deviations for various systems change slightly, the major findings are not affected.

Tables 3 and 4 also include the overall AAD%. In the following discussion about the overall AAD%, we use the simple average. Tables 3 and 4 also present the overall AAD% calculated using the total N_p for each system as the weighting factors. Since GERG-2008 can only be applied to 53 of the total 88 systems, we distinguish here between the overall deviations for all the 88 systems and those only for the 53 systems (called the "GERG systems" hereafter). Tables 3 and 4 also present the overall deviations excluding the atmospheric datasets in parentheses, which better reflect the model performance at high-pressures. The two types of overall deviations are generally close but exclusion of the atmospheric datasets tends to decrease the deviations for SRK and PR and increase those for the others. Tables 3 and 4 also include the overall deviations calculated without using the saturated densities. Exclusion of the saturated densities lowers the deviations but the general findings are similar. In the following discussion, we use the overall AAD% for all data including the saturated densities and the atmospheric ones unless otherwise mentioned.

From the results for the original EoS in Table 3, it is clear that GERG delivers the most accurate results for the GERG systems, giving an overall deviation of 0.86%. In comparison, the deviation is 1.87% for PC-SAFT, 1.21% for Soave-BWR, 8.64% for SRK, and 3.68% for PR. If we consider only the high-pressure datasets, the trend is similar, with GERG giving the smallest deviation of 0.93% for GERG as compared with 1.94%, 1.30%, 8.11%, and 3.66% for PC-SAFT, Soave-BWR, SRK and PR, respectively. In terms of deviations, PC-SAFT and Soave-BWR form the second best group and the cubic ones the third group. For the GERG systems excluding those pairs with only saturated densities, GERG typically gives a deviation lower than 1%. Only for three

systems CO_2-C_4, CO_2-C_7, and H_2S-C_3, GERG gives a larger deviation than both PC-SAFT and Soave-BWR. For CO_2-C_5, GERG gives a larger deviation than Soave-BWR but a smaller deviation than PC-SAFT. Among these systems, the quality for one CO_2-C_4 dataset [82] is questionable since GERG is generally more accurate than PC-SAFT and Soave-BWR for the neighboring pairs and the original paper for this dataset reports large deviations from REFPROP. It is also noted that the deviations are large for some near critical points in one CO_2-C_5 dataset [83]. In addition, GERG gives a slightly larger deviation than PC-SAFT for C_2-C_{10}, and than Soave-BWR for C_5-C_7, C_6-C_8 and C_7-C_8. The better performance of GERG is expected because the model has multiple component specific parameters than PC-SAFT and Soave-BWR, which provides necessary flexibility to describe the density variation for various components over a wide temperature and pressure range. It shows that the theoretical rigorousness of an EoS model (PC-SAFT) itself is not sufficient for achieving the best accuracy, and that any attempt to generalize a model (Soave-BWR) will somewhat compromise the description accuracy. Between PC-SAFT and Soave-BWR, Soave-BWR is more accurate for the GERG systems but similar to PC-SAFT when all the systems are included (1.65% for PC-SAFT and 1.70% for Soave-BWR). For relatively light components based on which Soave-BWR is developed, Soave-BWR has an advantage due to its functional form and better reproduction of critical points. However, for systems involving heavier hydrocarbons, like CO_2-C_{10}, CO_2-C_{11}, CO_2-C_{13}, CO_2-C_{14}, CO_2-C_{16}, CO_2-C_{30}, C_1-C_{10}, and C_1-C_{16}, Soave-BWR is inferior to PC-SAFT, indicating that the generalization for Soave-BWR to heavier hydrocarbons needs further improvement. It is fair to say that the performance for the second group EoS is not as good as GERG but relatively close. The three EoS are distinctively better than SRK and PR in the third group. For the GERG systems, SRK and PR give deviations of 8.64% and 3.68%, respectively. They increase to 13.85% and 7.20%, respectively, when all the systems are counted, indicating that they are particularly inaccurate for heavy hydrocarbons. Clearly, the cubic forms as used in SRK and PR are too simplistic to capture the density variation in a wide range of conditions. SRK shows larger deviations than PR because of its inaccurate critical compressibility factor.

The performance for the cubic models can be improved with volume translation. Table 4 presents the results for the volume translated models. For SRK, the deviations are reduced to 3.49% for the GERG systems and 4.46% for all the systems. For PR, they are reduced to 2.53% and 3.46%, respectively. Both SRK-VT and PR-VT are much better although still inferior to PC-SAFT and Soave-BWR in the second group. The improvement in SRK and PR can be seen for most systems but CO_2-C_{30} is a noticeable exception. PR-VT performs better than SRK-VT for the specific volume translation correlations (Eqs. (6)-(8)) used here, which may be caused by some model specific reasons. It could also be further discussed whether other correlations can further improve the performance of SRK. Table 3 also shows the results for volume translated PC-SAFT

and Soave-BWR. If we use Eqs. (9) and (10), the results for both models actually deteriorate, showing that it is not recommended to use the Rackett compressibility factor to design the correlations for PC-SAFT and Soave-BWR. If we use Eqs. (11) and (12) instead, which correspond to almost negligible translations, the results are almost the same, with PC-SAFT improving a bit for the GERG systems but deteriorating a bit for all the systems after the translation. The comparison with various volume translated EoS shows that the volume translation approach can significantly improve the performance for cubic models whose performance has a large room to improve, but for PC-SAFT and Soave-BWR, which already have decent density description, the effect of the volume translation is dubious. In our comparison, the volume translation parameters are determined using the approach of Peneloux et al., i.e., by matching saturated liquid densities at a certain condition. It should be noted that other ways can be used to develop the correlations for the volume translation parameters. For example, the parameters can be designed to minimize the density deviation in a certain range of temperature, pressure and composition. Such a possibility deserves investigation in the future model development or implementation but it is not discussed here. In general, despite the much-improved performance shown by SRK-VT and PR-VT, they are still inferior to the non-cubic EoS in the second group in density description.

Gonzalez Perez et al. [27] recently conducted a comparative study of several EoS, including SRK, PR, PC-SAFT, and SAFT-VR Mie [169], on their phase equilibrium and density modeling related to CO_2 capture and storage. According to their density evaluation using 57 binary mixtures, they divided the models into three groups: PC-SAFT and SAFT-VR Mie with ~2.8% AAD, SRK-VT and PR-VT with ~3.5% AAD, and SRK and PR with ~6.8% AAD, which is in general agreement with our results. Other subtle differences observed by them, like PR better than SRK and PR-VT a bit better than SRK-VT are also in agreement with our results. They also showed that SAFT-VR-Mie is generally more accurate in density than PC-SAFT for their systems studied, particularly for the pairs with C_1, C_2 or N_2. Actually, the overall performance of PC-SAFT in their study is between SAFT-VR Mie and the volume translated PR. It would be interesting to further compare SAFT-VR Mie with Soave-BWR and GERG 2008.

Table 3. AAD% in density for various EoS

System	N_p	GERG-2008	SRK	PR	PC-SAFT	SBWR
N_2CO_2	1387	0.82	2.47	3.84	1.92	1.32
N_2C_1	2301	0.16	1.84	5.32	1.25	0.67
N_2C_2	1154	0.30	2.28	2.40	0.88	0.48
N_2C_3	6	0.08	7.71	3.29	0.30	1.07
N_2C_8	144	0.13	12.23	2.16	0.74	0.46
CO_2C_1	1998	0.31	2.82	2.24	1.40	0.61
CO_2C_2	1796	0.73	4.25	2.80	2.37	1.16
CO_2C_3	1846	0.53	4.33	4.02	1.53	0.75
CO_2iC_4	124	1.40	6.27	3.84	4.35	1.62
CO_2C_4	403	3.57	4.11	5.35	2.10	0.98
CO_2C_5	812	3.12	11.34	5.88	3.88	2.38
CO_2C_7	1261	2.04	9.92	1.38	1.25	1.16
CO_2C_{10}	1153	1.05	14.59	4.96	1.63	2.53
CO_2C_{11}	150	-	16.84	7.09	2.01	3.58
CO_2C_{12}	445	-	16.82	7.72	1.39	1.37
CO_2C_{13}	459	-	19.75	10.50	2.72	4.70
CO_2C_{14}	136	-	21.47	12.32	2.54	7.50
CO_2C_{16}	82	-	22.20	13.41	1.02	6.06
CO_2C_{30}	158	-	34.38	26.96	1.29	5.34
H_2SC_1	1587	1.29	3.35	3.78	1.72	1.34
H_2SC_3	248	2.54	5.42	5.36	1.78	1.63
C_1C_2	923	0.36	2.46	2.82	1.14	0.67
C_1C_3	986	0.40	2.77	3.63	1.26	0.84
C_1iC_4	576	0.39	4.00	3.54	1.04	0.69
C_1C_4	906	0.49	4.00	2.79	1.19	0.61
C_1C_5	835	0.77	4.92	2.43	1.16	0.68
C_1C_6	55	1.79	9.30	1.62	0.39	1.60
C_1C_7	481	1.23	8.35	1.90	0.70	1.46
C_1C_{10}	826	0.66	13.48	4.66	0.92	3.13
C_1C_{16}	91	-	25.53	16.95	3.50	7.78
C_2C_3	648	0.17	8.61	4.06	0.59	0.54
C_2C_4	257	0.73	6.59	2.75	1.50	1.10
C_2C_5	1363	0.42	6.59	4.26	0.84	0.80
C_2C_7	212	2.47	7.18	2.31	2.70	2.50
C_2C_{10}	1404	0.62	13.09	3.44	0.59	2.67
C_3iC_4	668	0.08	4.71	6.72	1.03	1.03
C_3C_4	1112	0.40	10.36	8.62	6.09	4.76
C_3iC_5	597	1.37	2.81	4.66	4.98	4.16
C_3C_5	213	1.59	4.89	2.13	2.43	1.23
C_3C_6	228	1.99	8.59	3.42	4.68	2.12
C_3C_8	147	3.35	9.71	4.25	4.94	2.75
C_3C_{10}	1778	0.36	12.49	3.35	0.69	1.57
C_3C_{20}	177	-	17.86	9.39	2.86	3.08
iC_4C_4	270	0.10	4.26	7.01	1.59	1.90
C_4C_5	69	1.97	14.85	6.50	9.70	1.67
C_4C_6	156	1.25	13.13	5.24	5.51	1.21
C_4C_7	202	0.44	8.10	2.59	1.53	0.62
C_4C_8	90	2.16	13.25	5.61	5.77	1.77
C_4C_{10}	657	0.34	11.85	2.81	0.62	0.91
C_5C_6	318	0.13	8.85	2.55	0.75	0.33
C_5C_7	314	0.33	9.91	1.44	0.82	0.30
C_6C_7	379	0.08	10.73	0.70	0.66	0.31
C_6C_8	770	0.31	11.32	1.23	0.51	0.18
C_6C_9	9	0.04	13.50	2.65	0.77	0.10
C_6C_{10}	791	0.10	13.50	3.17	0.48	0.26
C_6C_{12}	41	-	18.00	8.57	2.36	1.62
C_6C_{14}	3	-	20.90	11.25	0.74	2.90
C_6C_{16}	174	-	21.39	12.63	2.16	2.42
C_7C_8	161	0.49	12.92	2.08	1.03	0.47
C_7C_9	9	0.01	14.11	3.39	0.82	0.14
C_7C_{10}	983	0.15	13.95	3.49	0.60	0.22
C_7C_{11}	894	-	15.44	5.19	0.48	0.47
C_7C_{12}	98	-	16.50	6.17	1.18	0.35
C_7C_{14}	14	-	20.01	10.24	0.88	2.07
C_7C_{16}	3	-	22.05	12.60	1.15	2.68

C_7C_{20}	34	-	21.99	12.51	0.74	1.63
C_7C_{22}	34	-	22.74	13.39	0.37	1.56
C_7C_{24}	21	-	23.45	14.19	1.39	2.22
C_8C_9	9	0.07	14.93	4.38	0.68	0.14
C_8C_{10}	770	0.05	14.60	4.21	0.41	0.10
C_8C_{12}	88	-	19.36	10.03	3.21	2.16
C_8C_{14}	14	-	20.54	10.87	0.69	1.94
C_8C_{16}	3	-	22.34	12.95	0.99	2.41
C_9C_{10}	9	0.03	16.55	6.28	0.68	0.19
C_9C_{12}	3	-	18.39	8.42	0.91	0.13
C_9C_{14}	3	-	21.03	11.45	0.52	1.80
C_9C_{16}	3	-	22.63	13.30	0.87	2.14
$C_{10}C_{12}$	597	-	18.48	8.89	0.98	0.59
$C_{10}C_{14}$	157	-	21.79	12.63	1.48	1.52
$C_{10}C_{16}$	154	-	21.56	12.47	1.25	1.76
$C_{10}C_{18}$	55	-	22.56	13.28	0.54	1.42
$C_{10}C_{20}$	24	-	24.00	14.89	0.53	1.17
$C_{10}C_{22}$	20	-	25.22	16.29	0.63	1.85
$C_{10}C_{24}$	16	-	26.06	17.28	1.19	1.80
$C_{12}C_{14}$	3	-	22.68	13.37	0.78	1.59
$C_{12}C_{16}$	84	-	24.11	15.39	1.37	1.52
$C_{14}C_{16}$	14	-	25.79	16.94	0.67	2.79
$C_{16}C_{20}$	35	-	26.98	18.31	0.63	2.07
Saturated densities included						
All (simple)	40688	-	13.85 (11.44)*	7.20 (5.80)*	1.65 (1.92)*	1.70 (1.77)*
All (N_p weighted)	40688	-	8.50 (8.47)*	4.37 (4.36)*	1.55 (1.57)*	1.36 (1.38)*
GERG (simple)	36401	0.86 (0.93)*	8.64 (8.11)*	3.68 (3.66)*	1.87 (1.94)*	1.21 (1.30)*
GERG (N_p weighted)	36401	0.71 (0.72)*	7.22 (7.15)*	3.70 (3.73)*	1.56 (1.57)*	1.25 (1.27)*
Saturated densities excluded						
All (simple)	39046	-	14.07 (11.46)*	7.43 (5.95)*	1.38 (1.59)*	1.71 (1.79)*
All (N_p weighted)	39046	-	8.55 (8.52)*	4.45 (4.44)*	1.48 (1.50)*	1.38 (1.40)*
GERG (simple)	34759	0.77 (0.84)*	8.24 (7.58)*	3.56 (3.52)*	1.44 (1.48)*	1.14 (1.25)*
GERG (N_p weighted)	34759	0.66 (0.67)*	7.12 (7.05)*	3.69 (3.72)*	1.43 (1.43)*	1.23 (1.25)*

* The values in the parentheses indicate the AAD% excluding the datasets only at atmospheric pressure. Exclusion of the atmospheric density data reduces the total N_p by 883 for all systems and by and 520 for the GERG systems.

Table 4. AAD% in density for volume-translated EoS

System	SRK-VT	PR-VT	PC-SAFT-VT Eq. (9)	SBWR-VT Eq.(10)	PC-SAFT-VT Eq.(11)	SBWR-VT Eq.(12)
N_2CO_2	2.65	1.75	1.89	1.29	1.95	1.31
N_2C_1	1.97	1.45	1.03	0.53	1.22	0.65
N_2C_2	1.54	1.22	0.79	0.46	0.87	0.48
N_2C_3	0.29	6.62	0.38	1.24	0.48	1.15
N_2C_8	3.91	0.87	3.12	1.03	1.54	0.50
CO_2C_1	1.61	1.38	1.39	0.62	1.39	0.61
CO_2C_2	2.75	2.53	2.34	1.17	2.35	1.16
CO_2C_3	2.88	2.11	1.45	0.75	1.48	0.72
CO_2iC_4	4.75	4.16	4.42	1.59	4.38	1.62
CO_2C_4	4.23	1.81	2.22	1.08	2.15	0.95
CO_2C_5	6.95	6.26	3.51	2.20	3.71	2.41
CO_2C_7	3.03	1.62	1.08	1.07	1.00	1.17
CO_2C_{10}	3.26	1.65	1.93	1.93	1.20	2.56
CO_2C_{11}	2.49	1.86	1.71	1.95	1.27	3.61
CO_2C_{12}	5.24	2.33	4.48	2.26	2.10	1.38
CO_2C_{13}	3.25	2.07	2.29	2.64	1.52	4.72
CO_2C_{14}	3.47	3.18	2.30	5.07	1.83	7.51
CO_2C_{16}	4.67	2.69	5.39	3.38	1.41	6.06
CO_2C_{30}	40.36	49.58	19.47	6.20	5.18	5.24
H_2SC_1	2.60	2.52	1.74	1.34	1.73	1.34
H_2SC_3	3.36	3.15	1.79	1.62	1.81	1.62
C_1C_2	1.76	2.21	1.15	0.74	1.14	0.67
C_1C_3	1.94	2.21	1.24	0.94	1.25	0.85
C_1iC_4	1.86	1.73	1.09	0.73	1.07	0.68
C_1C_4	2.11	1.72	1.20	0.67	1.22	0.62
C_1C_5	1.79	1.64	0.98	0.61	1.07	0.70
C_1C_6	1.38	1.74	0.98	1.17	0.47	1.65
C_1C_7	2.60	1.67	1.49	1.31	0.87	1.49
C_1C_{10}	2.83	1.78	2.81	2.65	1.29	3.16
C_1C_{16}	4.11	3.19	4.77	4.24	2.79	7.78
C_2C_3	5.12	4.71	0.59	0.72	0.61	0.58
C_2C_4	4.51	4.06	1.48	1.12	1.48	1.11
C_2C_5	3.10	2.12	0.85	0.78	0.83	0.82
C_2C_7	3.93	3.50	2.72	2.38	2.71	2.51
C_2C_{10}	3.02	1.93	2.42	1.89	0.93	2.71
C_3iC_4	3.55	1.64	1.16	1.00	1.14	0.98
C_3C_4	6.96	6.28	6.15	4.81	6.10	4.74
C_3iC_5	3.02	3.99	5.06	4.19	5.02	4.15
C_3C_5	3.57	2.91	2.37	1.21	2.40	1.23
C_3C_6	5.36	4.48	4.92	2.21	4.78	2.11
C_3C_8	5.56	4.82	5.30	2.78	5.05	2.75
C_3C_{10}	3.36	1.62	2.43	1.02	0.93	1.61
C_3C_{20}	10.79	8.61	8.92	2.41	4.57	3.09
iC_4C_4	4.57	1.60	1.91	2.00	1.77	1.84
C_4C_5	11.24	8.78	9.59	1.61	9.65	1.68
C_4C_6	8.97	6.88	5.83	1.38	5.63	1.20
C_4C_7	4.14	3.31	1.76	0.74	1.57	0.62
C_4C_8	7.80	6.33	6.37	1.85	5.98	1.77
C_4C_{10}	3.67	1.54	2.39	0.82	0.95	0.94
C_5C_6	2.24	0.94	0.63	0.97	0.54	0.30
C_5C_7	2.40	0.86	0.72	1.14	0.52	0.27
C_6C_7	2.35	0.87	1.08	1.31	0.45	0.28
C_6C_8	2.62	0.49	1.38	1.04	0.27	0.21
C_6C_9	1.86	1.11	1.51	1.38	0.18	0.13
C_6C_{10}	3.29	0.70	2.22	1.57	0.51	0.28
C_6C_{12}	3.16	2.11	5.95	3.83	3.21	1.60
C_6C_{14}	1.33	1.17	3.79	0.36	0.64	2.92
C_6C_{16}	2.96	2.40	7.14	2.65	3.41	2.41
C_7C_8	2.36	1.24	1.03	0.88	0.40	0.49
C_7C_9	2.13	0.95	1.68	1.76	0.18	0.09
C_7C_{10}	3.51	0.64	2.20	1.81	0.43	0.22
C_7C_{11}	3.58	0.68	2.78	1.74	0.57	0.49

C_7C_{12}	2.63	0.60	2.15	1.92	0.22	0.37
C_7C_{14}	1.64	1.18	3.56	0.75	0.70	2.09
C_7C_{16}	2.42	0.65	4.04	0.70	0.46	2.70
C_7C_{20}	7.75	7.07	5.84	2.81	1.29	1.61
C_7C_{22}	9.95	9.79	7.33	3.43	2.11	1.54
C_7C_{24}	12.47	13.23	6.72	3.26	1.02	2.18
C_8C_9	2.23	0.89	2.08	1.95	0.22	0.10
C_8C_{10}	3.64	0.67	2.60	1.99	0.56	0.10
C_8C_{12}	2.80	2.69	6.60	4.47	3.98	2.15
C_8C_{14}	1.72	1.03	3.82	1.00	0.69	1.96
C_8C_{16}	2.59	0.65	4.35	1.09	0.60	2.42
C_9C_{10}	2.67	0.41	2.65	2.43	0.38	0.16
C_9C_{12}	2.99	0.32	3.08	2.56	0.33	0.16
C_9C_{14}	2.03	0.67	4.21	1.30	0.91	1.82
C_9C_{16}	2.80	0.61	4.62	1.46	0.76	2.16
$C_{10}C_{12}$	3.91	1.07	3.98	2.64	1.27	0.60
$C_{10}C_{14}$	2.89	1.32	6.09	2.33	2.62	1.53
$C_{10}C_{16}$	5.46	2.70	6.71	2.34	2.58	1.77
$C_{10}C_{18}$	6.09	4.19	5.78	2.83	1.30	1.42
$C_{10}C_{20}$	8.77	7.78	6.91	3.84	1.60	1.17
$C_{10}C_{22}$	10.36	9.97	7.67	3.69	1.71	1.83
$C_{10}C_{24}$	14.52	15.19	8.24	4.59	1.42	1.77
$C_{12}C_{14}$	2.70	0.28	4.67	2.03	0.84	1.61
$C_{12}C_{16}$	4.42	1.58	7.55	2.81	2.89	1.53
$C_{14}C_{16}$	2.67	0.64	6.03	1.57	1.28	2.80
$C_{16}C_{20}$	8.48	7.71	7.97	3.65	1.79	2.06
Saturated densities included						
All (simple)	4.46 (4.36)*	3.46 (3.37)*	3.64 (3.31)*	1.95 (1.88)*	1.80 (2.12)*	1.71 (1.77)*
All (N_p weighted)	3.34 (3.38)*	2.34 (2.34)*	2.25 (2.26)*	1.46 (1.47)*	1.60 (1.62)*	1.36 (1.38)*
GERG (simple)	3.49 (3.63)*	2.53 (2.65)*	2.32 (2.37)*	1.46 (1.43)*	1.85 (1.97)*	1.21 (1.31)*
GERG (N_p	3.07 (3.09)*	2.14 (2.15)*	1.95 (1.96)*	1.32 (1.32)*	1.57 (1.58)*	1.26 (1.27)*
Saturated densities excluded						
All (simple)	4.22 (4.02)*	3.25 (3.07)*	3.53 (3.12)*	1.97 (1.91)*	1.55 (1.80)*	1.71 (1.79)*
All (N_p weighted)	3.29 (3.32)*	2.28 (2.27)*	2.21 (2.22)*	1.48 (1.49)*	1.53 (1.55)*	1.38 (1.40)*
GERG (simple)	2.92 (3.03)*	2.01 (2.11)*	1.93 (1.94)*	1.43 (1.39)*	1.40 (1.51)*	1.14 (1.25)*
GERG (N_p	2.93 (2.95)*	2.00 (2.02)*	1.82 (1.84)*	1.29 (1.30)*	1.43 (1.44)*	1.23 (1.25)*

* The values in the parentheses indicate the AAD% excluding the datasets only at atmospheric pressure

5. Model-to-model comparison in excess volume

As a relatively simple physical property, a huge number of experimental densities have accumulated over the years. However, even for hydrocarbon systems, the density data for many binary pairs are still missing and the available ones do not always cover the complete range of temperature, pressure and composition of interest to us. More experimental measurements, which are driven by either the need for various applications or a more generic scientific purpose, are definitely needed, but the growth in the high-pressure density data for hydrocarbon systems is gradual. Instead of waiting for an ideal database with complete data covering all the conditions of interest to evaluate different models, we consider it as a valuable and complementary approach to make a direct comparison between two models without using experimental data. Although such a comparison does not provide an answer on the accuracy of the compared models, it does provide the critical information on how different or alike the compared models are. A major advantage of this model-to-model comparison is that the study is no longer limited by the data availability, meaning that a more systematic comparison can be made covering more pairs and more relevant temperature, pressure and composition conditions.

Here we select SRK as the reference model and compare it with PC-SAFT and PR. It is well known that SRK is inferior to both PC-SAFT and PR in density description but we focus here on how different they are in describing excess volume. The model comparison is made for 41 components including N_2, CO_2, H_2S, 36 n-alkanes up to C_{60} (only C_{28}, C_{30}, C_{32}, C_{36}, C_{38}, C_{40}, C_{44}, C_{46}, C_{54}, C_{60} included above C_{26}) and two iso-alkanes (iC_4 and iC_5). These components are ordered in decreasing volatility and all the pairs with the first 25 components (up to C_{20}) are included, giving 500 pairs in total. For each pair, the comparison is made in the range of 300-500 K, 100-1000 bar and 0.1-0.9 for the mole fraction of the first component in the pair. The selected temperature and pressure range is more relevant to oil and gas production. The conditions used for comparison form a rectangular box in the temperature, pressure and composition space for each pair.

In the final comparison of excess volume, we have excluded some of the points in the rectangular box because of two reasons. First, a mixture at certain T and P may split into two phases. One can either assume that the mixture is a hypothetical single-phase mixture and calculate the corresponding molar volume, or calculate the two-phase molar volume as

$$v = \beta v^v + (1-\beta) v^l \tag{13}$$

where β is the vapor phase fraction, and v^v and v^l are the vapor and liquid molar volumes, respectively. The former approach is easier but tends to give large differences in excess volume in the two-phase region. The latter one requires flash calculation and the calculated difference in the two-phase region reflects both the difference in density and that in equilibrium composition.

Although the second approach appears more reasonable, it still has a problem since the two models give different two-phase regions and the comparison can be between a single-phase result and a two-phase one. To avoid this, we have excluded all the points in the two-phase regions predicted by the two models. Second, the calculated molar volume is very sensitive to pressure around the critical points of two pure components. In some cases, the pure component molar volume calculated by one model is gas-like and that by the other model is liquid-like, which results in large difference in the calculated excess volumes. The problem is exacerbated when comparing PC-SAFT and SRK since the two models correspond to different pure component critical points. Hence, we have excluded the regions adjacent to the critical points, defined arbitrarily as 0.8-1.2 T_{ci} and 0.5-1.5 P_{ci}, where T_{ci} and P_{ci} are the critical temperature and pressure of pure component *i*, respectively. Since the pressure used in the comparison is from 100 to 1000 bar, the restriction of 0.5-1.5 P_{ci} is effective mainly for CO_2 and H_2S. On average, around 10% of the points are excluded due to the above two reasons.

To measure the difference in the molar excess volumes (v^E) calculated by two models EoS1 and EoS2 at each point, we introduce the scaled deviation in excess volume as follows:

$$Dev\% = \frac{v^{E,EoS2} - v^{E,EoS1}}{v^{EoS2}} \times 100\% \tag{14}$$

EoS1 , i.e., SRK in our study, is used to calculate the reference molar excess volume $v^{E,EoS1}$; EoS2, e.g., PC-SAFT, calculates the other molar excess volume $v^{E,EoS2}$ for comparison and also the molar volume v^{EoS2} to scale the difference between the two molar excess volumes. The simple absolute and relative deviations are not used because these deviations do not convey a physical meaning as clear as the scaled deviation defined by Eq. (14). Furthermore, since the excess volume can be a small value close to zero, the resulting large relative deviation can be misleading. In contrast, the scaled deviation introduced in Eq. (14) indicates clearly how the difference in excess volume calculated by the two models affects the calculation of the final density. Other statistical parameters like AAD%, the mean (%), and the standard deviation (%) are further calculated based on the scaled deviation.

In the analysis of the results for the 500 pairs, we split them into 25 groups according to the first component in a pair. This gives 25 groups from N_2 to C_{20}. Each group can be defined in two different ways: in the first way, a group M consists of the pairs formed by M and all the other components; in the second way, it consists of the pairs formed by M and those heavier than M. For easy reference, we call these two types of groups “complete” group and “incomplete” group, respectively. The “complete” group comprises the interactions between M and all the other components. The incomplete one only accounts for the interactions with heavier compounds. The

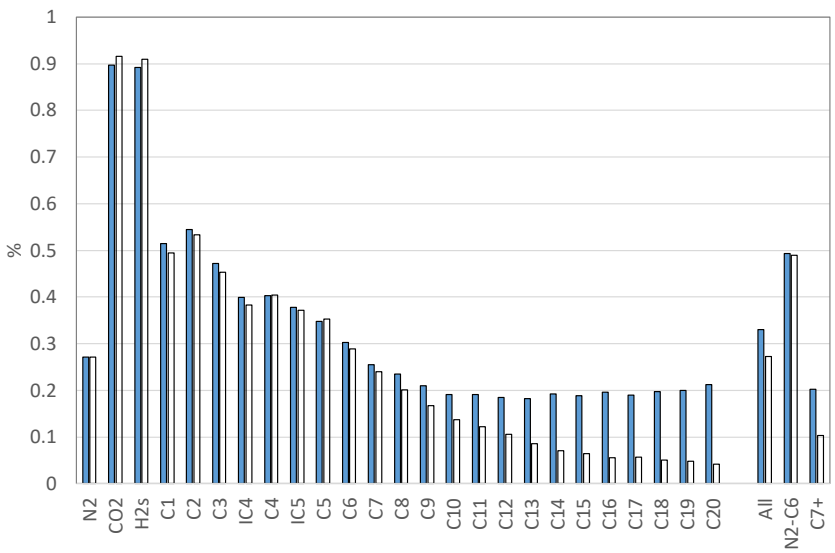
advantage of using an incomplete group is that the interactions with lighter components are screened out in the discussion for heavier groups and each binary pair is used only once. The complete and incomplete groups give slightly different statistics as shown below.

Figure 1 presents the statistics for the scaled deviations defined by Eq. (14) for the comparison between PC-SAFT and SRK. In addition to the information for each group, the averages for all the groups, the groups from N_2 to C_6, and those beyond C_6 (i.e., C_{7+}) are also presented. The AAD% generally decreases with the group index because the pair asymmetry decreases for heavier components. This is better shown when the incomplete groups are used since the complete groups will be affected by the large deviations between a heavy component and a very light one, e.g., between C_{20} and C_1. The trend is also reflected by the deviation contrast between the N_2-C_6 group and the C_{7+} group. From the means in Figure 1(b), we can see that PC-SAFT predicts smaller excess volumes than SRK except for the CO_2 group. The CO_2 and H_2S groups are a bit special, for which PC-SAFT and SRK give relatively large differences in excess volume. For the other groups, the differences are relatively modest between two models. For all the groups on average, we have an AAD% of ~0.3%, a mean of ~ -0.2%, and a standard deviation of ~0.2%. This means that if the mixture densities are calculated by combining the pure component densities from PC-SAFT and the excess volumes from SRK, the final density, on average, is ~ 0.2±0.2% different from the density calculated from PC-SAFT. Compared to the typical measurement uncertainty of 0.1% from a high-pressure vibrating tube density meter, the difference is very small. This, however, should not be narrowly understood as the difference always staying so small at all conditions. For particular pairs and at particular conditions, we can have large deviations.

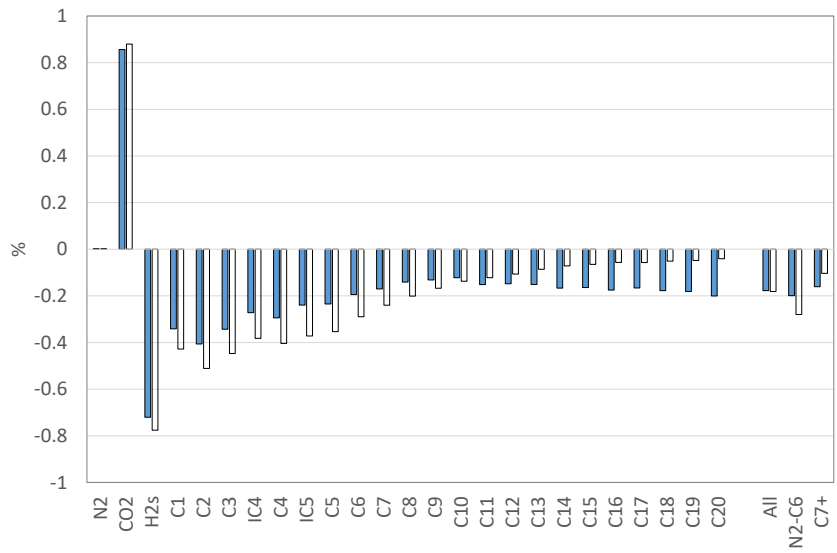
Figure 2 illustrates how the maximum and minimum scaled deviations are for various groups. The deviations are reported for the incomplete groups so that the same maximum/minimum will not be counted twice in two different groups. CO_2 and H_2S are again two particular components showing deviations not quite in alignment with the trend for the others. For alkanes, the minimum deviations give larger magnitude than the maximum ones. They are ~ -6% for the C_1 to C_4 groups and their magnitude die out quickly with the increasing carbon number. Figures 3 and 4 provide two examples, C_1-C_7 at x_{C1}=0.4 and C_2-C_{10} at x_{C2}=0.6, where the minimum deviations are observed for these two pairs. The minimum deviations as well as the maximum deviations happen at relatively low pressures. For these two cases, the minimum deviations happen at high temperatures. The vast majority of the conditions in the two examples give a very modest deviation of 0.5% and the large deviations appear in the low pressure region, say, 100-200 bar. It is not surprising to see the large deviations in this region because with relatively large excess volumes and smaller densities in this region, the influence of excess volume on the calculated density is larger. The two examples represent the typical deviation contour plots for most of the pairs. It is fair to state that in the vast

majority of conditions, the difference in excess volume calculation is small between PC-SAFT and SRK although the difference is significant in some particular regions typically at low pressures.

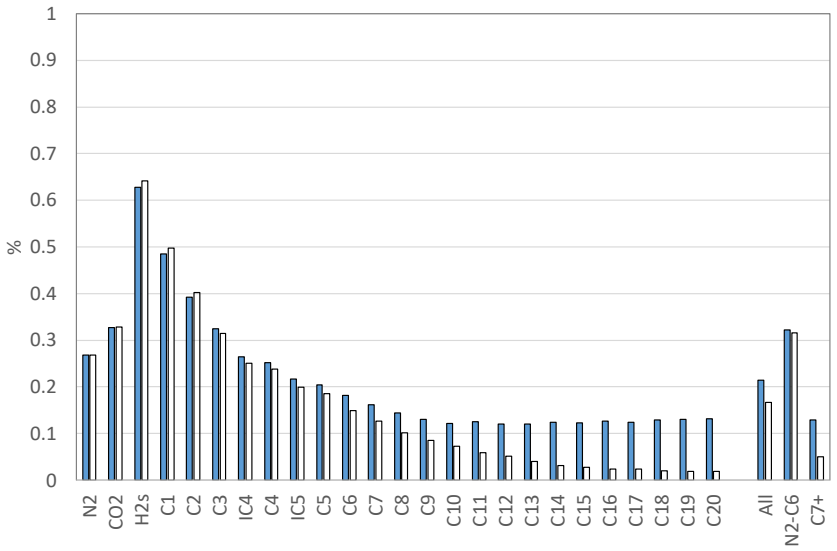
A similar comparison is made between PR and SRK with the results presented in Figure 5. The difference in excess volume between PR and SRK is even smaller. PR gives a bit larger excess volume than SRK for most groups except for the N_2 and H_2S groups. For all the groups on average, the AAD%, the mean and the standard deviations are 0.04%, 0.02% and 0.04%, respectively. It is commonly known that PR delivers a better density than SRK, and PC-SAFT a much better density than cubic EoS. In the **supplementary material**, we provide the comparisons in density between PC-SAFT and SRK, and between PR and SRK. For the same conditions as used in the excess volume comparison, the AAD% is 22% between PC-SAFT and SRK on average, and 11% between PR and SRK on average, with SRK giving larger volumes in both cases. Despite the obvious difference in density description between these models, in terms of the description of the volume change on mixing, our comparisons show that PC-SAFT is not particularly different from the other cubic models, and the two cubic models PR and SRK are essentially identical. This comes not like a complete surprise because in the development of these models, little consideration is given to the mixture densities. There is no interaction parameter for the packing density in PC-SAFT or for the co-volume in SRK or PR in their ordinary applications.



(a)



(b)



(c)

Figure 1. Statistics for the excess volume comparison between PC-SAFT and SRK: (a) AAD%; (b) mean (%); (c) standard deviation (%). Solid columns are for the complete groups and blank ones for the incomplete groups.

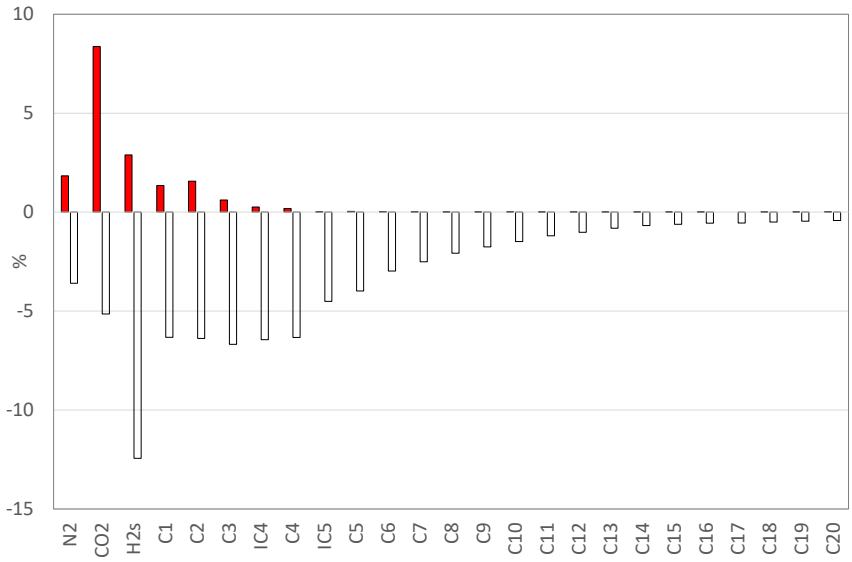


Figure 2. Maximum and minimum deviations (%) in excess volume between PC-SAFT and SRK for various groups (incomplete type): the solid columns for the maximum deviations and the blank ones for the minimum deviations.

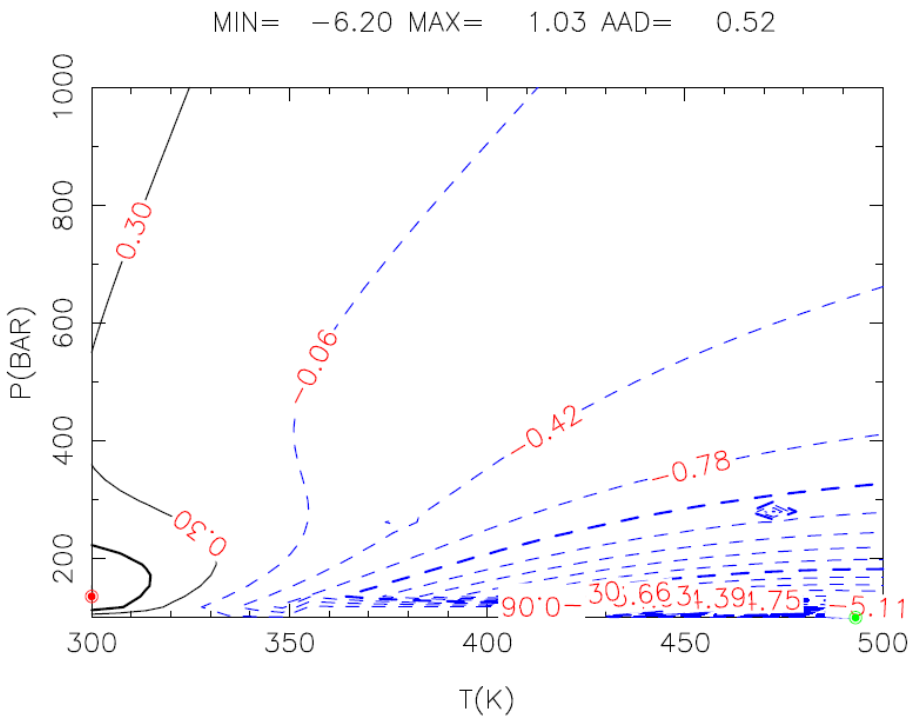


Figure 3. Contour map for AAD% in excess volume between PC-SAFT and SRK for C_1-C_7 at x_{C1}=0.4. The maximum and minimum are marked by red and green dots, respectively.

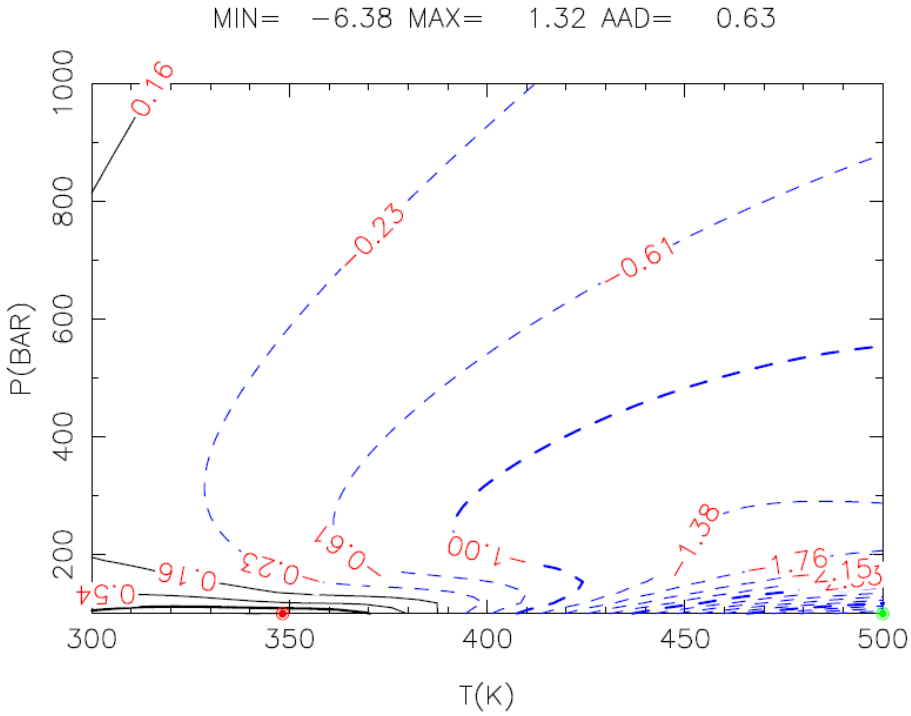
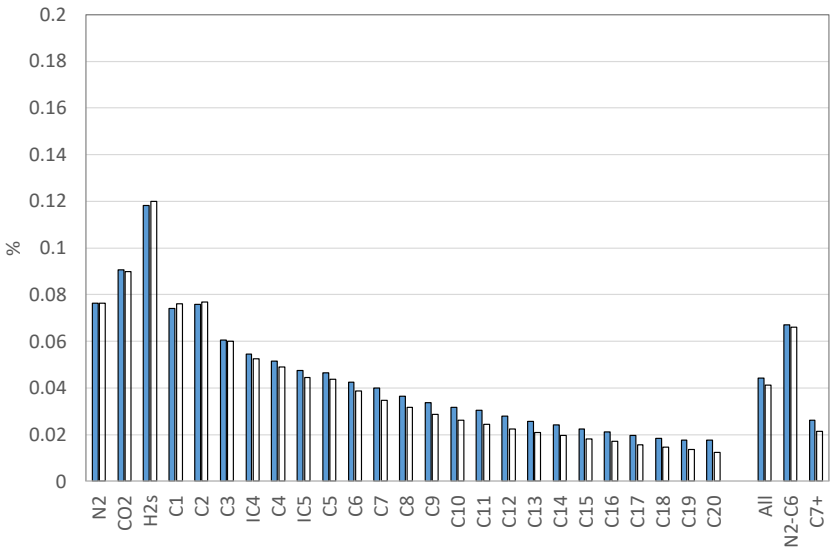
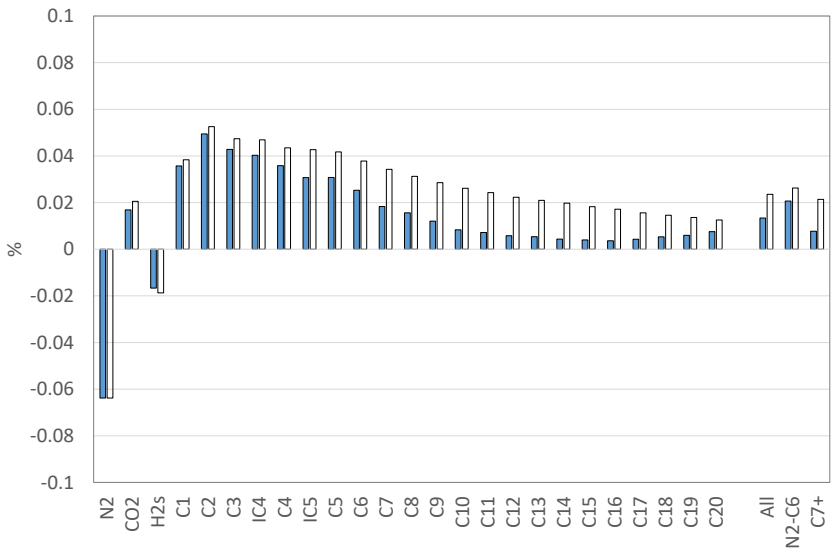


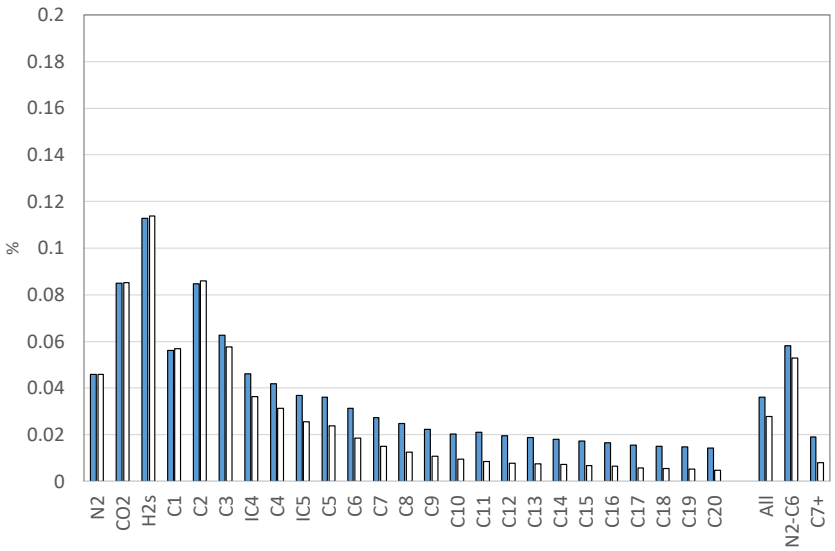
Figure 4. Contour map for AAD% in excess volume between PC-SAFT and SRK for C_2-C_{10} at x_{C2}=0.6. The maximum and minimum are marked by red and green dots, respectively.



(a)



(b)



(c)

Figure 5. Statistics for the excess volume comparison between PR and SRK: (a) AAD%; (b) mean (%); (c) standard deviation (%). Solid columns are for the complete groups and blank ones for the incomplete groups.

6. Estimation of high-pressure densities utilizing an excess volume method

The observation of relatively similar excess molar volumes calculated by various models motivates the discussion whether we can utilize the excess volume from a simple model to estimate the mixture density, and furthermore, whether the estimation can also generate other thermodynamic properties. We present below the theoretical implication of this excess volume method, the test of this method using our binary density database, and its potential application to high-pressure reservoir fluids.

6.1. Property estimation using v_i^p and v^E from two different models

The molar volume of a mixture can be expressed using its pure component molar volumes v_i^p (the superscript *p* denotes pure component) and its molar excess volume v^E evaluated at the same *T* and *P*:

$$v = \sum x_i v_i^p + v^E \tag{15}$$

We discuss here the calculation of v using v_i^p and v^E from two different models. The overall model for v is thus a "combined" one. We can show that if v is calculated this way, the molar excess properties for several functions, including enthalpy h, entropy s, Gibbs energy g and isobaric heat capacity C_p, are essentially the same properties as calculated by the model used for calculating v^E.

In a more general sense, the "models" for v_i^p and v^E can be considered as different sources for their values, not necessarily EoS models. For simplicity, our following discussion still assumes the use of general EoS models. If we use EoS II to calculate v_i^p and EoS I to calculate v^E, we have

$$v = \sum x_i v_i^{p,II} + v^I - \sum x_i v_i^{p,I} = \sum x_i v_i^{p,II} + v^{E,I} \tag{16}$$

The superscripts I and II denote EoS I and II, respectively. EoS II, a more sophisticated model like PC-SAFT or even reference EoS, provides more accurate description for v_i^p than EoS I. EoS I, a simpler model like SRK or PR, provides a reasonable v^E. Such a combination should in principle give a more accurate estimate of v than using EoS I alone. The treatment appears unnecessary if the more accurate EoS II can handle the mixture. However, if EoS II is not directly applicable to mixtures, or if the source of v_i^p is only experimental, such an estimate can be attractive in practice, as will be discussed in Section 6.3.

It is interesting to note that Eq. (16) corresponds to a new set of other commonly used thermodynamic properties and derivatives, such as fugacity coefficients, enthalpy, entropy, heat capacity, and Joule-Thomson coefficients. We can readily get the following derivatives from Eq. (16) :

$$\frac{\partial v}{\partial T} = \sum x_i \frac{\partial v_i^{p,II}}{\partial T} + \frac{\partial v^{E,I}}{\partial T} = \sum x_i \frac{\partial v_i^{p,II}}{\partial T} + \frac{\partial v^I}{\partial T} - \sum x_i \frac{\partial v_i^{p,I}}{\partial T} \tag{17}$$

$$\frac{\partial v}{\partial P} = \sum x_i \frac{\partial v_i^{p,II}}{\partial P} + \frac{\partial v^{E,I}}{\partial P} = \sum x_i \frac{\partial v_i^{p,II}}{\partial P} + \frac{\partial v^I}{\partial P} - \sum x_i \frac{\partial v_i^{p,I}}{\partial P} \tag{18}$$

The partial molar volume $\bar{v}_i$ is given by

$$\bar{v}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P} = \bar{v}_i^{\,I} + (v_i^{p,II} - v_i^{p,I}) \tag{19}$$

The fugacity coefficients can be expressed as

$$\ln\phi_i = \frac{1}{RT}\int_0^P \left(\bar{v}_i - \frac{RT}{P}\right) dP = \ln\phi_i^I + \ln\phi_i^{pure,II} - \ln\phi_i^{pure,I} \tag{20}$$

We can show that the temperature and pressure derivatives of $\ln\phi_i$ consist of three contributions in a similar manner and that the composition derivatives of $\ln\phi_i$ are the same as those of $\ln\phi_i^I$. Furthermore, we have various residual properties as

$$\frac{h^{res}}{R} = -T^2 \sum x_i \left(\frac{\partial \ln\phi_i}{\partial T}\right)_P = \frac{h^{res,I}}{R} + \sum x_i \left(\frac{h_i^{p,res,II}}{R} - \frac{h_i^{p,res,I}}{R}\right) \tag{21}$$

$$\frac{g^{res}}{R} = T\sum x_i \ln\phi_i = \frac{g^{res,I}}{R} + \sum x_i \left(\frac{g_i^{p,res,II}}{R} - \frac{g_i^{p,res,I}}{R}\right) \tag{22}$$

$$\frac{s^{res}}{R} = \frac{s^{res,I}}{R} + \sum x_i \left(\frac{s_i^{p,res,II}}{R} - \frac{s_i^{p,res,I}}{R}\right) \tag{23}$$

$$\frac{C_p^{res}}{R} = \frac{1}{R}\left(\frac{\partial h^{res}}{\partial T}\right)_P = \frac{C_p^{res}}{R} + \sum x_i \left(\frac{C_p^{p,res,II}}{R} - \frac{C_p^{p,res,I}}{R}\right) \tag{24}$$

Actually all the above molar residual properties have the form

$$m^{res} = m^{res,I} + \sum x_i m_i^{p,res,II} - \sum x_i m_i^{p,res,I} \tag{25}$$

It is obvious that

$$m^E = m^{res} - \sum x_i m_i^{p,res,II} = m^{res,I} - \sum x_i m_i^{p,res,I} = m^{E,I} \tag{26}$$

This indicates that if v^E for the "combined" model is calculated using a simple model EoS I, several other excess properties such as h^E, g^E, s^E, and C_p^E are also the same. This is important in implementation since we can simply use the following equation to calculate v, h, g, s, and C_p for the combined model:

$$m^{res} = m^{E,I} + \sum x_i m_i^{p,res,II} \tag{27}$$

It should be noted that the isochoric heat capacity cannot be calculated this way. But with the properties and derivatives given by Eqs. (16)-(27) , the other properties needed like $(\partial P/\partial T)_v$, Joule-Thomson coefficients, isochoric heat capacity, speed of sound can be readily obtained.

6.2. Test with the binary density database

The excess volume method is tested using the binary density database. We use either GERG-2008 or PC-SAFT as EoS II to calculate pure component volumes, and the other EoS to calculate the excess volumes. The detailed results are presented in the **supplementary information** and Table 5 summarizes the overall AAD% in comparison with the ADD% without using the excess volume approach. We distinguish between the results for the GERG systems and those for all the systems. For the GERG systems, we can use both GERG and PC-SAFT as EoS II; for all the systems, GERG cannot be used as EoS II and only PC-SAFT is used here. It should be noted that if EoS I and EoS II are the same in the excess volume method, the combined model is essentially the same as the original model (PC-SAFT or GERG) and the obtained deviations are the same—they are marked as bold letters in Table 5. It is obvious that for SRK and PR, combination of the excess volumes from these two EoS with the pure component properties from GERG or PC-SAFT can significantly reduce their deviations to a level comparable to those for GERG or PC-SAFT. Actually, the deviations are still a bit larger because SRK or PR cannot perfectly match the excess volume variation with temperature, pressure and composition in GERG or PC-SAFT.

Table 5. AAD% for the binary mixture densities by different methods

	GERG	SRK	PR	SAFT	SBWR
GERG systems					
Original EoS	**0.86**	8.64	3.68	**1.87**	1.21
Excess volume method (GERG as EoS II)	**0.86**	1.75	2.00	2.06	1.27
Excess volume method (PC-SAFT as EoS II)	2.05	2.19	2.47	**1.87**	1.96
All systems					
Original EoS	-	13.85	7.20	**1.65**	1.70
Excess volume method (PC-SAFT as EoS II)	-	1.85	2.02	**1.65**	1.93

Figure 6 shows the densities for the C_1-C_{10} system calculated by the excess volume method using PC-SAFT as EoS II and SRK as EoS I. Both the excess volume method and PC-SAFT give good agreement with the experimental data whereas SRK shows large deviations. The excess volume method can also generate other thermodynamic properties, such as the compressibility and expansivity for C_1-C_{10}, as shown in Figures 7 and 8, respectively. Among SRK, PC-SAFT and the excess volume method, the latter two give much better agreement. The results for the other properties including isobaric heat capacity, isochoric heat capacity, speed of sound, and Joule-Thomson coefficients are provided in the **supplementary information**. For these properties, PC-SAFT and the excess volume method are in better agreement for the speed of sound and Joule-

Thomson coefficients whereas the calculated two heat capacities are similar for all three models. It is worth noting that the compressibility curve at 278.15 K in Figure 5 shows an artificial maximum around 350 bar for the excess volume method. This exposes a major limitation of the excess volume method: although the method gives the reasonable estimates for the mixture density, it does not necessarily describe the derivatives of density with sufficient accuracy. For this example, the problem is in the second order derivatives or the compressibility variation with pressure. The incorrect trend in compressibility will further affect the speed of sound and the isochoric heat capacity, causing erroneous trends in the same pressure range, but the isobaric heat capacity and the Joule-Thomson coefficient are not affected. In some cases, if $(\partial v^E / \partial P)_T$ is dominant in the calculation of $(\partial v / \partial P)_T$ and EoS I and II give relatively different $(\partial v^E / \partial P)_T$, it can happen that the obtained compressibility becomes negative (non-physical). This happens usually below 200 bar for the binary systems tested. Therefore, the excess volume method should be used with caution for properties involving the derivatives of density.

There is another pitfall regarding the selection of the density root. In principle, we should select the same phase state for EoS I and II in the calculation. If both EoS have two density roots for a pure component in a mixture, the most stable root may not correspond to the same phase state for two EoS, and a bit arbitrary choice needs to be made here for the most suitable root for each EoS. Fortunately, this happens in the subcritical region of the pure components, usually at pressures lower than 50 bar (H_2S and CO_2 as exceptions in our list of components). However, the problem exists also in the single-phase region close to the critical point of a pure component. Owing to the sensitivity of volume to pressure, one EoS can give a gas-like density and another a liquid-like one. The situation is exacerbated if a model, like PC-SAFT, corresponds to a different critical point. This pitfall has caused particularly high deviations for some data points (<0.02% of the total points) and a small increase in the reported AAD% for the excess volume method in Table 5.

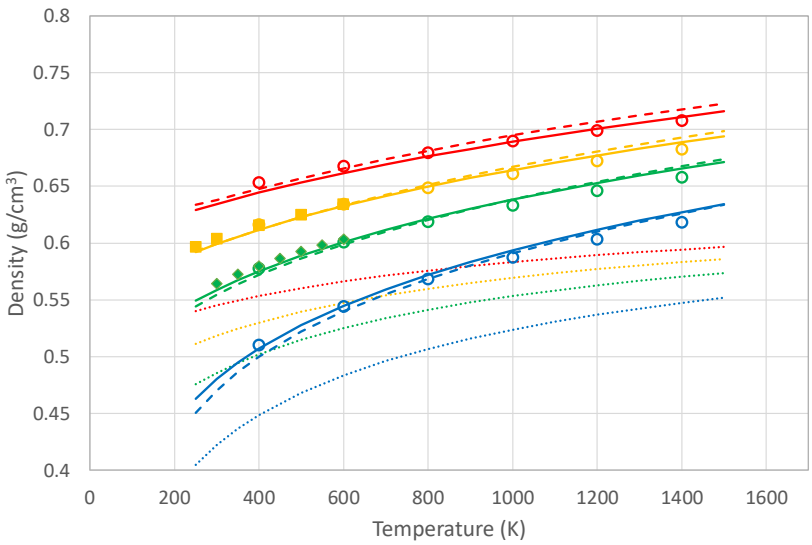


Figure 6. Density for the C_1-C_{10} mixture at x_{C1}=0.6 and temperatures 278.15, 323.15, 373.15, and 463.15 K (from top to bottom). Points represent the experimental data: (■) Audonnet and Padua (2004) at x_{C1}=0.601, (◆) Canet et al. (2002) at x_{C1}=0.6, (○) Regueira et al. (2016) at x_{C1}=0.6017. Lines represent the model calculations with x_{C1}=0.6017 : (•••) SRK, (—) PC-SAFT, (- - -) Excess volume method with PC-SAFT (EoS II) and SRK (EoS I).

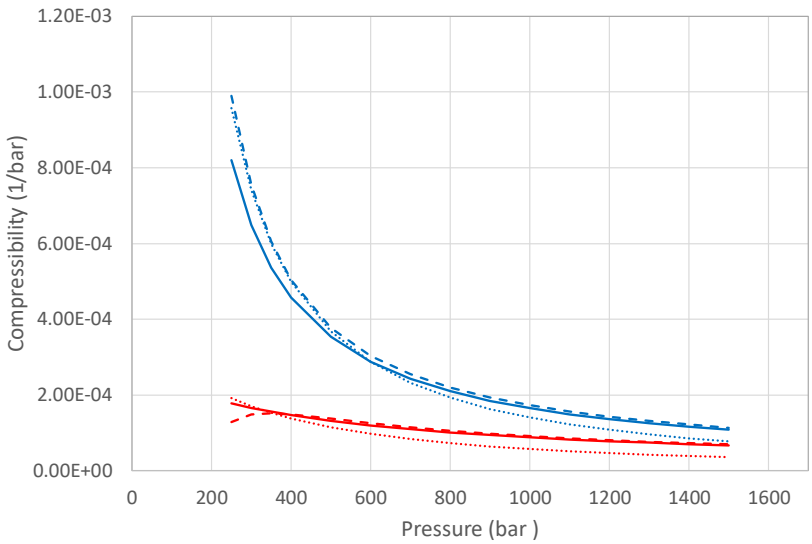


Figure 7. Calculated isothermal ompressibility for the C_1-C_{10} mixture at x_{C1}=0.6017. Red lines at 278.15 K and blue lines at 463.15 K: (•••) SRK, (—) PC-SAFT, (- - -) Excess volume method with PC-SAFT (EoS II) and SRK (EoS I).

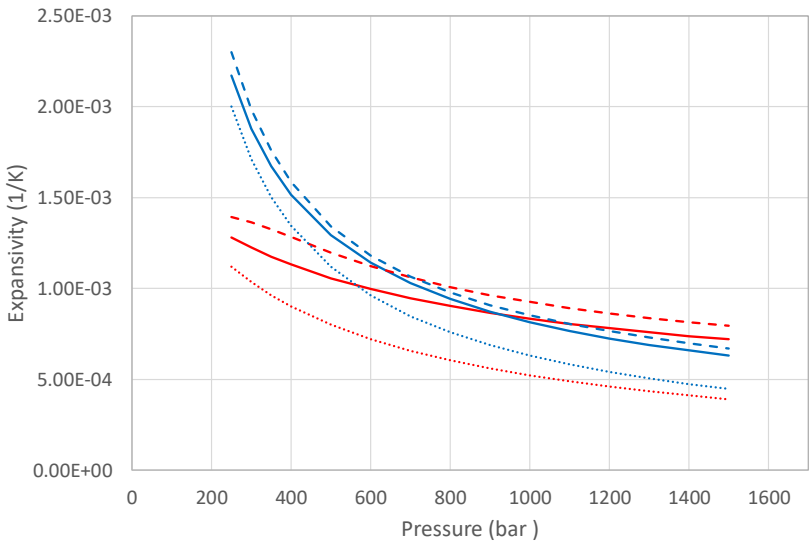


Figure 8. Calculated isobaric expansivity for the C_1-C_{10} mixture at x_{C1}=0.6017. Red lines at 278.15 K and blue lines at 463.15 K: (•••) SRK, (—) PC-SAFT, (- - -) Excess volume method with PC-SAFT (EoS II) and SRK (EoS I).

6.3. Potential application to high-pressure reservoir fluids

Although the excess volume method proves useful for generating relatively accurate density estimates from a simple EoS like SRK, it can be questioned whether the excess volume method is superfluous because an accurate EoS like GERG or PC-SAFT with its original mixing rules can already describe the mixture density satisfactorily. However, in many cases, the densities of the constituting components or groups are available experimentally or through correlations, but not from an accurate EoS. The excess volume method provides a pragmatic approach for estimating mixture properties with the equations presented in Section 6.1.

The high-pressure density of a reservoir fluid is usually measured in a high-pressure vibrating tube density meter or in a PVT cell. The former is more accurate but requires a separate test. A main challenge for the density measurement of a reservoir fluid is that the sample contains dissolved gas and needs to be kept in a single-phase state throughout the whole test. In comparison, it is much easier to work with the degassed reservoir fluid, known as the dead oil or stock tank oil (STO). Using the excess volume method, it is possible to combine the accurate high-pressure densities for a STO, which are more readily obtainable, with the model generated excess volume and other pure component volumes to estimate high-pressure densities for the reservoir fluid. For a reservoir fluid with known composition, its molar volume is given by

$$v = \sum_{i=1}^{N_G} x_i v_i^p + v^E \tag{28}$$

In the above equation, we treat all the pseudo components as real components in the modeling of this reservoir fluid. Since the stock tank oil is not a single component (not even a single pseudo component in normal modeling), we need to split the whole reservoir fluid into N_G artificial groups,

with STO as one of the groups. We can define the pseudo molar excess volume $v^{E,pseudo}$ using these groups:

$$v = \sum_{k=1}^{N_G} x_k^G v_k^G + v^{E,pseudo} \tag{29}$$

where x_k^G is the group mole fraction and v_k^G is the molar volume of group *k* at the same *T* and *P*. The groups other than STO can be lumped ones but it is convenient to use just individual pure components if they are well-defined. In such as case, we have

$$v = \sum_{i=1} x_i v_i^p + x_{STO}^G v_{STO}^G + v^{E,pseudo} \tag{30}$$

where the first term on the right hand side includes all the remaining well-defined components. The value of v_{STO}^G is determined experimentally whereas v_i^p for other pure components can be obtained from an accurate EoS like a reference EoS. We calculate $v^{E,pseudo}$ using an EoS like SRK. It should be noted that $v^{E,pseudo}$ is not equal to v^E in Eq. (28) unless there is no excess volume associated with the formation of STO from its constituting pseudo components. Since the volume change on mixing for the formation of STO is usually negligible, the difference between $v^{E,pseudo}$ and v^E can be neglected. The above provides a practical method to estimate high-pressure reservoir fluid densities by combining easily obtainable high-pressure STO experimental densities with EoS modeling. It can potentially reduce or even avoid the more difficult and expensive density measurement of live fluids (reservoir fluids containing dissolved gas). The method will be tested in our future work.

Eq. (30) also has some implications on the PVT modeling of high-pressure densities. It shows the importance of capturing the STO densities in the temperature and pressure range of interest in the development of a PVT model. This requires adequate considerations in C_{7+} characterization. The procedures for C_{7+} characterization for SRK and PR are well-established [33][170] and those for non-cubic models like PC-SAFT can be done in a similar manner [26]. These procedures by default do not match the STO density directly although matching of the atmospheric STO density can be introduced in the tuning step. Eq. (30) shows the importance of matching the density not just at atmospheric pressure, but over the whole temperature and pressure range of interest. Whether this can be achieved is determined by, besides the tuning techniques, the functional form of the EoS itself. Cubic models are presumably less accurate than non-cubic models in describing density over a wide range of conditions, but it has to be investigated for the specific systems how satisfactory a model is. It is nevertheless a good practice to check whether the chosen model can describe v_i^p and v_{STO}^G satisfactorily in the temperature and pressure range of interest. It

should also be checked whether phase equilibrium calculation is adversely affected by the tuning of C_{7+} parameters in matching v_{STO}^{G}.

Eq. (30) has the same advantages and limitations as discussed for the excess volume method in Sections 6.1 and 6.2. It provides a relatively simple and systematic way to assemble properties, which are not limited to densities, estimated from different models. However, there are potential risks of generating inaccurate or even non-physical trends particularly for derivative properties at pressures where excess volumes are relatively large. Therefore, using Eq. (30) as a combined model in a reservoir or process simulation is in principle possible but requires precaution and further evaluation in the context. We do not give general recommendations here but a relevant question is whether and how much we allow to model phase equilibrium and density inconsistently. We currently consider Eq. (30) mainly as a tool for estimating high-pressure densities and for guiding PVT modeling.

7. Conclusions

In this study, we evaluated some representative cubic and non-cubic EoS in modeling of mixture density particularly at high pressures and for petroleum-related applications. These models include SRK, PR, PC-SAFT, Soave-BWR and GERG-2008. For petroleum mixtures, the involved models are usually similar in phase equilibrium description if proper interaction parameters are used. However, they differ significantly in density description. This study attempts to answer how different they are in density description and to analyze why they are different.

For the purpose of evaluation, we established a large database for binary mixtures consisting of 88 systems and over 40000 points with most at high pressures, providing a solid basis for the evaluation of the selected models. For SRK, PR, PC-SAFT and Soave-BWR, their volume translated versions were also tested. The comparison shows that for systems where GERG-2008 is applicable, it gives the best accuracy because of the multiple component specific parameters used in the model. PC-SAFT and Soave-BWR form the second most accurate group, with Soave-BWR a bit better for light systems and PC-SAFT a bit better for heavier systems. The original SRK and PR are in the third group and their accuracies lag far behind. Volume translation can significantly improve the performance of SRK and PR to a level close but still inferior to that of the second group. The effect of volume translation on Soave-BWR and PC-SAFT is dubious although our test is only for some specific volume translation correlations. The above findings for various models are similar to the observations for the performance of these models for pure components, confirming the direct link between the mixture density modeling and the pure component density modeling. The current study is limited to binary mixtures and paraffinic hydrocarbons. It is worthwhile to extend the study

to ternary and multicomponent mixtures and systems containing aromatic hydrocarbons in the future.

We further made a direct comparison between models without the use of experimental data. This enables to test a larger number of systems consisting of 41 components and 500 pairs under more systematically chosen temperatures, pressures and compositions. SRK was compared with PC-SAFT and PR in terms of excess molar volume and molar volume. In the studied range over 100 bar, although SRK differs from PC-SAFT by 22% in density and from PR by 11% in density, the scaled deviations in excess volume, representing how much the difference can influence the calculated mixture density, are merely 0.3% and 0.04%, respectively. This further reveals that the difference in the mixture density modeling by various EoS mainly reflects their difference in the pure component density modeling. The difference in excess volume between the two cubic models is trivial, and the difference between the cubic SRK and the non-cubic PC-SAFT is also modest in comparison with the typical uncertainty in high-pressure density measurement (~0.1%). It should be noted that the difference in excess volume varies with conditions but it is usually small at high pressures.

Motivated by the similar excess volumes from different models, we proposed the excess volume method that combines the pure component densities from an accurate but complex EoS and the excess volume from a simple EoS like SRK. The other thermodynamic properties can also be obtained using the excess volume method. With the test using the binary database, we showed that the excess volume method can give reasonable density estimates even with the excess volumes estimated from a simple EoS like SRK. We also pointed out the limitations with the excess volume method. In particular, caution must be taken for the calculated properties involving the density derivatives. The practical significance of the excess volume method lies in its potential to reduce the need for direct experimental determination of high-pressure density of reservoir fluids with dissolved gas. It is possible to combine the more readily determined STO densities at different pressures with the excess volume from a model to estimate the high-pressure density of the reservoir fluids. This needs further experimental validation in the future.

It should be noted that this study emphasizes on the overall behavior rather than the peculiarity with a specific system or dataset. The difference between different systems should not be overlooked, especially for those pairs with N_2, CO_2 and H_2S. Comparisons can be made in a more detailed manner for specific types of systems in the future. We also note that binary mixture densities are seldom included in the development of an EoS model except for multiparameter equations emphasizing high accuracy in density. In contrast, the binary phase equilibrium data are always used to determine the binary interaction parameters for an EoS. The importance of binary excess volumes for mixture density modeling can be compared to that of binary VLE or LLE to

phase equilibrium modeling. It is recommended that the binary mixture densities or excess volumes are utilized in the ordinary EoS development for a better density description.

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