Dynamic Viscosity of Binary Fluid Mixtures: A Review Focusing on Asymmetric Mixtures

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Abstract

A literature review on experimental data for binary mixtures of methane and carbon dioxide with hydrocarbons up to *n*-hexadecane is presented. Based on these data, the extended corresponding states method, two entropy scaling approaches, and the friction theory are analyzed with respect to their capability of calculating viscosity values with increasing asymmetry of the binary mixture. It is shown that not only the viscosity model but also the underlying thermodynamic equation of state has a significant influence on the result of such calculations. Shortcomings are identified both in the experimental data and in the modeling approaches.

Keywords Asymmetry · Binary mixtures · Entropy scaling · Extended corresponding states · Friction theory · Viscosity

1 Introduction

The knowledge of thermophysical properties is essential to accurately predict the behavior of pure fluids or mixtures in engineering applications. While theoretical work on viscosities of pure fluids at mostly low density made large progress, systematic and accurate measurements on technically relevant mixtures were mainly carried out for equilibrium properties like density or speed of sound rather than for viscosity. A close cooperation between industry, research institutes and academic institutions enables, for example, to investigate thermodynamic properties of natural gases experimentally and theoretically on a very comprehensive scale. The increasing debate on climate change mitigation and the accompanying efforts to reduce carbon dioxide emissions are leading to similarly extensive research on CO₂-rich mixtures. The research in the field of alternative refrigerants is also continuously

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increasing. Despite all these efforts, the focus is mainly on thermodynamic state properties, but transport properties are examined much less closely. And all these applications have in common that at least the main components of the respective mixtures form rather symmetric mixtures. However, there are also many applications, which require thermophysical properties of asymmetric mixtures. Typical examples are enhanced oil recovery (mixtures of carbon dioxide, nitrogen, or natural gas with oil), screw expanders in organic Rankine cycles (mixtures of refrigerants with lubricants), or even quite simple applications such as pressurized cylinders with liquefied gases, which are pressurized with cushion gas (mixtures of helium, nitrogen, or argon with hydrocarbons). Another mixture that is often not mentioned in this context but also behaves strongly asymmetrically is, for example, CO₂ with water.

The terms *symmetrical* and *asymmetrical* are somewhat vague in the literature. There is no clear definition for this classification. A pragmatic approach is to differentiate on the basis of the boiling temperatures of the components involved at identical pressure. This approach is also related to the critical temperatures and molar masses of the components as long as simple fluids are involved. With increasing influence of electrostatic interactions, these relationships change. With quite similar molar masses, boiling and critical temperatures might differ significantly from each other (cf. mixtures with water or alcohols). However, the present study is restricted to “simple” mixtures so that the influence of the size and molar mass of the components can be analyzed without strong electrostatic interactions affecting the results.

To our best knowledge, a systematic investigation on the influence of increasing grade of asymmetry on the viscosity of mixtures is not available in the literature, yet. There are some works both experimentally and also theoretically on polyolefin mixtures [1–4], squalane mixtures [5–8], or CO₂ mixtures with long-chain hydrocarbons [5]. However, the database is very limited, which of course also applies to the models that were developed based on these data. In order to get an idea on the performance of different viscosity models, systems are evaluated here, which are experimentally investigated more comprehensively. The literature study carried out in this work revealed that methane and CO₂ mixtures with hydrocarbons have been investigated experimentally at least to the extent that a systematic investigation is possible. These systems are used here to analyze the performance of different models for the calculation of mixture viscosities, highlight gaps in the database even for such common mixtures, and point out next steps in future research.

2 Investigated Viscosity Models for Mixtures Reported in the Literature

Mathematical models for the calculation of the dynamic viscosity are commonly separated into a dilute gas contribution η^0 and a residual part η^r :

$$\eta(T, \rho, \bar{x}) = \eta^0(T, \rho, \bar{x}) + \eta^r(T, \rho, \bar{x}). \quad (1)$$

The dilute gas viscosity is calculated according to the Chapman–Enskog theory [9] for all models applied in the present work. It approximates the transport of a momentum through a gas assuming that the molecules are rigid and non-attractive spheres with a diameter σ , travel all with the same speed, and move Gaussian distributed in all three directions of space. It counts for the rate of collision of one molecule with others at a given temperature (speed, respectively) on a microscopic scale. Conversion to the macroscopic size is carried out using the Boltzmann's constant and the molar mass. There are several empirical approaches published for the collision integral, the most common being that of Neufeld et al. [10] based on the Lennard-Jones potential. Since only very few fluids approximately fulfill the assumptions of the Chapman–Enskog theory, an empirical factor was introduced later. This factor comprises, for example, the acentric factor or the polarity of a molecule, which enables a better description of non-spherical molecules or molecules with pronounced electrostatic interactions, cf. Chung et al. [11, 12]. In case of mixtures, simple approaches can be applied, which either combine the dilute gas viscosity of the pure fluids by means of the mole fractions and molar masses of the involved components (cf. Wilke [13, 14], Quiñones-Cisneros et al. [15] or Zéberg-Mikkelsen et al. [16]) or evaluate the size and energy parameters of the underlying pair-potential (commonly the Lennard–Jones potential) in a mixture (e.g., Huber et al. [17]).

Numerous models exist for the calculation of the residual dynamic viscosities of mixtures, which are often customized solutions for specific applications. Since the aim of this work is to analyze the performance of approaches with respect to an increasing asymmetry of mixtures, three approaches have been selected here for which the required parameters are available. In the literature, these models are broadly applied for the calculation of viscosities of fluid mixtures. In the following sections, a brief overview is given about the basic ideas of these approaches. Details and the comprehensive mathematical relations can be taken from the respective publications.

2.1 Extended Corresponding States Method

The most comprehensive model for the viscosity of fluid mixtures is the extended corresponding states method (ECS) as described by Chichester and Huber [18] and Huber et al. [17] and implemented in the software tools REFPROP [19], TREND [20], and CoolProp [21] (only pure fluids are included in CoolProp [21]). The list of available fluids (see Refs. [17] and [18]) was subsequently extended as soon as pure-fluid models became available and it currently comprises approximately 150 substances.

The basic idea of the corresponding states method is that thermophysical properties of different fluids are similar when being reduced by means of their critical properties. However, this approximation is only true as long as the investigated fluids have similar physical properties. A very simple case is for example a comparison of methane and ethane, for which the corresponding states principle would yield reasonable results. In contrast, the application of this approach to methane and

n-decane or methane and methanol yields rather inaccurate or even unreasonable results because of the different chain lengths and the significantly different physical behavior of the alcohol due to its associative characteristics. This issue can be at least partially mitigated if not only the critical parameters are considered.

The extended corresponding states method used for the calculations in the present work [17, 18] is based on the one-fluid extended corresponding states model published by Ely and Hanley in 1981 [22]. It consists of two main parts, the dilute gas and the residual contributions. The dilute gas part is calculated according to the previously discussed approach. However, in case that reference equations for pure-fluid viscosity models are available, the dilute gas contributions of these models are applied instead of the generalized approach of Chung et al. [11, 12]. The corresponding states principle relates the residual part of the pure fluid or mixture of interest to a well-known reference fluid (e.g., nitrogen or propane) by means of the critical parameters, the ratio of the molar masses (both composition-dependent in the case of mixtures), and so-called shape factors. The latter can be interpreted as a measure for the deviation of the investigated fluid from a spherical shape. The shape factors are determined so that the Helmholtz energy a and the compression factor Z of the pure fluid or mixture of interest and the reference fluid are the same at conformal states, cf. Ely [23].

2.2 Friction Theory

In general, friction describes the force resisting the movement of molecules relative to each other. This effect is defined on a microscopic scale and is well-known for centuries. On a macroscopic level, friction can be interpreted as the force hampering the motion of different layers of solid bodies or fluid layers. The friction theory used in this work attributes the viscosity to the shear stress (drag force), the respective velocity, and geometric characteristics of a dense fluid based on Newton's law of viscosity [24, 25]. Therefore, the approach is only valid for Newtonian fluids for which the ratio of shear stress and shear rate is a constant at given temperature and pressure; non-Newtonian fluids depending on the shear rate cannot be described, which also applies to the other two models discussed in this work. Quiñones-Cisneros et al. [15] introduced a mathematical approach for the calculation of viscosities of pure fluids in the gaseous and the liquid state. The basic idea is that the residual shear stress (overall shear stress minus the dilute gas collision term) can be separated into an attractive and a repulsive contribution. This classification is in line with the definition of the pressure being the sum of attractive and repulsive forces according to van der Waals [26]. Thus, the residual shear stress contributions are postulated to be analytical functions of the corresponding pressure contributions. There are different approaches available in the literature for the calculation of these analytical functions, e.g., linear or quadratic models, in conjunction with various equations of state with explicit distribution into attractive and repulsive parts (e.g., Peng-Robinson [27], Soave-Redlich-Kwong [28, 29], or PCP-SAFT [30–32] equations of state). Using suitable mixing rules for the analytical functions, the viscosity can be calculated not only for pure substances but also for fluid mixtures. In the last decades,

various modifications have been published that allow for the calculation of viscosities for a wide range of fluids and their mixtures, e.g., [3, 33–37]. However, since the friction theory requires substance-specific parameters, which have to be adjusted to experimental data, all of these modifications are only valid for the specific fluids analyzed in the respective publication. Moreover, the results of the friction theory are very sensitive to the underlying thermodynamic equation of state. The comprehensive calculation of the mixtures investigated in the present work is carried out with the approach of Quiñones-Cisneros et al. [38] with the Peng-Robinson equation [27] as basic function (labeled as FT in the following), because it includes parameters for methane, ethane, etc., up to long-chain hydrocarbons, and carbon dioxide. Since the simple cubic equations of state are known to exhibit shortcomings in the dense fluid region, Quiñones-Cisneros et al. [38] applied an empirical correction to the repulsive part of the Peng-Robinson equation [27] for a more accurate prediction of the compressibility in this region, especially for heavy hydrocarbons.

2.3 Entropy Scaling

The origin of the entropy scaling approach dates back to Rosenfeld's finding in 1977 [39] that transport properties such as the viscosity or thermal conductivity approximately exhibit a linear function of the residual entropy of a fluid when being scaled with a suitable reference value for the respective transport property. After this approach had received little attention for some time, Rosenfeld took up his idea again about 20 years later and proposed a scaling law for atomic transport in simple fluids [40]. However, practical application and more extensive research are only taking place in recent years. A very detailed summary of the theoretical background and mathematical relations of entropy scaling with respect to viscosity predictions was recently published by Dyre [41] and is, therefore, not repeated here. For the calculation of viscosities of real fluids, this approach was primarily used in connection with semi-empirical equations such as the PCP-SAFT [42–44] or the CPA [45] equation of state. After introducing a modified approach with a dimensionless residual entropy per unit volume as the independent scaling variable and a suitable choice of a reference fluid for refrigerants [46], the approach was first applied to model fluids in conjunction with accurate Helmholtz-energy equations of state [47]. Subsequently, comprehensive studies on pure hydrocarbons were carried out by Bell [48, 49]. First results for the calculation of viscosities in conjunction with Helmholtz-energy mixture equations of state were recently published by Binti Mohd Taib and Trusler [50], Mairhofer [51], and Yang et al. [52]. With respect to the fluids investigated in the present work, Binti Mohd Taib and Trusler [50] only published parameters for the carbon dioxide + *n*-decane system. The model proposed by Mairhofer [42] covers the 21 components of the GERG-2008 [53], and is, thus, applied for the evaluations in the present work. Yang et al. [52] focused on the representation of refrigerant mixtures. In contrast to Mairhofer [42], who applied the scaling as proposed by Novak [54], Yang et al. [52] used the plus-scaled reduced residual viscosity according to Bell [48]. Results with respect to the correlation of

Yang et al. [52] are presented here for systems in which the fluid-specific scaling factor is available for each component.

3 Representation of Experimental Data

In this work, a series of methane and carbon dioxide mixtures with other hydrocarbons is investigated in order to evaluate the performance of the previously described viscosity models with respect to increasing asymmetry. All models are applied according to the implementation in the software package TREND 5.1 [20]. Some general information on the properties of the involved fluids are listed in Table 1.

There are no parameters for the investigated mixtures available for the entropy scaling approaches in conjunction with accurate Helmholtz-energy equations of state for *n*-dodecane and *n*-hexadecane, cf. Table 1. The models investigated in this work are only valid for mixtures in homogeneous fluid states. Therefore, experimental state points, which are located in the heterogeneous vapor–liquid-equilibrium region are not considered in the evaluation. The determination of the phase boundaries depends on the underlying thermodynamic equation of state, which is different for all models. Since the GERG-2008 equation of state [53] is accepted as the ISO

Table 1 Characteristic properties of the substances investigated in this work taken from the publications of the corresponding reference equations of state for the calculation of thermodynamic properties

Fluid	Abbreviation	CAS No	T_c/K	$M/(g \cdot mol^{-1})$	References	Parameters available for: a: ECS [18] b: sScale [51] c: sScale [52] d: FT [38]
Methane	C ₁	74-82-8	190.564	16.0428	[55]	a, b, d
Ethane	C ₂	74-84-0	305.322	30.06904	[56]	a, b, c, d
Propane	C ₃	74-98-6	369.89	44.09562	[57]	a, b, c, d
<i>n</i> -Butane	C ₄	106-97-8	425.125	58.1222	[58]	a, b, c, d
<i>n</i> -Pentane*	C ₅	109-66-0	469.7	72.14878	[59]	a, b, c, d
<i>n</i> -Hexane	C ₆	110-54-3	507.82	86.17536	[60]	a, b, c, d
<i>n</i> -Heptane	C ₇	142-82-5	540.2	100.202	[61]	a, b, d
<i>n</i> -Octane*	C ₈	111-65-9	568.74	114.229	[62]	a, b, d
<i>n</i> -Nonane	C ₉	111-84-2	594.55	128.2551	[63]	a, b, d
<i>n</i> -Decane	C ₁₀	124-18-5	617.7	142.28168	[63]	a, b, d
<i>n</i> -Dodecane	C ₁₂	112-40-3	658.1	170.33484	[64]	a, d
<i>n</i> -Hexadecane	C ₁₆	544-76-3	722.1	226.441	[65]	a, d
Carbon dioxide	CO ₂	124-38-9	304.1282	44.0098	[66]	a, b, c, d

The last column indicates for which model pure-fluid parameters are available for the application of the investigated viscosity model

ECS extended corresponding states method, sScale entropy scaling approach, FT friction theory

*Component only listed for the sake of completeness. It is not further considered in this work, because no experimental data are available for mixtures of methane or carbon dioxide with this component

standard for the investigated mixtures, the assignment of the state region was made on the basis of this model. Experimental data points, which were found to be located in the heterogeneous region predicted with the GERG-2008 model [53], were not considered for the evaluation of any of these models. Such cases are marked with parentheses in Tables 2 and 3.

3.1 Statistical Evaluation

Compared to thermodynamic state properties, transport properties are studied less intensively. For example, for a well-measured system like methane + ethane there are approximately 3800 experimental data points available for the density and only 490 for the viscosity. This is also evident from the number of measurements for the binary mixtures relevant here. A total of 3351 data points is available for 17 binary mixtures, see Fig. 1. Due to the increasing interest of the industry in natural gas properties, most of the methane mixtures were studied in the 1960 to 1990s. Since then, this area has stagnated. CO₂ mixtures only came into focus in the late 1980s, but the number of available experimental data is still limited. This is particularly surprising in view of the debate about climate change, the associated reduction of CO₂ emissions, and the discussion about large scale CO₂ transport networks.

Average absolute relative deviations of the available experimental data for binary mixtures with methane (Table 2) and carbon dioxide (Table 3) are calculated with the three models according to

$$\text{AARD} = \frac{1}{N} \sum_{i=1}^N \left| 100 \frac{\eta_{\text{DATA}} - \eta_{\text{EOS}}}{\eta_{\text{DATA}}} \right| \quad (2)$$

for each author (cf. Tables 2 and 3) and are summarized for each binary system in Fig. 2. To obtain a fair comparison of the different models, one important aspect should always be kept in mind: The entropy scaling models are so far purely predictive for mixtures, while the other two models (ECS and FT) contain adjusted binary-specific parameters. Thus, there is still considerable potential for improvement, which is subject of ongoing research.

In Fig. 2, a general overview is given about the availability of experimental viscosity data for the binary systems investigated here together with the representation by means of the three different models. There are also some data available for methane + *n*-tetradecane and CO₂ + *n*-tetradecane, but none of the models includes parameters for *n*-tetradecane. Therefore, these data cannot be evaluated here.

In the left panel of Fig. 2, methane mixtures with higher-order hydrocarbons up to *n*-hexadecane are presented. Since methane to propane are the main components of natural gas, these components were more comprehensively studied than mixtures with higher hydrocarbons. In general, the number of data points decreases with increasing hydrocarbon order. This is partly due to the fact that the higher-order hydrocarbons are treated as trace elements in natural gas mixtures. As a result, they are given less importance than the main components. However, this should be treated with caution. Recent density measurements [67, 68] and a new mixture

Table 2 Average absolute relative deviation AARD (%) for the binary mixtures of methane + y

Author	Year	No. pts	No. pts. calc.	T/K	p/MPa	x_{C1}	AARD / %		
							ECS [18]	sScale [51]	FT [38]
y=ethane									
Abe et al. [77]	1978	5	5	298–469	0.101325	0.2639	0.55	10	1.5
		5	5	298–469	0.101325	0.4861	0.64	8.0	1.1
		5	5	298–469	0.101325	0.7518	0.60	5.3	0.51
Overall		15	15	298–469	0.101325	0.26–0.75	0.60	7.8	1.0
Diller et al. [78]	1984	93	93	100–300	1.6–32.1	0.3453	2.6	7.4	6.3
		124	124	100–300	1.5–34.9	0.5022	1.9	7.5	5.5
		109	109	100–300	1.6–32.9	0.6853	1.7	6.1	5.1
Overall		326	326	100–300	1.5–34.9	0.35–0.69	2.0	7.0	5.6
Humberg et al. [79]	2020	41	41	253–474	0.1–2.0	0.2498	0.48	8.6	1.6
		42	42	253–474	0.1–2.0	0.4942	0.70	6.4	1.3
		43	43	253–474	0.1–2.0	0.7512	0.66	4.0	0.73
Overall		126	126	253–474	0.1–2.0	0.25–0.75	0.61	6.3	1.2
Trautz and Sorg [80]	1931	4	4	289–524	0.101325	0.1903	0.73	10	2.2
		4	4	290–524	0.101325	0.2045	0.77	10	2.4
		4	4	287–524	0.101325	0.4874	1.4	7.3	1.8
Overall		4	4	289–524	0.101325	0.5670	1.2	6.2	1.9
		4	4	291–524	0.101325	0.8116	1.3	3.5	1.6
		20	20	287–524	0.101325	0.19–0.81	1.1	7.5	2.0
y=propane									
Abe et al. [77]	1978	5	5	298–469	0.101325	0.2807	0.64	12	2.5
		1	1	468.11	0.101325	0.4885	0.30	9.0	2.4
		4	4	298–419	0.101325	0.5421	0.27	8.5	2.7
Overall		5	5	298–469	0.101325	0.7805	0.21	5.7	1.3

Table 2 (continued)

Author	Year	No. pts	No. pts. calc.	T/K	p/MPa	x_{C1}	AARD / %		
							ECS [18]	sScale [51]	FT [38]
Overall		15	15	298–469	0.101325	0.28–0.78	0.38	8.8	2.1
Bicher and Katz [81]	1943	45	45	298–499	1.8–34.5	0.2	3.0	3.6	2.9
Czubinski et al. [82]	2018	57	57	202–424	2.6–30.4	0.8888	0.44	2.4	4.5
Giddings et al. [83]	1966	72	72	310–411	0.1–55.2	0.2207	1.9	4.7	1.1
		62	62	310–411	0.1–41.4	0.3878	1.9	4.9	2.1
		72	72	310–411	0.1–55.2	0.6139	1.2	3.2	2.1
		76	76	310–411	0.1–55.2	0.7910	1.2	2.4	2.2
Overall		282	282	310–411	0.1–55.2	0.22–0.79	1.5	3.8	1.9
Golubev [84, 85]	1970	60	60	373–524	0.1–60.8	0.2440	7.5	10	8.3
		60	60	373–524	0.1–60.8	0.5360	9.8	12	9.0
		90	90	348–524	0.1–60.8	0.8000	8.5	8.9	5.9
Overall		210	210	293–524	0.1–60.8	0.24–0.80	8.6	10	7.5
Huang et al. [86]	1967	53	(52)	123–311	3.4–34.5	0.7530	3.0	4.1	11
Locke et al. [87]	2014	14	14	280–299	0.6–7.0	0.9452	0.45	1.3	2.7
Stanwix et al. [88]	2015	26	26	199–424	10.4–31.1	0.9490	0.97	4.0	2.6
Trautz and Sorg [80]	1931	4	4	299–524	0.101325	0.1659	1.1	12	2.6
		4	4	297–525	0.101325	0.3616	0.74	10	3.9
		4	4	296–524	0.101325	0.6316	1.6	6.1	3.6
Overall		12	12	296–525	0.101325	0.17–0.63	1.1	9.4	3.5
y=n-butane									
Abe et al. [77]	1978	15	15	298–469	0.101325	0.16–0.74	0.59	8.1	2.8
Carmichael et al. [89]	1967	132	(118)	277–478	0.1–35.8	0.3940	3.9	5.2	2.9
Gozalpour et al. [90]	2005	8	(7)	310.95	<0.1–20.7	0.52–0.85	22	22	7.7

Table 2 (continued)

Author	Year	No. pts	No. pts. calc.	T/K	p/MPa	x_{C1}	AARD / %		
							ECS [18]	sScale [51]	FT [38]
Kestin and Yata [91]	1968	8	8	293–304	0.1–0.2	0.3553	0.31	8.0	4.3
		8	8	293–304	0.1–0.2	0.5421	0.12	6.2	4.8
		10	10	293–304	0.1–0.4	0.6974	0.19	4.7	4.1
		8	8	293–304	0.1–0.7	0.8432	0.64	3.3	2.6
Overall		34	34	293–304	0.1–0.7	0.36–0.84	0.31	5.5	4.0
Locke et al. [92]	2015	58	58	203–424	2.7–30.3	0.9484	1.0	2.4	5.0
y=n-hexane									
Bagzis [93] ^a	1971	4	4	255.93	0.7–8.3	0.06–0.48	8.5	5.7	5.8
Berstad [94]	1989	23	23	295–432	15.0–42.8	0.3590	2.8	7.7	1.5
		15	15	295–432	17.6–40.2	0.4980	3.3	3.3	2.5
		15	(13)	293–452	21.1–40.4	0.7490	9.0	3.9	9.2
Overall		53	(51)	293–452	15.0–42.8	0.36–0.75	4.5	5.4	3.7
y=n-heptane									
Kashefi et al. [95]	2013	28	28	323–474	34.6–138	0.4200	14	15	8.3
Rabe [96] ^b	1981	54	(0)	185–300	<0.1–11.9	0.01–0.78	–	–	–
y=n-nonane									
Bennet [97]	1969	32	(9)	238–299	1.0–8.3	0.05–0.38	15	3.4	11
y=n-decane									
Audonnet and Padua [98]	2004	32	32	303–394	9.8–76.1	0.2270	9.4	12	4.7
		28	28	303–394	20.0–75.6	0.4100	15	20	7.6
		24	24	303–394	24.8–75.2	0.6010	20	6.5	9.4
		20	20	303–394	40.0–75.2	0.7990	30	23	9.4
Overall		104	104	303–394	9.8–76.1	0.23–0.80	17	15	7.5

Table 2 (continued)

Author	Year	No. pts	No. pts. calc.	T/K	p/MPa	x_{C1}	AARD / %			
							ECS [18]	sScale [51]	FT [38]	
Bagzis [93]	1971	29	(1)	255 – 328	0.7–8.3	0.03–0.40	15	12	11	
Canet et al. [99]	2002	60	60	293–374	30.0–140	0.4867	23	21	5.4	
		60	60	293–374	30.0–140	0.6000	22	14	7.9	
		55	55	293–374	40.0–140	0.7567	31	13	6.9	
		55	55	293–374	40.0–140	0.9575	13	4.9	25	
Overall		230	230	293–374	30.0–140	0.49–0.96	22	13	11	
Daugé et al. [100]	2001	65	65	293–374	20.0–140	0.3124	14	17	3.6	
Gozalpour et al. [90] ^e	2005	30	(0)	310.95	<0.1–37.9	0.81–0.95	–	–	–	
Kashefi et al. [95]	2013	34	34	323–474	12.7–138	0.3900	13	25	9.8	
		17	17	294–431	9.8–42.0	0.3124	13	15	9.2	
		28	28	293–430	22.4–41.4	0.5575	15	7.4	10	
		28	(24)	292–430	28.9–41.7	0.6900	21	5.2	7.7	
Knapstad et al. [101]	1990	23	(4)	293–424	37.0–41.1	0.8467	3.0	12	4.2	
		96	(73)	292–431	9.8–42.0	0.31–0.85	16	8.8	8.9	
		35	35	310–411	10.3–34.5	0.3000	18	6.2	19	
		22	22	310–445	19.0–41.4	0.5000	30	11	30	
Overall	1966	14	14	310–411	31.0–48.3	0.7000	49	34	33	
		71	71	310–445	10.3–48.3	0.30–0.70	28	13	25	
y=n-hexadecane										
Klein et al. [103] ^d	2021	18	18	298–574	1.9–5.6	0.10–0.24	78	–	21	
Mohammed et al. [76]	2017	20	20	298–474	10.0–80.1	0.1013	25	–	19	
		24	24	298–474	10.0–80.2	0.2021	55	–	33	
		24	24	298–474	20.1–80.4	0.2976	59	–	44	

Table 2 (continued)

Author	Year	No. pts	No. pts. calc.	T/K	p/MPa	x_{C1}	AARD / %		
							ECS [18]	sScale [51]	FT [38]
Overall		23	23	298–474	13.9–80.2	0.3979	69	–	55
		91	91	298–474	10.0–80.4	0.10–0.40	53	–	38

The third column lists the overall number of state points, which is reported in the corresponding publication. The fourth column lists the number of points, which were considered in the present evaluation. State points not considered in this work are within the two-phase region according to the GERG-2008 [53] and, hence, are not evaluated with the three models. The composition x_{C1} is given in terms of mole fractions. The entropy scaling approach of Yang et al. [52] cannot be evaluated for methane mixtures, see Table 1

^aKinematic viscosities were measured and subsequently converted into dynamic viscosities. The compositions and densities used for the conversion were not measured but calculated from the Racket equation, which is rather inaccurate

^bAll values are located in the vapor–liquid equilibrium state according to the GERG-2008 [53]. However, the prediction of the phase boundaries is not reliable here, see Sect. 4

^cThe aim of the measurements of Gozalpour et al. [90] was to investigate the near-critical region. All measurements, which are stated to be in the homogeneous region, are actually located in the vapor–liquid equilibrium state according to the GERG-2008 [53]. Therefore, they are not considered for the evaluation in the present work. However, this might be a shortcoming of the GERG-2008 [53] rather than the measurements. To clarify the situation, a more detailed analysis and refit of the thermodynamic mixture model is required. The phase equilibrium measurements Gozalpour et al. [90] for the $CO_2 + n$ -decane system are not considered here, either, because no information on the mole fractions of the corresponding phases is given

^dOnly liquid-phase viscosity data are considered because vapor data were not measured but calculated

Table 3 Average absolute relative deviation AARD (%) for the binary mixtures of CO₂ + y

Author	Year	No. pts	No. pts. calc	T/K	p/MPa	x _{CO2}	AARD / %			
							ECS [18]	sScale [51]	sScale [52]	FT [38]
y=methane										
Davani et al. [104]	2013	168	168	310–456	34.5–173	0.1000	26	19	–	18
Jackson [105]	1956	12	12	298.14	0.101325	0.07–0.98	1.1	11	–	5.4
Locke et al. [87]	2014	18	18	280–329	1.5–6.5	0.4300	1.9	2.6	–	6.1
Locke et al. [106]	2015	119	119	229–348	1.4–31.9	0.5174	3.4	2.8	–	7.5
Kestin and Ro [107]	1974	5	5	298–474	0.101325	0.2620	1.2	6.7	–	6.4
		5	5	298–474	0.101325	0.4357	0.74	9.6	–	7.3
		5	5	298–474	0.101325	0.6438	0.33	13	–	6.5
		5	5	298–474	0.101325	0.7877	0.42	16	–	5.0
Overall		20	20	298–474	0.101325	0.26–0.79	0.67	11	–	6.3
Kestin and Yata [91]	1968	8	8	293–304	0.1–2.5	0.3257	0.28	5.7	–	7.0
		8	8	293–304	0.1–2.6	0.4806	0.12	7.7	–	7.1
		8	8	293–304	0.1–2.6	0.6624	0.14	10	–	5.8
		8	8	293–304	0.1–2.6	0.8565	0.13	12	–	3.1
Overall		32	32	293–304	0.1–2.6	0.33–0.86	0.17	8.8	–	5.7
y=ethane										
Abe et al. [108]	1979	5	5	298–469	0.101325	0.3978	1.2	17	3.1	3.6
		5	5	298–469	0.101325	0.7117	0.43	18	2.6	3.8
Overall		10	10	298–469	0.101325	0.40–0.71	0.81	18	2.8	3.7
Diller et al. [109]	1988	64	64	210–320	2.3–36.3	0.2517	7.2	10	7.1	16
		86	86	220–320	2.1–34.8	0.4924	3.9	5.7	4.5	21
		56	56	220–320	2.3–36.8	0.7398	13	9.6	11	5.4
Overall		206	206	210–320	2.1–36.8	0.25–0.74	7.4	8.1	7.0	15

Table 3 (continued)

Author	Year	No. pts	No. pts. calc	T/K	p/MPa	x _{CO2}	AARD / %			
							ECS [18]	sScale [51]	sScale [52]	FT [38]
y=propane										
Abe et al. [108]	1979	2	2	298–334	0.101325	0.2936	1.7	19	3.2	1.1
		3	3	373–469	0.101325	0.4452	1.5	19	3.0	1.3
		5	5	298–469	0.101325	0.6781	1.2	20	3.0	1.8
Overall		10	10	298–469	0.101325	0.29–0.68	1.4	20	3.0	1.5
Trautz and Kurz [110]	1931	4	4	300–551	0.101325	0.1893	0.96	16	0.71	2.0
		4	4	300–551	0.101325	0.4025	0.72	18	1.3	0.87
		4	4	300–551	0.101325	0.5776	0.74	18	1.3	0.55
Overall		4	4	300–551	0.101325	0.7883	0.84	18	0.74	0.41
		16	16	300–551	0.101325	0.19–0.79	0.81	18	1.0	0.95
		y=n-butane								
Abe et al. [108]	1979	12	12	298–469	0.101325	0.40–0.72	3.7	19	7.4	0.48
y=n-hexane										
Kian and Scurto [111]	2018	21	(12)	298–329	1.1–8.1	0.11–0.99	19	12	9	10
Koller et al. [112] ^a	2019	8	(4)	303.15	<0.1	0.07–0.76	2.2	17	14	14
y = n-heptane										
Rabe [96]	1981	53	53	220–300	0.2–5.7	0.02–0.90	9.4	8.9	–	4.0
y=n-decane										
Barrufet et al. [113]	1996	4	4	310–404	7.0	0.1510	4.9	7.4	–	1.7
		4	4	310–404	7.0	0.3010	9.2	11	–	6.1
		4	3	310–404	7.0–11.8	0.5050	14	8.5	–	4.0
Overall		12	11	310–404	7.0–11.8	0.15–0.51	9.0	9.1	–	3.9
Cullick and Mathis [114]	1984	20	(17)	310–404	6.7–34.7	0.1500	5.6	7.9	–	1.9

Table 3 (continued)

Author	Year	No. pts	No. pts. calc	T/K	p/MPa	x_{CO_2}	AARD / %			
							ECS [18]	sScale [51]	sScale [52]	FT [38]
Overall		20	(18)	310–404	6.8–34.5	0.3010	11	12	–	6.3
		17	(16)	311–404	6.9–30.9	0.5050	18	12	–	6.0
		13	13	312–404	8.7–28.0	0.6490	64	55	–	72
		13	13	312–404	8.7–28.0	0.8500	9.8	14	–	12
		83	(77)	310–404	6.7–34.7	0.15–0.85	20	19	–	17
Kariznovi et al. [115]	2013	6	6	323.20	<0.1	0.09–0.51	4.8	5.1	–	5.6
Kian and Scurto [111]	2018	23	23	298–329	1.1–10.1	0.10–0.69	20	21	–	23
Nourozieh et al. [116]	2013	6	6	373.20	1.0–6.6	0.07–0.37	4.1	3.6	–	3.3
y=n-dodecane										
Czubinski et al. [117]	2019	5	5	284–352	1.5–2.5	0.2009	50	–	–	6.7
Overall		5	5	284–351	2.5–5.5	0.4010	78	–	–	4.3
		5	5	284–351	3.7–9.3	0.5999	67	–	–	12
		5	5	283–351	4.6–14.3	0.8000	12	–	–	15
		20	20	283–352	1.5–14.3	0.20–0.80	52	–	–	9.7
		27	27	298–574	0.8–4.9	0.05–0.22	47	–	–	9.2
y=n-hexadecane										
Klein et al. [103] ^a	2021	25	25	298–424	10.4–102	0.0690	23	–	–	5.4
Mohammed et al. [76]		28	28	298–474	10.4–121	0.5877	47	–	–	22
Overall		29	29	298–474	21.2–121	0.7270	54	–	–	24
	2017	82	82	298–474	10.4–121	0.07–0.73	42	–	–	18

The third column lists the overall number of state points, which is reported in the corresponding publication. The fourth column lists the number of points, which were considered in the present evaluation. State points not considered in this work are within the two-phase region according to the GERG-2008 [53] and, hence, are not evaluated with the three models. The composition x_{CO_2} is given in terms of mole fractions

^aOnly liquid-phase viscosity data are considered because vapor data were not measured but calculated

Fig. 1 Number of available experimental data for the methane + y and CO₂ + y systems plotted against the year they were published

Fig. 2 Graphical overview of the representation of experimental viscosity data with the four different viscosity models. The AARD is summarized per binary mixture and the number of data are listed at the top of each plot

model for calculating thermodynamic properties [69], in particular for liquefied natural gas mixtures, showed that trace elements can certainly have a significant impact depending on the location in the fluid state region. On the other hand, measurements become more challenging with increasing asymmetry of the binary system. One of the reasons is that the shape of the vapor–liquid phase boundary can change significantly with only small variation in composition, i.e., the state region of interest becomes not easily accessible with a typical experimental setup and its limited possibilities of sample handling. This may directly impact the uncertainty in measurement since a subtle change of the sample composition due to mistaken sample handling will distort the measurement result. Thus, maintaining the well-known sample composition within highly accurate synthetic experiments is crucial, which is, however, a challenging task (particularly for sample liquefaction) as shown in many of our experimental studies [67, 70–75].

It is striking that a large amount of experimental data is available for the methane + *n*-decane mixture. This binary mixture is considered as a model for gas-condensate fluids in the literature since it presents dew and bubble points up to high pressures at room temperature. Moreover, *n*-decane is the highest hydrocarbon with a reliable Helmholtz equation of state and, concurrently, is a component of the most comprehensive and accurate mixture model in the literature [53]. For alkanes with longer chain length (e.g., *n*-hexadecane), there are accurate Helmholtz energy equations available, but they are not part of dedicated mixture models. With this, methane + *n*-decane is a suitable system for investigations on asymmetric mixtures not only with respect to viscosity but also other thermophysical properties. Therefore, a remarkable amount of thermophysical measurements is available in the literature.

The number of data points for the CO₂ + hydrocarbon mixtures is shown in the right panel of Fig. 2. The same trends can be observed as for the methane mixtures, except that the overall number of data are less for each system. This is because CO₂ is an undesirable minor component of natural gases and, therefore, plays a subordinate role in these mixtures. This might be different for CO₂ + refrigerants mixtures, which are not part of the present study.

The representation of all binary mixture data by means of the ECS model [18], the two entropy scaling approaches [51, 52], and the friction theory [38] is displayed as bar charts in Fig. 2. For the methane mixtures, a clear trend is visible. The representation of the experimental data becomes worse with increasing asymmetry of the mixture. Again, there are two reasons for this behavior. Most models work quite well as long as the involved components are physically similar. This prerequisite is most important for the ECS model [18], since it is directly related to the corresponding states principle, which is known to work reliably only for similar fluids. The entropy scaling approaches [51, 52] also have their limitations with respect to asymmetric mixtures [76]. In case of the friction theory [38], the same trend occurs, but it is less pronounced than for the other models. The reason for this is that the approach of Quiñones-Cisneros et al. [38] has been optimized primarily for the calculation of reservoir fluids and, thus, for heavy and long-chain fluids.

With regard to the different models, there are no significant differences in the AARD for the methane mixtures up to hexane. The ECS model [18] is slightly superior, followed by the friction theory [38] and the entropy scaling approach [51]. This trend reverses with increasing asymmetry so that the friction theory [38] becomes the model showing best representation of the experimental data. The representation of the CO₂ mixtures is more diffuse. In general, the friction theory [38] seems to be superior to the other models. Furthermore, the entropy scaling approach of Mairhofer [51] exhibits significant shortcomings for the CO₂ + propane and CO₂ + *n*-butane mixtures. Possible shortcomings of the representation of certain mixtures were already reported by Mairhofer [51]. However, it was not possible to identify a systematic reason for this effect. Therefore, the entropy scaling approach of Yang et al. [52] is used for comparison here. In contrast to Mairhofer [51], Yang et al. [52] apply a different reference viscosity as scaling factor. Equation parameters are only available for CO₂ mixtures including ethane, propane, *n*-butane, and *n*-hexane. This approach yields better results for

all mixtures, but still exhibits slight shortcomings, e.g., for the $\text{CO}_2 + n$ -butane mixture.

3.2 Analysis of Selected Binary Mixtures

In Sect. 3.1, a general overview about the representation of all binary mixtures of methane and CO_2 with hydrocarbons is presented. In this analysis, all datasets were summarized per mixture without taking into account the quality of the measurement data, different compositions, or the location of the state points in the homogeneous fluid region. Therefore, a more detailed analysis of exemplary mixtures is carried out in this section.

In a first step, the AARD of each dataset calculated with the three different models is evaluated for the binary systems for which more than two datasets are available, i.e., methane mixtures containing ethane, propane, n -butane, or n -decane (cf. Table 2) and CO_2 mixtures with methane or n -decane.

In Fig. 3, the overall AARDs of the available experimental datasets (named by author and year of publication) are illustrated for the four methane mixtures. Here, the colored areas show how well the three approaches can reproduce the experimental data. The trend, which was already noticed in the bar charts (Fig. 2), is confirmed here.

Fig. 3 Comparison of the AARDs of the mixtures methane + ethane (top left), methane + propane (bottom left), methane + n -butane (top right), and methane + n -decane (bottom right)

The most symmetric system is methane+ethane, which is represented best by the ECS model [18] (blue surface), followed by the friction theory [38] (yellow surface) and the entropy scaling [51] (red surface). Moreover, first impression of the quality of the data can be gained. The ECS model [18] reproduces all data with AARDs of less than 2 %. Therefore, the comparatively large deviations of the friction theory [38] with respect to the data of Diller et al. [78] and of the entropy scaling [51] with respect to all measurements are not related to the quality of the data but subject to the viscosity models. The deflection of the area of the friction theory [38] with respect to the data of Diller et al. [78] is very striking. When comparing to the other measurements, the temperature and composition ranges are similar, but the pressure range is significantly larger. This initially indicates that the large deviations are related to the high-pressure data, which will be discussed in more detail in the next section. The analysis of the second mixture (methane+propane) is no longer as conclusive as for the first one. The maximum AARDs are generally larger and the entropy scaling approach [51] exhibits the worst representation of the data. The ECS model [18] still seems to be the most appropriate one but exhibits larger AARDs than the friction theory [38] with respect to the data of Golubev [84, 85] and Bicher and Katz [81]. On the other hand, large deviations can be observed for the representation of the measurements of Huang et al. [86] and Czubinski et al. [82] with respect to the friction theory [38], whereas the ECS model [18] is significantly more appropriate. Comparing the corresponding temperature, pressure, and composition ranges does not reveal a definitive causality. The same impression results from the analysis of the methane + *n*-butane mixture, whereby the areas of the ECS model [18] and the friction theory [38] are approximately equal. However, also in this case, individual series of measurements are reproduced significantly different with both models. The methane + *n*-decane mixture gives a completely different impression than the previous ones. Except for the data of Kashefi et al. [95] and Daugé et al. [100], the AARD calculated with the ECS model [18] is significantly larger than the AARDs with respect to the friction theory [38] and the entropy scaling approach [51]. This was expected due to the underlying concept; the approach of corresponding states only works reliably for physically similar fluids. With increasing asymmetry of the mixture, the quality of the results becomes worse. The friction theory [38] is the most suitable model for this mixture, which is due to the focus on long-chain hydrocarbons during the development of the model (cf. Section 3.1).

CO₂ mixtures were less comprehensively investigated. Therefore, only for CO₂ + methane and CO₂ + *n*-decane more than two datasets are available. The corresponding spider plots are shown in Fig. 4. The CO₂ + methane mixture is best represented with the ECS model [18] except for the data of Locke et al. [106] and Davani et al. [104]. However, the AARDs of the latter dataset calculated with all three models (18 % to 26 %) is significantly higher than for all other datasets (maximum AARD=11 %). Therefore, the dataset of Davani et al. [104] is suspect to be less accurate than the remaining data. However, the maximum pressure of $p=173$ MPa is significantly higher than of the other datasets ($p_{\max}=32$ MPa [106]). Therefore, the large AARDs might also be subject to an incorrect behavior of the models in the high-pressure region. Except for the datasets of Locke et al. [87, 106], the friction theory [38] reproduces the experimental data better than the entropy scaling

Fig. 4 Comparison of the AARDs of the mixtures CO₂ + methane (left) and CO₂ + *n*-decane (right)

approach [51]. The plot for the CO₂ + *n*-decane mixture shows that the size of the three areas is approximately the same. Therefore, none of the models can be favored here. However, considering the illustrated AARD ranges, differences between the three models are rather small except for the dataset of Barrufet et al. [113] (friction theory [38]: 3.9 %, ECS [18]: 9.0 %, entropy scaling [51]: 9.1 %).

3.2.1 Methane + Ethane

In case of the methane + ethane system, the most interesting dataset is the one of Diller et al. [78], because the viscosity models calculate significantly different AARDs. In Sect. 3.2, issues are presumed in the high-pressure region for the friction theory [38]. Therefore, percentage deviations of experimental data with respect to the three models are presented as function of pressure, temperature, and composition in Fig. 5. In the top, right panel, deviations are within less than 3 % up to a pressure of approximately 2 MPa and increase up to more than 10 % with increasing pressure. This confirms the first assumption. However, in the lower pressure region, there are only pressure-dependent data of Humberg et al. [79] available, whereas the higher pressure region was only investigated by Diller et al. [78]. Therefore, it is difficult to assess if this effect is a problem related to the data or the model. When comparing to the ECS model [18] (top left panel), one may suspect an issue in the friction theory [38] because the data of Diller et al. [78] are significantly better reproduced by the ECS model [18]. Nevertheless, also this figure shows significant scatter of the data. The center, right panel shows a clear temperature-dependent trend. At a temperature of approximately 300 K, deviations with respect to the data of Diller et al. [78] are higher than with respect to the data of Humberg et al. [79], but they are equally distributed around the zero line. Deviations increase with decreasing temperature and exhibit an s-shaped trend in the deviation plot. A more distinct trend can be observed for the entropy scaling approach [51]. Even the ECS model [18] exhibits elevated deviations at very low temperatures. This effect becomes more distinct with decreasing content of methane in the mixture and is exemplary presented in Fig. 6. The distribution of the experimental measurements on the fluid surface is shown on a p, T plane for the three available compositions. The different colors indicate the

Fig. 5 Percentage deviations of experimental viscosity data for the methane+ethane system from values calculated with the ECS model [18] (left), entropy scaling approach [51] (center), and friction theory [38] (right) as function of the pressure (top), temperature (center), and composition in terms of the mole fraction of methane (bottom)

Fig. 6 p - T -diagram for the binary system methane+ethane presenting the percentage deviation of the experimental data of Diller et al. [78] calculated with the ECS model [18] by means of different colors (Color figure online)

percentage deviation of these state points [78] from the ECS model [18]. The overall view of this figure shows that the highest deviations occur in the low-temperature range and decreasing methane concentration.

However, since there are no other measurements available, these findings indicate either shortcomings of the three viscosity models in the cryogenic liquid region or increasing uncertainties in the measurements with decreasing temperature. A clear statement can only be made with additional measurements.

3.2.2 Methane + Propane

In Fig. 7, percentage deviations of the three models from the experimental viscosity data for the methane+propane system are illustrated. The only clear trend, which is in common for all models, is the increasing deviation of the data of Golubev [84, 85] with increasing pressure. Furthermore, the percentage deviation of the data of Huang et al. [86] is represented differently by the three

models in the low-temperature region. In general, percentage deviations increase with decreasing temperatures. However, the ECS model [18] exhibits positive deviations, whereas the other two models deviate negatively.

3.2.3 Methane + *n*-Butane and Methane + *n*-Decane

In Figs. 8 and 9, percentage deviations of the three models from the experimental data of the binary systems methane + *n*-butane and methane + *n*-decane are illustrated. In addition to the aforementioned aspect that the deviations increase with increasing chain length of the second component, they also show that a systematic evaluation of the individual systems is becoming more difficult. Each of the methods represents the available data in a different way. For the methane + *n*-butane system, deviations with respect to the ECS model [18] and the friction theory [38] exhibit a clear temperature-dependent trend, which is not the case for the entropy scaling [51]. On the other hand, this model shows distinct composition-dependent patterns. In the case of methane + *n*-decane, the ECS model [18] reveals shortcomings over the complete temperature, pressure, and composition range with deviations of up to 40 %. Although the friction theory [38] is generally more suitable than the other two, this method also shows temperature, pressure, and slight composition dependencies. More pronounced but opposite trends are obtained with the entropy scaling approach [51].

These different trends make both a comparison among the models and an evaluation of the experimental data very difficult. It is no longer possible to clearly state the preferred model for the individual binary system, since they all exhibit different strengths and weaknesses in different state regions.

3.2.4 CO₂ + Methane and CO₂ + *n*-Decane

The six datasets, which are available for the CO₂ + methane system, are significantly different reproduced by the three models, as illustrated in Fig. 10. The data of Kestin and Yata [91], Jackson [105], and Kestin and Ro [107] were measured over the entire composition range at low pressures and in a limited temperature range.

They are reproduced within 0.4 %, 1.6 %, and 2.5 %, respectively, with the ECS model [18]. Deviations with respect to the friction theory [38] are 8 %, 7.5 %, and 7.9 %, and even up to 19 % when using the entropy scaling approach [51]. This is a clear indicator that the data are accurate and the two models exhibit shortcomings in the low-pressure region. In case of the entropy scaling [51], an additional composition-dependent trend can be observed. The medium pressure range was experimentally investigated by Locke et al. [106] at equimolar composition. Deviations calculated with the ECS model [18] and the entropy scaling approach [51] are within 10 %, whereas the friction theory [38] deviates by up to 16 % at the lowest two isotherms. Finally, there are measurements available at elevated pressures and temperatures. Here, for all models, deviations increase to up to 30 % (entropy scaling [51] and friction theory [38]) and 40 % (ECS [18]) for increasing pressures with a slight temperature dependent trend.

Fig. 7 Percentage deviations of experimental viscosity data for the methane + propane system from values calculated with the ECS model [18] (left), entropy scaling approach [51] (center), and friction theory [38] (right) as function of the pressure (top), temperature (center), and composition in terms of the mole fraction of methane (bottom). Note that the y-axis is separated into a linear scale (white background) and a logarithmic scale (grey shaded area)

Fig. 8 Percentage deviations of experimental viscosity data for the methane + *n*-butane system from values calculated with the ECS model [18] (left), entropy scaling approach [51] (center), and friction theory [38] (right) as function of the pressure (top), temperature (center), and composition in terms of the mole fraction of methane (bottom)

Fig. 9 Percentage deviations of experimental viscosity data for the methane + *n*-decane system from values calculated with the ECS model [18] (left), entropy scaling approach [51] (center), and friction theory [38] (right) as function of the pressure (top), temperature (center), and composition in terms of the mole fraction of methane (bottom)

Fig. 10 Percentage deviations of experimental viscosity data for the $\text{CO}_2 + \text{methane}$ system from values calculated with the ECS model [18] (left), entropy scaling approach [51] (center), and friction theory [38] (right) as function of the pressure (top), temperature (center), and composition in terms of the mole fraction carbon dioxide (bottom)

Fig. 11 Percentage deviations of experimental viscosity data for the $\text{CO}_2 + n\text{-decane}$ system from values calculated with the ECS model [18] (left), entropy scaling approach [51] (center), and friction theory [38] (right) as function of the pressure (top), temperature (center), and composition in terms of the mole fraction carbon dioxide (bottom). Note that the y-axis is separated into a linear scale (white background) and a logarithmic scale (grey shaded area)

In Fig. 11, percentage deviations of the experimental viscosity data for the system $\text{CO}_2 + n$ -decane from values calculated with the three models are shown. The saturated-liquid viscosities of Kariznovi et al. [115] and Nourozieh et al. [116] are represented within 10 %. The data of Barrufet et al. [113] are represented within 10 % (friction theory [38]) and 30 % (ECS [18]) with increasing deviations with increasing CO_2 content in the mixture. For the data of Cullick and Mathis [114] and Kian and Scurto [111], no definite statement can be made which model might be more suitable. In case of the measurements of Cullick and Mathis [114], the composition of $x_{\text{CO}_2} = 65$ mol-% is conspicuous and suggests an error in the measurements. Deviations are greater than 60 %, whereas the remaining data of the same publication are reproduced within 30 % with all models. The measurements of Kian and Scurto [111] exhibit increasing deviations up to 60 % with increasing temperatures for all models.

4 Behavior of the Underlying Thermodynamic Equation of State

In addition to the performance of the actual viscosity models, the underlying thermodynamic equations of state also play an important role. Since it is not the actual subject of the present study, this aspect will not be analyzed comprehensively, but briefly explained on the basis of the GERG-2008 equation of state [53]. There are two crucial aspects, which have to be considered: (1) the prediction of the phase equilibria and (2) the uncertainty in the density calculations. In case of the entropy scaling approach, the accurate calculation of the residual entropy is also essential. However, since this is a model-specific aspect and considering that to date only little is known about this aspect, a more comprehensive analysis is required when analyzing the entropy scaling approach more closely.

4.1 Phase Equilibria

As stated in Sect. 2, the viscosity models discussed in this work are only valid for homogeneous fluid states as well as on the phase boundaries of fluid phase equilibria. Data in heterogeneous regions can no longer be treated as state properties but other aspects such as flow patterns and phase distributions have to be considered. Thus, the precise identification of homogeneous and heterogeneous regions is crucial for the correct calculation of viscosities from mathematical models. In this work, methane and CO_2 mixtures with other hydrocarbons are investigated. The most accurate equation of state available for these systems is the GERG-2008 of Kunz and Wagner [53]. This model was developed in order to accurately calculate thermodynamic properties for natural gases, especially at pipeline conditions and similar mixtures. As a result, methane, ethane and propane have comprehensively been studied experimentally and theoretically as the main components of natural gases, and higher-order hydrocarbons have been considered only as trace elements. This becomes apparent when analyzing the vapor–liquid phase boundary of these

Fig. 12 p - x -diagrams of the binary system $\text{CO}_2 + n\text{-decane}$ at selected temperatures including available experimental data and phase boundaries calculated with the GERG-2008 [53]. The composition x_{CO_2} is given in terms of the mole fraction

systems. In Fig. 12, exemplary p - x -diagrams are shown for the $\text{CO}_2 + n\text{-decane}$ system at selected isotherms. The prediction of the phase boundary with the GERG-2008 [53] is quite reasonable at low temperatures, whereas it deviates significantly at elevated temperatures. At $T=594$ K, the maximum pressure calculated from the equation of state is 14 MPa, whereas the data indicate a maximum pressure of 6 MPa. This also means that increased CO_2 concentrations are still in the two-phase region according to the equation of state (max. $x_{\text{CO}_2}=70$ mol %), although the phase boundary ends at $x_{\text{CO}_2}=45$ mol % according to Inomata et al. [118]. Such misbehavior of the equations of state, therefore, shifts the limits of the applicability of the viscosity equations. One example is the methane + n -heptane system. In Table 2, it is indicated that the entire dataset measured by Rabe [96] is located in the two-phase region and, therefore, cannot be evaluated here. In Fig. 13, p - x -diagrams for two isotherms are presented for which both viscosity data of Rabe [96] and vapor–liquid equilibrium measurements are available. At $T=220$ K, the GERG-2008 model [53] significantly overpredicts the saturation pressures of Chang et al. [119].

Fig. 13 p - x -diagrams of the methane+ n -heptane system at selected temperatures including available experimental data and phase boundaries as calculated with the GERG-2008 and the Lee-Kesler-Plöcker (LKP) equation of state [120, 121] ($k_{ij}=0$). The composition x_{C1} is given in terms of the mole fraction

Fig. 14 Percentage deviations of experimental homogeneous density data for the CO_2 + n -decane system from values calculated with the GERG-2008 [53] (left) and Lee-Kesler-Plöcker equation of state [120, 121] (right) as function of the pressure. $k_{ij}=0$ for the Lee-Kesler-Plöcker [120, 121] equation of state. Note that the y-axis is separated into a linear scale (white background) and a logarithmic scale (grey shaded area)

In order to get an idea of the influence of different equations of state, the Lee-Kesler-Plöcker (LKP) equation of state [120, 121] is shown for comparison. This model underpredicts the experimental data, and at pressures of $p > 5$ MPa the data of Rabe [96] are located in the homogeneous liquid state. At $T = 276$ K, the performance of both models is much better, but the GERG-2008 still

overpredicts the data of Reamer et al. [122], whereas the LKP equation [120, 121] calculates too low bubble-point pressures. However, when comparing the measurements of Rabe [96] with the experimental vapor–liquid equilibrium data [119, 122], they still seem to be located in the two-phase region. Therefore, they could not be evaluated with the present viscosity models even if the underlying thermodynamic equation of state would be more precise.

4.2 Homogeneous Density

According to Eq. 1, viscosity models are functions of temperature, density, and composition of the respective mixture. Therefore, accurate knowledge of the density is required in order to calculate reasonable viscosity data. As an example, the same mixtures as in the previous section will be analyzed here. However, it should be kept in mind that the performance of the thermodynamic models is significantly different for different binary mixtures. Therefore, such an analysis should actually be made for each mixture.

The illustration of the phase boundary data in Fig. 13 could lead to the assumption that instead of the GERG-2008 equation [53], the LKP equation [120, 121] should be used as the basic equation. However, this is a deceptive conclusion when evaluating the homogeneous density. The GERG-2008 equation [53] represented the available data better than the LKP equation [120, 121] although both models exhibit significantly larger deviations with respect to the data of Polikhronidi and Batyrova [123], cf. Fig. 14. The extent to which these density differences influence the results of the viscosity models has not yet been investigated and should, therefore, play a central role in further research.

4.3 Application of Different Thermodynamic Equations of State to the Entropy Scaling Approach

In this section a short case study on the impact of the equation of state on the results of the entropy scaling model is carried out. For this purpose, the most recent and most predictive viscosity model of Yang et al. [52] is used. The $\text{CO}_2 + n$ -decane system was chosen as a representative asymmetric mixture. The model is purely predictive except for a fluid-specific scaling factor ξ . In the original publication, $\xi_{\text{CO}_2} = 1.0215$ is given. For n -decane, there is no parameter given. Therefore, it has been adjusted here to best represent the investigated binary mixture with the corresponding equation of state. The equations of state, which are tested here are the GERG-2008 equation [53], the Lee–Kesler–Plöcker (LKP) equation [120, 121], the Peng–Robinson (PR) equation [27, 124], the PCP-SAFT equation [30, 31], and the Soave–Redlich–Kwong (SRK) equation [28, 29] as implemented in the software package TREND 5.1 [20]. In Fig. 15, comparisons of the AARDs for each dataset of the mixture $\text{CO}_2 + n$ -decane are presented. Results with respect to the entropy scaling approach of Mairhofer [51] are shown for comparison. The PCP-SAFT [30, 31] and the LKP [120, 121] equations are clearly inferior to the other models. The

Fig. 15 Representation of the AARDs of the viscosity data of the mixture $\text{CO}_2 + n$ -decane. The underlying thermodynamic equation of state as well as the adjusted fluid-specific scaling factor for n -decane ξ_{C10} are listed in the legend. Results with respect to the entropy scaling approach of Mairhofer [51] are shown for comparison. For the cubic equations, the LKP, and the PCP-SAFT equation, the mixing parameter $k_{ij}=0$ is applied

PR [27, 124] and SRK [28, 29] are better, but still exhibit increased deviations with respect to, e.g., the data of Kariznovi et al. [115]. The best representation of all experimental viscosity data is achieved with the GERG-2008 [53] as the basic equation of state. This is not very surprising, since other than the remaining models, the GERG-2008 equation [53] was not only adjusted to thermal but also caloric properties such as the speed of sound or isobaric heat capacity if available. Therefore, the prediction of the residual entropy is expected to be more accurate than for the other models. However, this needs to be analyzed more closely.

5 Conclusion

In this paper, a comprehensive analysis of the performance of three models for calculating viscosities of mixtures is presented. It is shown that the amount of available experimental data is rather limited and that there are significant differences in terms of accuracy. The data situation becomes worse with increasing asymmetry of the mixture. On the one hand, this is a consequence of the research focus in the last decades. Many datasets are more than 30 years old and focused on the main components of natural gas due to the interest of the natural gas industry. On the other hand, the measurement of binary mixtures with increasing degree of asymmetry is a major challenge in the laboratory. In line with the experimental data, a similar trend can be observed in the available mixture models.

In contrast to thermodynamic equations of state, there are no binary-specific functions for viscosities for dedicated systems that cover the entire state region. Instead, these data are calculated using generalized models such as the extended corresponding states principle [18], the friction theory [38], or the entropy scaling [51, 52]. Due to its nature, the extended corresponding states principle [18] performs quite well for mixtures comprising physically similar components, whereas it is not suitable for mixtures of increased asymmetry. The friction theory [38] reveals first

promising results. However, for mixtures it is so far limited to a combination with simple cubic (cf., Quiñones-Cisneros et al. [38]) or semi-empirical equations of state (cf., Czubinski et al. [4]). The application of highly accurate Helmholtz equations of state requires a separation into attractive and repulsive contributions according to the principle of the van der Waals equation of state. A first successful approach in this direction was recently presented by Quiñones-Cisneros et al. [125]. Although the idea of the residual entropy scaling method already dates back to the 1970s [39], this approach has only been taken up again in recent years. Even the application to pure substances has not yet been fully researched, so that the application to mixtures is still in its early stage. At this point we would like to point out again that the entropy scaling models for mixtures are purely predictive, but the other two models studied here contain adjusted binary-specific parameters. This should be kept in mind when evaluating the three models.

Finally, it was shown that the corresponding thermodynamic equation of state is of major importance. It is applied to determine the phase boundary, which defines the range of validity of the viscosity models. Furthermore, it is used to calculate the density (and in case of entropy scaling also the residual entropy), which is an input parameter of the model. Even the most accurate mixture model so far, the GERG-2008 equation [53], is restricted to molecules not larger than *n*-decane and already exhibits significant shortcomings with increasing asymmetry of the mixture. Thus, not only the viscosity models but also the corresponding thermodynamic equations of state need to be improved. The investigation of asymmetric mixtures should, therefore, be addressed more intensively in the future, both in the experimental and in the modeling area, whereby thermodynamic and transport properties are of equivalent relevance.

Compared to the viscosity studied here, the description of thermal conductivity in terms of both measurements and modeling is even worse. At least the modeling of this property is partly transferable from modeling of viscosity. Therefore, the thermal conductivity should also be addressed more thoroughly in future research projects.

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