Thermophysical Property Modeling of Lubricant Oils and Their Mixtures with Refrigerants Using a Minimal Set of Experimental Data

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ABSTRACT: Lubricant oils are used in many technical applications, e.g., in automotive, refrigeration technology, and many other industries. Reliable knowledge of thermophysical properties of such oils is essential, but modeling all of the important properties, including density, phase behavior, heat capacity, entropy, enthalpy, viscosity, and thermal conductivity, remains a key challenge today. To tackle this challenge, we propose a novel modeling approach based on treating the lubricant oil as a quasi-pure fluid, setting up a simple set of equations for all of the important properties of the oil, and developing a parameter fitting procedure using a minimal set of experimental data. This simple model set includes the Patel−Teja−Valderrama cubic equation of state, a simple expression for the ideal gas isobaric heat capacity as a linear function of temperature and residual entropy scaling for viscosity and thermal conductivity. To fit some of the parameters in this model set, two extra models are required: Raoult's law of boiling point elevation and the modified Rackett equation. As a result, fewer than 20 (at least 12) experimental points are needed to fit all 15 parameters of a pure or quasi-pure component, and one experimental mixture bubble-point pressure is required to enable a binary system prediction. For pure or quasi-pure components, in the liquid phase and not in the vicinity of the critical point, this modeling approach has an uncertainty over large temperature and pressure ranges of less than 7% for viscosity and less than 3% for all other properties. For binary mixtures, except for viscosity, the modeling approach still yields good predictions for all other properties, typically within 8%.
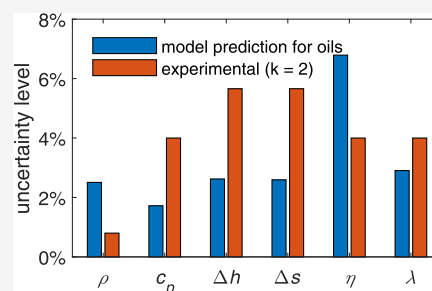
1. INTRODUCTION

A lubricant oil reduces the friction and heat generated when two contacting surfaces move over each other. In each year, tens of million tons of lubricants are consumed worldwide[1] in automotive (in internal combustion engines), energy (e.g., in compressors in systems based on thermodynamic cycles, such as refrigeration machines and heat pumps), and many other industries. Reliable knowledge of thermophysical properties of lubricants is essential, for example, to investigate the thermoeconomic performance of a thermodynamic cycle (chillers, heat pump, Rankine cycle, etc.) when the working fluid is mixed with lubricant oil. However, lubricants are generally composed of a base oil and a variety of additives to impart desirable characteristics. The components and composition of a lubricant are difficult to determine accurately, often not specified by the manufacturers, and treated as trade secrets. Traditional accurate thermophysical property modeling approaches such as multiparameter equations of state (EoS) cannot be used for lubricant oils because these approaches are generally developed for pure fluids or mixtures with known components and composition.

Fluid thermophysical properties required in the analysis of a thermodynamic cycle include mainly density, phase behavior, heat capacity, entropy, enthalpy, viscosity, and thermal conductivity. No single model can consider all of these

properties simultaneously. Instead, a set of thermodynamic and transport property models is needed. Typically, an EoS is necessary for the description of density and phase behavior, and together with an equation for the ideal gas isobaric heat capacity $c_p^o(T)$, heat capacity, entropy, and enthalpy can be calculated. Here, a reference state, e.g., entropy and enthalpy are both zero at $T = 298$ K and $p = 0.1$ MPa, should be given for the entropy and enthalpy calculation. Then, additional models are required for the calculation of the viscosity and thermal conductivity. Today, however, there is no such model set to rely on for oils. The existing models, e.g., see refs 2−4 for oils, are generally empirical equations for each property (mainly density and viscosity) fitted to experimental data; these equations are usually independent of each other, which leads to thermodynamic inconsistencies. Moreover, entropy and enthalpy are hard to measure accurately, and thus, there are barely any empirical equations for both properties. In this context, calculations of all of the needed thermophysical

properties of lubricants and lubricant + working fluid mixtures remain a challenge, where the working fluid is typically a pure refrigerant or refrigerant blend.

To tackle this challenge, we propose a novel modeling approach for all of the important thermophysical properties of lubricants and their mixtures with other fluids. In this approach, a lubricant oil is considered as a quasi-pure fluid; a model set with high thermodynamic consistency is created, and a parameter fitting procedure is developed to fit the oil's parameters (e.g., critical temperature, critical pressure, acentric factor, etc.) using a minimal set of experimental data. Section 2 describes how this modeling approach was developed in a feasibility study using well-studied pure fluids. In Section 3, applying this modeling approach to real lubricants and their mixtures with other fluids is described. This overall endeavor is part of subproject 3 within the KETEC (Research Platform Refrigeration and Energy Technology) project.[5] One important goal within subproject 3 of the KETEC project is to model thermophysical properties of lubricant + refrigerant mixtures.

2. FEASIBILITY STUDY

2.1. Model Set and Parameters. For the calculation of all thermophysical properties of a quasi-pure oil needed in the analysis of a thermodynamic cycle, an initial model set was chosen. It included a generalized three-parameter cubic equation of state (cubic EoS), a correlation of the ideal gas isobaric heat capacity as a linear function of temperature (linear $c_p^{\,o}(T)$), as well as residual entropy scaling for viscosity (RES-μ) and thermal conductivity (RES-λ). When a specific lubricant oil is considered, two extra models are required to fit the model parameters: Raoult's law of boiling point elevation (RBPE) and the modified Rackett equation (mRE). All of these models, which are more or less "textbook" knowledge, are described in as much detail as necessary in Section S1 and Table S1 in the Supporting Information (SI). Here, only the key information and parameter fitting procedures are presented. Please note that this model set can be easily extended for mixtures using mixing rules presented in Section S1 of the SI.

According to the model set described in Section S1, all parameters of a quasi-pure lubricant oil to be determined include molar mass M, critical temperature T_c, critical density ρ_c, critical pressure p_c, acentric factor ω, two parameters k_0, k_1 in the linear $c_p^{\,o}(T)$, Lennard-Jones (L-J) pair potential parameters ε/k_B and σ, RES fitted parameters for viscosity $n_{\mu k}$ ($k = 1-4$) and for thermal conductivity $n_{\lambda k}$ ($k = 1-4$), and three parameters for the critical enhancement of thermal conductivity (φ_0, Γ, q_D). The L–J parameters, ε/k_B and σ, can be estimated according to the predictive correlations of Chung et al.[6]

$$\varepsilon/k_B = T_c/1.2593 \tag{1}$$

$$\sigma^3 = 0.3189/\rho_c \tag{2}$$

A lubricant is normally used at conditions far away from its critical point (lubricants generally have a very high critical temperature and decompose well below the critical temperature), where the critical enhancement is negligibly small. Therefore, the related parameters φ_0, Γ, and q_D have almost no influence and are set as constants being the average values of the well-studied fluids as listed in Table S2. After reduction, only 15 parameters are needed for a quasi-pure lubricant: M, T_c, ρ_c, p_c, ω, k_0, k_1, $n_{\mu k}$, $n_{\lambda k}$ ($k = 1-4$), and mathematically, at

least 15 experimental points are needed to fit these 15 parameters. The exact required number of experimental points will be discussed in Section 2.2.

To investigate a proper parameter fitting procedure using a minimal set of experimental data, a feasibility study using well-studied pure fluids was carried out. Except for those with strong association force (heavy water, water, and ethylene glycol), all pure fluids in NIST's REFPROP database version 10.0[7] as well as in NIST report 8263[8] that have the feature of being in the liquid phase at atmospheric pressure $p_{atm} = 0.1$ MPa and in the temperature range from $T = 278.15$ to 368.15 K were selected for the feasibility study. These fluids were chosen because most lubricants have similar features, and the experiments required for parameter fitting are in the same $T-p$ range. The names of these fluids are listed in Table 1, and the reference values of their key parameters are listed in Table S2 in the SI. Unless otherwise stated, the fluid names used in this work are the same as used in REFPROP 10.0.[7] The reference values of the key parameters were either obtained directly from or fitted against values calculated using REFPROP 10.0[7] and NIST report 8263.[8]

The feasibility study was carried out by (1) calculating "experimental" values with REFPROP 10.0, (2) adding bias to these calculated values to imitate experimental expanded ($k = 2$) uncertainties U_{exp} (relatively $U_{r,exp} = 0.8, 4.0, 4.0, 4.0\%$ for density, heat capacity, viscosity, and thermal conductivity, respectively, considering commonly used techniques in industry), and then (3) fitting the parameters of each fluid in the model set. The used values (calculated and with bias) for the fitting are listed in Table S3 in the SI. The method to fit each of the 15 parameters is described in the following section.

2.2. Parameter Fitting Procedure. *2.2.1. Molar Mass.* The average molar mass of an unknown substance can be determined using many methods, such as RBPE, freezing point depression, and osmotic pressure. In the present study, the RBPE method was adopted, with which only two weight measurements (masses of the solvent and the solute) and two boiling temperature measurements are needed (see details in Section S1.1). To use the RBPE method, with a chosen solvent and pressure, the boiling point elevation constant K_b, which is essentially independent of the solute, should be determined in advance. Here, we show an example to calculate the value of K_b (with propane as the solvent at $p = 0.8$ MPa) using commonly used reference thermophysical property software packages (such as REFPROP 10.0,[7] TREND 5.0,[19] and CoolProp 6.4.1[20]). A small mass fraction 0.001 of a solute (pure fluid listed in Table 1) with known molar mass M was added to pure propane, and then, the boiling temperatures of the pure propane as well as the solution at $p = 0.8$ MPa were calculated using REFPROP 10.0. With the reversed equations given in Section S1.1, K_b can be calculated, which is averaged around 2028.5 K·g·mol^{-1} with a relative standard deviation of 0.6% among different solutes, as shown in Figure 1.

When calculating K_b, one should note that the solute mass fraction should be low enough (e.g., 0.001) to obtain accurate results. However, given a known K_b and the average molar mass M of a lubricant to be determined, the mass fraction of the solute should be high enough to cause an observable temperature rise but not too high to deviate from Raoult's law. For example, in a test calculation using well-studied fluids as solute, a solute mass fraction of 0.02 was added to pure propane at $p = 0.8$ MPa, and this yielded a boiling temperature increase on the order of 0.1−0.4 K, see Table S4 in the SI.

Table 1. Parameter[a] Values Fitted Using the Method Described in Section 2.2[b]

fluid name and reference EoS[c]	M (g·mol^{-1})	T_c (K)	p_c (MPa)	ω	k_0 (J·mol^{-1}·K^{-1})	k_1 (J·mol^{-1}·K^{-1})	$n_{\mu 1}$	$n_{\mu 2}$	$n_{\mu 3}$	$n_{\mu 4}$	$n_{\lambda 1}$	$n_{\lambda 2}$	$n_{\lambda 3}$	$n_{\lambda 4}$
						Feasibility Study (Fluid Name Used in REFPROP 10.0[7])								
C11[9]	161.472	599.626	1.91151	0.5002	300.491	375.600	0.7588	-0.1034	-0.0713	0.0249	-20.1842	-18.1355	19.1746	-3.0913
C12[10]	176.534	648.600	1.86693	0.5907	325.241	412.668	0.6823	-0.1578	-0.0163	0.0123	-2.0526	-6.9853	4.1266	-0.1362
C1CC6[7]	96.724	597.014	3.29095	0.4967	122.004	285.373	0.5961	-0.2633	0.0767	-0.0028	-4.8213	-9.3343	8.1096	-1.2221
C3CC6[7]	126.130	627.554	2.70892	0.5500	183.812	296.378	0.8899	-0.3857	0.0640	0.0032	7.4444	-6.6589	1.6530	0.1843
CHLOROBENZENE[7]	110.194	634.207	4.35481	0.5632	80.482	160.264	0.4288	-0.2675	0.1236	-0.0146	-1.0928	10.5203	-5.7334	1.0306
D5[11]	365.184	585.905	1.07862	0.4766	578.604	228.578	0.7900	-0.0490	-0.0958	0.0330	-29.3769	-28.3668	26.5537	-3.6224
D6[12]	441.596	584.238	0.90352	0.4733	640.262	406.375	0.9509	-1.0000	0.5643	-0.0852	-43.3474	-43.0384	40.7711	-5.9421
DECANE[13]	139.721	598.967	2.17660	0.4995	251.098	261.253	0.6977	-0.1884	-0.0017	0.0124	-1.5102	-14.0468	10.1974	-1.3268
EBENZENE[14]	109.484	626.140	3.40093	0.5477	128.011	213.615	0.5206	-0.2409	0.0799	-0.0060	0.3192	-9.6529	6.8780	-0.9414
HEPTANE[15]	98.559	555.490	2.74260	0.4359	168.821	214.726	0.4617	-0.2808	0.1426	-0.0171	2.9840	-2.2752	0.0875	0.5433
IOCTANE[7]	111.002	563.858	2.48949	0.4465	180.778	286.674	0.6149	-0.2093	0.0348	0.0058	2.7037	-6.6158	2.5474	0.1347
MD2M[16]	305.654	576.987	1.13215	0.4632	477.173	433.086	0.5797	-0.1324	0.0434	-0.0007	-20.6085	-20.0655	17.4807	-1.9074
MD3M[11]	323.274	580.068	1.10287	0.4677	501.217	348.699	0.6957	-0.0878	-0.0165	0.0111	-30.3204	-30.4374	31.3663	-5.0435
MD4M[11]	398.596	618.482	0.94975	0.5313	618.163	641.426	0.7436	-0.7808	0.4211	-0.0616	-26.4057	-28.8055	23.3771	-2.6708
MDM[16]	239.528	559.399	1.35779	0.4393	372.771	364.268	0.4349	-0.2659	0.1892	-0.0302	-8.2883	-11.7801	8.7561	-0.4791
MILPRF23699[5]	661.761	747.704	0.73515	0.8318	1000.000	2326.379	0.9396	0.2430	-0.2584	0.0419	-43.3165	-47.5001	25.4769	-2.1500
MLINOLEA[17]	262.695	749.399	1.65311	0.8379	500.393	10.000	0.7156	-0.1476	-0.0126	0.0064	-3.2317	-22.4014	12.2857	-1.3655
MLINOLEN[17]	340.012	744.970	1.29090	0.8248	613.192	297.463	0.9999	-0.4703	0.0964	-0.0049	-8.7406	-12.9076	8.3683	-0.8075
MM[18]	166.710	518.908	1.74089	0.3952	266.229	249.738	-0.0789	-0.0103	0.2384	-0.0579	-7.1668	-14.0666	13.1046	-1.8447
MOLEATE[17]	279.454	731.860	1.50777	0.7880	534.900	294.423	0.8629	-0.1530	-0.0437	0.0132	-24.0991	-31.8408	21.9339	-2.8106
MXYLENE[14]	103.415	625.252	3.57413	0.5462	112.185	201.666	0.5838	-0.2058	0.0355	0.0023	-0.0894	-7.8099	5.6943	-0.7443
NONANE[13]	124.871	587.068	2.35995	0.4804	218.245	260.843	0.5725	-0.1733	0.0381	0.0019	4.7669	-3.4447	0.5760	0.4531
OCTANE[7]	114.956	573.140	2.47209	0.4597	203.138	201.256	0.4280	0.1083	-0.1205	0.0289	1.6897	-3.6185	1.6874	0.2159
OXYLENE[14]	110.751	627.855	3.41806	0.5509	130.545	215.252	0.5848	-0.1340	-0.0122	0.0108	-19.5348	5.2963	3.2158	-0.6457
POE5[5]	405.063	720.306	1.19554	0.7567	625.987	813.718	0.9025	0.4444	-0.3793	0.0616	-7.6736	-10.8317	6.2819	-0.2830
POE7[5]	432.996	732.710	1.09032	0.7899	693.482	860.344	0.9806	0.3824	-0.3481	0.0557	-26.7906	-26.6986	18.8246	-2.1150
POE9[5]	492.116	737.175	0.93911	0.8022	844.626	932.849	0.9547	0.4122	-0.3465	0.0540	-31.7243	-33.3708	21.0307	-2.1218
TOLUENE[13]	97.274	588.090	3.66853	0.4825	107.129	181.192	0.6721	-0.2018	-0.0009	0.0129	-2.3820	-9.4034	8.3893	-1.3402
						Applied to Lubricants								
PEB8	640.900	764.871	0.74730	0.9400	200.000	500.000	0.9639	0.2369	-0.2410	0.0362	0.0000	0.0000	0.0000	0.0000
PAG68	200.000	750.688	2.43500	0.7157	286.940	457.802	1.0000	0.1271	-0.2248	0.0433	32.5579	7.6460	-9.3029	1.5942
POE ISO 68	200.000	954.491	3.10480	0.6525	282.703	510.491	0.0000	0.0000	0.0000	0.0000	-16.0310	-0.3803	3.8284	-0.4837
DIDP	446.672	777.691	1.09180	0.8117	649.057	1423.100	0.9893	0.4410	-0.3939	0.0627	0.0000	0.0000	0.0000	0.0000

[a]Parameters: molar mass M, critical temperature T_c, critical pressure p_c, acentric factor ω, two parameters k_0, k_1 in the ideal gas isobaric heat capacity equation, fitted parameters for viscosity $n_{\mu k}$ (k = 1–4) and for thermal conductivity $n_{\lambda k}$ (k = 1–4) in the residual entropy scaling approach. [b]The compressibility factor at the critical point, Z_c is 0.2663 for POE ISO 68 and 0.2563 for all other fluids. [c]For those without a published EoS, REFPROP 10.0[7] is cited.
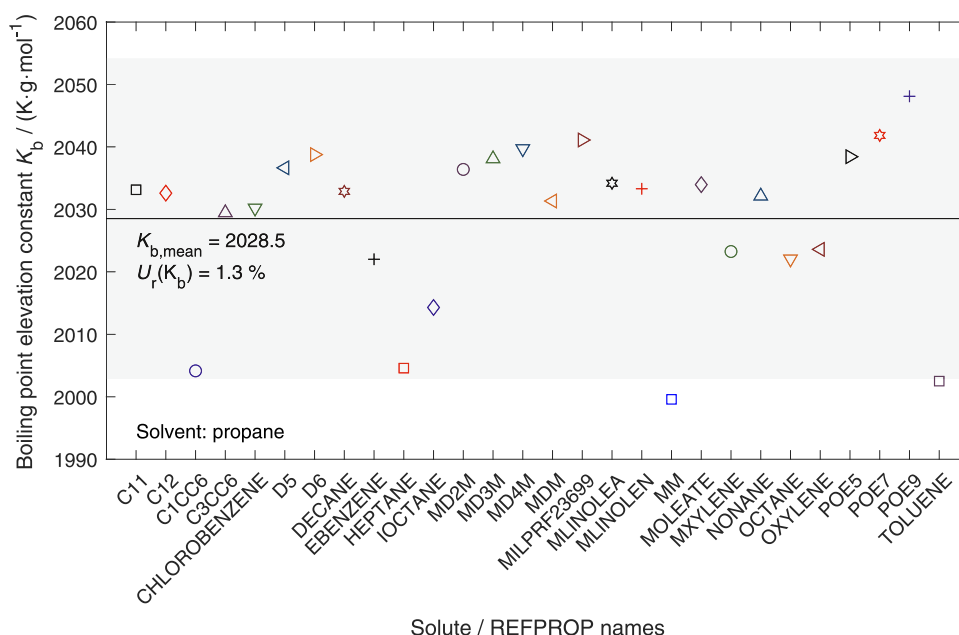
Figure 1. Boiling point elevation constant K_b with pure propane as the solvent at a pressure of 0.8 MPa. $K_{b,mean}$ is the averaged value (solid line) and $U_r(K_b)$ denotes the relative expanded uncertainty ($k = 2$).

With an expanded temperature measurement uncertainty of 0.04 K, the calculated molar masses M (listed in Table 1) typically deviate from reference values on the order of 5%, as shown in Table S4. Increasing pressure (note: K_b changes) will increase temperature elevation and thus yield more accurate values for M. If there is no experimental technique available to determine M, then a roughly estimated value (e.g., 200 g· mol^{-1}) can be given to M. The uncertainty attributed to this could somehow be compensated by the subsequent determination of parameters (e.g., critical pressure and binary interaction parameter; see discussion in Section 3.2).

2.2.2. Critical Point. According to the generalized three-parameter cubic EoS described in Section S1.3, it seems possible to fit T_c, p_c, and ω simultaneously using a few density measurements (p, ρ, T). However, unphysical results, especially those of ω, are always obtained. To overcome this problem, a modified Rackett equation (mRE) is proposed here

$$\rho_{atm} = \rho_c Z_c^{-(1-T/T_c)^{2/7}} \tag{3}$$

where ρ_{atm} is the liquid density at atmospheric pressure, and ρ_c, T_c, and Z_c are density, temperature, and compressibility factor at the critical point, respectively. Instead of ρ_{atm}, the original Rackett equation uses saturated liquid density, which however is very difficult to measure, as saturation pressures of lubricants are very low (typically less than 1.0 Pa absolute).

According to eq 3, ideally, three density measurements at three different temperatures at atmospheric pressure (p_{atm}, T, ρ) are enough to fit the three critical point information: ρ_c, T_c, and Z_c. However, in the feasibility study with the well-studied fluids, the fitted values for Z_c are generally unphysical. Therefore, a fixed value $Z_{c,fix} = 0.2563$ (recommended for esters by Vetere[21]) was given to Z_c, and the fitted ρ_c and T_c (as listed in Table 1) were then reasonable, i.e., not far away from reference values (as listed in Table S2 in the SI). If a more accurate Z_c was given to each of the well-studied pure fluids, the fitted results of ρ_c and T_c would be even better. This implies that in studying lubricants, Z_c does not have to be fixed

at 0.2563 but can be adjusted to yield the best agreement with the experimental ρ_{atm} (see Section 3.3). In the case where Z_c is fixed, two (p_{atm}, T, ρ) points are enough to determine ρ_c and T_c. However, we recommend four (p_{atm}, T, ρ) points in order to yield higher accuracy and to be in line with viscosity and thermal conductivity measurements, as discussed later. At last, the critical pressure p_c can be calculated according to the definition of Z_c and the fitted M, ρ_c, and T_c. Please note that the obtained critical point is not a true value but a pseudo one that works well within the proposed model set.

2.2.3. Acentric Factor. According to the definition of the acentric factor ω, it can be determined by measuring the saturation pressure at $0.7 \cdot T_c$. However, this is difficult to achieve for lubricants, as they most likely decompose before such high temperatures. Alternatively, with critical point information known, the cubic EoS can be adopted to fit ω using the same density measurements (p_{atm}, T, ρ) as in the critical point fitting. Here, we tried six different cubic EoS: Soave−Redlich−Kwong (SRK),[22,23] Peng−Robinson (PR),[24] Peng−Robinson−Stryjek−Vera (PRSV),[25] Wilson−Redlich−Kwong (WRK),[26] Patel−Teja−Valderrama (PTV),[27,28] and Redlich−Kwong (RK),[29] which are all formulated as special forms of the generalized three-parameter cubic EoS. As a result, except for the PTV EoS, all other five EoS generally yield unreasonable values of ω. The key reason for the success of the PTV EoS is that it can be used to calculate liquid density more accurately than the other EoS.[30,31] Therefore, only the PTV EoS was included in the model set and used for further calculations. The fitted results of ω using the PTV EoS are listed in Table 1.

2.2.4. Ideal Gas Properties. With the PTV EoS chosen and the parameters M, T_c, p_c, and ω fitted, the residual properties, such as residual entropy s^r, residual enthalpy h^r, and residual isobaric heat capacity c_p^r, can be calculated, as described in Section S1.3 in the SI. To account for the ideal gas part, a correlation of the ideal gas isobaric heat capacity as a linear function of temperature (linear $c_p^o(T)$), as described in Section S1.4, was adopted. There are only two parameters, k_0 and k_1 in
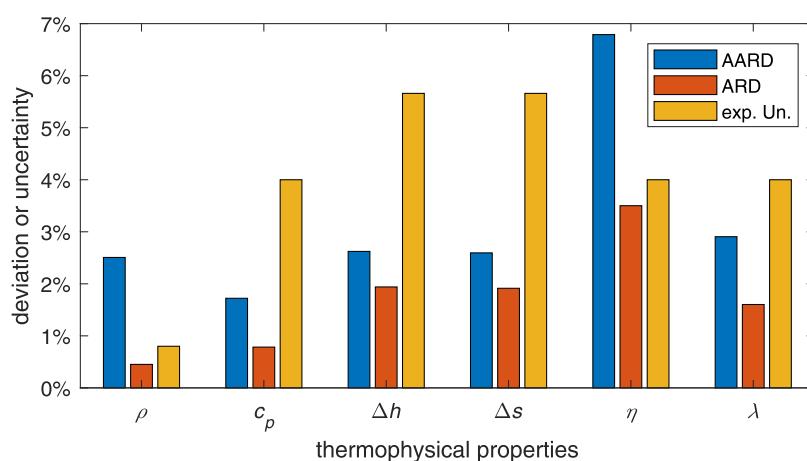
Figure 2. Average of the absolute value of relative deviation (AARD) and average relative deviation (ARD) between the model set and the reference models implemented in REFPROP[7] for the pure fluids listed in Table 1 and typical experimental expanded uncertainty (exp. Un, see Section 2.1). All pure fluids considered in the feasibility study were included in the calculation in the extended temperature (223.15−473.15 K) and pressure (up to 5.0 MPa) ranges.

the linear c_p^o (T), and ideally, two c_p^o measurements at two different temperatures at atmospheric pressure (p_{atm}, T, c_p) are enough to fit these two values. Nonetheless, like the density measurements, four measurements of (p_{atm}, T, c_p) are recommended, and the fitted results of k_0, k_1 are listed in Table 1.

2.2.5. Transport Properties. The RES approach links transport properties to residual entropy s^r using simple equations with a small number of adjustable parameters.[32−34] Many different approaches[35−40] based on RES have been developed in recent years, while, in this work, the approach developed by Yang et al.[41−43] was adopted. The methods are described in detail in Sections S1.5 and S1.6 in the SI for viscosity and thermal conductivity, respectively. Ideally, similar to ref 44, where the RES approach of Yang et al.[41−43] is applied to a thermodynamic cycle analysis, only one extra parameter is needed to calculate viscosity and another one for thermal conductivity. However, this requires that the global fitted parameters $n_{\mu k}$ and $n_{\lambda k}$ (k = 1−4) for lubricants are known in advance, which is not possible. In the feasibility study, even the best guess for the global fitted parameters (those reported for group 6 in the work of Yang et al.[43] for viscosity) does not yield satisfying results. Therefore, the four parameters $n_{\mu k}$ and $n_{\lambda k}$ (k = 1−4) have to be fitted for each lubricant. This requires four viscosity measurements (p_{atm}, T, μ) and four thermal conductivity measurements (p_{atm}, T, λ) at four different temperatures at atmospheric pressure. The fitted results are given in Table 1.

2.2.6. Binary Mixtures. According to all of the mixing rules presented in Sections S1.3−S1.6 in the SI, only one parameter, i.e., the binary interaction parameter k_{ij}, needs to be determined to enable calculations for a binary system. The k_{ij} is a parameter in the van der Waals mixing rule used for the cubic EoS; thus, suitable properties to fit k_{ij} are density and phase behavior. As will be discussed in Section 3.2, bubble-point pressure (a phase behavior property) is much more sensitive to k_{ij} than density. Therefore, ideally, only one experimental bubble-point pressure of a binary system is needed to fit the single unknown parameter k_{ij}. If no experimental bubble-point pressure is available for a binary system, k_{ij} can be set to zero (see Section 3.3). Furthermore, if there are many experimental data of other properties, k_{ij} could

be estimated as a value yielding the best statistical agreement with experiments (see Section 3.1).

In summary, the chosen model set for oils is PTV EoS + linear $c_p^o(T)$ + RES, while two extra models, RBPE and mRE, are needed for the parameter fitting. Some parameters (ε/k_B, σ, φ_0, Γ, q_D) have a negligible impact on the result and are therefore set as constants. All needed parameters of a specific lubricant oil are fitted as follows:

(1) two weight measurements and two boiling temperature measurements for M (might not be needed as M can be a rough-estimated value),

(2) Z_c fixed at a reasonable value (e.g., 0.2563 as recommended by Vetere[21] for esters),

(3) four data points of (p_{atm}, T, ρ) for T_c, p_c, and ω (when the temperature difference is large enough e.g., >80 K, it could be down to two points),

(4) four data points of (p_{atm}, T, c_p) for k_0 and k_1 (when the temperature difference is large enough e.g., >80 K, it could be down to two points),

(5) four data points of (p_{atm}, T, μ) for $n_{\mu k}$ (k = 1−4),

(6) four data points of (p_{atm}, T, λ) for $n_{\lambda k}$ (k = 1−4),

(7) for a binary system: one data point of mixture bubble-point pressure to determine k_{ij}.

Note: The temperature can be in the range of 278.15−368.15 K or in a slightly smaller range; pressure can differ from p_{atm} and does not have to be constant. As a result, less than 20 (at least 12) experimental points are needed to determine the needed parameters for the model set of a quasi-pure oil, and one experimental bubble-point pressure of a binary system is required to enable calculations of all needed properties of a binary system (e.g., an oil + a refrigerant).

2.3. Performance Tests. Using the fitted parameters of the pure fluids listed in Table 1, the prediction capability of the model set was tested by calculating ρ, c_p, μ, and λ in enlarged temperature and pressure ranges 223.15−473.15 K and up to 5.0 MPa and comparing with values calculated from REFPROP 10.0.[7] Here, the entropy increment Δs and enthalpy increment Δh were calculated as well. The results of the comparison are summarized in Figure 2. Note that in this figure, the calculations in the gas phase in the extended range are ignored because no lubricants are used in the gas phase. According to Figure 2, the systematic offset
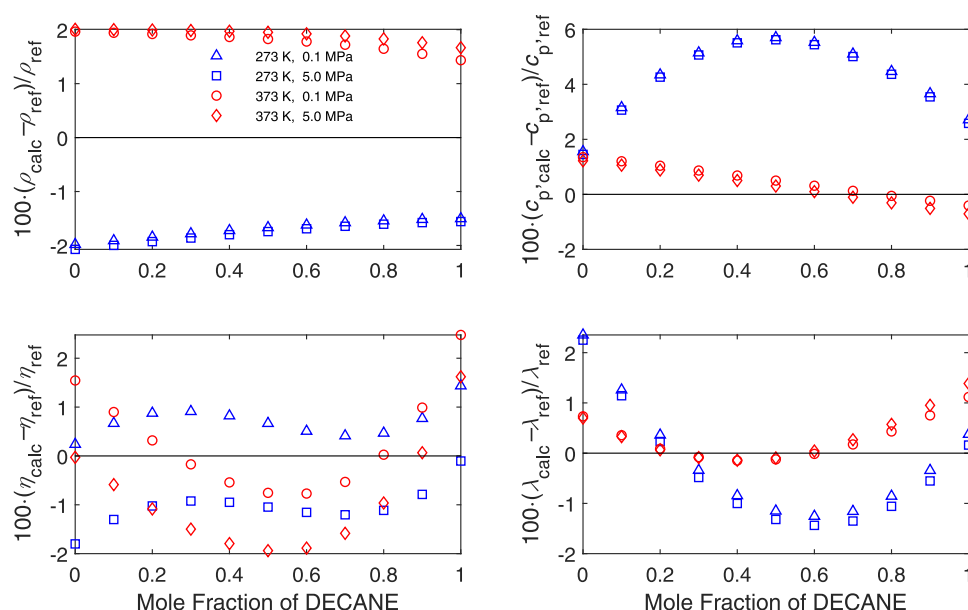
Figure 3. Relative deviations of the model set (subscripted with calc) from the reference models implemented in REFPROP 10.0[7] (subscripted with ref) for the binary system of DECANE + C12, a less asymmetric system.
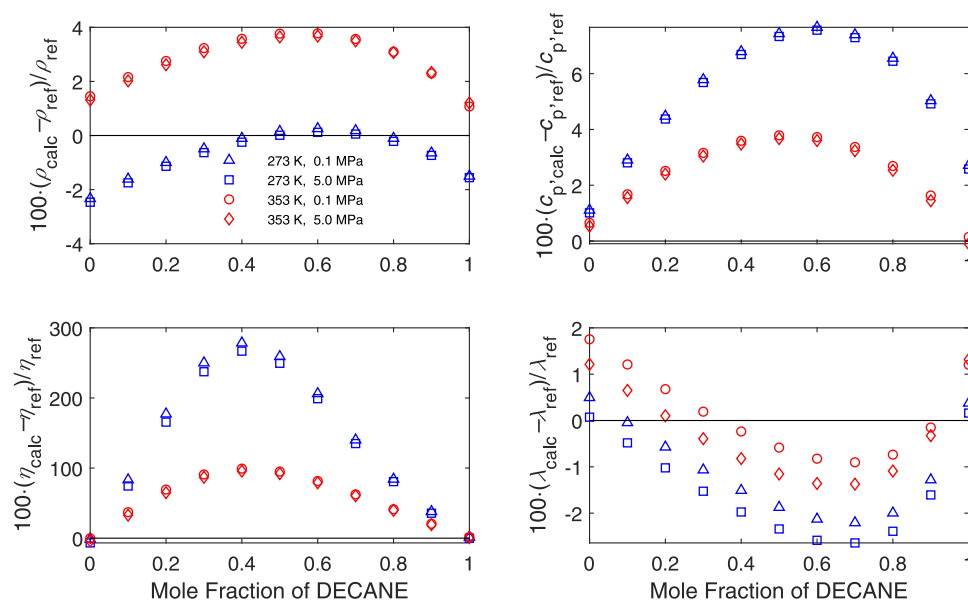

Figure 4. Relative deviations of the model set (subscripted with calc) from the reference models implemented in REFPROP 10.0[7] (subscripted with ref) for the binary system of DECANE + MLINOLEA, an asymmetric system.

(corresponds to the average of relative deviation, ARD) of the model set from the reference values is less than the measurement uncertainty U_{exp}, and the scattering (corresponds to the average of the absolute value of relative deviation, AARD) is more or less at the same level of U_{exp}. The model set was estimated to have an uncertainty of less than 7% for viscosity and less than 3% for all other properties. Viscosity predictions have larger uncertainty mainly because it shows a strong exponential relation to temperature, while other properties show largely linear relations.

Two binary systems are selected to evaluate the prediction capability of the model set for mixtures: DECANE + C12 as a representative of a less asymmetric system and DECANE + MLINOLEA of an asymmetric system (fluid names in REFPROP 10.0 are used). Here, same as Thol and Richter,[45]

we use the term "asymmetric" in a rather macroscopic and pragmatic way, i.e., we differentiate based on 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." The binary interaction parameter k_{ij} used in the cubic EoS for both selected systems was set to zero. The calculation results over the whole composition range (mole fraction of the first component from 0 to 1) and at extended temperature (273 and 373 K) and pressure (0.1 and 5.0 MPa) ranges were compared to reference values calculated with default models implemented in REFPROP 10.0.[7] Comparison results are illustrated in Figures 3 and 4 for both systems, respectively. For the less asymmetric system, see Figure 3, relative deviations for ρ, c_p, μ, and λ are generally within 2, 6, 2,

and 2%. This is a good representation of the data as they are at the same level of the typical experimental uncertainty (see Section 2.1). For the asymmetric system, see Figure 4, relative deviations for ρ, c_p, and λ are generally within 5, 8, and 3%, which is still a very good outcome. However, deviations for viscosity are as high as 300%, and the prediction performance can only be slightly improved if another reasonable value for k_{ij} is adopted, e.g., deviations down to 200% if $k_{ij} = 0.04$. This really poor viscosity prediction for asymmetric systems is attributed to the strong exponential relationship of viscosity to temperature and composition (more details in Section 3.2), and there are no proper mixing rules for asymmetric systems using the RES-μ approach today. Improving viscosity prediction of asymmetric binary systems using the RES approach is challenging and is part of our future work in the KETEC project.

3. APPLICATION OF THE MODELING APPROACH TO REAL LUBRICANTS

In this section, the proposed modeling approach (the model set and the parameter fitting procedure) was applied to real lubricants and their mixtures with other fluids. The testing cases are a less asymmetric binary system, an asymmetric binary system, and two extremely asymmetric binary systems.

3.1. Less Asymmetric Binary System. Experimental density and viscosity data of a lubricant pentaerythritol tetra(2-ethylhexanoate), abbreviated as PEB8, were collected from Fandiño et al.[46] and Pensado et al.,[47] respectively. Both publications are from the same research group that published experimental density[48] and viscosity[49] data of a binary system PEB8 + POE7 (full name: pentaerythritol tetraheptanoate, the abbreviation PEC7 was used in the original papers[48,49]). No isobaric heat capacity and thermal conductivity data of pure PEB8 or PEB8 + POE7 mixtures were found in the literature.

First, four density and viscosity data points each of pure PEB8 at $p = 0.1$ MPa from the literature[46,47] were used to fit the parameters of pure PEB8 (see Figure 5). The fitting parameters are listed in Table 1, where parameters associated with the heat capacity and thermal conductivity are set to zero. Then, all experimental literature data,[46,47] at pressures up to 60 MPa, were compared to the model prediction, yielding relative deviations for density and viscosity generally within 2 and 20%, respectively, as shown in Figure 5. The relative deviations for viscosity increase with increasing pressure; if only data with pressures lower than 15 MPa are of interest, then the agreement is within 3% for viscosity.

For the prediction of density and viscosity of the PEB8 + POE7 mixture, parameters of POE7 are collected from Table 1 (determined in the feasibility study). Both components are oils; therefore, the accurate measurement of bubble-point pressure and then the accurate fitting of the binary interaction parameter k_{ij} are difficult. In this context, k_{ij} was set to zero for this binary system. The relative deviations of all experimental literature data[48,49] from our model predictions are generally within 3 and 30% for density and viscosity, respectively, as shown in Figure 6. Changing k_{ij} by trial and error might improve the prediction of viscosity which, however, slightly deteriorates the prediction of density.

3.2. Asymmetric Binary System. Bubble-point pressure, density, heat capacity, viscosity, and thermal conductivity measurements of PAG68 and PAG68 + propane mixtures (an asymmetric binary system) were carried out at ILK Dresden, Germany. The information on the experimental setups is
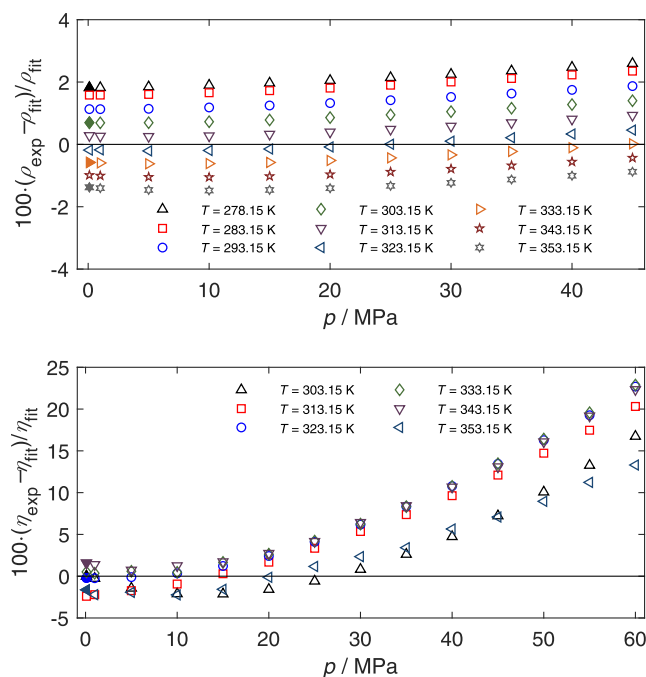

Figure 5. Relative deviations of experimental densities[46] and viscosities[47] of pure PEB8 from predictions of the model set. Data in full symbol were used to fit the parameters of pure PEB8.
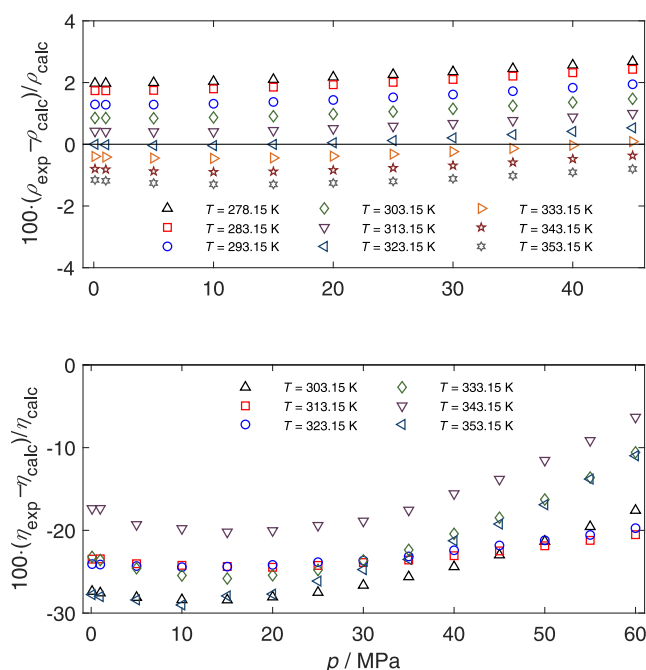

Figure 6. Relative deviations of the experimental density[48] and viscosity[49] of PEB8 + POE7 from predictions of the model set.

summarized in Table 2, and the measurement results are given in Tables S5−S8 in the SI. PAG68 can be considered as a quasi-pure lubricant, which is a commercially available refrigeration lubricant, especially formulated for hydrocarbon refrigerants by the manufacturer. According to the confidentiality agreement with the manufacturer, no further information about PAG68 can be provided here. Please note, in the PAG68 measurements, pressure was typically at atmospheric pressure or slightly higher; while in the PAG68

Table 2. Experimental Setups for the PAG68 and PAG68 + Propane Measurements

property	technique and reference	uncertainty ($k = 2$)
bubble-point pressure	direct method (self-developed, ILK Dresden)[50]	0.15 bar or 1%
density	vibrating tube densimeter (DMA HPM, Anton Paar)[50]	0.1 kg·m^{-3}
heat capacity	differential scanning calorimetry (stepwise method, μDSC 7 evo, Setaram)[51]	3%
viscosity	oscillating piston (VISCOpro 2000, Cambridge Viscosity)[50]	10%
thermal conductivity	ring-gap apparatus (self-developed, ILK Dresden)[52]	5%
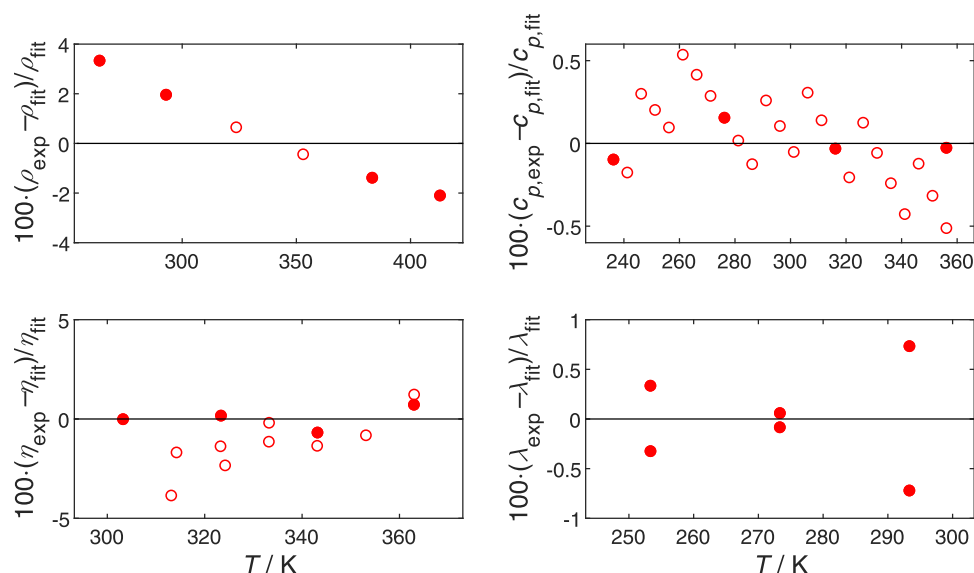
Figure 7. Relative deviation of the measured data of quasi-pure PAG68 from predictions of the model set. Data in full symbol are used to fit the parameters of PAG68.
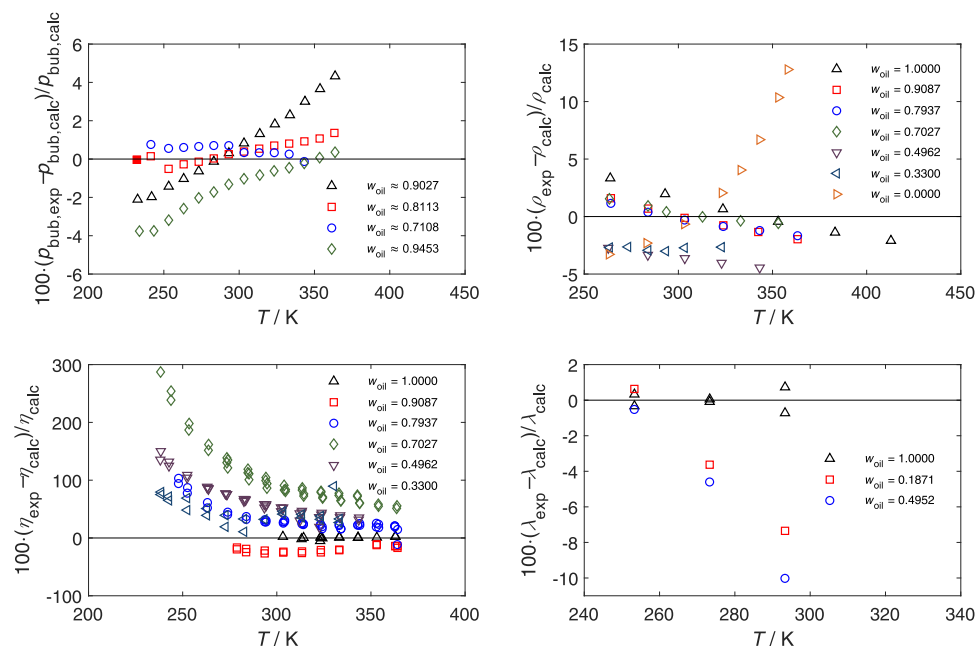
Figure 8. Relative deviations of the measured data of the PAG68 + propane mixtures from the predictions of the model set. Only one data point (the one in full symbol in the top left subfigure) was used to fit the binary interaction parameters of PAG68 + propane; w refers to mass fraction.

+ propane measurements, pressure was typically slightly higher than the bubble-point pressure to keep the mixtures in the liquid phase. Pressure values, apart from bubble-point pressure measurements, were not measured accurately; therefore, they are not provided in the SI. Bubble-point pressure of the PAG68 + propane mixtures was calculated using the PTV EoS

with the vdW mixing rule. It is important to note that the equation for the mixture's component fugacity contains a typo in the last equation of the original paper:[27] the "+" symbol in front of the term "$2Qd/(Q^2 - d^2)$" should be replaced with "$-$" symbol. No measurements were carried out to obtain the average molar mass of PAG68; here, we roughly chose a value

of M_{PAG68} = 200 g·mol^{-1}. Changing M_{PAG68} will not obviously affect the model performance as will be discussed later. Furthermore, although PAG is not an ester, its Z_c value was still fixed at 0.2563 (recommended for esters in ref 21). Such a rough-estimated Z_c value can already yield good results, as shown in the following.

Four data points each of density, heat capacity, and viscosity at four different temperatures and six points of thermal conductivity at three different temperatures of PAG68 were used to fit the parameters of PAG68. Together with the remaining data of PAG68, the relative deviations of the measured data from the model predictions are shown in Figure 7 (where data used for fitting are highlighted). The fitted parameter data of quasi-pure PAG68 are listed in Table 1. The relative deviations for density, isobaric heat capacity, viscosity, and thermal conductivity are generally within 2.0, 0.5, 4.0, and 1.0%, which is at the same level of experimental uncertainties. Changing the value of M_{PAG68} resulted in the change of some fitted parameters, mainly critical pressure, but had no obvious effect on the prediction performance for quasi-pure PAG68, i.e., Figure 7 remained almost the same. It can be seen from Figure 7 that the relative deviation of the experimental density from the model prediction decreases with increasing temperature. This can also be observed for all other studied quasi-pure oils, e.g., PEB8 in Figure 5, and later POE ISO 68 and DIDP in their corresponding figures in Section 3.3. Attempts to vary the Z_c value by trial and error improved the prediction of density but worsened the predictions of other properties as well as mixtures. We suggest that maybe an improved α-function in the PTV EoS (α is a function of temperature, see Table S1 in the SI) could solve this problem, which is, however, part of future work.

For thermophysical property calculations of the PAG68 + propane mixtures, the needed parameters of propane[53] were obtained from REFPROP 10.0 as listed in Table S2 in the SI, and the binary interaction parameter k_{ij} = 0.0381 of the PAG68 + propane mixture was fitted using one randomly picked bubble-point pressure point, as indicated in Figure 8. The bubble-point pressure rather than density was used for k_{ij} fitting because the bubble-point pressure is much more sensitive to k_{ij}. As shown in Figure 9, in the range of k_{ij} = 0.030−0.046, the root mean square (RMS) of the relative

deviation of experimental densities from calculated values barely changes but varies significantly with bubble-point pressures.

The relative deviations of the experimental PAG68 + propane data from the model prediction are illustrated in Figure 8. Changing the value of M_{PAG68} (= 200 g·mol^{-1}) resulted in a change of the fitted k_{ij} but will not obviously affect the prediction performance for the mixtures. For such an asymmetric system, the relative deviation for bubble-point pressure, density, and thermal conductivity are quite satisfying: generally, within 5, 5, and 10%, respectively. It is worth noting that, for density prediction of pure propane, as the critical temperature of pure propane (369.89 K) is approached, the relative deviation increases up to 14%, while for the PAG68 + propane mixture, the relative deviation is only up to 5%.

However, in the case of viscosity, the deviation is up to 300%, as can be seen in Figure 8. To further evaluate the ability of the model to predict viscosity, the experimental data and model predictions are plotted along isotherms (303, 323, 343, and 363 K) in viscosity versus mass fraction in Figure 10.
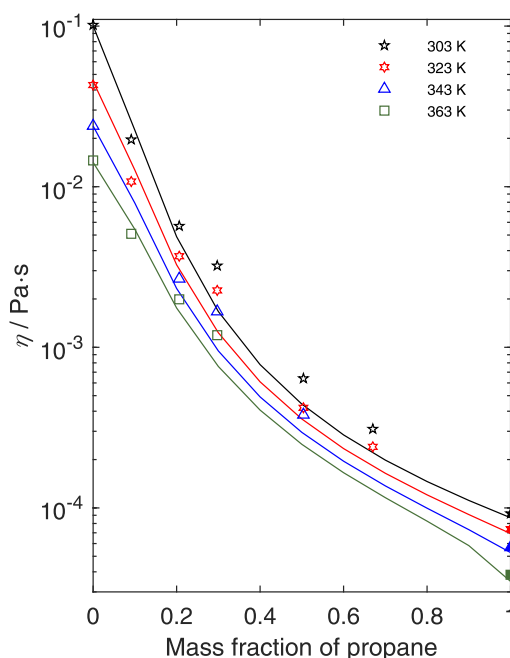
Figure 10. Viscosity of the PAG68 and propane system. Solid curve: predictions of the model set; empty symbols: experimental data of this work; filled symbols: calculations with REFPROP 10.0.[7]

These isotherms (with a tolerance of 1 K, e.g., the data at 302 K belong to the 303 K isotherm) were selected because there are experimental data from both PAG68 and PAG68 + propane mixtures. No viscosity measurement of pure propane was performed in this work, so the "experimental data" of pure propane in Figure 10 were calculated using REFPROP 10.0.[7] In the model prediction, the pressure, as an input value, was the same as in the corresponding experimental data, i.e., the pressure was the saturated liquid pressure for propane and PAG68 + propane mixtures and was 0.1 MPa for PAG68.

As can be seen in Figure 10, although the pressure is not constant, the model predictions along each isotherm follow a relatively smooth curve from the pure PAG68 end to the pure propane end, with both ends agreeing well with the experimental data. However, the experimental data do not
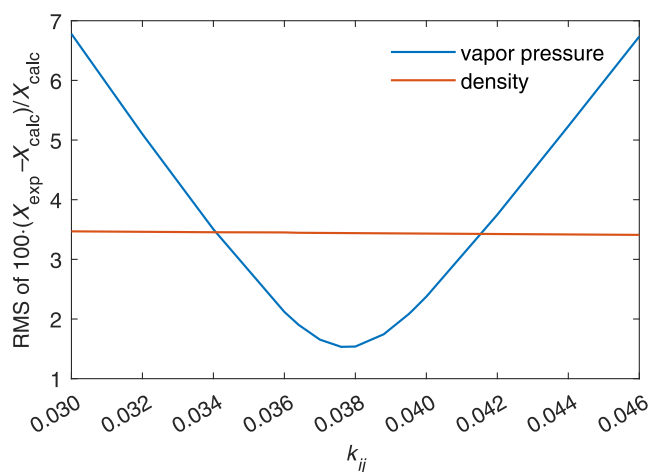

Figure 9. Sensitivity of the calculated density and bubble-point pressure of the PAG68 + propane mixtures to binary interaction parameter k_{ij}. RMS refers to root mean square.

follow the trend as smoothly as the model prediction. For example, the data generally show a spike in the trends at a propane mass fraction of 0.3, and the extension of the mixing data to the pure propane end does not appear to agree well with the REFPROP 10.0[7] calculation. The nonsmooth properties of the experimental data (if we assume they are correct) pose a major challenge to model prediction. Moreover, the viscosity changes significantly on the order of 1000 times from pure PAG68 to pure propane under similar temperature and pressure conditions. This means that a small change in the mass fraction of the mixture would result in a huge change in viscosity. Take as an example the point at 303 K and a propane mass fraction of 0.2, where the model prediction deviates from the experiment by about 30%: if the propane mass fraction was changed to 0.18, the deviation would drop to less than 2%. This means that a 30% increase in viscosity might be due to a 0.02 decrease in propane mass fraction, which is almost equal to the uncertainty in mixture preparation[33,34,54,55] plus unexpected evaporation of propane throughout the mixture measurement. In short, the huge viscosity change (on the order of 1000 times) from a pure refrigerant to quasi-pure oil poses another major challenge for model prediction.

Using a different RES approach for viscosity prediction, larger deviations had also been observed by Binti Mohd Taib and Trusler[56] with increasing molecular asymmetry of the system. The models used in REFPROP 10.0 are also imperfect for such systems. In this work, attempts to use other mixing rules without adjustable parameters did not yield an obviously better result. Therefore, in order to improve the viscosity prediction of the current model for asymmetric binary systems, highly reliable experimental data (especially with accurately known composition) are needed to develop a better mixing rule, including adjustable parameters fitted to the experimental data. Further studies based on the collection of accurate experimental data should be conducted.

3.3. Extremely Asymmetric Binary Systems. Literature data[2,57−59] of two extremely asymmetric binary systems—POE ISO 68 + CO_2 and di-isodecyl phthalate (DIDP) + CO_2—were collected from the research group of Prof. Martin Trusler at Imperial College London, UK. POE ISO 68 is a polyol ester synthetic oil and was considered as a quasi-pure fluid in this work. Density, heat capacity, and thermal conductivity of POE ISO 68 and POE ISO 68 + CO_2 were taken from the master thesis of Weerakajornsak.[58] Only three isothermal data of POE ISO 68 were available in this thesis work; therefore, density at 0.1 MPa, heat capacity at 0.1 MPa, and thermal conductivity at both 0.1 and 15.0 MPa (measured maximum pressure) at each of the three isotherms were used for parameter fitting; the fitted parameters of POE ISO 68 are listed in Table 1. Thermal conductivity data at 15.0 MPa were adopted for the fitting as well because there were four parameters $n_{\lambda k}$ ($k = 1-4$) to be fitted, but there are only three isothermal data available. In fitting the parameters of POE ISO 68, its Z_c was set to 0.2663 to yield the best agreements between the experimental data and model prediction. The relative deviations of all experimental data of POE ISO 68[58] from predictions of the model set are generally within 1.0, 0.1, and 1.2% for density, heat capacity, and thermal conductivity, respectively, as illustrated in Figure 11. For the predictions of the POE ISO 68 + CO_2 mixtures, the needed parameters of CO_2[60] were obtained from REFPROP 10.0 as listed in Table S2, and the binary interaction parameter k_{ij} was simply set to zero. The
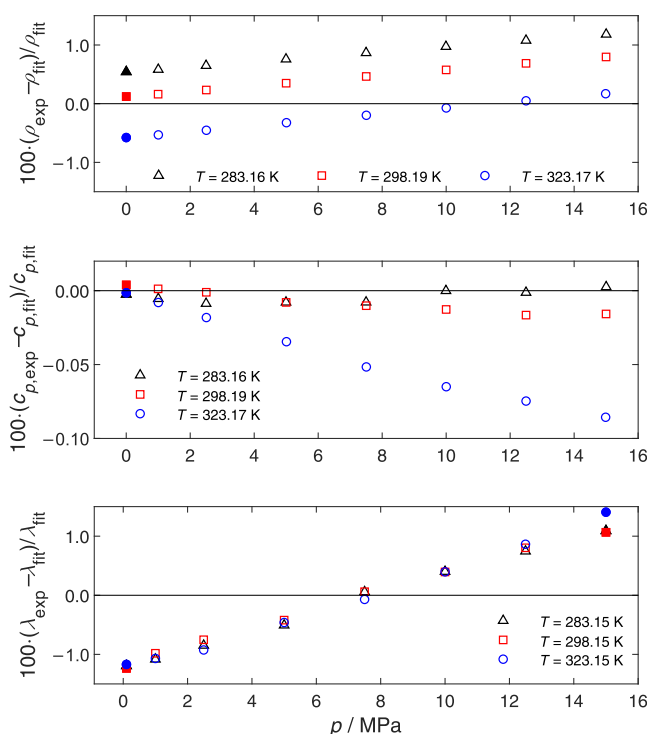

Figure 11. Relative deviations of experimental data[58] of quasi-pure POE ISO 68 from predictions of the model set. Data in full symbols were used to fit the parameters for POE ISO 68.

relative deviations of the experimental data[58] from the model predictions are generally within 5.0% for density and 8.0% for thermal conductivity but up to 70% for heat capacity, as shown in Figure 12. The key reason for the large deviation in the heat capacity is that the heat capacity was generally measured in the vicinity of the critical point of CO_2, where the critical enhancement could be clearly observed from the experimental data. This implies that the used simple model is not able to accurately predict heat capacity near the critical point.

Experimental density and heat capacity data of DIDP were collected from Peleties et al.[59] A correlation function for viscosity of DIDP in the temperature range from 288.15 to 308.15 K was developed by Caetano et al.,[2] and its calculation results were adopted as "experimental" data in this work. Density and viscosity data of DIDP + CO_2 were collected from Taib et al.[57] Four data points each of density, heat capacity, and viscosity at four different temperatures at 0.1 MPa were adopted to fit the parameters of DIDP, which are listed in Table 1. Together with the remaining experimental data of pure DIDP, the relative deviations of the measured data from the model predictions are shown in Figure 13 (data used for fitting are highlighted). The relative deviations are generally within 5.0, 1.0, and 1.0% for density, isobaric heat capacity, and viscosity; this is excessively good considering that density was measured up to 140.0 MPa. The binary interaction parameter k_{ij} was set to zero for the DIDP + CO_2 mixture calculations. As shown in Figure 14, the relative deviations of the experimental data from the model predictions are within 5.0% for density, which is very good, and up to 400% and even more for viscosity, the reason for which was explained in Sections 2.3 and 3.2.
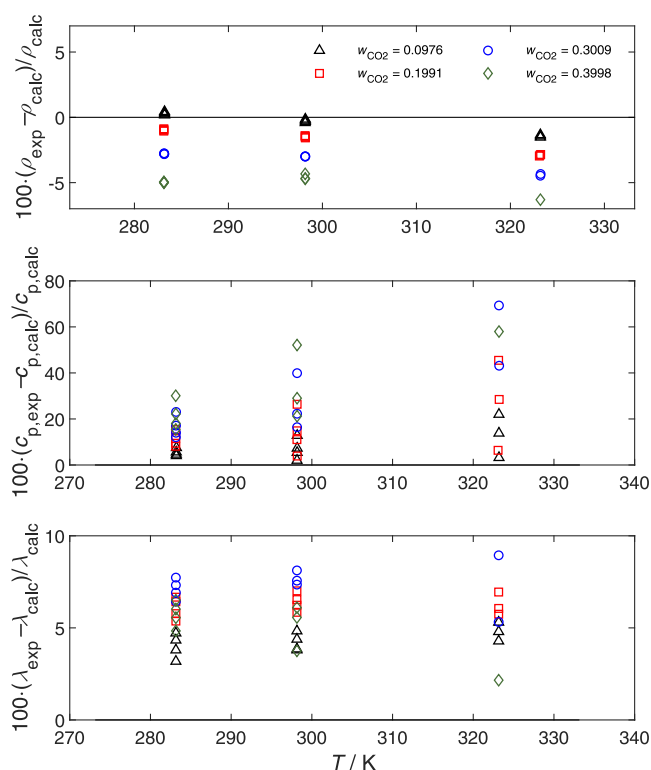
Figure 12. Relative deviations of experimental data[58] of POE ISO 68 + CO_2 mixtures from predictions of the model set; w refers to mass fraction.
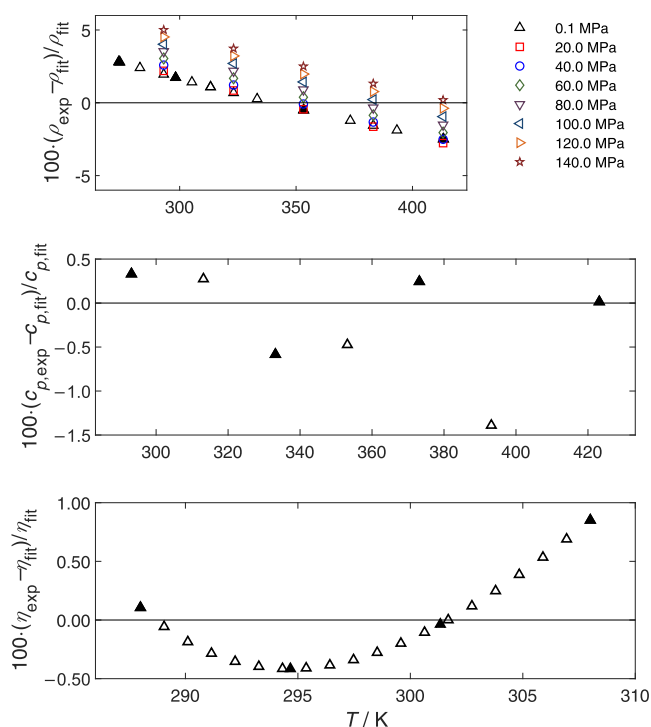

Figure 13. Relative deviations of experimental data[2,59] of pure DIDP from predictions of the model set. Data in the full symbol are used to fit the parameters of pure DIDP.
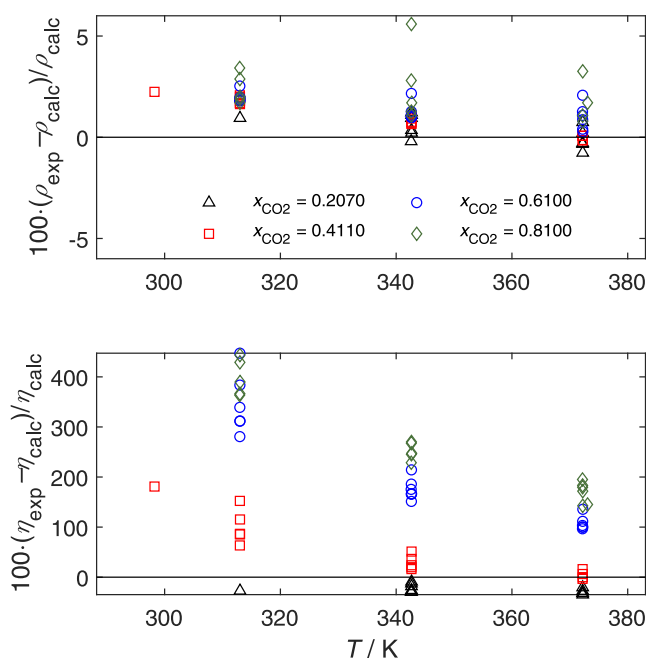
Figure 14. Relative deviations of experimental data[58] of DIDP + CO_2 mixtures from predictions of the model set; x refers to mole fraction.

entropy, enthalpy, viscosity, and thermal conductivity) of a lubricant oil remains a key challenge today. To address this challenge, we propose a novel modeling approach, in which a lubricant oil is considered as a quasi-pure fluid, a simple model set is used for the property calculations, and a procedure for fitting the required parameters using only a few experiments is developed. This model set includes the Patel–Teja–Valderrama cubic equation of state, the ideal gas isobaric heat capacity as a linear function of temperature, and residual entropy scaling for viscosity and thermal conductivity. All needed parameters to be fitted include molar mass, critical temperature, critical density, critical pressure, acentric factor, two parameters for heat capacity, and four parameters for viscosity and thermal conductivity. To fit the molar mass and critical point, two extra models are required, namely, Raoult's law of boiling point elevation and a modified Rackett equation. Fitting the molar mass of a lubricant is not entirely necessary; a rough-estimated value can be given to it, and the effect to the performance of the modeling approach is very small. Within the scope of determining the model set (mainly the cubic EoS) and the parameter fitting procedure, a feasibility study using well-studied pure fluids was carried out. The pure fluids include almost all dense pure fluids available in NIST's REFPROP database 10.0.[7] As a result, less than 20 experimental points (a minimum of 12) are needed to fit all of the parameters of a pure or quasi-pure component, and one experimental point is required to enable a binary system prediction. It is important to note here that six cubic EoS candidates were studied, but only the PTV EoS yielded reasonable results because it can predict liquid densities more accurately than other cubic EoS.

The performance of the proposed modeling approach (the model set and the parameter fitting procedure) was first tested by calculating the properties of the well-studied pure fluids and their mixtures in enlarged temperature and pressure ranges and comparing to REFPROP 10.0 calculations. Then, the modeling approach was further tested by being applied to real cases of

4. CONCLUSIONS

Modeling all of the important thermophysical properties (mainly including density, phase behavior, heat capacity,

lubricants and their mixtures with other fluids. A less asymmetric binary system (pentaerythritol tetra(2-ethylhexanoate) + pentaerythritol tetraheptanoate, abbreviated as PEB8 + POE7, both are lubricants), an asymmetric binary system (PAG68 + propane), and two extremely asymmetric binary systems (POE ISO 68 + CO_2 and di-isodecyl phthalate + CO_2) were investigated. Experimental data of these binary systems were either obtained from the literature or provided within the scope of this work. As a result, in the liquid phase and not in the vicinity of the critical points, for pure fluids and less asymmetric binary systems, this modeling approach has an estimated uncertainty ($k = 2$) of less than 7% for viscosity and less than 3% for all other properties. For the asymmetric binary system, except for viscosity, the modeling approach still yields good predictions, typically within 8%.

The large uncertainty in predicting viscosity is due to the strong exponential relationship of viscosity to the temperature and composition. For example, the viscosity in the liquid phase changes about 1000 times from pure propane to pure PAG68 at the same temperature and pressure. It is widely recognized that accurate prediction of the viscosity of asymmetric systems using the RES approach is very difficult, and even the models used in REFPROP 10.0 are imperfect for such systems. The current results presented are the best we can achieve using a mixing rule without adjustable parameters. Future work will be to develop a mixing rule with adjustable parameters that can be fitted to the experimental data. A prerequisite for this is to obtain very reliable experimental data, especially with accurate compositional information. Such data are unfortunately rarely available.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.3c02474.

> Detailed model description; data used in the feasibility study, including reference values of the constants of real fluids, values used for parameter fitting, and molar mass determination using the Raoult's law of boiling point elevation; and experimental data of PAG68 and its mixture with propane (PDF)

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Notes

The authors declare no competing financial interest.

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