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Predictive methods for density and refractive index of naphthenic lubricating oils during solvent extraction process

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A B S T R A C T

Lubricating oils are usually produced by solvent extraction to separate aromatics in order to achieve the desired specifications and better quality products. Among the different properties of lubricating oils, density and refractive index are some of the most important properties which can both be used for petroleum fluid characterization. Predictions of density and refractive index for naphthenic oils during solvent extraction by DMSO obtained by the pseudo-component approach and the quadratic correlation were both examined. The pseudo-component approach is a method to predict density and refractive index from composition while the latter merely relates density to refractive index. Results indicated that the predictions yielded by the pseudo-component method were in good agreement with experimental data for naphthenic oils. And the use of a function of refractive index (FRI_{20}) as a pseudo-component property remarkably improved n_{20} predictions for the naphthenic mixtures. However, the density and refractive index predictions obtained by the quadratic correlation exhibited significantly higher deviations for naphthenic oils than those for paraffinic oils. Thus a new modified correlation of the same functional form was proposed for naphthenic oils. The modification significantly improved predictions for naphthenic oils, which presented similar accuracy as the pseudo-component approach. And the previous correlation was still used for paraffinic oils.

Additionally, effect of temperature on density and refractive index of naphthenic oils was examined. Results showed that the modified quadratic correlation was accurate for describing the relationship between density and refractive index of naphthenic oils at 20−90 °C. The temperature dependence of density and refractive index for the raffinates and the extracts could be accurately described by the thermal coefficients for saturates and aromatics, respectively. Regarding the refractive index variation of the extracts with temperature, the empirical equation was proved to be a better option compared with the method using the thermal coefficient for aromatics.

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1. Introduction

Nowadays, the application of lubricating oils is considerably increased in order to reduce the adverse effects caused by friction. Some types of lubricants require low aromatic content (Hoseini et al., 2008; Mohammad et al., 2021), while others such as eco-friendly aromatic-rich rubber processing oils need to retain high aromatic content while removing polycyclic aromatic hydrocarbons (PCAs) as much as possible (Dasgupta et al., 2009; Luo et al., 2018; Han et al., 2021). Usually, various types of lubricating oils are produced by the liquid-liquid extraction to separate aromatics in order to achieve the desired specifications and better quality products. The solvent is selected to separate a target amount of aromatics from the oil based on the solubility of the aromatics in the solvent. In addition to furfural (Grieken et al., 2005; Coto et al., 2006a, b; Espada et al., 2007; Espada and Rodríguez, 2017; Cui et al., 2022), which is one of the most widely used solvents for this process, the commonly used solvents include N-methylpyrrolidone (Mostafa et al., 2019), N,N-dimethylformamide (Cui et al., 2022; Ding et al., 2022; Sun et al., 2022), dimethyl sulfoxide (DMSO) (Ding et al., 2022), glycol ether (Fu et al., 2012), ionic liquids (Sun et al., 2021), and so on. Compared to experimental data on solvent

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extraction with furfural, data concerning other solvents are relatively insufficient.

Physical properties of mixtures are of vital importance to describe the solvent extraction process in which they are involved. The relevant physical properties, such as density and refractive index, can be both used for petroleum fluid characterization and to determine other properties (Albahri et al., 2003; Mehrkesh et al., 2010). Density is a key parameter for almost all process calculations, and is meanwhile an input for many property correlations and simulating processes. Refractive index is strongly related to density in hydrocarbon and petroleum systems. And refractive index can also be used for the calculation of other properties, such as solubility parameters (Wang and Buckley, 2003; Vargas and Chapman, 2010), viscosity and thermal conductivity (Vargas and Chapman, 2010). Moreover, refractive index is also important as it is commonly used to check the quality of the distillates produced during the solvent extraction processes, regarding their aromatic content (Espada et al., 2008).

A pseudo-component approach based on the composition of samples in terms of hydrocarbon-type (i.e. saturates, aromatics and polars) using mixing rules to determine the density and refractive index of lubricating oils during solvent extraction of vacuum distillates have been reported by many studies (Grieken et al., 2005; Coto et al., 2006a, b; Espada et al., 2007; He et al., 2016; Espada and Rodríguez, 2017). But the method was limited to experimental data on solvent extraction of paraffinic lubricating oils. Few papers have referred to prediction of properties for naphthenic lubricating oils.

On the other hand, it is desirable to find an accurate way to predict density and refractive index from correlations between the two properties especially when information on composition is unavailable. Many connections which relate density with refractive index or a function of refractive index (*FRI*) have been established. For example, the "One-Third" rule proposed by Vargas and Chapman (2010), which suggests a value of *FRI*/ρ approximately equal to one-third for several pure hydrocarbons and its mixtures,

explains the origin of the correlation between density and refractive index (or *FRI*). Yet it has been observed that there is a significant deviation from this one-third rule for different distillates (Yarranton et al., 2015). With regard to other correlations, some relate density linearly to only refractive index itself or a function of refractive index (*FRI*) (Vargas and Chapman, 2010; Yarranton et al., 2015; Angle et al., 2006; Khan, 1998), while others relate density to

solvent extraction. However, previous studies mostly focused on paraffinic oils, which made it difficult to confirm if correlations were suitable for naphthenic lubricating oils. Therefore, it has been ambiguous what form of correlation is sufficient to describe a broad range of oils, especially for naphthenic oils.

As regards the effect of temperature on density and refractive index, both the density and the function of refractive index of liquid oils decrease linearly with temperature with the exception of near the saturation pressure or critical point (Yarranton et al., 2015). Yet there are few papers for assessing the magnitudes of the density and the *FRI* temperature dependence of petroleum distillates, especially for naphthenic oils.

In this work, the density and refractive index values of the studied naphthenic mixtures during solvent extraction with DMSO were predicted by two methods, which included the pseudo-component approach and the quadratic correlation, for assessing the accuracy of these methods. Thereafter, the quadratic correlation was modified for better fitting the relationship between density and refractive index (or *FRI*) of naphthenic oils during solvent extraction. And the modified quadratic correlation was further examined on other experimental data involving naphthenic oils. Furthermore, the temperature dependence of the properties and the relationship between density and refractive index (or *FRI*) at different temperatures for naphthenic oils were also examined.

2. Characterization methods

2.1. Pseudo-component approach

The pseudo-component approach considered that mixtures were formed by three groups of pseudo-components, viz: saturates (S), aromatics (A) and polars (Po) in lubricating oil systems during solvent extraction process (Grieken et al., 2005; Coto et al., 2006a, b; Espada et al., 2007). Density and refractive index of mixtures were calculated by applying the following mixing rules:

$$(1/\rho_{20})_{\text{mix}} = \left[(X_S/100)(1/\rho_{20})_S + (X_A/100)(1/\rho_{20})_A + (X_{Po}/100)(1/\rho_{20})_{Po} \right] \tag{1}$$

$$(n_{20}/\rho_{20})_{\text{mix}} = \left[(X_S/100)(n_{20}/\rho_{20})_S + (X_A/100)(n_{20}/\rho_{20})_A + (X_{Po}/100)(n_{20}/\rho_{20})_{Po} \right] \tag{2}$$

where ρ_{20} and n_{20} are density and refractive index at 20 °C, respectively. X_S, X_A and X_{Po} are the values of composition in terms of saturates, aromatics and polars, respectively.

Another mixing rule employing a function of refractive index (or *FRI*) proposed by Espada and Rodríguez (2017) is listed below:`

$$(1/FRI_{20})_{\text{mix}} = \left[(X_S/100)(1/FRI_{20})_S + (X_A/100)(1/FRI_{20})_A + (X_{Po}/100)(1/FRI_{20})_{Po} \right] \tag{3}$$

FRI in a quadratic form (Espada and Rodríguez, 2017; Yarranton et al., 2015). Espada and Rodríguez (2017) have validated that predictions of density and refractive index by the pseudo-component approach exhibited similar accuracy as the quadratic correlation for the studied paraffinic lubricating oil mixtures during

$$FRI_{20} = \frac{n_{20}^2 - 1}{n_{20}^2 + 2} \tag{4}$$

This mixing rule, as against Eq. (2), does not require the

knowledge of density to calculate the refractive index of mixtures.

Therefore, the density and refractive index of a mixture can be calculated by applying the above-mentioned mixing rules (Eqs. (1)–(3)) if its composition (in terms of saturates, aromatics and polars), as well as average pseudo-component properties are known. And the average pseudo-component properties were determined by regression.

2.2. Correlations between density and refractive index (or FRI)

Regarding hydrocarbon and petroleum systems, where polar interactions are weak, intermolecular attractions are determined by the polarizability, which can be directly related to the refractive index through the Lorentz-Lorenz equation (Vargas et al., 2009):

$$\alpha = \left(\frac{3}{4\pi N_A}\right) R_m = \left(\frac{3}{4\pi N_A}\right) \frac{n^2 - 1}{n^2 + 2} V \tag{5}$$

where α is the electronic polarizability, R_m is the molar refractivity, N_A is the Avogadro's number, n is refractive index, and V is the molar volume. As reported in literature (Vargas et al., 2009), the molar refractivity of different families of pure hydrocarbons can be correlated to their molecular weight based on the Lorentz-Lorenz model, as shown in Eq. (6):

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2}\right) \frac{M_w}{\rho} = FRI \frac{M_w}{\rho} \tag{6}$$

where FRI is a function of the refractive index n (as shown in Eq. (4)), M_W is the molecular weight, and ρ is the mass density.

In combination with the above two equations, it can be seen from Eq. (7) that density and refractive index are closely related. It has been proved that molar refractivity (R_m) is approximately proportional to molecular weight for a wide range of hydrocarbons, which implies that the function of the refractive index (FRI) divided by the mass density is also a constant.

$$\frac{FRI}{\rho} = \frac{R_m}{M_w} = \frac{4\pi N_A \alpha}{3 M_W} \tag{7}$$

The "One-Third" rule presumed that the ratio of FRI/ρ is a constant approximately equal to one-third for a wide range of hydrocarbons and crude oil systems (Eq. (8)) (Vargas and Chapman. 2010). The value of one-third is common for many pure hydrocarbons and mixtures. However, there is a deviation from the one-third value for light and very heavy hydrocarbons. When data for aliphatic (C_1–C_{20}), aromatic (C_6–C_{13}) and polyaromatic (C_{10}–C_{19}) hydrocarbons at 20 °C were correlated by Vargas and Chapman (2010), Eq. (9) which is known as the Lorentz-Lorenz expansion (Achtermann et al., 1992) was obtained:

$$\left(\frac{n^2 - 1}{n^2 + 2}\right) \frac{1}{\rho} = \frac{R_m}{M_w} \approx \frac{1}{3} \tag{8}$$

$$\frac{FRI}{\rho} = \frac{1}{\rho^o} = 0.5054 - 0.3951\rho + 0.2314\rho^2 \tag{9}$$

In addition to the "One-Third" rule, other correlations between density and refractive index (or FRI) were proposed by many researchers. Yarranton et al. (2015) proposed the following quadratic expression (Eq. (10)), which was proved to provide a better fit to a wide range of data including pure hydrocarbons (paraffins, single ring cyclics, and aromatics) and petroleum fractions. Besides, several linear correlations between density and refractive index (or FRI) were suggested by Angle et al. (2006) and Khan (1998).

Nevertheless, it has been reported that linear correlations between the two properties showed obviously larger deviations than the quadratic relationship (Espada and Rodríguez, 2017; Yarranton et al., 2015). Thus the linear correlations were not described in detail.

$$\rho_{20} = -0.6656 + 7.375 FRI_{20} - 6.984(FRI_{20})^2 \tag{10a}$$

$$FRI_{20} = 0.5280 - 0.3784(1.2813 - \rho_{20})^{0.5} \tag{10b}$$

2.3. Effect of temperature on density and refractive index (or FRI)

As Vargas and Chapman (2010) noted, FRI/ρ can be assumed independent of temperature. Therefore, Eq. (11) can be readily obtained

$$\frac{FRI(T)}{\rho(T)} = \frac{FRI(T_{\text{ref}})}{\rho(T_{\text{ref}})} \tag{11}$$

where T and T_{ref} represent the desired temperature and the reference temperature, respectively. When information about density and refractive index at the reference temperature is known, the refractive index (or the density) at the desired temperature can be readily obtained through Eq. (11) and the density (or the refractive index) at the desired temperature.

Moreover, the effect of temperature should be accurately predicted when neither density nor refractive index data are available. Yarranton et al. (2015) found that both specific volume (reciprocal of density) and FRI were linearly related to temperature for different samples (saturates, aromatics, and bitumens). For density, the variation with temperature can be expressed in terms of coefficient of thermal expansion, α_V, defined as following:

$$\alpha_V = \frac{1}{v}\left(\frac{dv}{dT}\right) \tag{12}$$

where v is the specific volume (reciprocal of density). Then Eq. (13) can be derived from the integral relation.

$$v = v_{20} \exp(\alpha_V(T - 20)) \tag{13}$$

where v_{20} is the specific volume at 20 °C in cm³/g, T is temperature in °C.

It was found that the thermal expansion coefficients of saturates and n-alkanes versus the specific volume follow one approximately linear trend, while the data for aromatics follow another approximately linear trend. The thermal expansion coefficients of saturates and aromatics are linearly correlated with the specific volumes at 20 °C, as shown in Eq. (14) and Eq. (15) (Yarranton et al., 2015), respectively.

$$\alpha_V(\text{sat}) = -0.0008278 + 0.001375\, v_{20}$$
$$= -0.0008278 + 0.001375/\rho_{20} \tag{14}$$

$$\alpha_V(\text{aro}) = -0.001500 + 0.002224\, v_{20}$$
$$= -0.001500 + 0.002224/\rho_{20} \tag{15}$$

Thus the density of petroleum fractions at any temperature and atmospheric pressure (in the liquid state) can be related to the density measured at 20 °C, as shown in Eq. (16):

$$\rho = \rho_{20} \exp\left(-\alpha_V(T-20)\right) \tag{16}$$

and for $\alpha_V T \ll 1$, Eq. (16) can be approximated as:

$$\rho = \rho_{20}(1 - \alpha_V(T-20)) \tag{17}$$

Similarly, a thermal FRI coefficient, α_F, can be defined as follows:

$$\alpha_F = \frac{1}{FRI}\left(\frac{dFRI}{dT}\right) \tag{18}$$

The thermal FRI coefficients for saturates and aromatics are developed similar to the thermal expansion coefficient α_V (Yarranton et al., 2015):

$$\alpha_F(\text{sat}) = -0.002276 + 0.005567 FRI_{20} \tag{19}$$

$$\alpha_F(\text{aro}) = -0.002619 + 0.006168 FRI_{20} \tag{20}$$

where FRI_{20} is the FRI at 20 °C, $\alpha_F(\text{sat})$ and $\alpha_F(\text{aro})$ are the thermal FRI coefficients for saturates or aromatics, respectively.

Therefore, the FRI of saturates and aromatics at any temperature and atmospheric pressure are related to the FRI measured at 20 °C as follows:

$$FRI = FRI_{20} \exp\left(\alpha_F(T-20)\right) \tag{21}$$

and for $\alpha_F T \ll 1$:

$$FRI = FRI_{20}(1 - \alpha_F(T-20)) \tag{22}$$

Moreover, the relationship of refractive index to temperature can be described by an empirical equation (Vargas et al., 2009):

$$n_{T_1} = n_{T_2} + 0.0004 \cdot \Delta T \quad (T_1 < T_2) \tag{23}$$

2.4. Carbon-type analysis of petroleum fractions

The carbon-type analysis of petroleum fractions was mainly used to assess the structural group composition of oils. According to the carbon-type analysis determined on the basis of physical properties, the distribution of aromatic, naphthenic, and paraffinic structural groups in hydrocarbon mixtures can be obtained. Correlations between composition (in paraffins, naphthenes and aromatics groups) and physical properties (such as density, refractive index) for petroleum mixtures have been proposed by Riazi and Daubert (1986). Another similar method is described in ASTM D2140 (2017), which is usually applied for lubricating oils, to determine the carbon-type composition, expressed as the percentage of paraffinic carbons (C_P), the percentage of naphthenic carbons (C_N), and the percentage of aromatic carbons (C_A). ASTM D2140 is a graphical method for determining the carbon-type composition of oils through the viscosity, density and relative density, and refractive index measurement. In addition, for oils containing sulfur content of no less than 0.8 wt%, the accuracy of the method may be improved by applying a sulfur correction. The corrections are listed as follows:

$$\text{Sulfur correction for } \%C_N = -\%S/0.288 \tag{24a}$$

$$\text{Sulfur correction for } \%C_P = +\%S/0.216 \tag{24b}$$

$$\text{Sulfur correction for } \%C_A = 100 - (\text{corrected } \%C_N + \text{corrected } \%C_P) \tag{24c}$$

In this work, the carbon-type composition of the studied mixtures was determined using the above-mentioned standard method to facilitate the quantitative classification of paraffinic and naphthenic oils.

3. Experimental section

Experimental data on solvent extraction experiments of naphthenic lubricating oils under different conditions using DMSO (dimethylsulfoxide) were used in this work. In the extraction process, a certain amount of feedstock and DMSO was placed in a 500-mL glass reactor, the temperature was by recirculating silicone oil from a thermostatic bath and controlled within ±0.1 °C. The mixture was agitated at 500 rpm for 1 h and settled for another 1 h to achieve complete phase separation. Then, the raffinate and extract phase were collected in different sampling bottles, and the solvent was removed from each sample via rotary evaporation under vacuum. Vacuum distillation was performed at about 3 kPa to remove the solvent at a temperature under 373 K to avoid thermal cracking. The obtained raffinates and extracts were accurately weighed using an electronic balance in order to calculate the yields of raffinates and extracts. The composition and properties of the raffinates and the extracts were both analyzed as discussed below.

In this work, the ρ_{20} values were determined by ASTM D1298 with the accuracy of ±0.00005 g/cm^3 by using a vibrating tube densimeter (Rudolph DDM291), while the n_{20} values were measured by a refractometer (Rudolph J457) according to ASTM D1747 with the accuracy of ±0.00002. The viscosity was measured based on ASTM D445 by using a rotational viscometer (Anton Paar SVM3000) with the uncertainty of ±0.35%. The hydrocarbon composition of oils was determined by means of ASTM D2007. And the uncertainty values in measurement of composition for saturates, aromatics and polars were 1.6%, 1.5% and 0.3%, respectively. The carbon-type composition of oils were determined by ASTM D2140 based on the experimental data of viscosity, density, and refractive index.

The quality of experimental data was checked by mass balance. The feed composition calculated from the composition and yield of raffinates and extracts of each experiment was compared with the experimental value. Average absolute deviations between experimental and calculated composition values for saturates, aromatics and polars were 1.5%, 2.2% and 0.6%, respectively. The deviations were all within the limits of reproducibility indicated by the ASTM D2007 standard test method.

Table 1 summarizes the hydrocarbon composition (in terms of saturates, aromatics and polars), the carbon-type composition (in terms of paraffinic carbons, naphthenic and aromatic carbons) and the properties of each fraction, viz: liquid density at 20 °C (ρ_{20}) and refractive index at 20 °C (n_{20}).

F1 and F2 represent the raw and the prehydrotreated naphthenic vacuum distillates, respectively. Each mixture is denoted by a letter (R for raffinate, E for extract), followed by the corresponding number of the experiment. It should be noted that the hydrocarbon composition (in terms of saturates, aromatics and polars) was used in the pseudo-component approach and the carbon-type composition was used to determine if an oil was paraffinic or naphthenic in this work. In addition, density and refractive index of naphthenic

Table 1
Experimental results for the solvent extraction experiments of naphthenic oils (F: feed, R: raffinate, E: extracts).

Fraction	Composition[a], wt%			ρ_{20}, g/cm^3	n_{20}	Viscosity at 100 °C, cSt	Carbon-type composition[b], %		
	X_S	X_A	X_{Po}				C_A	C_N	C_P
F1	66.91	29.83	3.26	0.92312	1.50470	6.54	11.3	49.1	39.6
F1-R1	75.93	22.44	1.63	0.91209	1.49808	5.81	7.7	49.5	42.8
F1-R2	78.60	21.55	1.85	0.91093	1.49733	5.63	7.4	49.8	42.8
F1-R3	78.71	20.19	1.10	0.90918	1.49643	5.83	6.7	49.2	44.1
F1-R4	79.79	18.84	1.37	0.90850	1.49577	5.84	6.0	49.8	44.2
F1-R5	80.61	17.48	1.91	0.90783	1.49559	5.82	6.1	49.3	44.6
F1-R6	78.56	17.91	3.53	0.90657	1.49496	5.85	5.8	49.0	45.2
F1-R7	76.80	18.87	4.33	0.90930	1.49633	5.73	6.6	49.7	43.7
F1-R8	75.73	20.65	3.61	0.90856	1.49564	5.61	6.0	50.5	43.5
F1-R9	77.47	19.50	3.03	0.90745	1.49534	5.72	6.1	49.4	44.5
F1-E1	7.83	87.54	4.63	1.00940	1.54506	11.02	32.5	67.5	0.0
F1-E2	9.01	86.63	4.36	1.00769	1.54339	11.14	32.3	67.7	0.0
F1-E3	10.23	85.62	4.16	1.00039	1.54538	11.33	30.5	66.4	3.1
F1-E4	11.03	84.01	5.96	0.99686	1.53859	11.08	25.9	65.2	8.9
F1-E5	11.49	83.07	5.44	0.99458	1.54287	10.78	29.0	63.4	7.6
F1-E7	8.07	88.83	3.10	1.00536	1.54588	10.32	32.0	68.0	0.0
F1-E8	10.64	84.26	5.10	0.99558	1.5418	10.11	28.6	67.5	3.9
F1-E9	14.00	80.19	5.81	0.99158	1.53943	9.61	27.3	66.8	5.9
F2	68.76	31.05	0.19	0.91022	1.49909	5.24	10.7	44.5	44.8
F2-R1	74.64	25.36	0.00	0.90612	1.49566	4.92	7.9	47.4	44.7
F2-R2	75.80	24.20	0.00	0.90403	1.49498	5.16	7.8	45.7	46.5
F2-R3	76.20	23.80	0.00	0.90323	1.4943	5.05	7.3	46.3	46.4
F2-R4	76.36	23.64	0.00	0.90378	1.49398	4.93	6.7	48.1	45.2
F2-R5	77.00	23.00	0.00	0.90266	1.49348	4.94	6.5	47.7	45.8
F2-R6				0.90454	1.49448	5.17	6.8	47.7	45.5
F2-R7				0.90333	1.49373	5.18	6.3	47.8	45.9
F2-R8				0.90278	1.49359	5.05	6.4	47.5	46.1
F2-E1	19.04	80.68	0.28	0.98391	1.55532	5.59	37.5	34.2	28.3
F2-E2	19.50	80.20	0.30	0.97708	1.54897	5.30	36.0	36.6	27.4
F2-E3	19.90	79.79	0.31	0.97201	1.54435	4.81	35.0	40.3	24.7
F2-E4	20.40	79.67	0.33	0.96435	1.53610	5.34	34.7	38.2	27.1
F2-E5	21.20	79.46	0.34	0.96428	1.53576	5.51	30.4	43.0	26.6
F2-E6				0.98438	1.54917	5.42	36.0	46.5	17.5
F2-E7				0.97130	1.54335	5.35	33.5	38.9	27.6
F2-E8				0.97058	1.53751	4.81	30.4	47.9	21.7

The composition (X_S, X_A and X_{Po}), density, refractive index and viscosity were measured and the carbon-type composition was calculated.

[a] X_S, X_A and X_{Po} are the values of composition in terms of saturates, aromatics and polars, respectively.
[b] Determined by ASTM D2140 based on the density, refractive index and viscosity measurement.

oils at different temperatures (40 °C, 70 °C and 90 °C) were also measured and compared. The data measured at elevated temperatures are provided in Table A1 (Appendix).

4. Results and discussion

4.1. Predictions by pseudo-component approach

As it is not possible to identify all the individual compounds present in complex mixtures such as petroleum fractions, it is common to apply the pseudo-component method to reduce the number of compounds in petroleum fractions. The pseudo-component approach based on the hydrocarbon composition (in terms of saturates, aromatics and polars) was widely used in prediction of density and refractive index for lubricating oils and LLE

Table 2
Optimized pseudo-component properties of naphthenic oils and deviations.

Property	Saturates (S)	Aromatics (A)	Polars (Po)	AAD[a]	MAD[b]
ρ_{20}, g/cm^3	0.8816	1.0066	1.2599	0.0047	0.0184
n_{20}[c]	1.4770	1.53290	1.9778	0.0058	0.0277
$n_{20}(FRI_{20})$[d]	1.4824	1.5467	1.6772	0.0024	0.0115

[a] AAD-average absolute deviation.
[b] MAD-maximum absolute deviation.
[c] Pseudo-component n_{20} obtained by using Eq. (2).
[d] Pseudo-component n_{20} obtained by using Eq. (3).

modeling (Grieken et al., 2005; Coto et al., 2006a, b; Espada et al., 2007; Espada and Rodríguez, 2017.).

As presented by Coto and his colleagues (Grieken et al., 2005; Coto et al., 2006a, b; Espada et al., 2007), the mixtures were comprised of three pseudo-components (saturates (S), aromatics (A) and polars (Po)) through the compositions presented in Table 1 by applying the pseudo-component approach. The pseudo-component approach assumes that the average pseudo-component properties do not change throughout all of the raffinates and extracts. That is because that compared to the difference between the molecular composition of saturates, aromatics and polars, the difference between the chemical structure of saturates (or aromatics/polars) of feed, raffinates, and extracts is relatively small and could be ignored.

The data in Table 1 were divided into two groups: one dataset including F1 and its raffinates and extracts was used by the pseudo-component approach to obtain the average properties of pseudo-components, while the other including F2 and its raffinates and extracts was used to test the accuracy of the pseudo-component method.

According to the mixing rules of density (Eq. (1)) and refractive index (Eqs. (2) and (3)), the optimum values of ρ_{20} and n_{20} of each pseudo-component were obtained by minimizing the objective function (OF) (Eq. (25)) defined as the sum of squared deviations between experimental (P^{exp}) and calculated values (P^{cal}) for each property of the studied mixtures:
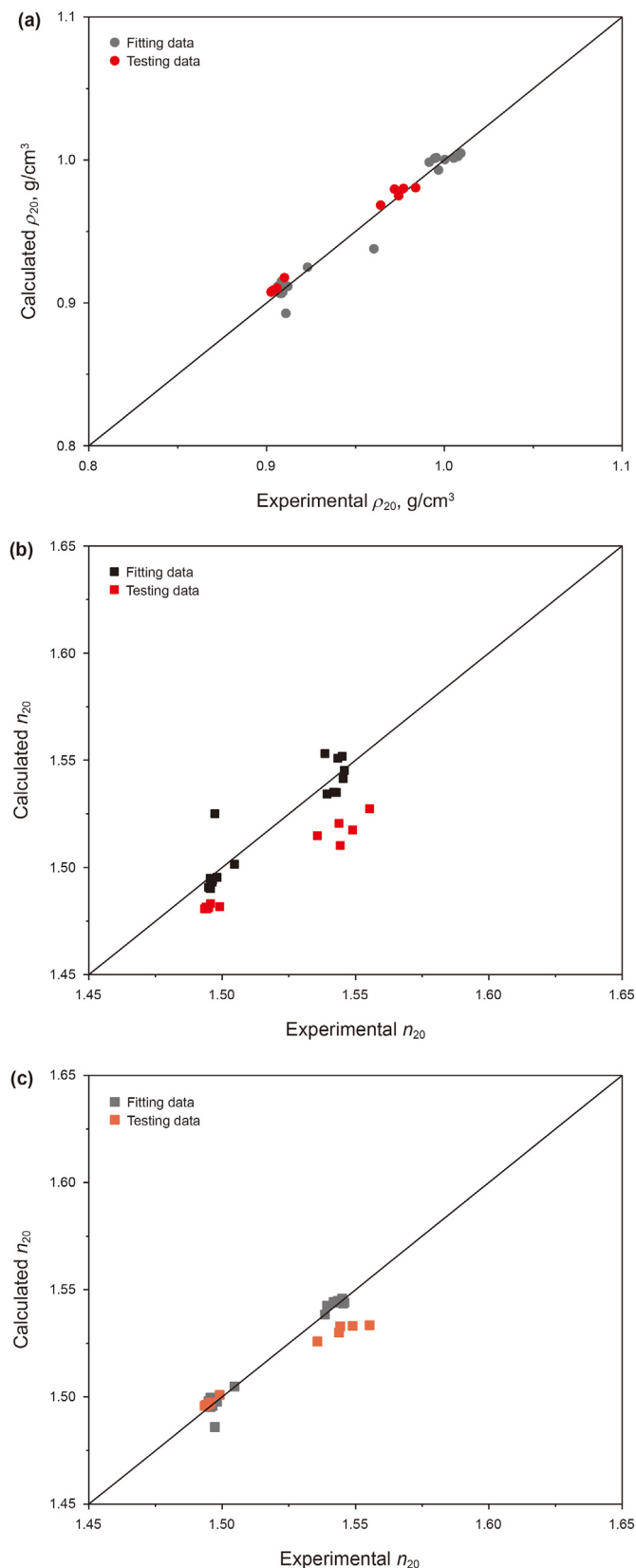
Fig. 1. Comparison of the experimental data and calculated ρ_{20} and n_{20} values by the pseudo-component approach for napthenic oils.
(**a**) ρ_{20} using Eq. (1), (**b**) n_{20} using Eq. (2), (**c**) n_{20} using Eq. (3).

Table 3
Average absolute deviations (AAD) and maximum absolute deviations (MAD) of ρ_{20} and n_{20} predictions for prehydrotreated naphthenic oils obtained by the pseudo-component method.

Property	AAD	AARD[a], %	MAD	MARD[b], %
ρ_{20}, g/cm³	0.0044	0.48	0.0074	0.79
n_{20}[c]	0.0200	1.31	0.314	2.21
$n_{20}(FRI_{20})$[d]	0.0008	0.50	0.0219	1.41

[a] AARD-average absolute relative deviation.
[b] MARD-maximum absolute relative deviation.
[c] Predicted n_{20} obtained by using Eq. (2).
[d] Predicted n_{20} obtained by using Eq. (3).

$$OF = \sum_{i=1}^{N} \left(P_i^{cal} - P_i^{exp} \right)^2 \tag{25}$$

The optimized average pseudo-component properties calculated from experimental data (F1 and its raffinates and extracts) are listed in Table 2. Deviations of predictions were calculated by means of average absolute deviation (AAD) and maximum absolute deviation (MAD). The limitation used for Eq. (1) was $\rho_{Po} > \rho_A > \rho_S$. The n_{20} values of pseudo-components obtained by using Eqs. (2) and (3) were under the limitations of $n_{Po} > n_A > n_S$ and $FRI_{Po} > FRI_A > FRI_S$, respectively. As can be seen, the average absolute deviations of ρ_{20} and n_{20} using mixing rules of Eqs. (1) and (2) were 0.0047 g/cm³ and 0.0058, respectively. But deviations of n_{20} were obviously lower when Eq. (3) was employed than those obtained by using Eq. (2), which was in consistent with the results obtained by Espada and Rodríguez (2017).

Furthermore, the testing data (F2 and its raffinates and extracts) in Table 1 were used for checking the accuracy of the pseudo-component method. As the distillation range for F1 and F2 was approximately the same, the average pseudo-component properties could be assumed as the same. ρ_{20} and n_{20} predictions for the fitting data and the testing data using mixing rules of Eqs. (1)–(3) were compared with experimental values, as shown in Fig. 1. Deviations derived from the pseudo-component method for the testing data were listed in Table 3. Results showed that AADs of ρ_{20} and n_{20} using mixing rules of Eqs. (1) and (3) were 0.0044 g/cm³ and 0.0008, respectively, which further validated the accuracy of the pseudo-component method. It also indicated that the mixing rule employing FRI was superior for n_{20} predictions.

An alternative approach is to characterize the oil into paraffins, naphthenes, and aromatics instead of saturates, aromatics, and polars. Fouladvand et al. (2021) divied lubricating oils into three pseudo-components in terms of paraffinic, naphthenic, and aromatic components. In this case, the pseudo-component contents according to ASTM D3238 were calculated based on the properties (density, refractive index and molecular weight) of oils instead of experimental analysis. And the average pseudo-component properties were determined in a similar way as described in this work. However, it was shown that the results of pseudo-component SG for naphthenes and aromatics (1.8861 and 1.0200, respectively) were unreasonable, as the density of aromatics is theoretically higher than naphthenes with the same boiling point. Therefore, the pseudo-component method in terms of saturates, aromatics and polars would be more appropriate.

4.2. Correlations between density and refractive index (or FRI)

Previous research (Espada and Rodríguez, 2017; Yarranton et al., 2015) has indicated that the quadratic correlation between density and refractive index (Eq. (10)) was evidently superior to other correlations. And deviations obtained by using Eq. (9) (derived from
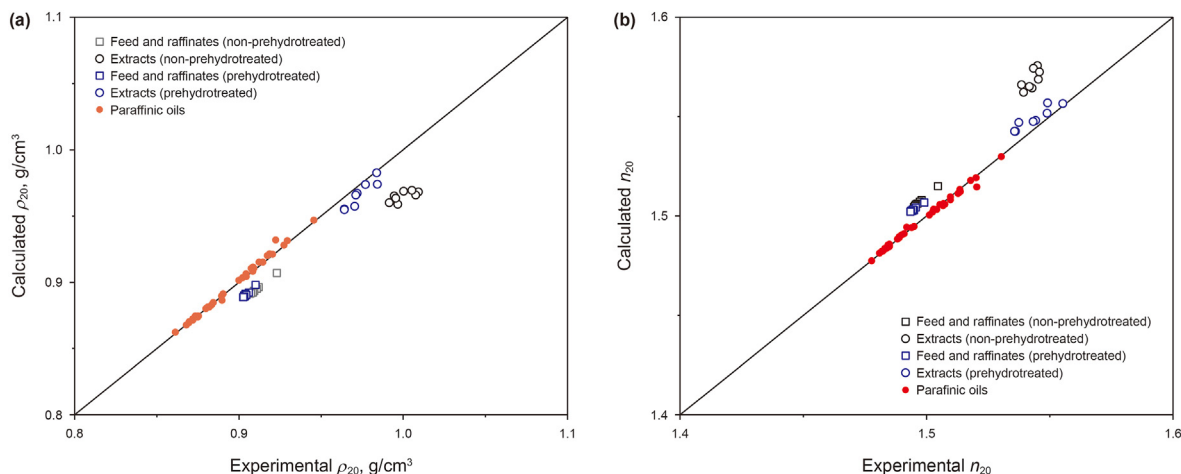
Fig. 2. Comparison of the experimental data and calculated ρ_{20} (**a**) and n_{20} (**b**) values obtained by the quadratic correlation for naphthenic and paraffinic distillates.

Table 4
Average absolute deviations (AAD) and maximum absolute deviations (MAD) of ρ_{20} and n_{20} predictions for naphthenic oils and paraffinic oils obtained by the quadratic correlation.

Source	ρ_{20}				n_{20}			
	AAD, g/cm³	AARD[b], %	MAD, g/cm³	MARD[b], %	AAD	AARD[b], %	MAD	MARD[b], %
Naphthenic oils	0.0178	1.87	0.0420	4.17	0.0120	0.79	0.0308	2.00
Paraffinic oils[a]	0.0012	0.14	0.0093	1.00	0.0007	0.05	0.0059	0.39

[a] Source: Ref. (Achtermann et al., 1992; Riazi and Daubert., 1986).
[b] AARD-average absolute relative deviation, MARD-maximum absolute relative deviation.

the One-Third rule) which were listed in Table A1 (Appendix) also presented significantly larger values than those derived from the quadratic correlation, which was in good agreement with situations when applying this correlation to heavy petroleum fractions (Yarranton et al., 2015). Thus, only ρ_{20} and n_{20} predictions by the quadratic correlation (Eq. (10)) were discussed in this paper.

4.2.1. Predictions by the quadratic correlation

ρ_{20} and n_{20} values of the studied naphthenic mixtures (F1, F2 and their raffinates and extracts) in Table 1 were calculated by the quadratic correlation. Results for ρ_{20} and n_{20} predictions obtained by applying the correlation were compared with experimental values, as shown in Fig. 2. In addition, predictions and experimental

data of paraffinic distillates during solvent extraction in the literature (Singh and Kishore, 2010; Mostafa et al., 2019) were also compared in Fig. 2 in order to clarify the difference between naphthenic and paraffinic oils.

The paraffinic data is from the literature (Singh and Kishore, 2010; Mostafa et al., 2019).

Fig. 2 showed that the calculated ρ_{20} and n_{20} values were in good agreement with experimental data for paraffinic distillates, which revealed the suitability of this quadratic relationship between density and refractive index for paraffinic mixtures. However, the ρ_{20} predictions of naphthenic oils obtained by the quadratic correlation were apparently lower than the experimental values. And systematic overestimation for n_{20} was yielded for the naphthenic
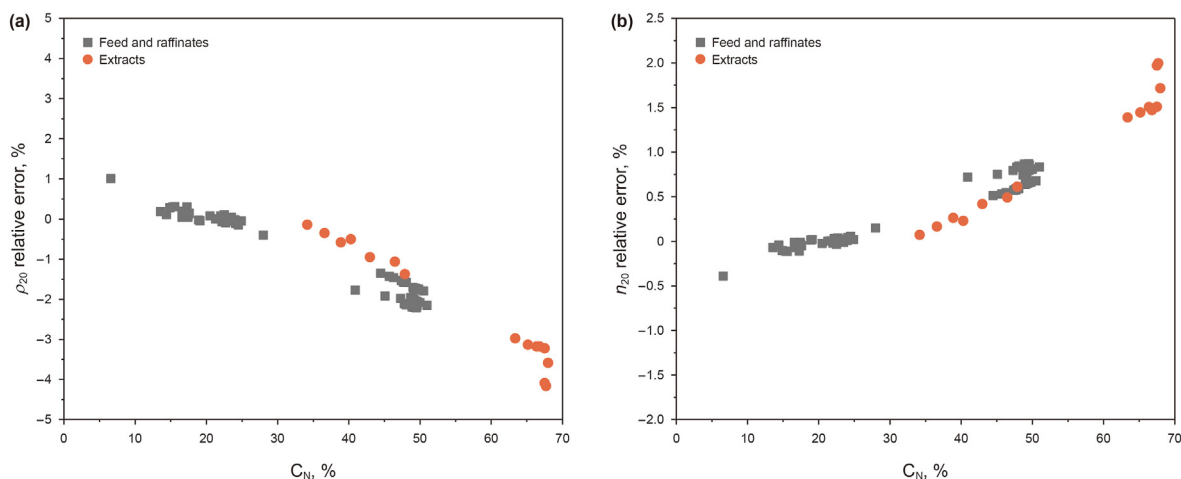

Fig. 3. The relative errors of ρ_{20} and n_{20} derived from the quadratic correlation versus C_N values of oils.

mixtures. As shown in our previous paper (Xu and Liu, 2021), deviations of the quadratic correlation for pure hydrocarbons, such as paraffins, monocyclic naphthenes, monocyclic aromatics, condensed ring naphthenes, and condensed ring aromatics, were compared. Results showed that deviations of condensed ring naphthenes were the largest. Hence the higher deviation of the quadratic correlation for naphthenic oils was probably attributed to the higher concentration of condensed naphthene rings.

Table 4 showed AAD (average absolute deviation) of ρ_{20} and n_{20} predictions obtained by the quadratic correlation. Results further indicated obviously higher deviations for naphthenic oils (AAD about 0.0178 g/cm^3 and 0.0120 in the case of ρ_{20} and n_{20} predictions, respectively) than those for paraffinic oils (AAD about 0.0012 g/cm^3 and 0.0007 in the case of ρ_{20} and n_{20} predictions, respectively). It was further evidence of the statement that the quadratic correlation was more suitable for paraffinic oils rather than naphthenic oils.

It can also be seen from Fig. 2 that deviations for the extracts were clearly larger than those for the raffinates in the case of the raw naphthenic oils, while the opposite behavior was observed for the prehydrotreated distillates. The results were closely related to the carbon-type composition. As for the raw naphthenic oils, the C_N values of the extracts were evidently higher than those of the raffinates. But the lower C_N values of the extracts than those of the raffinates for the prehydrotreated oils weakened the effect of naphthenic rings.

For further exploring the effect of carbon-type composition (in terms of paraffinic carbons, naphthenic and aromatic carbons) on predictions obtained by the quadratic correlation, the relative errors of ρ_{20} and n_{20} derived from the quadratic correlation versus C_N values of oils were plotted in Fig. 3 based on the data of naphthenic and paraffinic oils. As can be observed, the relative errors of ρ_{20} and n_{20} predicted by the quadratic correlation were approximately linearly correlated with the C_N values of oils. The absolute relative errors increased with increasing C_N values regardless of extracts and raffinates, which further implied that the quadratic correlation suggested by Yarranton et al. (2015) was more suitable for paraffinic oils with lower C_N values. When the C_N value of oils was higher than 20%, ρ_{20} predictions obtained by the quadratic correlation underestimated experimental values, and overestimation was yielded for n_{20} predictions. Moreover, the prediction errors of ρ_{20} and n_{20} increased sharply with the increase of C_N values when the C_N value of oils (extracts) was larger than 67%, which suggested the linear trend was no longer suitable. Therefore, it can be concluded that predictions obtained by the quadratic correlation were not satisfactory for naphthenic oils with higher C_N values.

4.2.2. Predictions by the modified quadratic correlation

The quadratic correlation was further modified to fit the experimental data of naphthenic oils shown in Table 1. Then the optimal parameters in Eq. (10) were obtained by minimization of the objective function (Eq. (25)), the modified quadratic correlation was given by:

$$\rho_{20} = -0.6934 + 7.3429 FRI_{20} - 6.665(FRI_{20})^2 \qquad (26a)$$

$$FRI_{20} = 0.6633 - 0.4450(1.601 - \rho_{20})^{0.5} \qquad (26b)$$

Fig. 4 presented the ρ_{20} and n_{20} predictions for the naphthenic oils from the original and modified version of the quadratic correlation. The average and maximum absolute deviations for the original and modified correlations were summarized in Table 5.

Fig. 4 showed that predictions of density and refractive index for most oils were obviously improved by the modification. However, predictions for the enlarged area (corresponding to the extracts of
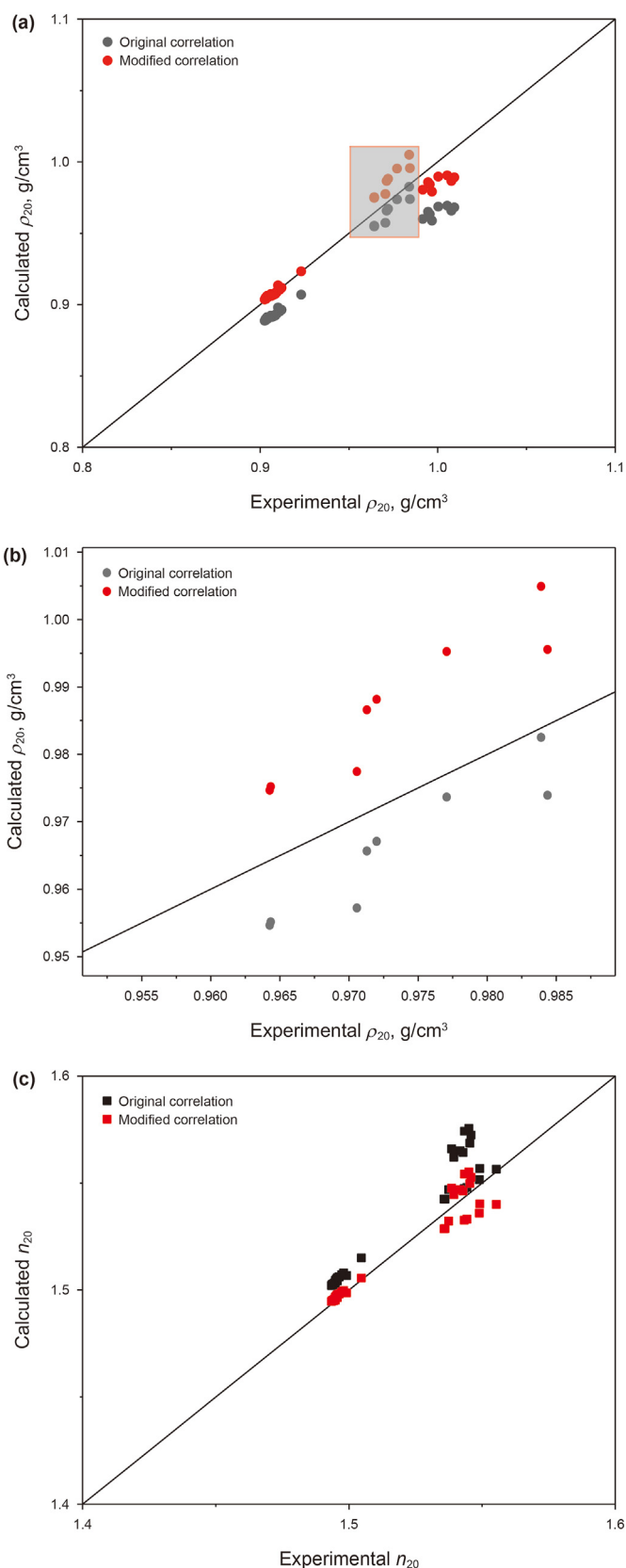

Fig. 4. Comparison of the ρ_{20} (**a**,**b**) and n_{20} (**c**) predictions derived from the original and modified version of the quadratic correlation for the naphthenic oils. (**b**) enlarged area of (**a**).

Table 5
Average absolute deviations (AAD) and maximum absolute deviations (MAD) of ρ_{20} and n_{20} predictions for naphthenic oils obtained by the original quadratic correlation and modified quadratic correlation.

Correlation	ρ_{20}				n_{20}			
	AAD, g/cm^3	AARD[a], %	MAD, g/cm^3	MARD[b], %	AAD	AARD[a], %	MAD	MARD[b], %
Original	0.0178	1.87	0.0420	4.17	0.0120	0.79	0.0308	2.00
Modified	0.0034	0.36	0.0210	2.13	0.0026	0.17	0.0153	0.99

[a] AARD-average absolute relative deviation.
[b] MARD-maximum absolute relative deviation.
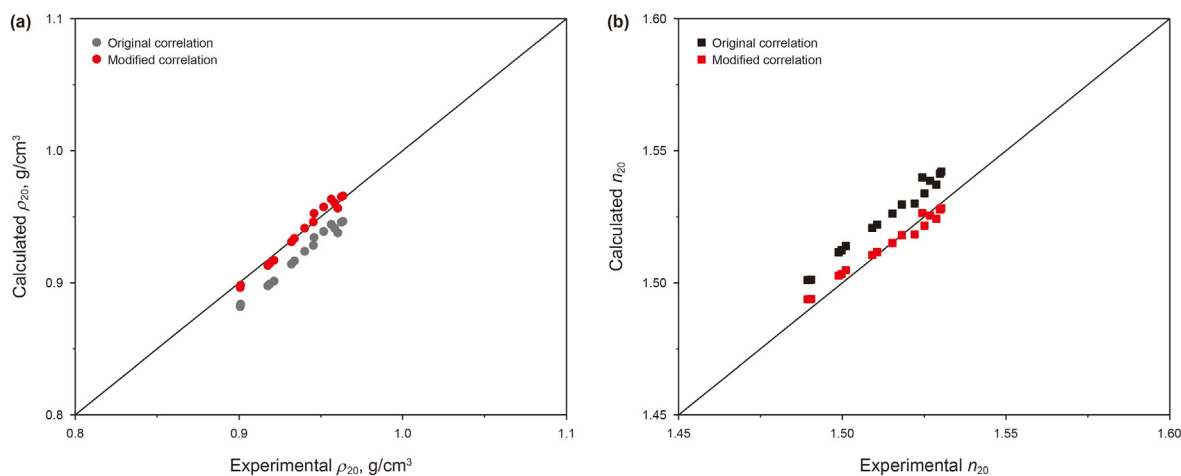
Fig. 5. Comparison of the ρ_{20} (**a**) and n_{20} (**b**) predictions for the naphthenic oils in literature (Wang, 2019; Liu et al., 2013) from the original and modified version of the quadratic correlation.

the prehydrotreated oils) by the modified correlation were not clearly improved compared with the original correlation. This was probably due to the lower C_N values (in the range of 30.4%–37.5%) of the oils in the enlarged area, which made it more suitable for the original correlation. It can be seen from Table 5 that deviations for prediction of ρ_{20} and n_{20} were both significantly reduced (from 1.87% to 0.36% for ρ_{20} and from 0.79% to 0.10% for n_{20}). Therefore, it can be concluded that the prediction accuracy of the modified correlation of the same functional form for the naphthenic oils has been significantly improved. Moreover, the prediction accuracy of naphthenic oils by using the modified correlation was nearly close to that by applying the pseudo-component method (Section 3.1). Hence a viscosity measurement is also required for knowing if the oil is paraffinic or naphthenic before the use of quadratic correlation.

In order to verify the reliability of the modified quadratic correlation for naphthenic oils during solvent extraction, the new correlation was also tested on experimental data of naphthenic vacuum distillates from literature (Wang, 2019; Liu et al., 2013). Fig. 5 showed the ρ_{20} and n_{20} predictions from the original and modified quadratic correlation, which suggested better prediction

accuracy from the modified quadratic correlation for naphthenic oils. The average absolute and relative deviations for the original and modified correlations were summarized in Table 6. As can be observed, the average absolute relative deviation of density was reduced from 1.86% to 0.14%, and that of refractive index was decreased from 0.75% to 0.05%. Thus it can be inferred that the new correlation greatly improved the predictions of naphthenic oils in comparison with the original correlation, which validated the reliability of the modified quadratic correlation for naphthenic distillates.

4.3. Effect of temperature

Effect of temperature was mainly analyzed from two aspects: one was the influence of temperature on the relationship between density and refractive index, the other was the variation of density and refractive index with temperature. Accurate predictions of density and refractive index for naphthenic oils at different temperatures would be acquired through the analysis of these two aspects.

Table 6
Average absolute deviations (AAD) and maximum absolute deviations (MAD) of ρ_{20} and n_{20} predictions for naphthenic oils in literature (Wang, 2019; Liu et al., 2013) obtained by the quadratic correlation.

Correlation	ρ_{20}				n_{20}			
	AAD, g/cm^3	AARD[a], %	MAD, g/cm^3	MARD[b], %	AAD	AARD[a], %	MAD	MARD[b], %
Original	0.0174	1.86	0.0227	2.36	0.0113	0.75	0.0154	2.00
Modified	0.0012	0.14	0.0093	1.00	0.0007	0.05	0.0059	0.39

[a] AARD-average absolute relative deviation.
[b] MARD-maximum absolute relative deviation.

Table 7
FRI/ρ ratios of naphthenic feed oils, raffinates and extracts at different temperatures.

Fraction	FRI/ρ			
	at 20 °C	at 40 °C	at 70 °C	at 90 °C
F1	0.3211	0.3219	0.3225	0.3231
F1-R1	0.3214	0.3220	0.3228	0.3233
F1-R2	0.3214	0.3220	0.3228	0.3233
F1-R3	0.3215	0.3221	0.3232	0.3234
F1-R4	0.3214	0.3221	0.3228	0.3233
F1-R5	0.3216	0.3222	0.3232	0.3224
F1-R6	0.3217	0.3227	0.3228	0.3239
F1-R7	0.3214	0.3221	0.3228	0.3240
F1-R8	0.3213	0.3220	0.3227	0.3235
F1-R9	0.3216	0.3222	0.3229	0.3232
F1-E1	0.3132	0.3139	0.3150	0.3157
F1-E2	0.3130	0.3137	0.3146	0.3164
F1-E3	0.3162	0.3169	0.3182	0.3186
F1-E5	0.3169	0.3176	0.3187	0.3203
F1-E7	0.3149	0.3157	0.3167	0.3174
F1-E8	0.3160	0.3171	0.3179	0.3195
F1-E9	0.3161	0.3168	0.3179	0.3193
F2	0.3226	0.3232	0.3241	0.3246
F2-R1	0.3222	0.3228	0.3236	0.3241
F2-R2	0.3226	0.3228	0.3235	0.3242
F2-R3	0.3225	0.3228	0.3235	0.3243
F2-R4	0.3221	0.3227	0.3235	0.3240
F2-R5	0.3222	0.3228	0.3235	0.3240
F2-R6	0.3221	0.3228	0.3235	0.3244
F2-R7	0.3221	0.3228	0.3235	0.3246
F2-R8	0.3222	0.3228	0.3236	0.3241
F2-E1	0.3264	0.3272	0.3282	0.3292
F2-E3	0.3249	0.3244	0.3243	0.3263
F2-E6	0.3232	0.3231	0.3251	0.3261
F2-E7	0.3247	0.3255	0.3265	0.3272
F2-E8	0.3220	0.3223	0.3220	0.3239

4.3.1. Effect of temperature on correlations between density and refractive index

Based on the FRI/ρ ratios at different temperatures in Table 7, it can be observed that the FRI/ρ ratio of naphthenic oils increased slightly with increasing temperature. As with any ratio method (Eq. (11)), the errors for predicting density and refractive index would increase as temperature increases. Hence, the deviations of density and refractive index at other temperatures predicted by Eq. (11) would be larger as temperature difference increases. However, according to the modified quadratic correlation (Eq. (26)), the FRI/ρ ratio changes with density, which also varies with temperature.

Whether the modified quadratic correlation was suitable for density and refractive index of naphthenic oils at other temperatures remains unknown. Therefore, the prediction accuracy obtained by the modified quadratic correlation for naphthenic oils at other temperatures were examined.
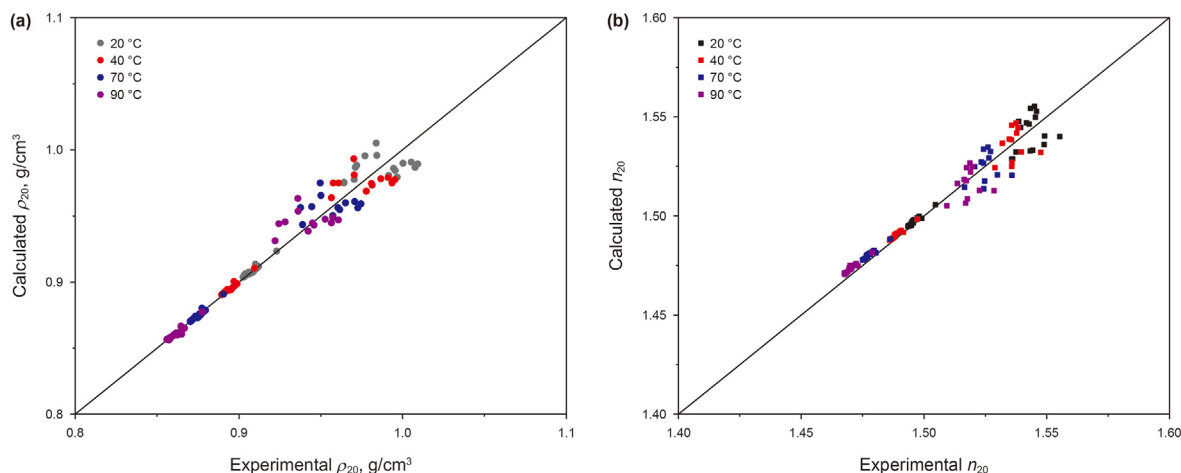
Predictions of density and refractive index from the modified quadratic correlation were compared to the experimental values measured at different temperatures for naphthenic oils, as depicted in Fig. 6. Deviations of predictions for naphthenic oils shown in Table 8 illustrated that AARDs of the modified quadratic correlation for predictions of density and refractive index at 20–90 °C were in the range of 0.36%–0.58% and 0.17%–0.30%, respectively. Results showed that deviations of density and refractive index were not evidently increased with increasing measuring temperature. And when the C_N value of oils was below 37%, the maximum deviations for ρ_{20} and n_{20} were observed. According to the previous study (Xu and Liu, 2021), the original quadratic correlation was more suitable for paraffinic oils with a C_N value of lower than 37%. Thus, it was presumed that the modified quadratic correlation was more suitable for naphthenic oils with a C_N value of higher than 37%.

In conclusion, the modified correlation of the same functional form could well describe the relationship between density and refractive index of naphthenic oils at 20–90 °C.

4.3.2. Temperature dependence of density and refractive index

According to the method described in Section 2.3, the density at any temperature in the liquid region was calculated using Eqs. (14)–(17), and the effect of temperature on refractive index was examined using Eqs. (19)–(22). Based on the ρ_{20} and n_{20} data, the density and refractive index of raffinates (with low aromatic concentration) and extracts (with high aromatic content) at 40 °C, 70 °C and 90 °C were calculated by using the thermal coefficients for saturates and aromatics, respectively. Experimental data and the calculated density and refractive index of raffinates and extracts at different temperatures were compared in Fig. 7. It can be seen from Fig. 7 that the predictions were very consistent with the experimental values, indicating that the temperature dependence of density and refractive of raffinates and extracts can be accurately described by the thermal coefficients for saturates and aromatics, respectively.

Deviations of the density and refractive index at 40 °C, 70 °C and 90 °C for the thermal coefficients were shown in Table 9. The deviations of density and refractive index slightly increased for
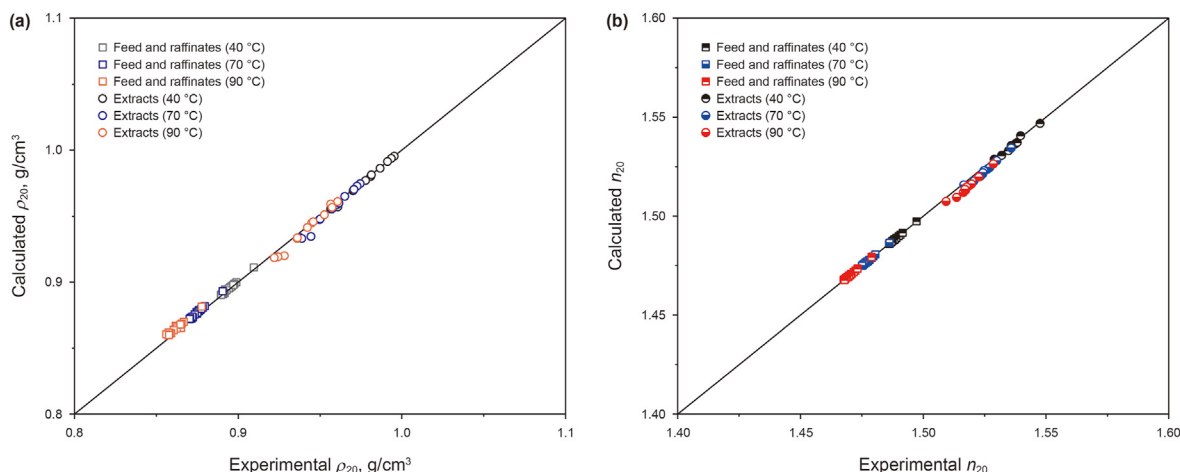

Fig. 6. Comparison of experimental values measured at different temperatures and the calculated values of density (**a**) and refractive index (**b**) derived from the modified quadratic correlation for naphthenic oils.

Table 8
Average absolute deviations (AAD) and maximum absolute deviations (MAD) of ρ and n predictions for naphthenic oils obtained by the modified quadratic correlation.

Temperature, °C	ρ_T				n_T			
	AAD, g/cm³	AARD[a], %	MAD, g/cm³	MARD[b], %	AAD	AARD[a], %	MAD	MARD[b], %
20	0.0034	0.36	0.0210	2.13	0.0026	0.17	0.0153	0.99
40	0.0056	0.58	0.0229	2.36	0.0039	0.25	0.0156	1.01
70	0.0052	0.55	0.0249	2.63	0.0041	0.28	0.0154	1.00
90	0.0053	0.57	0.0270	2.89	0.0044	0.30	0.0158	1.03

[a] AARD-average absolute relative deviation.
[b] MARD-maximum absolute relative deviation.

Fig. 7. Comparison of experimental data and the calculated density (**a**) and refractive index (**b**) of raffinates and extracts at different temperatures.

raffinates and extracts as the difference between the measured temperature and the reference temperature (20 °C) was larger. And it can be seen that the predictions of raffinates were slightly more accurate than those of extracts at different temperatures.

As for density, when the equations were modified to a more general type (Eq. (27)), deviations could be further decreased by selecting a reference temperature T_0 closer to the measured temperature T. Similar modification could be made for refractive index (or *FRI*) (Eq. (28)).

$$\rho = \rho_{20} \exp(-\alpha_V(T - T_0))$$
$$\alpha_V(\text{sat}) = -0.0008278 + 0.001375/\rho_{T_0} \qquad (27)$$
$$\alpha_V(\text{aro}) = -0.001500 + 0.002224/\rho_{T_0}$$

$$FRI = FRI_{20} \exp(-\alpha_F(T - T_0))$$
$$\alpha_F(\text{sat}) = -0.002276 + 0.005567 FRI_{T_0} \qquad (28)$$
$$\alpha_F(\text{aro}) = -0.002619 + 0.006168 FRI_{T_0}$$

Moreover, the temperature dependence of refractive index can

also be determined by the empirical equation (Eq. (23)). The refractive index predictions at different temperatures calculated by Eq. (23) were compared to those obtained from Eqs. (19)–(22), as shown in Table 9. Results indicated that the predictions of refractive index obtained by the thermal coefficients were more accurate for the raffinates. But the empirical equation was proved to be more accurate for the refractive index predictions of the extracts.

5. Conclusions

With regard to naphthenic oils during solvent extraction, predictions of density and refractive index obtained by the pseudo-component approach and the quadratic correlation were both evaluated. The pseudo-component approach is a method to predict density and refractive index from composition while the correlation method merely relates density to refractive index. Results illustrated that predictions yielded by the pseudo-component method were in good agreement with the experimental values

Table 9
Average absolute deviations (AAD) of ρ and n predictions for naphthenic oils at different temperatures.

Oil	T, °C	ρ_T		n_T			
				α_F		Rule	
		AAD, g/cm³	AARD[a], %	AAD	AARD[a], %	AAD	AARD[a], %
Feed and raffinates	40	0.0008	0.09	0.0002	0.01	0.0006	0.04
	70	0.0018	0.20	0.0002	0.01	0.0016	0.11
	90	0.0029	0.33	0.0002	0.01	0.0023	0.15
Extracts	40	0.0011	0.11	0.0010	0.01	0.0006	0.04
	70	0.0027	0.29	0.0023	0.15	0.0010	0.07
	90	0.0026	0.27	0.0034	0.22	0.0017	0.11

[a] AARD-average absolute relative deviation.

for naphthenic oils. And the use of a function of refractive index (FRI_{20}) as a pseudo-component property remarkably improved n_{20} predictions for the naphthenic mixtures. Therefore it can be concluded that the pseudo-component method was accurate for predicting the density and the refractive index of both paraffinic distillates and naphthenic oils. However, the quadratic correlation exhibited systematic deviations, which presented significantly higher deviations for naphthenic oils than those for paraffinic oils. The absolute relative errors of ρ_{20} and n_{20} predicted by the quadratic correlation increased with increasing C_N values of oils regardless of extracts and raffinates. Therefore the correlation was modified to fit for naphthenic oils with higher C_N value. Results indicated that predictions for naphthenic oils obtained by the modified quadratic correlation were similar to those ones yielded by the pseudo-component approach, which were both in good agreement with the experimental data. And it was implied that the new quadratic correlation of the same functional form was more suitable for naphthenic oils with a C_N value of higher than 37%. And the previous correlation was still suitable for paraffinic oils. Furthermore, it should be noteworthy that a viscosity measurement is also required to know if the oil is paraffinic or naphthenic before the use of quadratic correlation.

Effect of temperature on density and refractive index of naphthenic oils was also examined for predicting those properties at different temperatures. Results suggested that the modified quadratic correlation was accurate for describing the relationship between density and refractive index of naphthenic oils at 20–90 °C. The temperature dependence of the density and the refractive index for raffinates and extracts could be accurately predicted by the thermal coefficients for saturates and aromatics, respectively. Regrading the extracts, the empirical equation was proved to be more accurate for predictions of the refractive index compared with the method by applying the thermal coefficient.

Declaration of competing interest

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

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.petsci.2023.01.003.

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