Temperature coefficients of the refractive index for hydrocarbons and binary mixtures

Qing Wen [a], Jun Shen [a,*], Zheng Shi [a], Eben Dy [a], Kirk H. Michaelian [b], Craig Fairbridge [b], Nelson G.C. Astrath [c], Jurandir H. Rohling [c], Mauro L. Baesso [c]

[a] Institute for Fuel Cell Innovation, National Research Council of Canada, 4250 Wesbrook Mall, Vancouver, British Columbia, Canada V6T 1W5
[b] CanmetENERGY, Natural Resources Canada, One Oil Patch Drive, Devon, Alberta, Canada T9G 1A8
[c] Departamento de Física, Universidade Estadual de Maringá, Av. Colombo 5790, Maringá, Paraná 87020-900, Brazil

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ABSTRACT

Temperature coefficients of the refractive index (dn/dT) for nine hydrocarbons and two sets of binary mixtures were investigated in this work. The measured $-dn/dT$ values for the pure hydrocarbons were found to be inversely proportional to their molar volumes (V_m) and molecular weights (M). Experimental data for binary mixtures show that $-dn/dT$ varies linearly with volume and mass fractions, consistent with theory derived from the linear relationships of $-dn/dT$ with $1/V_m$ and $1/M$ for individual hydrocarbons. This study should aid the interpretation of the observed correlations of dn/dT with physical and combustion properties of diesel fuels.

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1. Introduction

The temperature coefficient of the refractive index (dn/dT) is a parameter that may potentially be used to evaluate hydrocarbon fuel quality. Castro et al. previously reported that dn/dT can be utilized to discriminate different types of biodiesel oils and determine their degree of purity [1]. Recent studies in our laboratory reveal that dn/dT is clearly correlated to the performances of diesel fuels in both Homogeneous Charge Compression Ignition (HCCI) and Premixed Charge Compression Ignition (PCCI) engines, which offer the potential for diesel-like fuel conversion efficiency and ultra-low nitrogen oxide and particulate matter emissions [2,3]. Significant effort has been dedicated to investigate the effects of various fuel properties on combustion and emission in HCCI and PCCI engines previously [2–6]. In general, fuels with high $-dn/dT$ values were found to yield low fuel consumption, and require high combustion phasing to achieve optimal performance. Additionally $-dn/dT$ is strongly correlated with other physical and combustion parameters. For example, $-dn/dT$ varies inversely with cetane number (a measure of ignition delay), distillation temperature, flash point, and viscosity. These relationships may lead to the identification of key property parameters which can be used to measure diesel fuel quality and compare it to accepted standards.

Several studies involving molecular-level interpretations of dn/dT have been reported previously [1,7,8]. It is generally accepted that dn/dT depends on molecular size, concentration, and electronic polarizability; however, quantitative information on the relationships between dn/dT and these molecular properties is not available. The goal of the present work is to understand dn/dT on a molecular level so as to interpret the correlations observed for diesel fuels. Representative major hydrocarbon species present in these fuels were selected for this investigation.

A conventional diesel fuel consists primarily of n-paraffins, iso-paraffins, cycloparaffins and aromatics; the carbon numbers of the species in such a fuel range from approximately 10–22, with an average of 14 or 15 [9]. Based on these trends, several common hydrocarbons can be proposed as major components in the development of surrogate fuels. These compounds are n-hexadecane, 2,2,4,4,6,8,8-heptamethylnonane, 2-methyloctadecane, n-butylcyclohexane, cis-decalin, 1,3,5-trimethylbenzene, n-dodecylbenzene, 1-methylnaphthalene, and tetralin. These species were investigated in this work as a starting point for understanding the dn/dT properties of diesel fuels. The dn/dT values of the nine pure hydrocarbons and two sets of binary mixtures were measured and interpreted in this work.

2. Experimental

n-Hexadecane, 2,2,4,4,6,8,8-heptamethylnonane, cis-decalin, 1-methylnaphthalene and tetralin, purchased from Sigma–Aldrich, had stated purities of 99%, 98%, 99%, 95%, and 99%, respectively. n-Butylcyclohexane (99%), n-dodecylbenzene (97%), and 1,3,5-trimethylbenzene (>98%) were obtained from Alfa Aesar. 2-Methyloctadecane was obtained from ChemSampCo Inc. at a purity of 95%. Densities at 25 °C (ρ), molecular weights (M), and molar volumes (V_m) of these compounds are listed in Table 1. All chemicals were used as supplied without further purification. Two sets of

* Corresponding author. Fax: +1 604 221 3001.
E-mail address: jun.shen@nrc-cnrc.gc.ca (J. Shen).

Table 1
Density (ρ) at 25 °C,[a] molecular weight (M),[a] molar volume (V_m),[b] and measured $-dn/dT$ values of the pure hydrocarbons.

	ρ (g cm^{-3})	M (g mol^{-1})	V_m (cm^3 mol^{-1})	$-dn/dT$ [c] (10^{-4} K^{-1})
n-Hexadecane	0.773	226.44	293	4.05 ± 0.01
2,2,4,4,6,8,8-Heptamethylnonane	0.793	226.44	286	3.95 ± 0.02
2-Methyloctadecane	0.783	268.52	342	3.98 ± 0.01
n-Butylcyclohexane	0.818	140.27	172	4.35 ± 0.01
cis-decalin	0.897	138.25	154	4.30 ± 0.01
1,3,5-Trimethylbenzene	0.864	120.19	139	4.91 ± 0.02
n-Dodecylbenzene	0.856	246.43	288	4.04 ± 0.01
1-Methylnaphthalene	1.001	142.20	142	4.73 ± 0.01
Tetralin	0.973	132.20	136	4.61 ± 0.03

[a] Provided by the manufacturers.
[b] Calculated as M/ρ.
[c] Measurement uncertainties reflect standard deviations of five measurements.

binary mixtures, [1-methylnaphthalene (1) + n-hexadecane (2)] and [1,3,5-trimethylbenzene (1) + n-dodecylbenzene (2)], were prepared using mass fractions determined with an analytical balance (precision ± 0.0001 g). Volume fractions were calculated using densities of the pure hydrocarbons (Table 1) and their mass fractions in the mixture; volumes were assumed to be additive, i.e., that they are unaffected by mixing. This assumption accords with the densities of mixtures measured by weighing a fixed volume of the liquids. The excess volumes were estimated to be less than 0.5% of the total volumes; these small contributions are not expected to affect the results presented below significantly.

The dn/dT values of the individual hydrocarbons and binary mixtures were measured using an optical interferometer system and are listed in Table 1. Details of the theory and experimental setup are given in Ref. [10]. Briefly, a liquid sample contained in a 10-mm quartz cuvette is uniformly irradiated by a weak He–Ne laser (633 nm); reflections from the two inner surfaces of the cuvette interfere to create fringes. A heating device induces a slow and uniform temperature variation in the sample, causing the fringes to move. Experiments were performed at temperatures from 25 to 35 °C. The temperature-dependent interferograms were used to calculate the magnitude of dn/dT. The dn/dT values in this narrow temperature interval are nearly constant for a given sample, hence average values are reported here.

3. Results and discussion

The parameter, dn/dT, can be expressed as the derivative of the Lorenz–Lorentz relation with respect to temperature [1,7,8]:

$$dn/dT = \frac{(n^2 - 1)(n^2 + 2)}{6n}(\varphi - \beta) \qquad (1)$$

where φ and β are the temperature coefficients of electronic polarizability and thermal expansion, respectively. $\frac{(n^2-1)(n^2+2)}{6n}$ is a function of number density (inversely proportional to molecular size) and
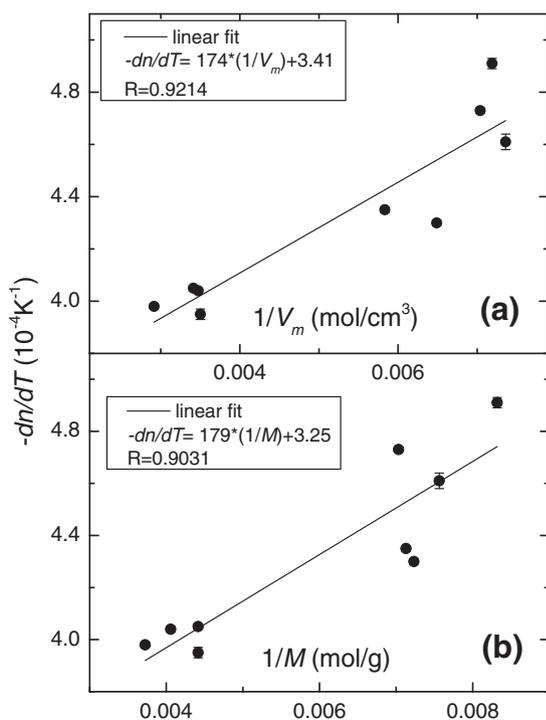

Figure 1. Measured $-dn/dT$ values of hydrocarbons as a function of (a) $1/V_m$ and (b) $1/M$. Error bars represent standard deviations of five measurements. Points, experimental data; solid lines, linear fits.
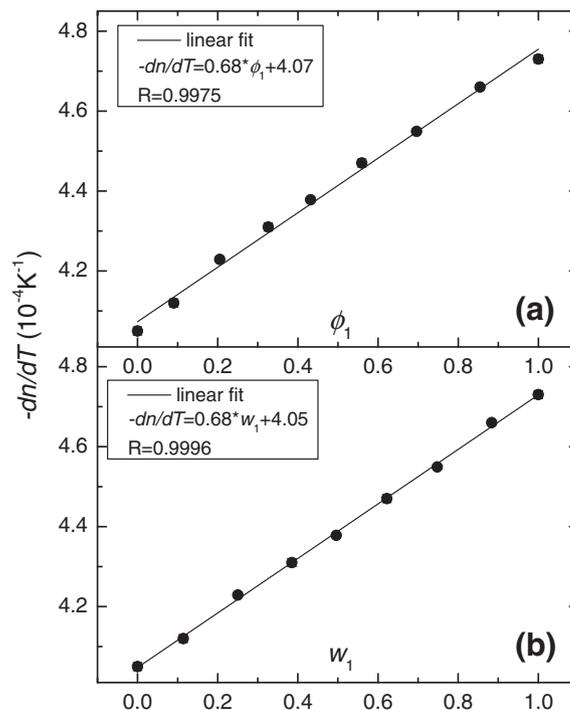

Figure 2. Measured $-dn/dT$ values of [1-methylnaphthalene (1) + n-hexadecane (2)] binary mixtures as functions of (a) volume fraction ϕ_1 and (b) mass fraction w_1 of 1-methylnaphthalene. Details are the same as in Figure 1. Lines in (a) and (b) were fitted using Eqs. (4) and (5), respectively.
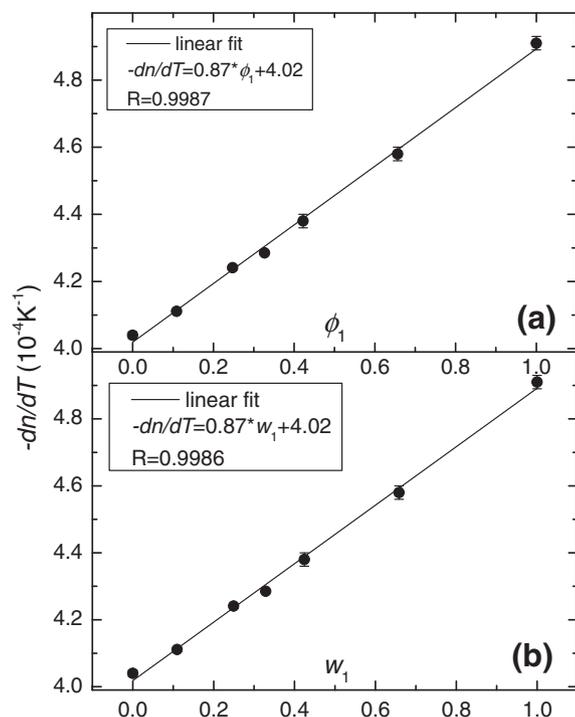
Figure 3. Measured −dn/dT values of [1,3,5-trimethylbenzene (1) + n-dodecylbenzene (2)] binary mixtures as functions of (a) volume fraction ϕ_1 and (b) mass fraction w_1 of 1,3,5-trimethylbenzene. Details are the same as in Figure 2.

electronic polarizability. φ is associated with the electronic polarizing power Z/a^2 where Z is charge magnitude and a denotes separation between charged particles, and thus depends on the electric dipole moment, size, and concentration of the molecules [1,7]. β Can be written as $-\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)$ and for most hydrocarbons $\frac{\partial\rho}{\partial T}$ varies inversely with molecular weight [11]. As a result, dn/dT conveys information about molecular size (or weight). For nonpolar molecules such as the hydrocarbons investigated in this study φ is generally much less than β, and thus the dn/dT values are always negative. For convenience, $-dn/dT$ quantities are therefore used when discussing the magnitude of this parameter.

Figure 1 illustrates the variation of measured $-dn/dT$ with $1/V_m$ and $1/M$ for the nine hydrocarbons. The parameters $1/V_m$ and $1/M$ are the inverse of molecular size and weight, respectively. The error bars in Figure 1 show the standard deviations of five measurements. The figure shows that $-dn/dT$ generally increases with $1/V_m$ and $1/M$, in other words, $-dn/dT$ decreases as molecular size or weight increases. Correlations of $-dn/dT$ with $1/V_m$ and $1/M$ can be approximately fitted using linear functions, with both correlation coefficients greater than 0.9. Similar linear relationships between $-dn/dT$ and $1/V_m$ (or $1/M$) were also found for 10 other hydrocarbons; their $-dn/dT$ values are reported in Table 5.2 of Ref. [12]. These compounds are n-paraffins (with carbon number

from 5 to 10), cyclohexane, benzene, toluene, and o-xylene. It should be noted that the $-dn/dT$ values for organic materials containing heteroatoms such as oxygen (e.g., alcohols and ketones) may deviate from this linear relationship due to significantly changed electronic polarizability arising from the heteroatoms. However, in general, smaller $-dn/dT$ values are expected for larger hydrocarbon molecules. This is consistent with the observations that $-dn/dT$ decreases with distillation temperature, flash point and viscosity for diesel fuels with low heteroatom contents.

The $-dn/dT$ values of binary hydrocarbon mixtures can be deduced from the following relationships:

$$\frac{1}{(V_m)_{mix}} = \frac{\phi_1}{(V_m)_1} + \frac{\phi_2}{(V_m)_2} \qquad (2)$$

$$\frac{1}{M_{mix}} = \frac{w_1}{M_1} + \frac{w_2}{M_2} \qquad (3)$$

where ϕ_i and w_i ($i = 1,2$) are volume and mass fractions of pure component i, respectively, with the relationships $\phi_1 + \phi_2 = 1$ and $w_1 + w_2 = 1$. Taking into account the approximately linear relationships between $-dn/dT$ and $1/V_m$ (or $1/M$), the following expressions can be written for binary mixtures:

$$\left(-\frac{dn}{dT}\right)_{mix} = \left(-\frac{dn}{dT}\right)_1\phi_1 + \left(-\frac{dn}{dT}\right)_2\phi_2$$
$$= \left(-\frac{dn}{dT}\right)_2 + \phi_1\left(\left(-\frac{dn}{dT}\right)_1 - \left(-\frac{dn}{dT}\right)_2\right) \qquad (4)$$

$$\left(-\frac{dn}{dT}\right)_{mix} = \left(-\frac{dn}{dT}\right)_1 w_1 + \left(-\frac{dn}{dT}\right)_2 w_2$$
$$= \left(-\frac{dn}{dT}\right)_2 + w_1\left(\left(-\frac{dn}{dT}\right)_1 - \left(-\frac{dn}{dT}\right)_2\right) \qquad (5)$$

Eqs. (4) and (5) show that $-dn/dT$ is expected to vary linearly with the volume and mass fractions for binary mixtures. Figures 2 and 3 show experimental $-dn/dT$ data as functions of volume and mass fractions of component 1 for two sets of binary mixtures; linear curve fitting of the data using Eqs. (4) and (5) was also carried out. The slopes and intercepts of the fitted curves were used to determine $-dn/dT$ for the pure components, yielding the results in Table 2. These calculated values agree well with the experimental results. It can also be noted that the correlation of $-dn/dT$ with volume fraction becomes equivalent to that with mass fraction in the limiting case where the densities of the two hydrocarbons are identical. This is consistent with the expressions for the fitted curves in Figure 3a and b where the two constituents, 1,3,5-trimethylbenzene and n-dodecylbenzene, have similar densities (Table 1). An analogous linear variation of dn/dT with concentration was reported previously for binary gas mixtures [13].

4. Summary

The $-dn/dT$ values of nine pure hydrocarbons, namely n-hexadecane, 2,2,4,4,6,8,8-heptamethylnonane, 2-methyloctadecane, n-butylcyclohexane, cis-decalin, 1,3,5-trimethylbenzene, n-dode-

Table 2
Comparison of measured $-dn/dT$ values ($10^{-4}K^{-1}$)[a] of pure hydrocarbons with those determined by linear curve fitting in Figures 2 and 3.[b]

	1-Methylnaphthalene	n-Hexadecane	1,3,5-Trimethylbenzene	n-Dodecylbenzene
Figure 2a	4.75 ± 0.03	4.07 ± 0.01		
Figure 2b	4.73 ± 0.01	4.05 ± 0.01		
Figure 3a			4.89 ± 0.03	4.02 ± 0.01
Figure 3b			4.89 ± 0.03	4.02 ± 0.01
Measured	4.73 ± 0.01	4.05 ± 0.01	4.91 ± 0.02	4.04 ± 0.01

[a] Uncertainties are standard deviations of five measurements.
[b] Uncertainties of calculated values were determined from the standard errors of the fitted parameters.

cylbenzene, 1-methylnaphthalene, and tetralin, were measured using an optical interferometer system in this work. The results show that, to a first approximation, the $-dn/dT$ values for hydrocarbons increase linearly with $1/V_m$ and $1/M$; stated differently, $-dn/dT$ decreases as the molecular size or weight becomes larger. However, this trend does not occur for compounds containing heteroatoms, such as alcohols and ketones. The relationship between $-dn/dT$ and molecular size (or molecular weight) is consistent with observations that $-dn/dT$ decreases with distillation temperature, flash point and viscosity for diesel fuels with low heteroatom contents.

Two sets of binary mixtures, [1-methylnaphthalene (1) + n-hexadecane (2)] and [1,3,5-trimethylbenzene (1) + n-dodecylbenzene (2)], were also investigated. The measured $-dn/dT$ values were found to be proportional to the volume and mass fractions. This is consistent with a theory based on the linear relationships of $-dn/dT$ with $1/V_m$ and $1/M$ for single hydrocarbons. The $-dn/dT$ values for these hydrocarbons can be determined by fitting data for binary mixtures to the theory, the determined values being in good agreement with experimental data. The correlation of $-dn/dT$ with volume fraction becomes equivalent to that with mass fraction when the densities of the two mixed hydrocarbons are equal.

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