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Experimental Thermal and Fluid Science 29 (2005) 681–684
Experimental Thermal and Fluid Science
www.elsevier.com/locate/etfs

Refractive index temperature and wavelength dependencies of normal saturated fatty acids in liquid state

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Received 13 August 2004; received in revised form 1 November 2004; accepted 9 November 2004

Abstract

Measurements of the refractive index from 293 to 321 K at four fixed wavelengths, from 587.6 to 404.7 nm, are reported for valeric acid (pentanoic acid), caproic acid (hexanoic acid), oenantic acid (heptanoic acid), caprylic acid (octanoic acid), and pelargonic acid (nonanoic acid). We also report the temperature and wavelength dependencies of the refractive index obtained from a least-squares routine. The agreement between the measured and calculated refractive indices lies within the experimental uncertainty.

Keywords: Refractive index; Pentanoic acid; Hexanoic acid; Heptanoic acid; Octanoic acid; Nonanoic acid

1. Introduction

Refractive index in the visible range is an important physical property in the characterization and identification of pure organic liquids. Precise values of this optical property are required at different wavelengths and temperatures. On the other hand, fatty acids are compounds of major interest by their industrial usefulness as reagents, lubricants, and food precursors. Also, many alkanoic acids play an important role in the manufacture of many synthetic materials [1].

Nevertheless, few systematic studies of optical and thermo-optical properties of these apparently very common organic solvents are reported. A rather fragmentary and incomplete information is usually found in the literature. Most of the available data for these organic liquids are related to the Na-D line and experimental values are usually referred to arbitrary and scattered temperatures [2–4]. To our knowledge, there are only two references where refractive index for fatty acids is reported as a function of temperature, but these studies are restricted to the Na-D line [5,6].

We have measured the refractive indices of the normal saturated fatty acids in the liquid state, from valeric to pelargonic inclusive, at a sufficient number of temperatures between 293 and 321 K to correlate temperature and refractive index for each acid, and at four experimental wavelengths in the visible, namely, 587.6, 546.1, 435.8, and 404.7 nm. As previously reported for benzene and benzene derivatives [7], a complete equation correlating n, T, and λ in the visible range, from 293 to 321 K at room pressure, is given for the five fatty acids under study.

We have compared the refractive indices calculated from our equation with some published data relatives to the Na-D line for these systems. The agreement is quite satisfactory.

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0894-1777/$ - see front matter
doi:10.1016/j.expthermflusci.2004.11.002

Nomenclature

A	n_λ vs. T zero order fitting parameter, dimensionless	n	refractive index, dimensionless
a_0	$n(T,\lambda)$ vs. λ and T fitting parameter, dimensionless	n_D	refractive index at sodium—D line, dimensionless
a_2	$n(T,\lambda)$ vs. λ and T fitting parameter, nm^2	n_λ	refractive index at fixed wavelength λ, dimensionless
B	n_λ vs. T first-order fitting parameter, K^{-1}	T	temperature, K
b_0	$n(T,\lambda)$ vs. λ and T fitting parameter, K^{-1}	λ	wavelength, nm
b_2	$n(T,\lambda)$ vs. λ and T fitting parameter, $nm^{-2}\,K^{-1}$	σ	standard deviation of fittings, dimensionless

2. Experimental section

Chemicals with purities of 99% or greater purchased from Fluka were used without further purification, although all compounds were degassed twice and dried over a molecular sieve before using. Purity had been previously checked by gas chromatography.

Refractive indices were measured with a Carl Zeiss Jena Pullfrich refractometer. Thermal control and apparatus description have been previously reported [7]. The experimental uncertainty has been estimated to be 1×10^{-4} at most. The slight accuracy decrease found for fatty acids experiments with regard to the benzene derivatives measured before with the same experimental equipment is attributed to the use of a different optical prism. The replacement of the prism is unavoidable due to the aggressive chemical behavior of fatty acids.

The measurement of the refractive index was carried out at seven temperatures (around 293, 298, 303, 308, 313, 318 and 321 K). Mercury, helium, and hydrogen light sources provided the four optical lines used in our experiments (587.6, 546.1, 435.8, and 404.7 nm). All the refractive indices reported in this paper are relative to air, nominally at 293.15 K and 0.1 MPa.

3. Results and discussion

The refractive indices n of valeric acid, caproic acid, oenantic acid, and pelargonic acid have been measured from 293 K to 321 K at the four wavelengths before mentioned. Caprilyc acid was not studied at 404.7 nm, corresponding to the Hg-h line, because of the poor experimental detection. In Table 1 we give our rough data for n at each temperature, T, for the four fixed wavelengths. Each reported value represents the average of at least three individual runs. The uncertainty of the tabulated values is estimated to be 1×10^{-4}.

At each wavelength, our rough experimental results have been fitted to an equation of the form

$$n_\lambda(T) = A + B\cdot T \tag{1}$$

where $n_\lambda(T)$ is the refractive index, and A and B are constants for each liquid and wavelength. As previously reported for benzene derivatives, a linear fit provides an adequate representation consistent with the accuracy of our measurements. The fitting coefficients A and B for each compound and wavelength, together with the corresponding standard deviation σ, are recorded in Table 2.

The temperature dependence of the refractive index, given by B's coefficients in Table 2, is very similar for the five fatty acids studied here. This feature can be visualized in Fig. 1, where we show our rough n values against T, together with the fits, at 546.1 nm, a central wavelength in the visible. As seen in the figure, the refractive index steadily increases when more and more carbon atoms are included in the organic chain.

A Cauchy formula has been used to represent the wavelength dependence of n. So, we have constructed a complete (n,T,λ) equation in the form

$$n(T,\lambda) = (a_0 + a_2\cdot\lambda^{-2}) + (b_0 + b_2\cdot\lambda^{-2})\cdot T \tag{2}$$

where a_0, a_2, b_0 and b_2 are constants for each system. Table 3 summarizes the fitting parameters. More digits than statistically significant have been included in the table in order to avoid round-off errors in the calculation of n. As seen in Table 3, the standard deviation σ of the fit is in agreement with our experimental uncertainty, not exceeding in general 1×10^{-4}, a value similar than those obtained from the use of Eq. (1).

In Table 4 we have compared the refractive indices calculated from Eq. (2), rounded to the fourth decimal place, with some published data relative to the Na-D line, a wavelength not directly measured here. The agreement is satisfactory, especially because the Na-D line lies beyond our experimental wavelength range. As previously established for benzene and benzene derivatives, the equation reported here is very competent to represent the combined dependence of n with temperature and wavelength for the studied systems.