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Study of the structure and refractive parameters of diethylamine and triethylamine

Nalan Tekin[a,*], Celik Tarimci[b]

[a]Department of Chemistry, Science and Art Faculty, Balikesir University, 10100 Balikesir, Turkey
[b]Engineering Physics Department, Ankara University, 06100 Ankara, Turkey

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Abstract

The refractive index (n) and thermal coefficient of the refractive index (dn/dt) are measured at four wavelengths for the diethylamine and triethylamine. The measurements are carried out using the Bellingham + Stanley model 60/ED high-accuracy Abbe refractometer. The optical permittivity (ε) and its variation with temperature are calculated. Applying the Cauchy equation, the following refractive properties are obtained: the optical dispersion $dn/d\lambda$, the dielectric dispersion $d\varepsilon/d\lambda$, the variation of $-dn/dT$, $d\varepsilon/dT$, as a function of wavelength (λ), and Cauchy's constants against temperature. Additionally, molar refractivity versus temperature and wavelength are determined.

Keywords: Diethylamine; Triethylamine; Refractive index; Cauchy's constants

1. Introduction

Physical and chemical properties of molecule depend on atoms, the stretch and the species of chemical bonding. A vast majority of chemical reactions takes place in solutions. Both H-bonding and Van der Waals bonding are important in solution media [1].

Accordingly the knowledge of the pure solvent's physical constants, macroscopic and microscopic, which reflect its behaviour and structure is necessary. The physical properties of solvents are already reported in the literature, which were measured using an electrical method at low frequency ranges; see for example Ref. [2]. But in fact the solvents are used at high frequencies (UV and visible) and therefore it is of interest to study its properties at these high frequencies.

The refractive and structure properties of laser dye solvents have been investigated by using laser interferometry in Refs. [3–6]. Additionally, Hawranek and co-workers have studied liquid triethylamine by using a Bellingham + Stanley model 60/ED high-accuracy Abbe refractometer [7,8].

The refractive index can be measured with a much higher degree of accuracy than permittivity ε; in many cases the measurement of optical and electrical properties of a substance can be replaced by measuring the refractive index. Therefore, the present measurements depend on accurate determinations of the refractive index (n) and its thermal coefficients (dn/dT) at Hg 435.8 nm, Hg 546.1 nm, Na 589.6 nm (D-line) and Cd 643.8 nm. In this study, the following refractive properties were determined by using the same method for refractive index in Refs. [7,8]:

(i) the optical dispersion $dn/d\lambda$
(ii) the dielectric dispersion $d\varepsilon/d\lambda$
(iii) the thermal coefficient of refractive index $-dn/dT$ as a function of wavelength

*Corresponding author. Tel.: +90 266 249 33 58; fax: +90 266 249 33 60.
E-mail addresses: nisik@balikesir.edu.tr, nalan_tekin35@hotmail.com (N. Tekin).

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(iv) the thermal coefficient of optical permittivity ($d\varepsilon/dT$) versus wavelength and
(v) the Cauchy's constants A and B versus temperature
(vi) molar refractivity versus wavelength and the reciprocal of temperature
(vii) thermal volume expansion coefficient as a function of wavelength and temperature.

2. Experimental

The refractive indices at selected wavelengths in the VIS region were obtained with a Bellingham + Stanley model 60/ED high-accuracy Abbe refractometer, at 293.15–323.15 K range. The following lines were used in the measurements: Hg 435.8 nm, Hg 546.1 nm, Na 589.6 nm (D-line) and Cd 643.8 nm. The refractometer cell was connected with a thermostated bath.

The density of the solutions, which is required to determine other physical properties, was measured from 293.15 to 323.15 K by a pycnometric method, the pycnometer volume being between 20 and 25 mL. The temperature of the thermostatic bath was controlled within ±0.5 °C in the range between 0 and 60 °C.

3. Results

The permittivity, ε, of nonpolar solvents can be determined by both the properties of the isolated molecules and the effects of molecular interactions. At different densities, the variations of permittivity with temperature is calculated from theories that take account only of pair interactions. The classic calculation of the average field at a molecule due to identically polarized neighbours in a structure of cubic symmetry leads to the Clausius–Mossotti equation, which relates a microscopic property α with a measurable macroscopic property ε [9,10]:

$$\frac{\varepsilon-1}{\varepsilon+2}\frac{M}{\rho}=\frac{4\pi N_0\alpha}{3}, \tag{1}$$

where ρ is the density, M the molecular weight and α the total polarizability of the isolated molecule, assumed to be independent of interactions with neighbours.

At optical high frequencies the permittivity of a material cannot be measured by the use of electrical methods. However, it is known from Maxwell's theory for electromagnetic waves that for non-magnetic materials the permittivity is related to the refractive index as follows [3–6]:

$$n^2=\varepsilon. \tag{2}$$

Using the data of refractive index and according to Maxwell's theory ($n^2=\varepsilon$) for transparent non-magnetic materials (permeability ≈ 1), we are able to calculate the optical permittivities (ε) at the mentioned wavelengths. Tables 1 and 2 show good agreement when compared with the values at low frequencies extracted from

Table 1
Important physical parameters of diethylamine calculated according to ($n^2=\varepsilon$)

Parameters	$\lambda=435.8$ nm (Hg)	$\lambda=546.1$ nm (Hg)	$\lambda=589.6$ nm (Na) (D-line)	$\lambda=643.8$ nm (Cd)
Refractive index at 20 °C	1.388060	1.387337	1.387010	1.386697
Thermal coefficient of refractive index (dn/dT)	-5.568253×10^{-4}	-5.482643×10^{-4}	-5.407285×10^{-4}	-5.226071×10^{-4}
Optical permittivity ($n^2=\varepsilon$)	1.926711	1.924704	1.923796	1.922928
Thermal coefficient of permittivity ($d\varepsilon/dT$)	-1.534893×10^{-3}	-1.511892×10^{-3}	-1.491721×10^{-3}	-1.442829×10^{-3}
Specific refraction	0.236002	0.235611	0.235434	0.235265
Molar refraction	24.3115	24.2713	24.2525	24.2356

Table 2
Important physical parameters of triethylamine calculated according to ($n^2=\varepsilon$)

Parameters	$\lambda=435.8$ nm (Hg)	$\lambda=546.1$ nm (Hg)	$\lambda=589.6$ nm (Na) (D-line)	$\lambda=643.8$ nm (Cd)
Refractive index at 20 °C	1.401875	1.400934	1.400333	1.400099
Thermal coefficient of refractive index (dn/dT)	-4.735071×10^{-4}	-4.730071×10^{-4}	-4.723785×10^{-4}	-4.674228×10^{-4}
Optical permittivity ($n^2=\varepsilon$)	1.965253	1.962616	1.960932	1.960277
Thermal coefficient of permittivity ($d\varepsilon/dT$)	-1.319328×10^{-3}	-1.318749×10^{-3}	-1.31789×10^{-3}	-1.65245×10^{-3}
Specific refraction	0.243428	0.242924	0.242602	0.242477
Molar refraction	33.8823	33.8123	33.7675	33.7500