Research Article

Experimental Verification of Vuks Equation Using Hollow Prism Refractometer

Anita Kanwar¹ and Priya S. Yadav²

¹ Department of Physics, VES College of Arts, Science and Commerce, Sindhi Society, Chembur, Maharashtra, Mumbai 400071, India

² Department of Physics, Atharva Engineering College, Malad West, Maharashtra, Mumbai 400095, India

Correspondence should be addressed to Anita Kanwar, anita_s_kanwar@yahoo.com

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The refractive indices of the cholesteric liquid crystal solution were measured using multiwavelength (visible range) refractometer for three different wavelengths. Measurements were made at different temperatures for various concentrations of the solution, mixing CLC in a soluble solvent. Vuks equation describes the wavelength and temperature dependence of refractive indices of anisotropic crystalline materials. We have used a simplified version of Vuks equation relating only to macroscopic indices and verified its validity for five-different-concentration solution at various temperatures. The result is also used to obtain molecular polarizabilities and temperature dependent material constants of our sample.

1. Introduction

The importance of liquid crystals lies in their thermal, electrical, and optical properties [1–3]. After understanding these properties one can hope to exploit the full range of possible device and materials applications. In many applications the knowledge of optical anisotropy [4, 5] and refractive indices of liquid crystals, and their temperature dependence is desirable [6]. Temperature-induced refractive index change is used in many liquid-crystal (LC) devices to modulate light [7]. Since LC shows optical anisotropy and is birefringent [8] in nature, its refractive index is quite different from that of an isotropic liquid. There are various methods used for the determination of refractive index of liquid crystals [9, 10].

Vuks [11] proposed a semiempirical model which is analogous to the classical Clausius-Mossotti equation for correlating the microscopic molecular polarizabilities to the macroscopic refractive indices of some crystalline materials. The Vuks paper is cited and used by many researchers to study properties of liquid crystals [12, 13]. Vuks made a bold assumption that the internal field in a liquid crystal is the same in all directions and gave a semi-empirical

equation correlating the refractive indices with the molecular polarizabilities for anisotropic materials [9]:

$$\frac{n_{e,o}^2 - 1}{\langle n^2 \rangle - 2} = \frac{4\pi}{3} N \alpha_{e,o}, \quad (1)$$

where n_e and n_o are the refractive indices for the extraordinary and ordinary ray, respectively, $\alpha_{e,o}$ are the corresponding molecular polarizabilities, N is the number of molecules per unit volume, and $\langle n^2 \rangle$ is given by

$$\langle n^2 \rangle = \frac{n_e^2 + 2n_o^2}{3}. \quad (2)$$

Li and Wu [14] modified this equation and showed that the validity of Vuks equations can be easily examined by measuring the temperature and wavelength-dependent refractive indices of liquid crystals. The modified equation (detailed derivation in [14]) given by them is

$$\langle n^2 \rangle + 2 \approx \sqrt{10} \langle n \rangle - 0.5, \quad (3)$$

where average refractive index is

$$\langle n \rangle = \frac{n_e + 2n_o}{3}. \quad (4)$$

TABLE 1: Measured refractive indices (n_e and n_o) of 1-molar solution and validity of Vuks equation.

Temp. (K)	n_e	n_o	$\langle n \rangle$	$\langle n^2 \rangle$	LHS of $\langle n^2 \rangle + 2$	RHS of $\sqrt{10} \langle n \rangle - 0.5$
Wavelength (404 nm)						
343	1.5156	1.4726	1.4869	2.2114	4.2114	4.2016
333	1.5151	1.4767	1.4895	2.2189	4.2189	4.2098
323	1.5186	1.4861	1.4969	2.2410	4.2410	4.2332
313	1.5188	1.4916	1.5007	2.2522	4.2522	4.2452
303	1.5188	1.5027	1.5081	2.2743	4.2743	4.2686
Wavelength (546 nm)						
343	1.5037	1.4577	1.473	2.1703	4.1703	4.1576
333	1.5061	1.4705	1.4824	2.1977	4.1977	4.1873
323	1.5044	1.4714	1.4824	2.1978	4.1978	4.1873
313	1.5033	1.4775	1.4861	2.2086	4.2086	4.1990
303	1.5013	1.4853	1.4906	2.2220	4.2220	4.2133
Wavelength (578 nm)						
343	1.501	1.4547	1.4701	2.1618	4.1618	4.1485
333	1.5046	1.4632	1.477	2.1819	4.1819	4.1703
323	1.5025	1.4684	1.4798	2.1900	4.1900	4.1791
313	1.5018	1.4735	1.4829	2.1993	4.1993	4.1889
303	1.5084	1.4834	1.4917	2.2254	4.2254	4.2168

TABLE 2: Measured refractive indices (n_e and n_o) of 2-molar solution and validity of Vuks equation.

Temp. (K)	n_e	n_o	$\langle n \rangle$	n^2	LHS of $\langle n^2 \rangle + 2$	RHS of $\sqrt{10} \langle n \rangle - 0.5$
Wavelength (404 nm)						
343	1.5137	1.4715	1.4856	2.2073	4.2073	4.1975
333	1.512	1.4786	1.4897	2.2196	4.2196	4.2104
323	1.5132	1.4873	1.4959	2.2380	4.2380	4.2300
313	1.5134	1.4893	1.4973	2.2421	4.2421	4.2345
303	1.5131	1.494	1.5004	2.2512	4.2512	4.2443
Wavelength (546 nm)						
343	1.5059	1.4627	1.4771	2.1822	4.1822	4.1706
333	1.5056	1.4725	1.4836	2.2011	4.2011	4.1911
323	1.5008	1.4676	1.4787	2.1867	4.1867	4.1756
313	1.5085	1.4766	1.4872	2.2121	4.2121	4.2025
303	1.5067	1.4774	1.4872	2.2119	4.2119	4.2025
Wavelength (578 nm)						
343	1.5045	1.4616	1.4759	2.1787	4.1787	4.1668
333	1.5017	1.4686	1.4796	2.1896	4.1896	4.1785
323	1.4969	1.4656	1.476	2.1789	4.1789	4.1671
313	1.5028	1.4745	1.4839	2.2022	4.2022	4.1921
303	1.5019	1.4765	1.485	2.2053	4.2053	4.1956

The importance of modified Vuks equations (3) is that the sophisticated microscopic Vuks equation can now be validated by two simple macroscopic parameters: $\langle n^2 \rangle$ and $\langle n \rangle$. These two parameters can easily be obtained by measuring the individual refractive indices (n_e and n_o) of the liquid crystal. In this paper we tried to verify this equation by finding out refractive indices of Cholesteric LC solution of five different concentrations prepared by us with varying its temperature.

2. Experimental Method

The most commonly used method to measure refractive indices is using an Abbe refractometer [15]. We have used hollow prism multiwavelength refractometer to measure refractive indices [16, 17] of a Cholesteric LC solution (n_e and n_o) and observed that these indices vary with both the temperature and the concentration. The solutions of five different molar concentrations were prepared using cholesteryl

TABLE 3: Measured refractive indices (n_e and n_o) of 3-molar solution and validity of Vuks equation.

Temp. (K)	n_e	n_o	$\langle n \rangle$	$\langle n^2 \rangle$	LHS of $\langle n^2 \rangle + 2$	RHS of $\sqrt{10} \langle n \rangle - 0.5$
Wavelength (404 nm)						
343	1.5222	1.4828	1.4959	2.2382	4.2382	4.2300
333	1.5187	1.4934	1.5018	2.2556	4.2556	4.2487
323	1.5165	1.494	1.5015	2.2546	4.2546	4.2477
313	1.5145	1.4924	1.4998	2.2494	4.2494	4.2424
303	1.5157	1.498	1.5039	2.2618	4.2618	4.2553
Wavelength (546 nm)						
343	1.5164	1.4663	1.483	2.1998	4.1998	4.1892
333	1.5094	1.4733	1.4853	2.2065	4.2065	4.1965
323	1.5074	1.4769	1.4871	2.2116	4.2116	4.2022
313	1.4993	1.4696	1.4795	2.1891	4.1891	4.1782
303	1.5074	1.4793	1.4887	2.2163	4.2163	4.2073
Wavelength (578 nm)						
343	1.5012	1.4632	1.4759	2.1785	4.1785	4.1668
333	1.5002	1.4655	1.4771	2.1820	4.1820	4.1706
323	1.5069	1.474	1.485	2.2054	4.2054	4.1956
313	1.4905	1.4607	1.4706	2.1630	4.1630	4.1500
303	1.5066	1.4825	1.4905	2.2218	4.2218	4.2130

TABLE 4: Measured refractive indices (n_e and n_o) of 4-molar solution and validity of Vuks equation.

Temp. (K)	n_e	n_o	$\langle n \rangle$	$\langle n^2 \rangle$	LHS of $\langle n^2 \rangle + 2$	RHS of $\sqrt{10} \langle n \rangle - 0.5$
Wavelength (404 nm)						
343	1.5189	1.477	1.491	2.2234	4.2234	4.2145
333	1.5143	1.4751	1.4882	2.2150	4.2150	4.2057
323	1.5135	1.4748	1.4877	2.2136	4.2136	4.2041
313	1.5036	1.4751	1.4846	2.2042	4.2042	4.1943
303	1.5025	1.4757	1.4846	2.2043	4.2043	4.1943
Wavelength (546 nm)						
343	1.5128	1.4667	1.4821	2.1970	4.1970	4.1864
333	1.499	1.4643	1.4759	2.1784	4.1784	4.1668
323	1.4987	1.4641	1.4756	2.1778	4.1778	4.1658
313	1.4987	1.4671	1.4776	2.1836	4.1836	4.1722
303	1.4969	1.4662	1.4764	2.1801	4.1801	4.1684
Wavelength (578 nm)						
343	1.4988	1.4567	1.4707	2.1635	4.1635	4.1504
333	1.4932	1.4553	1.4679	2.1551	4.1551	4.1415
323	1.4921	1.4542	1.4668	2.1519	4.1519	4.1380
313	1.4892	1.4545	1.4661	2.1496	4.1496	4.1358
303	1.4866	1.4538	1.4647	2.1457	4.1457	4.1314

pelargonate and toluene as solvent. This refractometer is designed using a specially constructed hollow prism and optical spectrometer [18]. First the spectrometer is adjusted using optical leveling and Schuster's method. Angle of prism (A) is obtained. Then minimum deviation angles for three wavelengths: 404 nm, 546 nm, and 578 nm of mercury source were measured. Refractive indices were calculated using the following formula:

$$\mu = \frac{\sin((A + \partial m)/2)}{\sin(A/2)}. \quad (5)$$

A polarizer was used to identify ordinary and extraordinary spectrum. While to check the validity of the method initially refractive indices of few known liquids were obtained. A temperature variation was obtained using an indigenously designed heating coil and a digital thermometer. The same procedure was repeated for different concentrations of the mixture. For each concentration reading was taken with varying the temperature. The prism minimum deviation technique is commonly used for extremely accurate measurements [19, 20]. Refractive index measurements correct up to

TABLE 5: Measured refractive indices (n_e and n_o) of 5-molar solution and validity of Vuks equation.

Temp. (K)	n_e	n_o	$\langle n \rangle$	$\langle n^2 \rangle$	LHS of $\langle n^2 \rangle + 2$	RHS of $\sqrt{10} \langle n \rangle - 0.5$
Wavelength (404 nm)						
343	1.518	1.4745	1.489	2.2175	4.2175	4.2082
333	1.5154	1.4741	1.4879	2.2141	4.2141	4.2047
323	1.5189	1.4839	1.4956	2.2370	4.2370	4.2291
313	1.5128	1.491	1.4983	2.2449	4.2449	4.2376
303	1.5179	1.4998	1.5058	2.2676	4.2676	4.2613
Wavelength (546 nm)						
343	1.5104	1.4667	1.4813	2.1946	4.1946	4.1839
333	1.5003	1.4617	1.4746	2.1747	4.1747	4.1627
323	1.5118	1.475	1.4873	2.2123	4.2123	4.2028
313	1.5058	1.4775	1.4869	2.2111	4.2111	4.2016
303	1.5013	1.4766	1.4848	2.2049	4.2049	4.1949
Wavelength (578 nm)						
343	1.5007	1.4567	1.4714	2.1654	4.1654	4.1526
333	1.4965	1.4598	1.472	2.1672	4.1672	4.1545
323	1.5075	1.4759	1.4864	2.2097	4.2097	4.2000
313	1.4989	1.4679	1.4782	2.1854	4.1854	4.1741
303	1.4977	1.4671	1.4773	2.1826	4.1826	4.1712

TABLE 6: Variation of average refractive index with temperature for three wavelengths.

T (K)	Average RI (404 nm)	Average RI (546 nm)	Average RI (578 nm)
343	1.48968	1.4793	1.4728
333	1.49142	1.48036	1.47472
323	1.49552	1.48222	1.4768
313	1.49614	1.48346	1.47634
303	1.50056	1.48554	1.48184

TABLE 7: Showing A and B values, for three wavelengths.

Wavelength (nm)	A	B (K^{-1})
404	1.503	3.02×10^{-4}
546	1.4865	1.65×10^{-4}
578	1.4830	2.1×10^{-4}

four to five decimal places are common using this technique with good control of the sample temperature.

3. Observations

Cholesteryl pelargonate in five different proportions was dissolved in the solvent to obtain different concentration solutions by properly stirring the solution at room temperature then heating it up to the isotropic temperature. Homogeneous solutions were heated, and refractive indices were obtained for every 10 K rise in the temperature using the multiwavelength refractometer. Using FPSS technique [21], we found that these solutions have nearly the same clearing temperature variations over the range of 1.5 K, hence temperature in Kelvin and not reduced temperature is used in the calculations. We studied the variation of refractive index (n_e and n_o) with the temperature for various

concentrations [22, 23]. The results obtained are compiled in Tables 1, 2, 3, 4, and 5. The measurements were made for three different wavelengths in the visible range. The validity of the modified Vuks equation is checked for each sample.

Secondly we obtained average refractive index for each colour at different temperature (Table 6) using above data, and tried to correlate it with the equation given below according to which the average refractive index $\langle n \rangle$ decreases linearly as the temperature increases [24]. Figure 1 shows the variation of average refractive index for with temperature for three wavelengths. We also found the values of the constants A and B as per (6). These values are tabulated in Table 7 for three wavelengths used by us:

$$\langle n \rangle = A - BT. \quad (6)$$

We have also found the values of polarizabilities α_e and α_o for one molar solution using equations

$$\alpha_e = \frac{3M}{4\pi\rho N_A} \cdot \frac{n_e^2 - 1}{\langle n^2 \rangle + 2}$$

$$\alpha_o = \frac{3M}{4\pi\rho N_A} \cdot \frac{n_o^2 - 1}{\langle n^2 \rangle + 2}, \quad (7)$$

TABLE 8: Polarizabilities α_e , α_o , and $\langle\alpha\rangle$ in $\times 10^{-23}$ cm³ unit for one molar solution at various temperatures for three different wavelengths.

T (K)	Wavelength (404 nm)			Wavelength (546 nm)			Wavelength (578 nm)		
	α_e	α_o	$\langle\alpha\rangle$	α_e	α_o	$\langle\alpha\rangle$	α_e	α_o	$\langle\alpha\rangle$
343	6.7033	6.0392	6.2606	6.5818	5.8709	6.1078	6.5528	5.8372	6.0757
333	6.6835	6.0909	6.2884	6.5763	6.0269	6.2100	6.5777	5.9382	6.1513
323	6.7032	6.2020	6.3691	6.5496	6.0405	6.2102	6.5321	6.0059	6.1813
313	6.6887	6.2695	6.4092	6.5157	6.1180	6.2506	6.5068	6.0704	6.2158
303	6.6541	6.4064	6.4889	6.4640	6.2177	6.2998	6.5689	6.1836	6.3121

FIGURE 1: Shows the variation of average refractive index with temperature for three wavelengths.

where ρ is the LC density, M is the molecular weight (in our case it is 526.88), and N_A is the Avogadro's number. The average value of α is obtained using the following equation:

$$\langle\alpha\rangle = \frac{(\alpha_e + 2\alpha_o)}{3}. \quad (8)$$

The values of α_e , α_o and $\langle\alpha\rangle$ are tabulated in Table 8.

4. Results and Discussion

We have applied modified Vuks equation number (3) on five different solutions of Cholesteric liquid crystals and measured the extraordinary and the ordinary refractive indices using the hollow prism method. The experiments conducted by us not only validate the modified Vuks equation but also validate our method of finding refractive indices of liquid crystal solutions. There is an average error of nearly 0.2%.

In the second part we are successful in obtaining values of the constants A and B for the equation which shows the variation of average refractive index with temperature. We are also able to show that average refractive index decreases with the increasing temperature linearly as specified by (6).

In the third part we have obtained values of average polarizability for three different wavelengths. The value of polarizability for Cholesteryl pelargonate predicted by chem.Spider data generated using the ACD/Labs, ACD/PhysChem Suite is 6.604×10^{-23} cm³ at room temperature. This again is very close to the values calculated by us at various temperatures with the average error of 0.22 percent.

We have developed the hollow prism method to find refractive indices of liquid crystals. This method is validated by the simplified version of Vuks equation. Using this we are able to calculate birefringence, average refractive index, and molecular polarizabilities at various temperatures and concentrations.

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