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An Innovative Investigation of Viscosity, Relaxation Time, Tilt Angle and Radiation Force Variations by Using a Laser Interferometer Method of a Laser Dye Solvent

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Abstract. In the present work an interferometer laser technique was applied to determine the values and behavior of some physical parameters of one of most important laser dye solvent, benzene. Density, viscosity, relaxation time, tilt angle, radiation power, work done, and scattering factor were determine as values and behavior as function of temperature, thermal behavior d/dT, and wavelength, dispersion behavior, $d/d\lambda$. The viscosity values and its thermal behavior were determined by using the following derived equation: $(d\tau/dT) = (3/kT^2)\{T[\eta_\lambda(dV/dT)] - \eta_\lambda V_\lambda\}$. It was found that the relation between η and λ obeys the empirical relation $\eta_T(\lambda) = \eta_{20}(\lambda) + (d\eta/d\lambda)_T\lambda$. The relaxation time τ values were determined with the aid of $\tau_\lambda(T) = (3/kT)V\eta_\lambda(T)$, in addition the values of $(d\tau/dT)_\lambda$ and $(d\tau/d\lambda)_T$ were determined. The dispersion behavior of τ was fitted with the form $\tau = 2.029 \times 10^{-4} \exp(-2.060 \times 10^{-4}\lambda)$. The interrelation between both τ and η under the effect of temperature was verified too. The maximum radiation power exerted by one molecule of that laser dye solvent, $F_{\max}$, as a function of T and λ was investigated. It was found that its thermal behavior follows $F_{\max} = 1.366 \times 10^{-31} \exp(-2.31 \times 10^{-2}T)$. Its wavelength behavior was $F_{\max}(\lambda)T = 2.581 \times 10^{-27} \exp(-2.31 \times 10^{-2}\lambda)$. The scattering power γ_s was estimated with its thermal change $(d\gamma_s/dT)_\lambda$ and its wavelength change $(d\gamma_s/d\lambda)_T$ were studied. The tilt angle θ of the laser dye cell was determined with its thermal and wavelength change $(d\theta/dT)_\lambda$ and $(d\theta/d\lambda)_T$, respectively. The work W and power P exerted by the dye solvent molecule were determined by using one of thermodynamical formula $W = V\beta TP$ both $(dW/dT)_\lambda$ and $(d\theta/d\lambda)_T$ were studied. The temperature and wavelength dependence of W was estimated during the derived relation $W = 3.7817 \times 10^{-24}(T_2 - T_1) + 4.6754 \times 10^{-25}(\lambda_2 - \lambda_1)$. The viscosity dependence of the refractive index $n_{T,\lambda}(\eta)$ was studied which was found that it obeys for $\lambda = 458$ nm $n_{T,\lambda}(\eta) = 1.4270 + 2.1869 \times 10^{-47} \exp(1.589 \times 10^4 \eta_{T,\lambda} - 1)$. The density dependence of the refractive index $n_{T,\lambda}(\rho)$ was investigated show-

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ing a relation $n_{T,\lambda}(\rho) = 1.079 + \rho_{T,\lambda}(dn/d\rho)_{T,\lambda}$, from which the value of $(dn/d\rho)_{20,458} = 0.4954$ holds. Three triplet relations were investigated: 1) the n–ρ–T relation to be $n_\lambda(T) = 1.243 - 5.295 \times 10^{-4} T + 0.3204 \rho_\lambda(T)$, 2) the n–η–ρ relation follows $n(T) = -4.699 \times 10^{-2} - 2.329 \times 10^{-2} \rho(T) + 4.893 \times 10^{-2} n_\lambda(T)$ and 3) the η–ρ–T relation obeying $\eta_\lambda(T, \rho) = -7.063 \times 10^{-3} \exp\{-0.5[(T + 7.101 \times 10^{-2}/2.005 \times 10^{3}) + (\rho - 0.8409/0.7863)]\}$. All of these numerical values are selected for $\lambda = 458$ nm, as an example. From these triplet relations the values of $(dn/d\rho)_{\mathrm{cal}}$, $(d\eta/dT)_{\mathrm{cal}}$, $(d\eta/d\rho)_{\mathrm{cal}}$, $(dn/d\eta)_{\mathrm{cal}}$ and $(d\eta/dn)_{\mathrm{cal}}$ were estimated and compared with that experimental values.

Keywords: dye laser, laser dyes, viscosity, radiation force, refractive index, dispersion
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1. Introduction

Dye lasers are most useful systems for biological, medical, scientific and technical applications because of the following reasons [1]:

- wavelength tunability over a wide spectral range,
- single-frequency radiation source with high spectral power, and
- a continuous wave (CW) dye laser eliminates several limitations of the standing wave dye laser such as spatial hole burning, or small output power.

Organic liquid are characterized by several properties that make them suitable for dissolving and for providing reaction media for various types of solutes. These properties include physical quantities, such as the liquid range (freezing to normal boiling temperatures), vapor pressure, density, refractive index, relative permittivity, etc. [2].

Many authors [3–5] showed that the photo physical properties of many laser dyes are affected by the solvent polarity. Where the Stokes shifts $\Delta\nu = \nu_{\mathrm{abs}} - \nu_{\mathrm{em}}$, quantum yields, and fluorescence lifetimes show more or less linear correlation with the solvent polarity function

$$\Delta f = \{(\varepsilon - 1)/(2\varepsilon + 1)\} - \{(n^2 - 1)/(2n^2 + 1)\} . \tag{1}$$

All these parameters are unusually lower in non-polar solvents. Unlike in other solvents, both quantum yield and fluorescence lifetime in non-polar solvents are also strongly temperature dependent.

Radiationless transition from the first excited state to the ground state or triplet state reduce the quantum yield q of fluorescence, defined as the ratio of the Einstein coefficient of spontaneous emission A and the sum of the rate K_{tr} of radiationless transitions and A:

$$q = A/(A + K_{\mathrm{tr}}) . \tag{2}$$

Since all laser action starts from spontaneous emission, it becomes increasingly difficult to operate a dye laser the stronger the quenching of the fluorescence by radiationless transitions for the dye used. For a long time it was thought that a quantum yield of about 10% was the limit for practicable dye laser operation. One way around this limitation would be to force the dye molecule to make a transition to the ground state by stimulated emission immediately after excitation, before radiationless transitions has had a chance to deactivate the molecule. Ingenious solution of this problem was found independently by two groups [6]. A pecosecond pulse is sent through a beam-expanding cylinder–lens telescope to illuminate N lines of an optical grating under the blaze angle so that most of the energy is diffracted into the first order.

It is known that when the pump laser incidence upon the laser dye medium it will be completely absorbed by the medium which re-emittes it as a fluorescence from which the dye laser beam comes out. As a result, the absorbed laser beam will heat of the active laser dye medium causing changing its density which tends to change its refractive index and the correlated parameters. Taking into account that any temperature fluctuation in the active medium of the laser dye causes a change in the length of the laser cavity L (mirror separation) tending to change both the laser wavelength λ by the fraction $\Delta\lambda$ which is given by $\Delta\lambda/\lambda = \Delta d/d + \Delta n/n$ and the laser frequency ν by the fraction $\Delta\nu$ which is given by $\Delta\nu/\nu = \Delta d/d + \Delta n/n$.

On the molecular scale one can look at the friction and viscosity of the dye solution. If molecular obstructions are taken into account, for pure liquids, the effect of friction is very different, the ellipsoids of revolution being pressed against each other, rotating about or oscillating along the major axis. The effects, although very small in the first case, are considerable in the second. In practice there will be as many viscosity effects as there are modes of oscillation.

The emission line-width of CW single-mode dye laser is broadened by fluctuations of the optical path length of the laser cavity. The fluctuations are caused mainly by density and thickness fluctuations of the dye jet and by some insignificant mechanical instabilities of the laser cavity. The density and thickness fluctuations are created by the thermal fluctuations of the dye solution, power fluctuations of the pump laser, pressure fluctuations, and surface waves of the dye jet.

2. Theoretical Background

2.1. Viscosity and relaxation time effect

It is evident that the term molecular viscosity η, cannot be calculated by a macroscopic measurement of viscosity, is related to the relaxation time τ and molecular volume [7, 8]

$$\tau = 3V\eta/kT\,, \tag{3}$$

where V is the molecular volume, k is the Boltzmann constant and T is the absolute temperature.

A high optical quality of the region can only be achieved by restricting the solution flow rate to the laminar flow regime. Therefore, the viscosity of the liquid solvent must be sufficiently large. The use of a highly viscous solvent has some additional advantages. Although the flow rate of the dye jet is kept in the laminar flow regime, the jet surface is determined by surface waves, which are produced by irregularities in the nozzle and by pressure fluctuations. The damping of these surface waves is high for a high-viscosity solvent. In addition a higher maximum laminar flow velocity can be reached, which leads to a more effective mechanical triplet quenching and reduces thermal problems [9].

2.2. Radiation force

Radiation force means the total force arising upon interaction between pump laser beam and a liquid molecule of laser dye medium. Depending on the spatial and temporal structure of the laser light field, its wavelength and strength, radiation force may be an extremely complex function of the molecular position and velocity. Since all the known studies on the application of light pressure forces have been carried out using three types of light fields, namely a plane wave, a Gaussian laser beam and a standing light wave, or their combination. The theory of molecular motion in such fields has been developed quite well [10, 11]. The behavior of the radiation pressure force in them is only quantitively considered.

Consider a plane pump laser wave directed along an axis and having its frequency tuned to the resonance with the absorption frequency of a molecule placed in it. The molecule absorbs the pump laser photons directed along the same axis and re-emits them spontaneously in all directions. As a result, the molecule is acted upon in the direction of the wave by a radiation force whose maximum magnitude is given by the product of the photon momentum $\hbar k$ by the photon scattering factor γ_s [12], i.e.

$$F_{\max} = \hbar k \gamma_s \,, \tag{4}$$

where $k = 2\pi/\lambda$ and $\hbar$ is Plack's constant.

The scattering factor is related with the refractive index of the laser dye solution through the equation [13]:

$$n - 1 = (\lambda^2/2\pi)(\gamma_s N)^{1/2} \,, \tag{5}$$

where λ is the laser wavelength and N is the number of molecules per unit volume.

2.3. Density fluctuations ρ

The emission linewidth of CW single-mode dye laser is broadened by fluctuations of the optical path length of the laser cavity. The fluctuations are caused mainly by density and thickness fluctuations of the dye jet and by some insignificant mechanical instabilities of the laser cavity. The density and thickness fluctuations are created by the thermal fluctuations of the dye solution, power fluctuations of the pump laser, pressure fluctuations, and surface waves of the dye jet.

Of the statistical effects which influence the linewidth, three have been considered [14] spontaneous emission or phase diffusion, Brownian motion of the resonator, and statistical fluctuations in the density of the active medium. Only the last of these is large enough to be important in practical systems.

Many authors have treated the density fluctuations in a liquid due to the statistical fluctuation in the number of molecules per unit volume. An early treatment by Einstein (1910) yields the rms fluctuation in density ρ as

$$(\Delta\rho/\rho) = (\mu kT/V_c)^{1/2}\,, \tag{6}$$

where μ is the isothermal compressibility, T is the absolute temperature, k is the Boltzmann constant and V_c is the volume under consideration.

The appropriate volume for the dye laser is the active volume of the system. In determining the frequency shift associated with these density changes it is assumed that the polarizability is proportional to the number of molecules per unit volume. The refractive index is proportional to the square root of the polarizability so that

$$(\Delta n/n) = (1/2)(\Delta\rho/\rho)\,. \tag{7}$$

To determine the frequency change $\Delta\nu$ produced by this fluctuation in refractive index

$$(\Delta\nu/\nu) = (\Delta d/d) = (\Delta nd/nD)\,, \tag{8}$$

where d is the active length and D is the length laser resonator.

The focused pump beam of a high-power dye laser causes local thermal heating of the dye solution due to radiationless transitions [15]. Since the pump intensity has a uniform distribution, an inhomogeneous temperature distribution is created which is related to refractive index variations Δn by

$$|\Delta n|\alpha(1/\rho c)|dn/dT|\,, \tag{9}$$

where ρ is the density, c is the heat capacity and dn/dT is the temperature variation of the refractive index of the dye solution.

The refractive index variations can be noticed as a thermal lens effect, which has some astigmatism [16]. Therefore, this thermal lens effect is hard to compensate and reduces the maximum pump power.

2.4. Tilt angle

From elementary theory of diffraction it is clear that the contribution to the diffracted beam from each line has a delay of one wavelength with respect to the neighboring line, so that the delay between the left and the right border of the diffracted beam in N wavelengths. This means that the pulse front is tilted by an angle θ. Now this pulse is focused by a cylinder lens on the inner surface of a dye cell containing a weekly fluorescent dye solution with a refractive index n at the wavelength of the fluorescence maximum. It is immediately obvious that the pulse hitting first the near end of the cell will travel towards the far end across the cell with exactly the same speed as the fluorescence light emitted in the same direction, provided that the tilt of the pulse front is correctly chosen so that [17]

$$\tan\theta = n\,. \tag{10}$$

If the intensity of the pump pulse is sufficiently high, a few fluorescence photons will start at the near end in the direction towards the far end of the cell always seeing dye molecules that were excited into the lasing level less than 1 ps ago, so that stimulated emission has a higher probability than radiationless transitions, the fluorescence photon flux is strongly amplified, and a strong output beam of amplified spontaneous emission exits from the far end of the cell.

3. Experimental

The determined parameters under investigations are based on the values of the refractive index of benzene. The refractive index of benzene as a laser dye solvent has been measured by the aid of laser interferometric method. The refractive index of benzene has been measured as a function of temperature at constant laser wavelength, on one side, and as a function of laser wavelength at constant temperature, on the other side. The technical arrangement of refractive index measurement of benzene has been reported in Ref. [18].

4. Results and Discussions

4.1. Viscosity

4.1.1. Temperature behavior

By using Eq. (3) one can get:

$$d\tau/dT = (3/kT^2)\{T[\eta(dV/dT) + V(d\eta/dT)] - \eta V\}\,, \tag{11}$$

supposing that $d\eta/dT = 0$ during a small temperature range, therefore one gets

$$d\tau/dT = (3/kT^2)\{T[\eta(dV/dT)] - \eta V\}\,, \tag{12}$$

where dV/dT is the rate of change of molecular volume of benzene with respect to the temperature and $d\tau/dT$ is the rate of change of the molecular relaxation time of benzene molecule with respect to the temperature.

By using Eq. (12) and substituting with the values of $T = 293$ K, $\eta = 6.49 \times 10^{-3}$ Poise, $(dV/dT)_\lambda$ and $(V_{20})_\lambda$. The value of $(d\tau/dT)_\lambda$ could be calculated. By using the value of $(d\tau/dT)_\lambda$ in Eq. (12) and the value of $(dV/dT)_\lambda$ and $(V_T)_\lambda$ the values of $\eta_\lambda(T)$ were calculated as function of temperature at constant wavelength λ. The obtained values of $\eta_\lambda(T)$ were plotted as shown in Fig. 1. From that figure the values of $(d\eta/dT)_\lambda$ were obtained showing a decreased behavior following the known facts for liquids.

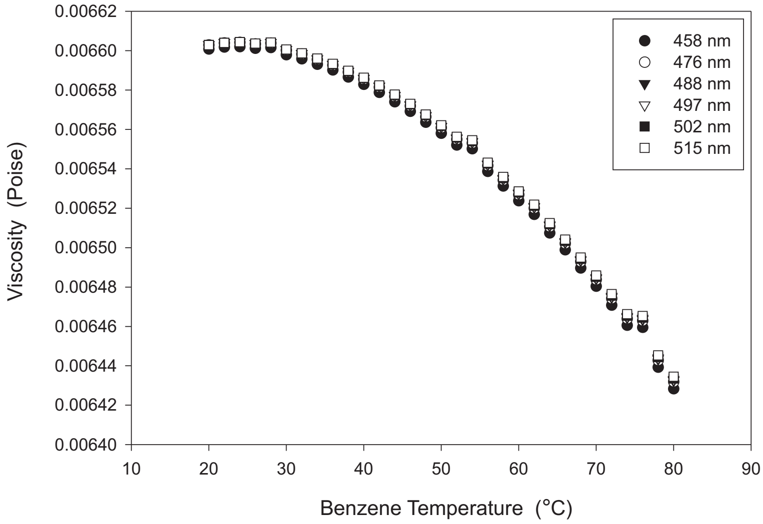

Fig. 1. Thermal behavior of the viscosity of laser dye solvent at constant wavelengths, $(d\eta/dT)_\lambda$

4.1.2. Wavelength behavior $\eta_T(\lambda)$

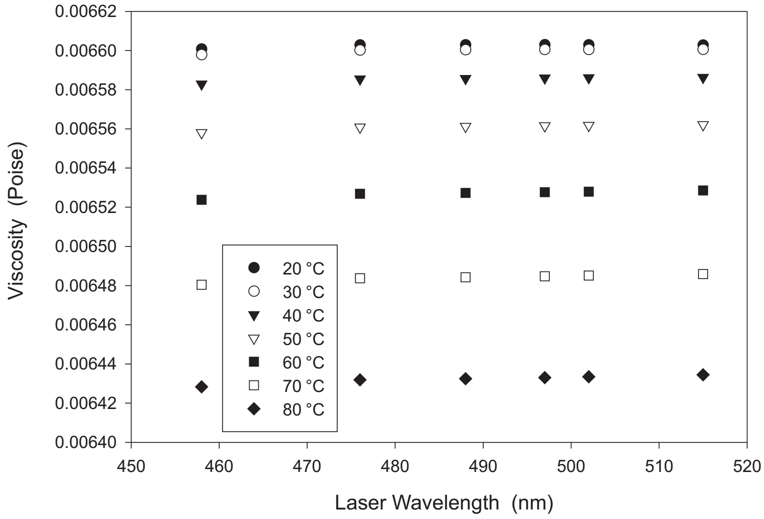

Fig. 2. Wavelength dependence of the benzene as a laser dye solvent at selected temperatures, $(d\eta/d\lambda)_T$

The values of the benzene's viscosity as function of different laser wavelengths and constant temperature $\eta_T(\lambda)$ were calculated with the aid of Fig. 1. The obtained values of $\eta_T(\lambda)$ were plotted as shown in Fig. 2 at constant temperatures 20, 30, 40, 50, 60, 70 and 80 °C. From Fig. 2 the rate of change of $\eta_T(\lambda)$ with respect to λ, at constant values of T, was estimated to be $(d\eta/d\lambda)_T$ with the values of given in Table 2. The wavelength behavior of $\eta_T(\lambda)$ was found to follow the following empirical relation:

$$\eta_T(\lambda) = \eta_{20}(\lambda) + (d\eta/d\lambda)_T\lambda\,, \tag{13}$$

where $\eta_{20}(\lambda)$ is the benzene's viscosity at ambient and $(d\eta/d\lambda)_T$ is the slope of the curve.

4.2. Relaxation time effect (τ)

4.2.1. Temperature behavior $\tau_\lambda(T)$

By using Eq. (3) and substituting with the values of the obtained values of both $\eta_\lambda(T)$ and $V_\lambda(T)$ at different values of temperature and constant values of λ. The values of $\tau_\lambda(T)$ for benzene were calculated and plotted against T to show its temperature behavior as shown in Fig. 3 from which the rate of change of τ with respect to T at constant λ was calculated to be $(d\tau/dT)_\lambda$ with the values given in Table 1. This behavior shows an inverse proportional relation with the temperature obeying Eq. (3) which means a good agreement between the experimental results and theory.

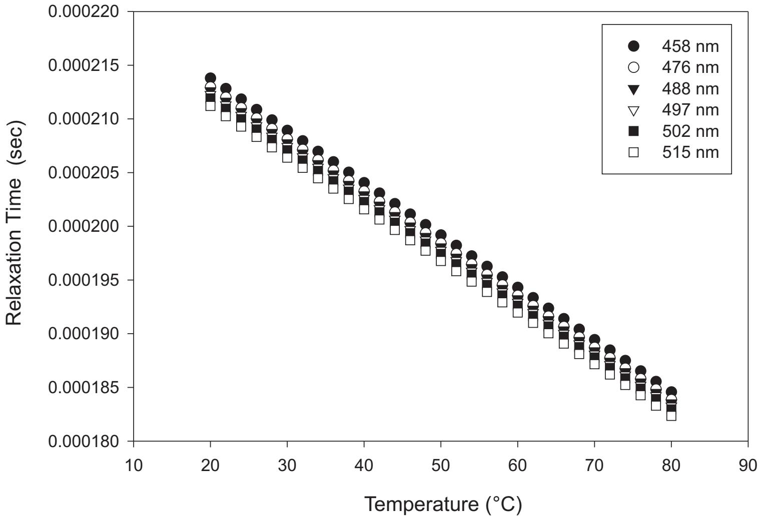

Fig. 3. The dependence of the relaxation time τ of the benzene on the temperature at constant wavelengths λ, $(d\tau/dT)_\lambda$

Table 1. Rate of change of some physical parameters of a laser dye solvent with respect to the solvent's temperature at constant pumped laser wavelengths

Laser wavelength (nm)	$-(\frac{d\eta}{dT})_\lambda$ $\times 10^6$	$-(\frac{d\tau}{dT})_\lambda$ $\times 10^7$	$-(\frac{dF_{\max}}{dT})_\lambda$ $\times 10^{34}$	$-(\frac{d\gamma_s}{dT})_\lambda$ $\times 10^7$	$(\frac{dW}{dT})_\lambda$ $\times 10^{24}$	$(\frac{dP}{dT})_\lambda$ $\times 10^{20}$	$-(\frac{d\theta}{dT})_\lambda$ $\times 10^2$
458	2.8958	4.8701	3.8256	2.6443	3.8280	3.4513	2.7180
476	2.8706	4.8512	3.3799	2.4281	3.7940	3.4371	2.7203
488	2.8619	4.8432	3.1281	2.3038	3.7863	3.4327	2.7209
497	2.8532	4.8353	2.9530	2.2150	3.7752	3.4283	2.7216
502	2.8520	4.8273	2.8581	2.1653	3.7646	3.4243	2.7222
515	2.8268	4.8111	2.6470	2.0574	3.7420	3.4151	2.7236

Table 2. Rate of change of some physical parameters of a laser dye solvent with respect to the pumped laser wavelength at constant solvent's temperatures

Temp. °C	$(\frac{d\eta}{d\lambda})_T$ $\times 10^7$	$-(\frac{d\tau}{d\lambda})_T$ $\times 10^{-4}$	$(\frac{dF_{\max}}{d\lambda})_T$ $\times 10^{34}$	$-(\frac{d\gamma_s}{d\lambda})_T$ $\times 10^7$	$-(\frac{dW}{d\lambda})_T$ $\times 10^{25}$	$-(\frac{dP}{d\lambda})_T$ $\times 10^{22}$	$-(\frac{d\theta}{d\lambda})_T$ $\times 10^3$
20	3.5405	4.5775	3.9609	1.5378	4.2419	9.2009	2.3525
30	3.3988	4.4693	3.7422	2.2892	4.3867	9.7346	2.3613
40	3.0352	4.3611	3.5239	3.0444	4.5315	1.0296	2.3703
50	2.4380	4.2807	3.3122	5.4660	4.6763	1.0885	2.3793
60	1.6181	4.1725	3.1071	2.9620	4.8210	1.1508	2.3881
70	1.3151	4.0731	2.9085	1.5803	4.9658	1.2153	2.3968
80	1.0131	3.9649	2.7164	0.1986	5.1106	1.2837	2.4055

4.2.2. Wavelength dependence $\tau_T(\lambda)$

From the data given in Fig. 3 the values of $\tau_T(\lambda)$ were estimated and plotted against λ at constant $T = 20$, 30, 40, 50, 60, 70 and 80 °C as shown in Fig. 4. From the slope the values of $(d\tau/d\lambda)_T$ were estimated with the given values in Table 2. This wavelength dependence of τ was found to obey the following empirical form:

$$\tau = a\exp\{-b\lambda\}\,, \tag{14}$$

where $a = 2.029 \times 10^{-4}$ and $b = 2.060 \times 10^{-4}$. This means that the relaxation time decays exponentially with the increasing wavelength.

4.2.3. Verification of both η and τ values

From Eq. (3)

$$3\eta(T)V(T)/\tau(T)T = k\,.$$

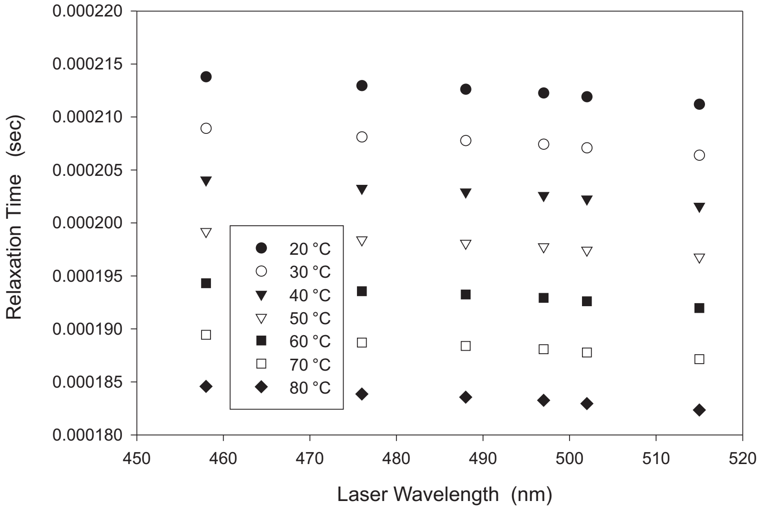

Fig. 4. The dependence of the relaxation time τ on the pumped laser wavelength λ at constant temperatures T, $(d\tau/d\lambda)_T$

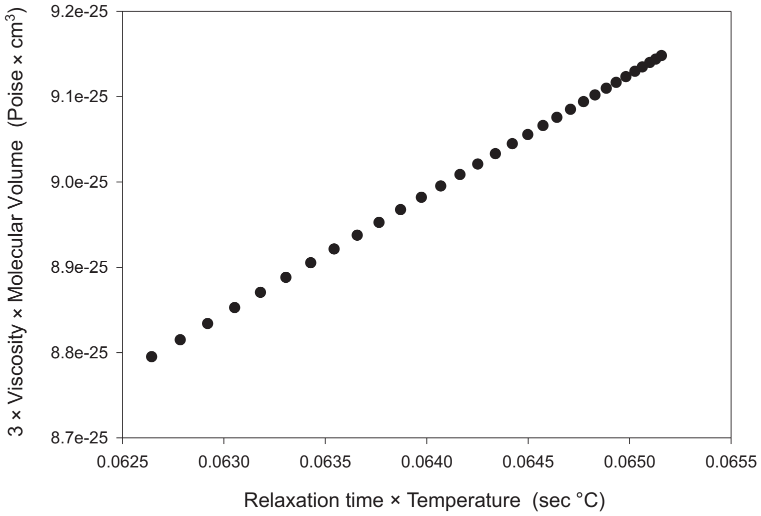

Fig. 5. The result verification of both benzene's viscosity η and its relaxation time τ, $(3\eta V/\tau T) = k$

By plotting $3\eta(T)V(T)$ as the y axis and $\tau(T)T$ as the x axis, for each value of temperature T and volume $V(T)$, Fig. 5 was appeared with a straight line its slope equals 1.4040×10^{-23} which must equals the value of Boltzmann's constant with the known value 1.38×10^{-23}. By comparing these two values the difference between theoretical and experimental studies was equal to $\pm 0.024 \times 10^{-23}$ which is an acceptable value. This means that the experimental determination values of η and τ are in good agreement with the theoretical study.

4.3. Maximum radiation force

By combining Eqs. (4) and (5) a relation between refractive index, photon momentum, scattering factor and the maximum radiation force of a laser dye solvent molecule was given by:

$$F_{\max} = [4\pi^2 \hbar (n-1)^2]/(N\lambda^5)\,, \tag{15}$$

where $\hbar$ is Planck's constant with the value 6.66×10^{-34} Joule·sec (SI units), N is the number of molecules per unit volume, n is the refractive index and λ is the incident laser wavelength.

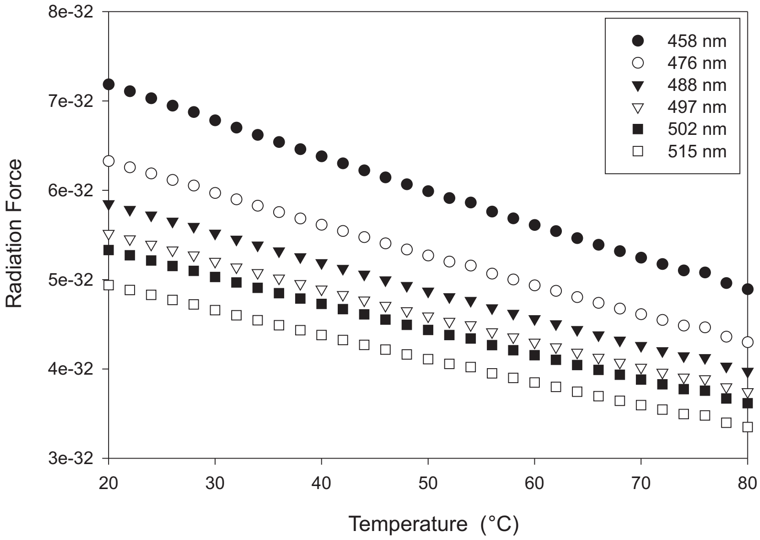

Fig. 6. The thermal dependence of the benzene's maximum radiation force at constant wavelengths, $(dF_{\max}/dT)_\lambda$

For $N = 1$, the values of $F_{\max}$ were calculated as a function of T for each temperature value T. The dependence of $F_{\max}$ on T was plotted as shown in Fig. 6 and the slope of each curve corresponding to each λ, $(dF_{\max}/dT)_\lambda$, was calculated with the values given in Table 1. An empirical relation was found to govern the

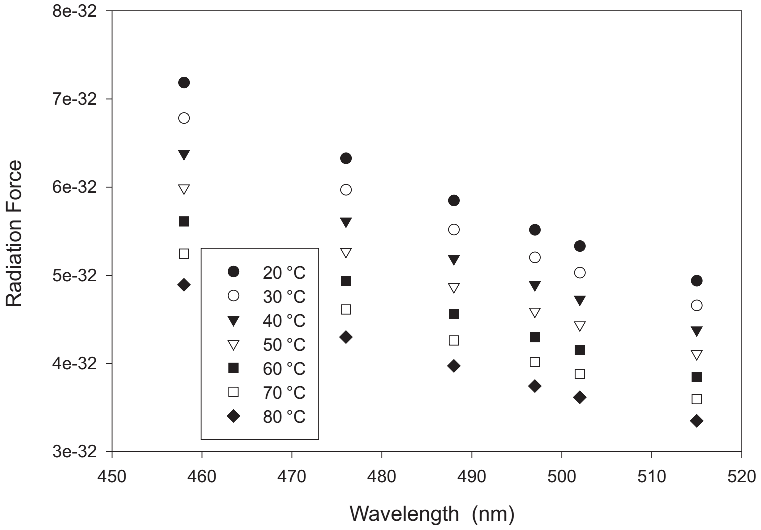

Fig. 7. The wavelength dependence of the maximum radiation force at constant temperatures, $(dF_{\max}/d\lambda)_T$

temperature dependence of $F_{\max}$, which shows an exponential decay, as:

$$F_{\max} = a\exp(-bT)\,, \tag{16}$$

where $a = 1.366 \times 10^{-31}$ and $b = 2.31 \times 10^{-2}$.

From Fig. 5 and Eq. (16) it is seems that the maximum radiation force of laser dye solvent molecule decreases as its temperature increases, which means that when the temperature of the laser dye active medium becomes high the radiation power of the laser dye molecule will be decrease. This tends to decrease the emitted power of the dye laser. Therefore the temperature of the laser dye active medium must be optimized at suitable lower temperature.

Also, the dependence of $F_{\max}$ on λ was investigated as shown in Fig. 7 and the rate of change $(dF_{\max}/d\lambda)_T$ was estimated as given in Table 2 for selected temperatures. This dependence was found to follow the following exponential form:

$$F_{\max}(\lambda)_T = a\exp(-b\lambda)\,, \tag{17}$$

where $a = 2.581 \times 10^{-27}$ and $b = 2.31 \times 10^{-2}$.

According to Fig. 7 the pumped laser wavelength must be selected to be constant at a definite wanted wavelength. Taking into account that when the temperature of the active medium changed this tends to change the dimensions of the laser cavity which shifts the emitted laser frequency and its wavelength consequently.

4.4. Scattering factor γ_s

In view of the maximum radiation power on the scattering factor the behavior of γ_s was studied depending on both temperature and wavelength as shown in Figs. 8 and 9, respectively. From both figures $(d\gamma_s/dT)_\lambda$ and $(d\gamma_s/d\lambda)_T$ were evaluated as given in Tables 1 and 2, respectively.

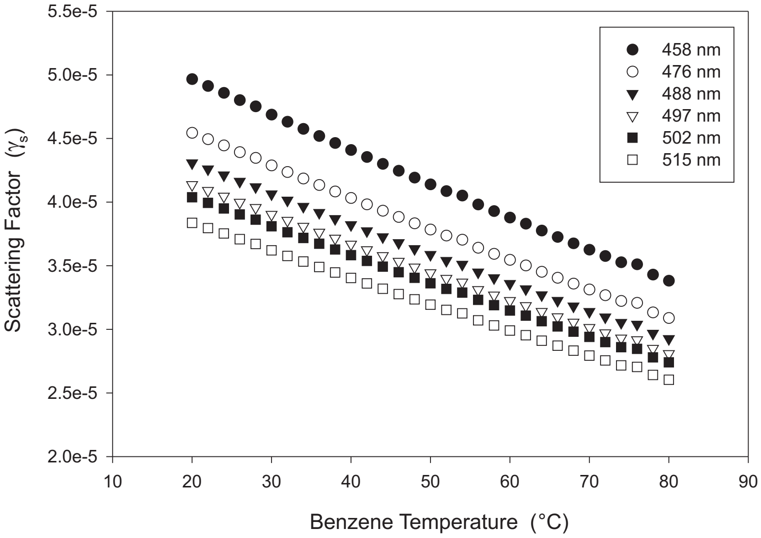

Fig. 8. The scattering factor γ_S variation with the benzene's temperature at constant pumped laser wavelengths, $(d\gamma_S/dT)_\lambda$

4.5. Work (W) and power (P)

By using the thermodynamical formula:

$$W = V\beta pT \tag{18}$$

or

$$W = (\delta V/\delta T)_p pT\,, \tag{19}$$

where V is the molecular volume, $\beta = (1/V)(\delta V/\delta T)_p$ is the volume expansion coefficient, p is the atmospheric pressure, and T is the absolute temperature.

By substituting with values of V, (or $(\delta V/\delta T)_p$), p and T, the work done by one laser dye solvent molecule was calculated for each temperature at constant wavelength. The results were plotted as shown in Fig. 10 from which $(dW/dT)_\lambda$ was calculated with the values tabulated in Table 1. It is shown that the work done by the laser dye solvent molecule increases with increasing the temperature whereas it was decreased with increasing wavelength. One can calculate that although the

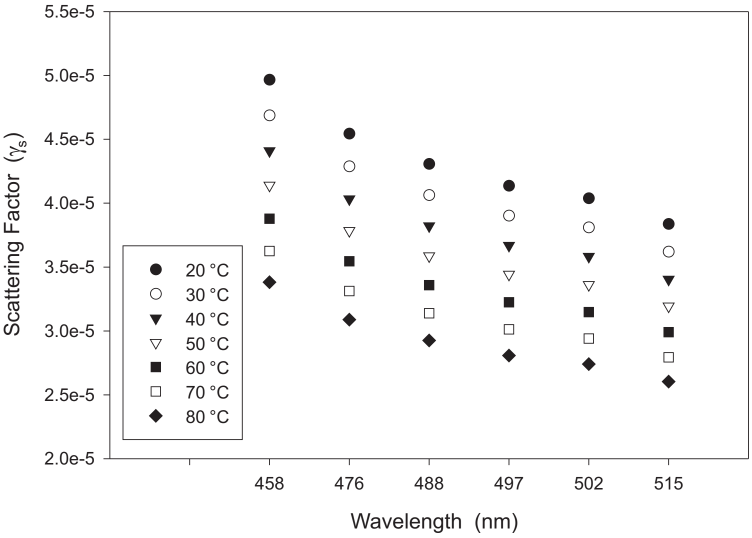

Fig. 9. The scattering factor γ_S variation with pumped laser wavelength of the laser dye solvent, benzene, at constant temperatures $(d\gamma_S/d\lambda)$

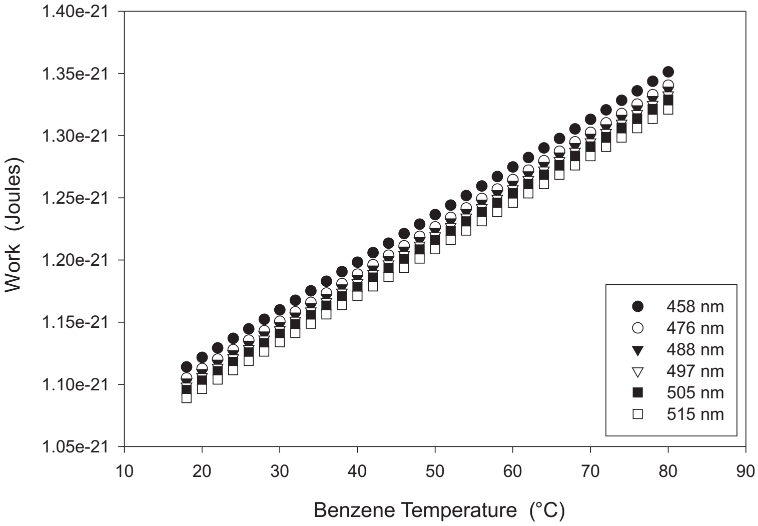

Fig. 10. Temperature dependence of the work done by one molecule laser dye solvent W at constant pumped laser wavelengths, $(dW/dT)_\lambda$

work done by the molecule under investigation directly with its temperature but the radiation force emitted was decreased. This means that the higher temperature despites the radiation power emitted by the laser dye solvent molecules.

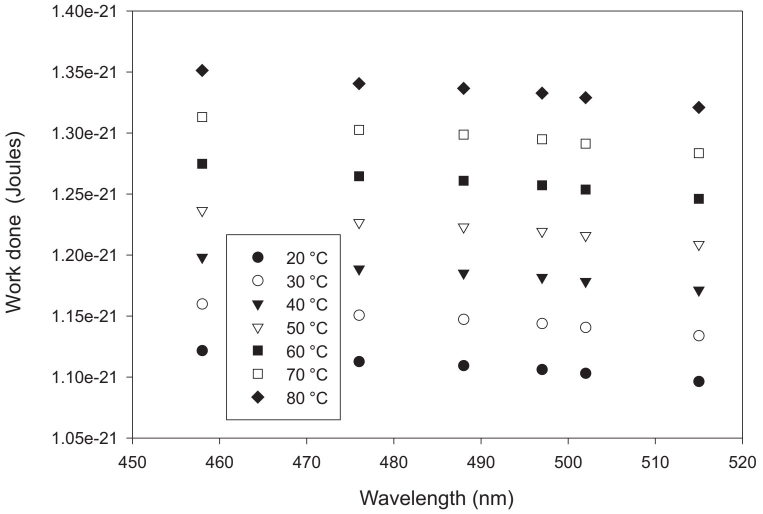

Fig. 11. Wavelength dependence of the work done by one molecule laser dye solvent W at constant laser dye solvent temperatures, $(dW/d\lambda)$

The dependence of W on λ was shown in Fig. 11 from which the values $(dW/d\lambda)_T$ were calculated with the values given in Table 2. The dependence of W on both T and λ is given by:

$$dW = (dW/dT)_\lambda dT + (dW/d\lambda)_T d\lambda\,. \tag{20}$$

By knowing both $(dW/d\lambda)_T$ and $(dW/dT)_\lambda$, one obtains the following relation:

$$dW = 3.7817 \times 10^{-24} dT - 4.6754 \times 10^{-25} d\lambda\,.$$

Therefore

$$dW = 3.7817 \times 10^{-24} \int dT - 4.6754 \times 10^{-25} \int d\lambda\,, \tag{21}$$
$$W = 3.7817 \times 10^{-24}(T_2 - T_1) + 4.6754 \times 10^{-25}(\lambda_1 - \lambda_2)\,.$$

By substituting for T_1, T_2, λ_1 and λ_2, one gets the work done by benzene laser dye solvent molecule.

It is known that the power = work/time, therefore the work done by a molecule during each relaxation time was calculated. Hence the power exerted by the whole number of molecules within a unit volume could be calculated and its behavior with the temperature was studied as shown in Fig. 12. The values of $(dP/dT)_\lambda$ for benzene corresponding to each wavelength were calculated as given in Table 1.

In addition the dispersion behavior of $P(\lambda)$, for the laser dye solvent under investigation, was studied at constant selected temperatures with the aid of Fig. 12. Figure 13 shows this dispersion behavior from which the rate of change of the power

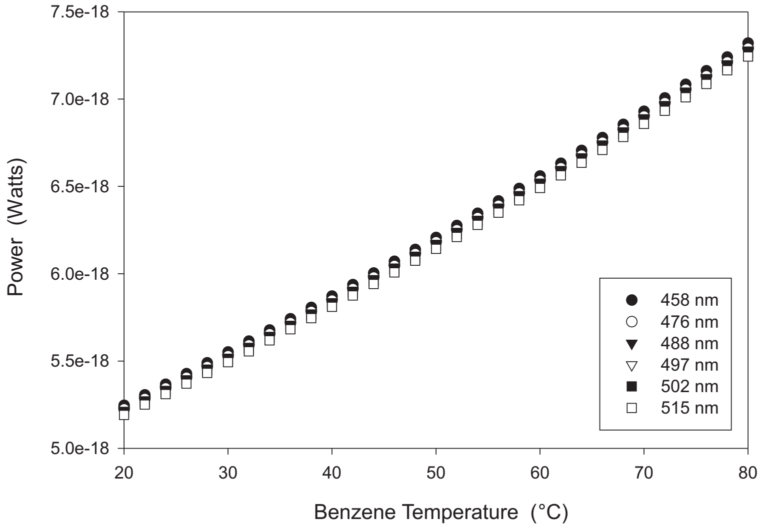

Fig. 12. Thermal dependence of the power P exerted by one molecule of laser dye solvent at constant pumped laser wavelengths, $(dP/dT)_\lambda$

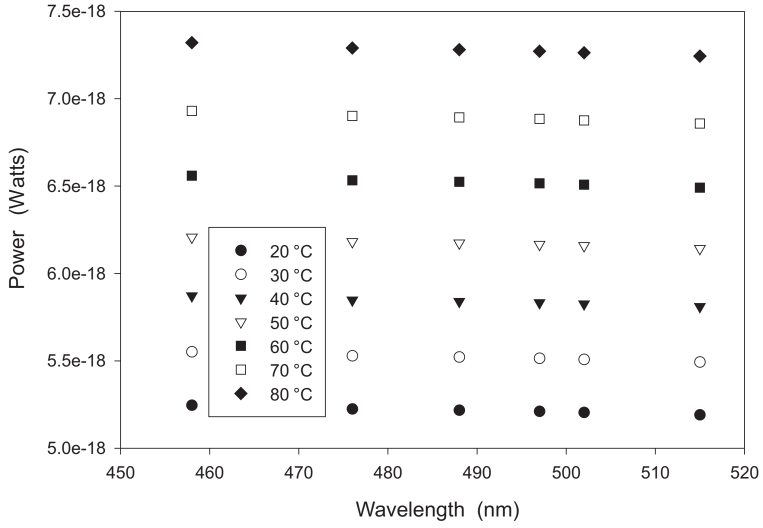

Fig. 13. Dispersion of the power P of a laser dye solvent of benzene solvent at constant temperatures, $(dP/d\lambda)$

exerted by one molecule of benzene $(dP/d\lambda)_T$ were calculated with the values given in Table 2.

4.6. Tilt angle θ

The effect of tilt angle θ of the laser dye solution cell was studied under the effect of temperature change $(d\theta/dT)_\lambda$ and wavelength change $(d\theta/d\lambda)_T$. When the temperature of the laser dye solvent becomes higher the angle of tilt of that cell will changed with little variation. This variation changes the refractive index of that medium. By using Eq. (10) the values of θ were calculated at each temperature. Figures 14 and 15 show the temperature and wavelength dependence of θ, respectively. The values of $(d\theta/dT)_\lambda$ and $(d\theta/d\lambda)_T$ are given in Tables 1 and 2, respectively.

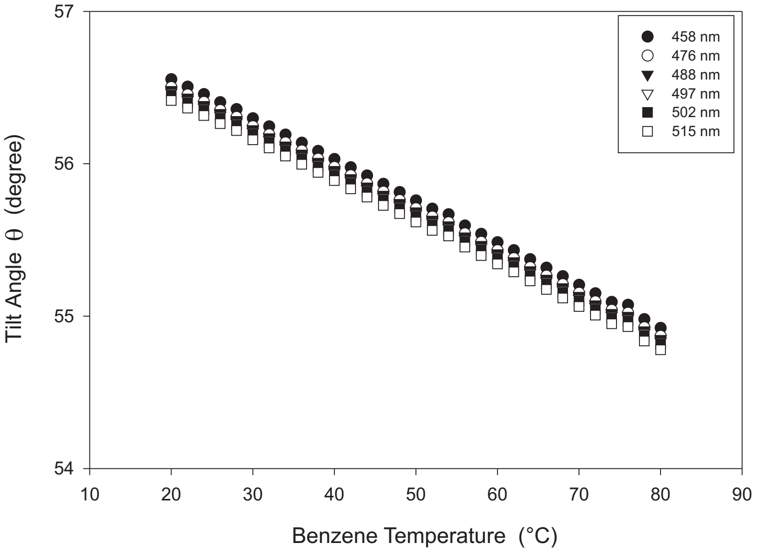

Fig. 14. Temperature change of the tilt angle θ laser dye cell at constant pumped laser wavelengths, $(d\theta/dT)_\lambda$

4.7. Density dependence of refractive index $n(\rho)$

Since the density of the laser dye solvent was changed inversely with the temperature, $d\rho/dT$. Also the refractive index n depends on the temperature of that medium inversely, dn/dT. Therefore the rate of change of n with respect to ρ, i.e. $dn/d\rho$ was studied by plotting the relation between n and ρ at different temperatures and a constant wavelength, as shown in Fig. 16. From that figure the values of $[(dn/d\rho)_\lambda]_{\text{exp}} = 0.4954$, for $\lambda = 458$ nm, were estimated with the given values in Table 3. This result was verified as follows.

Since $(dn/d\rho)_{\text{cal}} = (dn/dT)/(d\rho/dT)$, by using the values of $dn/dT = -1.4984\times 10^{-3}$, and $d\rho/dT = -3.0239 \times 10^{-5}$ [19], corresponding to $\lambda = 458$ nm, as an example, the value of $[(dn/d\rho)_\lambda]_{\text{cal}} = 0.49552$. The difference $[(dn/d\rho)_\lambda]_{\text{cal}} -$

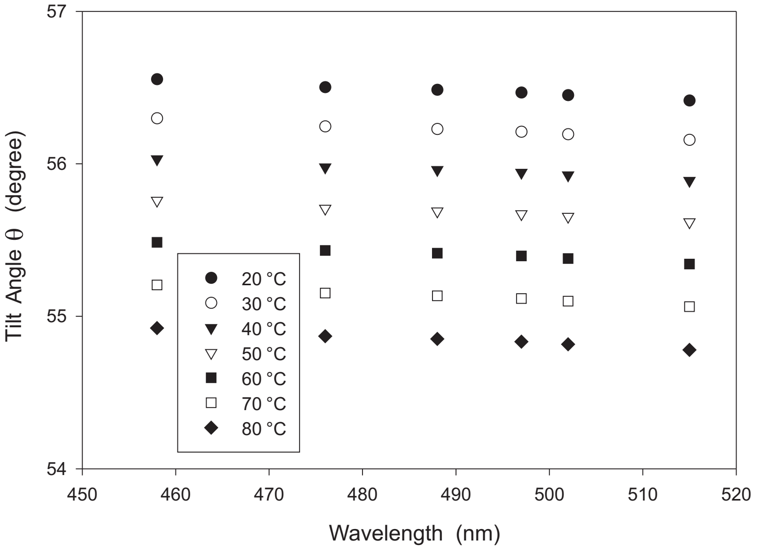

Fig. 15. Wavelength dependence of the tilt angle θ laser dye cell at constant laser dye temperatures, $(d\theta/d\lambda)_T$

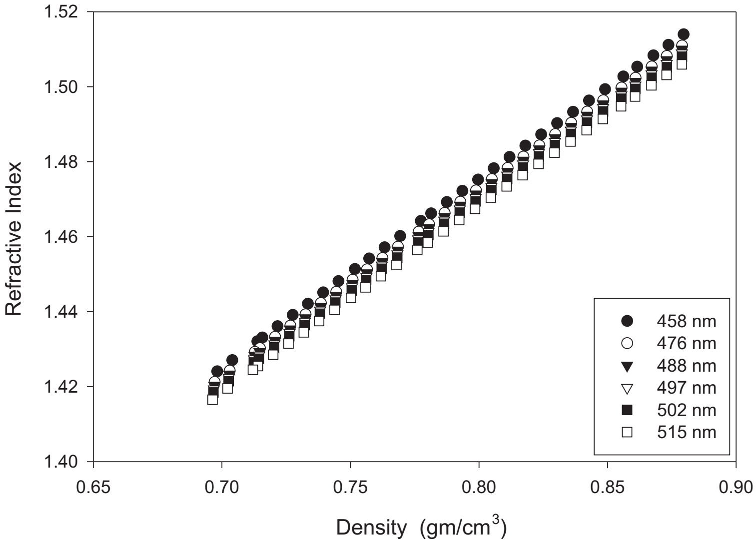

Fig. 16. The rate of change of the refractive index n with respect to the laser dye solvent's density ρ at constant pumped laser wavelengths λ and temperatures T, $(dn/d\rho)_{T,\lambda}$

Table 3. Rate of change of the refractive index, viscosity, density and tilt angle with respect to each other of laser dye solvent according to the investigated triplet relation

λ (nm)	$\left(\frac{dn}{d\rho}\right)$		$\left(\frac{dn}{d\eta}\right)$		$\left(\frac{dn}{d\theta}\right)$ $\times 10^2$		$\left(\frac{d\eta}{d\rho}\right)$ $\times 10^3$	
	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal
458	0.4954	0.4955	522	532	5.511	5.5129	2.144	0.9576
476	0.4935	0.4936	527	536	5.496	5.4972	2.104	0.9475
488	0.4925	0.4927	528	538	5.492	5.4903	2.090	0.9438
497	0.4920	0.4921	530	540	5.487	5.4872	2.076	0.9402
502	0.4913	0.4913	531	544	5.482	5.4823	2.063	0.9389
515	0.4898	0.4898	534	551	5.472	5.4722	2.035	0.9290

$[(dn/d\rho)_\lambda]_{\text{exp}} = \pm 0.00012$. This means that the determined values of $[(dn/d\rho)_\lambda]_{\text{exp}}$ at different wavelengths were in good matching with that calculated.

4.8. Viscosity dependence of refractive index $n(\eta)$

Because the inverse dependence of the viscosity η with the temperature T of the investigated laser dye solvent with the rate of change $(d\eta/dT)_\lambda$. In addition, dn/dT is a negative change value. Therefore the dependence of n on η was studied through Fig. 17 from which the values of $(dn/d\eta)_\lambda$ were appeared with the given values in Table 1. These values were verified through $[(dn/d\eta)_\lambda]_{\text{cal}} = (dn/dT)_\lambda/(d\eta/dT)_\lambda$ by substituting with given values [19] of both $(dn/dT)_{\lambda 1} = -1.4984 \times 10^{-3}$ and $(d\eta/dT)_{\lambda 1} = -4.5055 \times 10^{-6}$, during the linear part of the curve i.e. during the temperature range 56–80 °C, $[(dn/d\eta)_\lambda]_{\text{cal}} = 332.571$. But $[(dn/d\eta)_\lambda]_{\text{exp}} = 327.654$ with the difference $[(dn/d\rho)_\lambda]_{\text{cal}} - [(dn/d\rho)_\lambda]_{\text{exp}} = \pm 4.917$. Also, during the second linear part within the temperature range 24–54 °C the value of $[(dn/d\eta)_{\lambda 1}]_{\text{cal}} = 731.355$, whereas $[(dn/d\rho)_\lambda]_{\text{exp}} = 717.637$ with the difference ± 13.718. But at a temperature less than 24 °C the behavior was completely different because it is found that the curves shown in Fig. 17 satisfy the following stirling exponential growth equation

$$n_\lambda(T) = n_{0\lambda}(T) + (a/b)\{\exp[b\eta_\lambda(T) - 1]\} \tag{22}$$

with the constant values ($\lambda = 458$ nm, as an example):

$$n_0 = 1.4270\,, \qquad a = 3.475 \times 10^{-43} \qquad \text{and} \qquad b = 1.589 \times 10^{+4}\,.$$

By using the exponential growth Eq. (22) and substituting with the values of n_0, a, b and η at different λ and T. The corresponding values of $n_\lambda(T)$ has

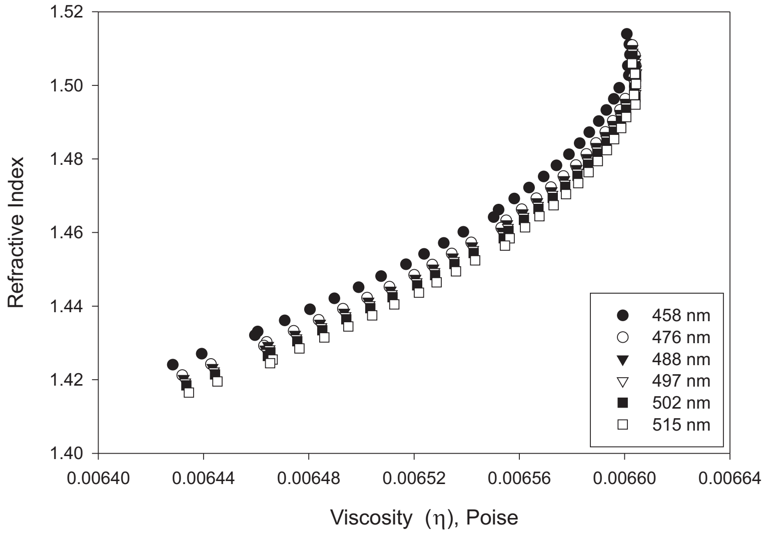

Fig. 17. The viscosity dependence of the refractive index n of the laser dye solvent at constant pumped laser wavelengths λ and temperatures T, $(dn/d\eta)_{T,\lambda}$

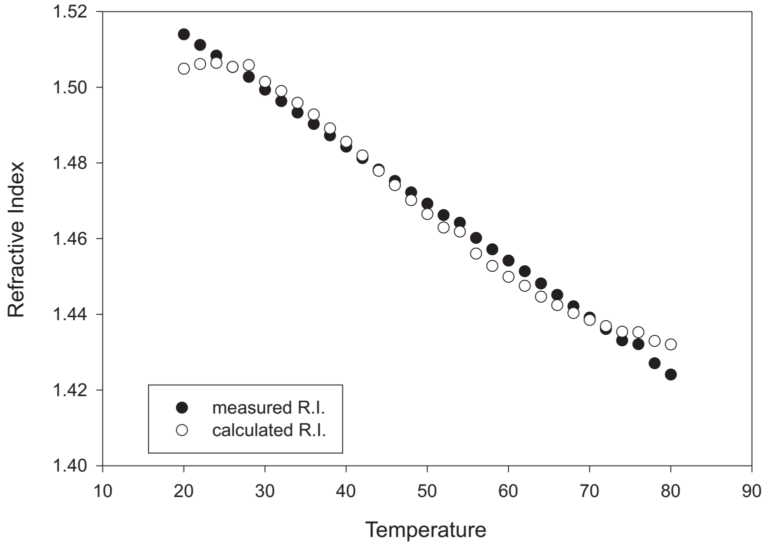

Fig. 18. Graphical comparison between the measured values and calculated values of the refractive index n at constant pumped laser wavelengths λ

been calculated with a very little difference with the measured values. This means that the relation (23) could be used to determine $n_\lambda(T)$ or $\eta_\lambda(T)$. Taking into account that the constant n_0 is the value of refractive index of the laser dye solvent under investigation at temperature higher than 80 °C at which the behavior is linear. Therefore the temperature corresponding to this refractive index can be calculated. In addition, the refractive index of this solvent can be calculated at any temperature higher than 80 °C. The same procedure can be taken for the viscosity of that solvent. The refractive index $[n_\lambda(T)]_{\mathrm{cal}}$ was calculated at $\lambda = 458$ nm with the slope $(dn/dT)_{\mathrm{cal}} = -1.4526 \times 10^{-3}$ and compared with that of measured value, at the same wavelength, which was equals $(dn/dT)_{\mathrm{exp}} = -1.4984 \times 10^{-3}$ as shown in Fig. 18. Therefore one could conclude that the relation (22) can be used to calculate either $n_\lambda(T)$ or $\eta_\lambda(T)$ with a good matching with the experimental determination. The values of $dn/d\eta$ were given in Table 3.

4.9. Angle dependence of refractive index $n(\theta)$

By using Eq. (10) the dependence of refractive index n of the laser dye solvent on the tilt angle θ of the sample cell which contains the laser dye solution was studied. This investigation was done under constant values of both temperature T and wavelength λ was shown in Fig. 19. The values of $(dn/d\theta)_{T,\lambda}$ were evaluated with the values given in Table 3. As an example, the value of $(dn/d\theta)_{T,\lambda}$ at $\lambda = 458$ nm was equal to 5.511×10^{-2}. Since $(dn/d\theta)_{\mathrm{cal}} = (dn/dT)/(d\theta/dT) = 5.5129 \times 10^{-2}$ with the difference $(dn/d\theta)_{\mathrm{exp}} - (dn/d\theta)_{\mathrm{cal}} = \pm 3.82 \times 10^{-3}$ which shows a good matching between the measured and calculated values of $(dn/d\theta)_{T,\lambda}$.

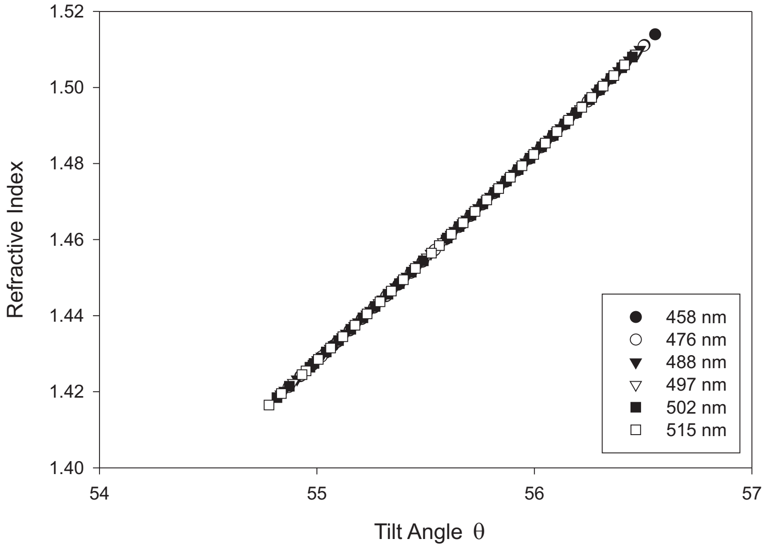

Fig. 19. The rate of change of the refractive index n of the laser dye solvent with respect to the tilt angle of the laser dye cell at constant pumped laser wavelengths λ and temperatures T, $(dn/d\theta)_{T,\lambda}$

4.10. *Density dependence of viscosity $\eta(\rho)$*

Because the temperature dependence of both density ρ and viscosity η of the laser dye solvent. A relation between density and viscosity of this solvent was studied as shown in Fig. 20 following the expression;

$$\eta = a(1 - \exp\{-b\rho\})\,, \tag{23}$$

where $a = 3.858$ and $b = 2.144 \times 10^{-3}$, for $\lambda = 458$ nm, as an example.

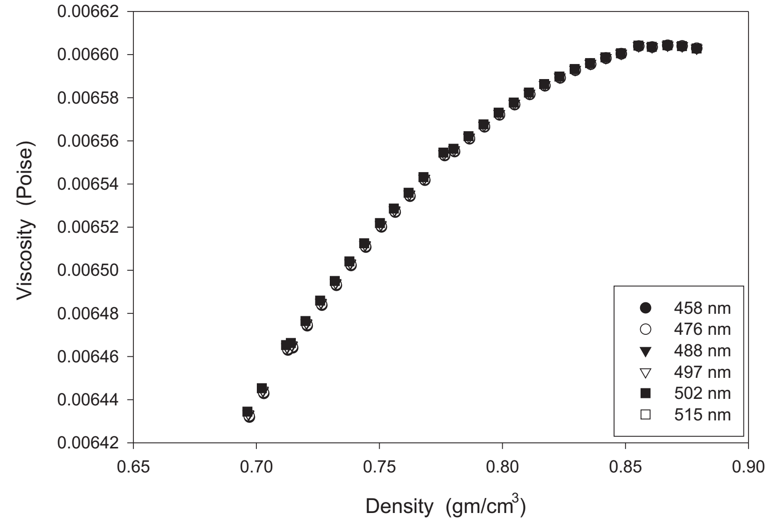

Fig. 20. The interrelation between viscosity and density of the laser dye solvent at constant pumped laser wavelengths λ and temperatures T, $(d\eta/d\rho)_{T,\lambda}$

The rate of change $(d\eta/d\rho)_{T,\lambda}$ was estimated with the values given in Table 3. Since $d\eta/d\rho = (d\eta/dT)/(d\rho/dT)$, therefore the calculated value $(d\eta/d\rho)_{\text{cal}}$ was calculated and compared with that experimental value with a difference $\pm 1.19 \times 10^{-3}$.

4.11. *Triplet relations*

4.11.1. n–ρ–T relation

The dependence of the refractive index n on the density ρ which depends on the temperature T of the laser dye solvent was studied through the triplet graph plotted between n, ρ and T shown in Fig. 21 from which the dependence of n on both ρ and T was estimated through the following fitted relation:

$$n_\lambda(T) = a_\lambda + b_\lambda T + c_\lambda \rho_\lambda(T)\,, \tag{24}$$

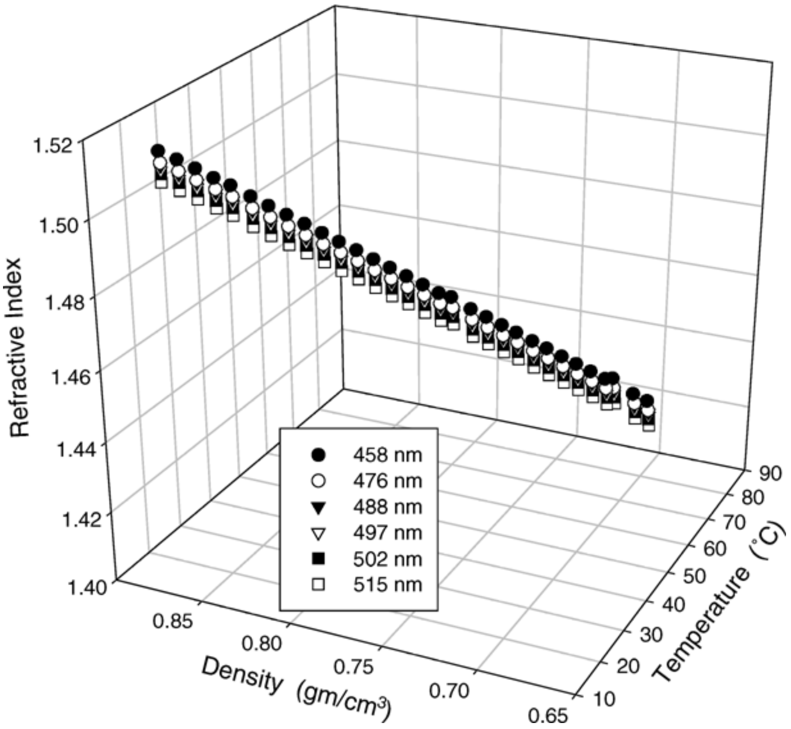

Fig. 21. The dependence of the refractive index of the investigated laser dye solvent on both the density and the temperature $n_\lambda(\rho, T)$

where a, b and c were constants with given values equal to 1.243, -5.295×10^{-4} and 0.3204, respectively, for $\lambda = 458$ nm, as an example. By this equation which fitted the plotted data the values of the refractive index n at a given values of T and ρ, at constant wavelength calculated. The calculated values of the refractive index $n_\lambda(T, \rho)$ were calculated at $T = 20$ °C, $\rho_{20} = 0.8970$ gm/cm^3 to give $n_{\mathrm{cal}} = 1.51404$ with a difference equals $\pm 5 \times 10^{-4}$ from that measured values. In addition, the value of $(dn/dT)_\lambda = a + b(d\rho/dT)_\lambda$ from which the value of $[(dn/dT)_\lambda]_{\mathrm{cal}} = -1.4984 \times 10^{-3}$ which was found to be equal to the experimental value $[(dn/dT)_\lambda]_{\mathrm{exp}} = -1.4984 \times 10^{-3}$. Also, the value of $[(dn/d\rho)_\lambda]_{\mathrm{cal}} = a[1/[(d\rho/dT)_\lambda]_{\mathrm{exp}}] + b = 0.4955$ which was compared with the experimental of $[(dn/d\rho)_\lambda]_{\mathrm{exp}} = 0.4954$ [19]. Therefore the triplet relation (24) was found that it has a good application to determine the refractive index n in terms of T and ρ. Also, the rate of change of $(dn/dT)_\lambda$ and $(dn/d\rho)_\lambda$ could be calculated in a good agreement with experimental values.

4.11.2. n–η–ρ relation

Figure 22 shows the triple relation between n, η and ρ of the laser dye solvent which was found that it is fitted with the relation:

$$\eta_\lambda(T) = a_\lambda + b_\lambda \rho_\lambda(T) + c_\lambda n_\lambda(T)\,, \tag{25}$$

where a, b and c are constants given with the values -4.699×10^{-2}, -2.329×10^{-2} and 4.893×10^{-2}, respectively. From Eq. (25) one has:

$$(d\eta/dT)_\lambda = a_\lambda (d\rho/dT)_\lambda + b_\lambda (dn/dT)_\lambda\,, \tag{26}$$

$$(d\eta/d\rho)_\lambda = a_\lambda + b_\lambda (dn/d\rho)_\lambda\,, \tag{27}$$

$$(d\eta/dn)_\lambda = b_\lambda + a_\lambda [1/(dn/d\rho)_\lambda]\,, \tag{28}$$

$$(dn/d\eta)_\lambda = b_\lambda + a_\lambda (dn/d\rho)_\lambda\,. \tag{29}$$

From Eq. (26) $[(d\eta/dT)_\lambda]_{\mathrm{cal}} = -2.8897 \times 10^{-6}$ Poise °C^{-1} which was compared with that $[(d\eta/dT)_\lambda]_{\mathrm{exp}} = -2.8958 \times 10^{-6}$ Poise °C^{-1}. Equation (27) gives

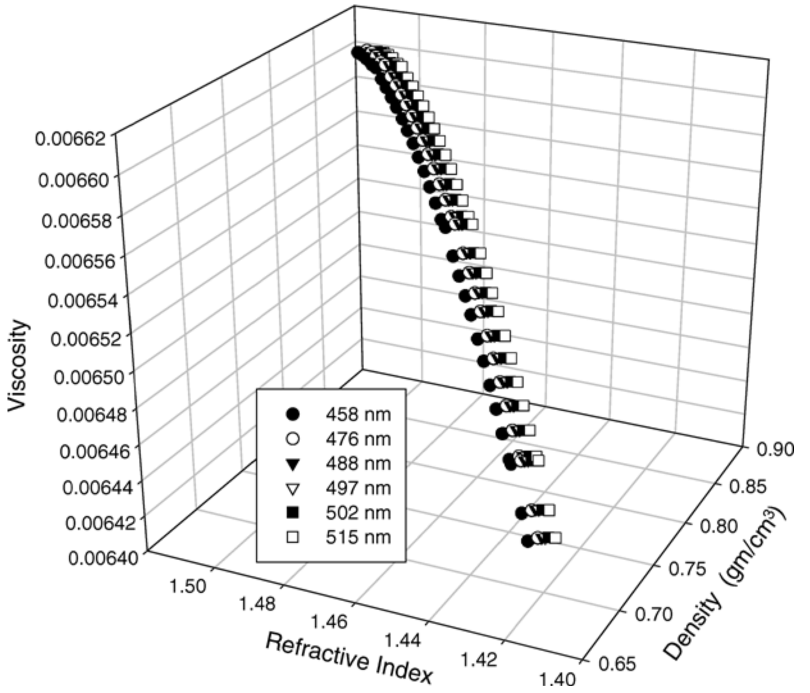

Fig. 22. The investigated triplet relation between viscosity, refractive index and density of the laser dye solvent at constant pumped laser wavelengths and constant temperatures, $\eta_{\lambda,T}(\rho, n)$

$[(d\eta/d\rho)_\lambda]_{\mathrm{cal}} = 9.4992 \times 10^{-3}$ Poise gm^{-1}cm^3 and the experimental value $[(d\eta/d\rho)_\lambda]_{\mathrm{exp}} = 2.144 \times 10^{-3}$ Poise gm^{-1}cm^3. By using Eq. (28) it was shown that the value of $[(d\eta/dn)_\lambda]_{\mathrm{cal}} = 1.9175 \times 10^{-3}$ Poise. But Eq. (29) gives $[(dn/d\eta)_\lambda]_{\mathrm{cal}} = 522.6005 \times 10^{-3}$ Poise^{-1} which was found to be equal to the mean average value of the slope of the two linear parts of Eq. (22).

4.11.3. η–ρ–T relation

Figure 23 shows the triplet relation between viscosity η, the density ρ and the temperature T of the laser dye solvent under investigation. The relation which fits this figure was:

$$\eta_\lambda(T, \rho) = a \exp\{-0.5[(T - T_0)/b] + [(\rho - \rho_0)/a]\}\,, \tag{30}$$

where $a = 7.063 \times 10^{-3}$, $b = 2.005 \times 10^3$, $c = 0.7863$, $T_0 = -7.101 \times 10^2$ and $\rho_0 = 0.8409$ are constants, for $\lambda = 458$ nm.

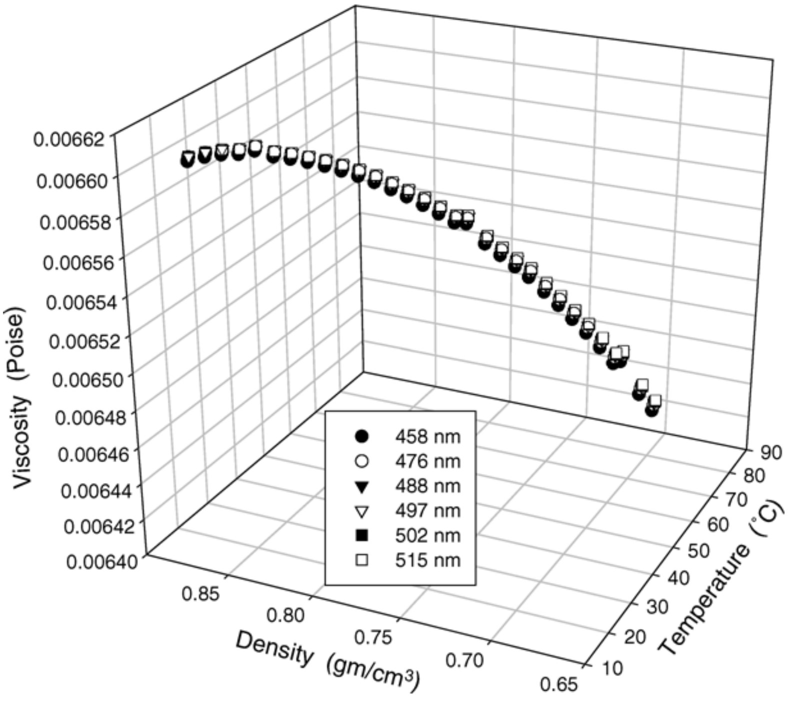

Fig. 23. The dependence of the viscosity of the laser dye solvent on both the density and the temperature of the investigated laser dye solvent at constant pumped laser wavelengths, $\eta_\lambda(\rho, T)$

To examine the correction of this equation the values of $[\eta_\lambda(T,\rho)]_{\mathrm{cal}}$ were calculated showing a difference equals $\pm 2.5\times 10^{-4}$. This means that there is a good matching between this equation and the experimental results for η as a function of both ρ and T.

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