Some Physical Properties of Master Oil (MO) and Lophira Lanceolata Oil (LLO) and their Temperature Dependence

Abstract

This study demonstrated that the viscosity, surface tension, and refractive index of MO and LLO all vary inversely with temperature. The thermodynamic parameters (exponent n, residual surface tension γ^*, critical temperature T_c, molar volume, and Eotvos constant were calculated using a novel model that was developed from the surface tension and viscosity observations at various temperatures. Both oils are non-Newtonian liquids, and according to the results LLO has higher values for all thermodynamic parameters than MO. The results also show that the refractive index of MO decreases faster than that of LLO. This shows that a smaller angle of incidence is required in MO than in LLO to produce total internal reflection during heating. Depending on the conditions, the rate (slow or fast) at which the refractive index of a liquid varies with temperature is a useful signature in optics.

Keywords: Surface tension, viscosity, refractive index, temperature, thermodynamic parameters

Introduction

In mechanics, liquids are known to be one of the basic states of matter. A liquid has definite volume and void of elasticity of form (absence of a shear modulus). Liquids are distinguished for their strong molecular interactions and consequently low compressibility since small reduction in the already small intermolecular distances gives rise to large intermolecular forces of repulsion [15]. Liquids exist in various forms such as water, oils, solutions, molten solids and condensed gases to mention but a few. Oils are naturally occurring inorganic or organic substances that are not soluble in water. Most oils containing organic materials are made up of carbon, hydrogen, oxygen and some elements like phosphorus. Oils are mostly extracted from living animals and plants as well as their dead remains in rocks underground. Liquids like other states of matter have both physical and chemical properties which make them to have wide applications in everyday life. For example, surface tension has made liquids to have applications in washing industry, design of rain coats and umbrellas, survival of pond skater and mosquito eggs on the surface of stagnant water, rise of kerosene in wicks of stoves and bush lamps, absorption of nutrients from the soil by plants and breathing in embryo in the womb. Because of the importance of surface tension, a host of authors have worked on surface tension of liquids such as; variation of surface tension with temperature [1], thermodynamic parameters of five vegetables oils using capillary rise method [16]; the effect of sodium chloride concentration on the surface tension of water using drop weight method [14] the effect of eight commercial detergents on surface tension of water using capillary rise method [13] the effect of temperature on the surface tension of palm oil and ground oil using capillary rise method [17]; and the effect of saliva on the surface tension of water and soft drinks using capillary method [17] to mention but a few. There are several factors that affect surface tension of liquid which include temperature, pressure, contaminants, solute, contact angle, homogeneity and viscosity of the liquid to mention but a few.

On the other hand, viscosity has made liquids useful as lubricants in moving parts of machines. Also, viscosity is known to be a good parameter for oil quality control because it is sensitive to small changes in temperature, concentration, homogeneity, and shape and size of molecules. For example, the viscosity and density of some pure vegetable oils have been shown to decrease with temperature [6,15], Liquid flow can be hindered by strong intermolecular attractions and molecular shapes. Long chain liquid polymers resist flow because the chains become entangled with one another during flow. The viscosity of lubricants and their blending agents affects the rate at which the sensitive components suffer oxidation at the surface of the liquid [2].

Another significant physical property is the refractive index of a substance; and is defined as the velocity of light in vacuum divided by velocity of light in the substance. The optical property of a medium to slow down light travelling through it leads to its optical refractive index. Refractive index has been found to play a vital role in many areas of material science with special reference to various optical technologies and measurement of refractive indices of liquids. The measurements of refractive index and density are often required in physics and chemistry to determine the concentration of solutions. The refractive indices of liquids are determined by various methods and a common method is the measurement of angle of minimum deviation produced by a light beam that passes through the liquid contained in a hollow prism made of glass called Abbe refractometer [3,12]

In this work, surface tensions, viscosities and refractive indices of Lophira Lanceolata oil and Master oil were determined at various temperatures using tensiometer, viscometer and Abbe refractometer, respectively. A new relationship that enables the determination of the molar volume from viscosity measurements was established. The thermodynamic parameters such as the exponent index n, the critical temperature, T_c and Eotvos constant, K were determined from surface tension measurements.

Theory

The study of physical properties of liquids such as surface tension, viscosity and refractive index has revealed the importance of liquids in everyday life. The theories of the dependence of these properties on temperature are presented in this section.

(a) Surface tension-temperature relation

Surface tension (γ) is the fundamental property of a liquid surface which makes the free liquid surface to behave like a stretched elastic membrane. It is defined as the force F per unit length L acting perpendicularly to the surface of a liquid or may be thought of as work required to create a unit area of surface at a given temperature and mathematically expressed as $\gamma = \frac{F}{L}$. In general, surface tension γ is dependent on temperature T it decreases with increase in temperature vanishing at a temperature called the critical temperature T_c. The general formula for surface tension as a function of temperature is given by [1,8]

$$\gamma = \gamma^{*}\left(1-\frac{T}{T_C}\right)^{n} \qquad 1$$

and $$\gamma^{*} = \gamma_0\left(1-\beta T_0\right) = \frac{KT_C}{V^{\frac{2}{3}}} \qquad 2$$

where γ^* is a constant being the surface tension of a liquid at absolute zero, V_m is the molar volume of a liquid, T_c is the critical temperature, n is an empirical factor (n=11/9) yields good result for organic liquids and K is the Eotvos constant valid for almost all substances, a typical value of $K=2.1\times10^{-7}\ JK^{-1}Mol^{-2/3}$ [7]. For example, for water V_m =18 ml/Mol and T_c = 374 °C. However, for any substance, equation (1) contains three unknown quantities namely γ^*, n and T_c. Obviously, it is difficult to solve a single equation containing three unknown quantities. Nevertheless, such equation can be solved by making some mathematical manipulations. Hence, we present two possible ways to solve equation (1);

a) If the temperature variation is small, we use the fact that $n\approx1$ for the linear estimate, then equation (1) reduces to

$$\gamma = \gamma^{*}\left(1-\frac{T}{T_C}\right) \qquad 3$$

Then from the plot of surface tension against temperature according to equation (3), the slope gives the critical temperature T_c while the intercept gives the critical surface tension γ^*.

b) Alternatively, to solve equation (1) we require at least three (3) values each of γ and T. Thus, using three set of values γ_1, γ_2, γ_3 and their corresponding temperatures T_1, T_2, T_3, in equation (1) yields three simultaneous equations.

$$\gamma_1 = \gamma^{*}\,(1-\frac{T_1}{T_c})^{n} \qquad 4$$

$$\gamma_2 = \gamma^* \left(1 - \frac{T_2}{T_c}\right)^n \qquad 5$$

$$\gamma_3 = \gamma^* \left(1 - \frac{T_3}{T_c}\right)^n \qquad 6$$

Dividing equation (4) by equation (5)

$$\frac{\gamma_1}{\gamma_2} = \left(\frac{T_c - T_1}{T_c - T_2}\right)^n \qquad 7$$

Dividing equation (5) by (6)

$$\frac{\gamma_2}{\gamma_3} = \left(\frac{T_c - T_2}{T_c - T_3}\right)^n \qquad 8$$

From equation (7), T_c can be obtained as

$$T_c = \frac{T_1 - T_2\left(\frac{\gamma_1}{\gamma_2}\right)^{\frac{1}{n}}}{1 - \left(\frac{\gamma_1}{\gamma_2}\right)^{\frac{1}{n}}} \qquad 9$$

Substituting equation (9) into equation (8), we obtain

$$(T_2 - T_3)\left(\frac{\gamma_1}{\gamma_3}\right)^{1/n} + (T_3 - T_1)\left(\frac{\gamma_2}{\gamma_3}\right)^{1/n} = T_1 - T_2 \qquad 10$$

Equation (10) is a transcendental equation from which the value of n can be determined. Putting this value of n in equation 1 then the values of γ^* and T_c can be determined from the plot of $\gamma^{1/n}$ against T, where the slope is equal to $\frac{\gamma^{*\frac{1}{n}}}{T_c}$ and the intercept is equal to $\gamma^{*1/n}$. However, if there is significant variation in the calculated γ values from the measured values which may arise due to large spans between two values of the independent variable T and the dependent variable γ, then, a better alternative should be pursued. This requires smaller spans in T values say, 2° C for three T values and say 2 mN/m for three γ values. The value of n for small span in T values and γ values can be used to obtain the corresponding values of γ^* and T_c. This is the model adopted in this work.

(b) Viscosity- temperature relationship

Different liquids have different viscosities, depending on the nature of the liquid. When liquids are heated, their intermolecular distances increase and the flow of their molecules pass one another become easier. Thus, the viscosity decreases with temperature and vice-versa. The viscosity (η)-temperature (T) relation has been established in the form of decreasing exponential function given by [4, 5, 10, 15].

$$\eta = \eta_o \, e^{\frac{G}{RT}}, \text{ where } \eta_o = \frac{N_A h}{V}$$

or $$\ln \eta = \ln \eta_o + \frac{G}{R} \cdot \frac{1}{T} \qquad 11$$

where N_A = Avogadro number, h = Planck's constant, n_o = Viscosity as T tends to infinity, V_m = Molar volume, G = Molar activation energy and R =Molar gas constant. It is clear that from the plot of $\ln\eta$ versus $\frac{1}{T}$, the values of V_m and G can be deduced from the intercept and slope respectively.

(c) Refractive index-temperature relation

The refractive index determines how much light is bent, or refracted, when entering a material at a given temperature. This is the first documented use of refractive indices and is described by Snell's law of refraction [11]

$$n = \frac{n_2}{n_1} = \frac{\sin\theta_1}{\sin\theta_2} \qquad 12$$

where n is the refractive index of the second medium, θ_1 and θ_2 are the angles of incidence and refraction respectively, of a ray crossing the interface between two media with refractive indices n_1 and n_2. Note that if the first medium is vacuum or air, $n_1=1$ and equation (11) reduce to $n=n_2$. The refractive index also determines the amount of light that is reflected when reaching the interface, as well as the critical angle for total internal reflection. In optics, the refractive index or index of refraction n of a material is a dimensionless number that describes how light propagates through that medium. It is defined as [9]

$$n = \frac{c}{v} \qquad 13$$

where c is the speed of light in vacuum and v is the phase velocity of light in the medium. For example, the refractive index of water is 1.333; meaning that light travels 1.333 times faster in a vacuum than it does in water. Therefore, the knowledge of the refractive index of a liquid tells us the scope of application of the liquid in optics. But when the temperature of the second medium increases it expands and the angle of refraction increases and hence the refractive index decreases. Therefore, the variation of refractive index n with temperature T can be written as

$$n = AT + B \qquad 14$$

where A is a negative constant and B could be positive or negative since n decreases with T.

Materials and Methods

The materials used for the experiments in this research work are: water bath, stirrer, retort stand and clamp, beakers, pippette, sensitive digital balance of accuracy ±0.01g, lophira lanceolata oil, Abbe refractometer, tensiometer, viscometer, Bunsen burner, thermometers, sewing machine oil (Master oil), water, petric dish, ethanol.

The procedures of the experiments to produce or obtain the lubricants and measurements of each of their physical properties (surface tension, viscosity and refractive index) of Master oil and Lophira lanceolata oil at different temperatures are presented as follows:

(a) Sample acquisition/extraction of MO and LLO

Fruits of Lophira lanceolata were obtained from lophira trees located in Ganye Local Government Area of Adamawa State. The fruits were dried for several days and partially crushed to remove out seeds. The seeds were fried and grounded into powder. Boiling water was added to it and stirred to form a paste. It was kept for two days after which the oil was decanted into a clean bottle. The Master oil was bought from the Jimeta market, Yola, Nigeria.

(b) Surface Tension of MO and LLO at Various Temperatures.

A sample of Lophira Lanceolata oil was placed in a thermostatically controlled container of Sigma 702 tensiometer of accuracy ± 0.01N/m^2. The temperature was adjusted to 313.15 K on a Screen using the temperature control botton. The ring (platinum) was placed in the sample by the help of the upper Knob and it was adjusted gently to the surface by the help of the lower knob. Thereafter care was taken in adjusting the ring from the surface untill the meniscus produced by the ring was broken of and the ring jerked off. This upward pull of the ring was indirectly the surface tension at that temperature which was read off from the screen. The experiment was repeated for temperatures 323.15 K, 333.15 K, 343.15 K, 353.15 K, 363.15 K, 373.15 K. These procedures were repeated for Master oil.

(c) Viscosity of MO and LLO at Different Temperatures.

The viscosities of Lophira lanceolata oil (LLO) and master oil (MO) at various temperatures (313.15-373.15 K) were measured at the same time using a digital Viscometer ASTMD2162-06. This is a digital instrument which is standardized based on the kinetics viscosity of water at 20 ºC. This instrument has two tubes in which the liquids under investigation were placed in order to measure simultaneously their viscosities at different temperatures. In addition, attached to its side is a digital stop watch that can measure the time at which the viscosities were recorded at a particular temperature. The values of the viscosities of LLO and Master oil at various temperatures were determined.

(d) Refractive Index of MO and LLO at Various Temperatures.

An Abbe Refractometer of accuracy ± 0.05 units, with a thermostatically controlled water bath was used for all the measurements of refractive index. Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermostatic water bath for all the measurements in the temperature range 313.15-373.15 K. The prism box was opened and a few drops of Lophira Lanceolata oil was placed on the ground surface of the lower prism at each temperature, starting with 313.15 K.

The prism box was closed and the box flattened again, making sure that the liquid did not flow away. The cross wires of the telescope were focused by rotating the eye piece and adjusting the mirror so as to get good illumination. By means of the lower knob, the prism box was turned slowly backwards and forwards until the field of view became coloured fringe. By means of the upper knob the compensator was rotated until the coloured fringe disappeared and the lighted image showed a sharp edge. The prism box was rotated until the sharp edge was in coincidence with the intersection of the cross-wires in the telescope. The index of refraction was read off on the scale through the eye piece. The experiment was repeated at temperatures 323.15 K, 333.15 K, 343.15 K, 353.15 K, 363.15 K, 373.15 K. These procedures were repeated for Master oil.

Results and discussion

The experimental values of the viscosities and the corresponding times taken for viscosity and shear force to reach equilibrium at various temperatures in Master oil (MO), Lophira Lanceolata oil (LLO) and Water are presented in Table 1.

Table 1. Viscosity of Master oil, LLO and Water at different temperatures.

Temp (K)	**Viscosity η (mPa.s)**			**Time (seconds)**	
	Master oil	**LLO**	**Water***	**MO**	**LLO**
313	29.34	153.82	11.91	10.41	55.49
323	20.21	101.87	9.85	7.17	36.75
333	15.39	71.02	9.56	5.46	25.67
343	12.82	51.70	8.96	4.55	18.65
353	9.05	38.65	7.99	3.21	14.21
363	7.97	30.65	4.61	2.83	11.27
373	5.47	27.33	4.09	1.94	9.86

*(*Source: International Association for Properties of Steam (IAPS, 1985)*

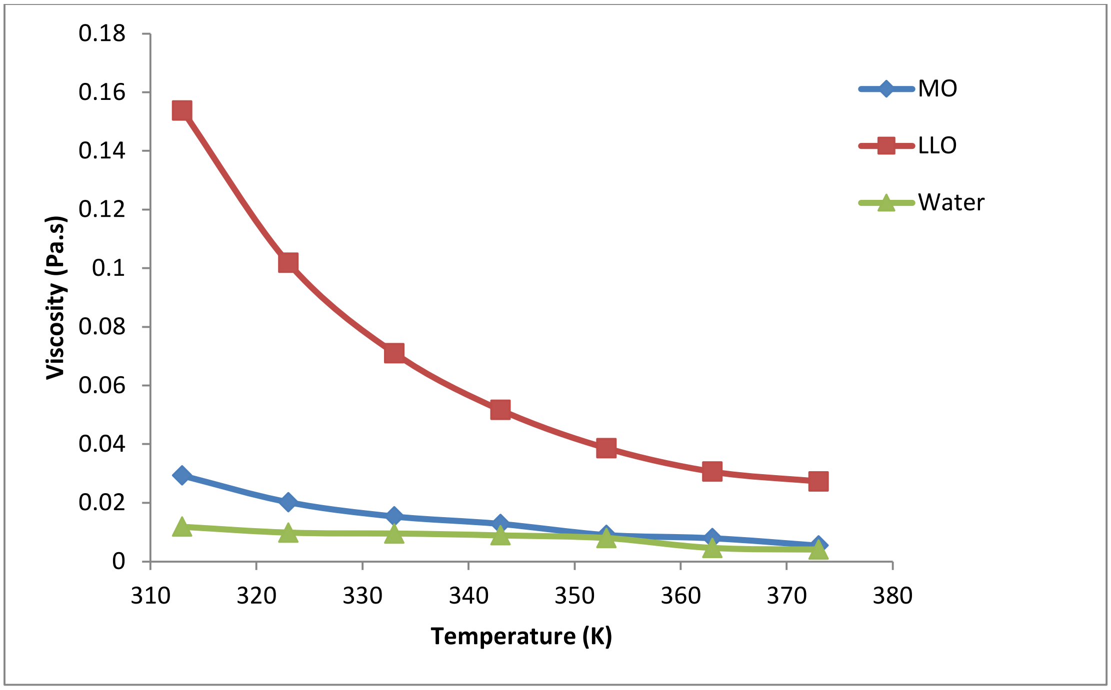

Fig. 2. Viscosity-temperature curves for MO, LLO and water

Figure 2, shows that the viscosities, η of the liquids decrease with temperature, T according to the general relation $\eta = \eta_o e^{\frac{G}{RT}}$ where η_O is the critical viscosity of liquid as T tends to infinity, R=8.3145 J/mole-K is the universal gas constant and G is the molar activation energy.

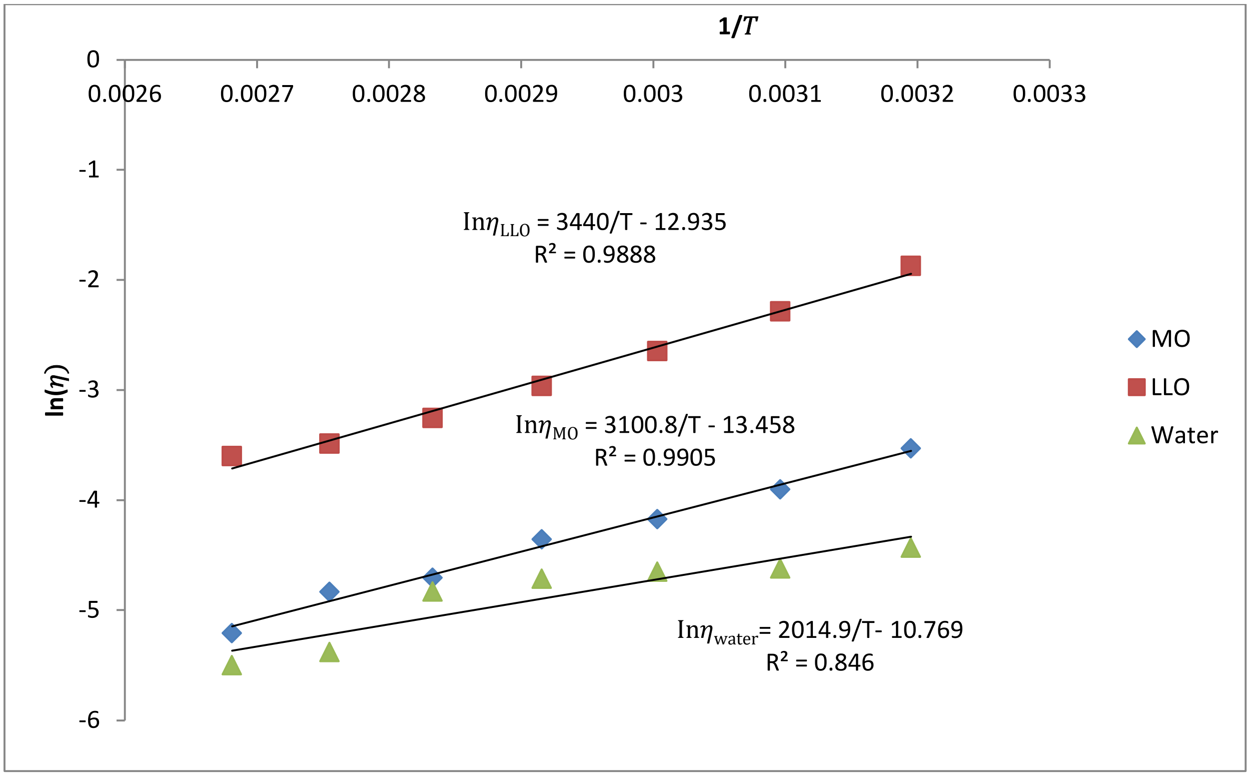

Fig.3. Plots of ln(η) versus 1/T for MO, LLO and water

Figure 3, shows the graph of ln(η) against $\frac{1}{T}$ which yields the following regression lines

$$\ln(\eta)_{\mathrm{MO}} = 3100.8\frac{1}{T} - 13.458, \ \ R^2 = 0.9905 \quad 15$$

$$\ln(\eta)\mathrm{llo} = 3440\frac{1}{T} - 12.935, \ \ R^2 = 0.9888 \quad 16$$

$$\ln(\eta)_{water} = 2014.9\frac{1}{T} - 10.769, \ \ R^2 = 0.8460 \quad 17$$

where R^2 is the goodness of fit of the lines, the coefficients of $\frac{1}{T}$ equals $\frac{G}{R}$ and the constants represent ln(η_o). The values of the critical viscosity and molar activation energy (η_o, G) for MO, LLO and water respectively were obtained as (η_o=1.43176 **μ**Nm^{-2}, G=25781.60 J/mole), (η_o=2.41537 **μ**Nm^{-2}, G=28601.88 J/mole) and (η_o=2.10653 **μ**Nm^{-2}, G=16752.89 J/mole). Also, the molar volumes, $V_m = \frac{N_A h}{\eta_o}$, for MO, LLO and water are 279 ml, 165 ml and 18.9 ml respectively where $N_A=6.02\times10^{23}$ and $h=6.626\times10^{-34}$Js. The calculated molar volume of water 18.9 ml is very close to the actual molar volume of water 18 ml.

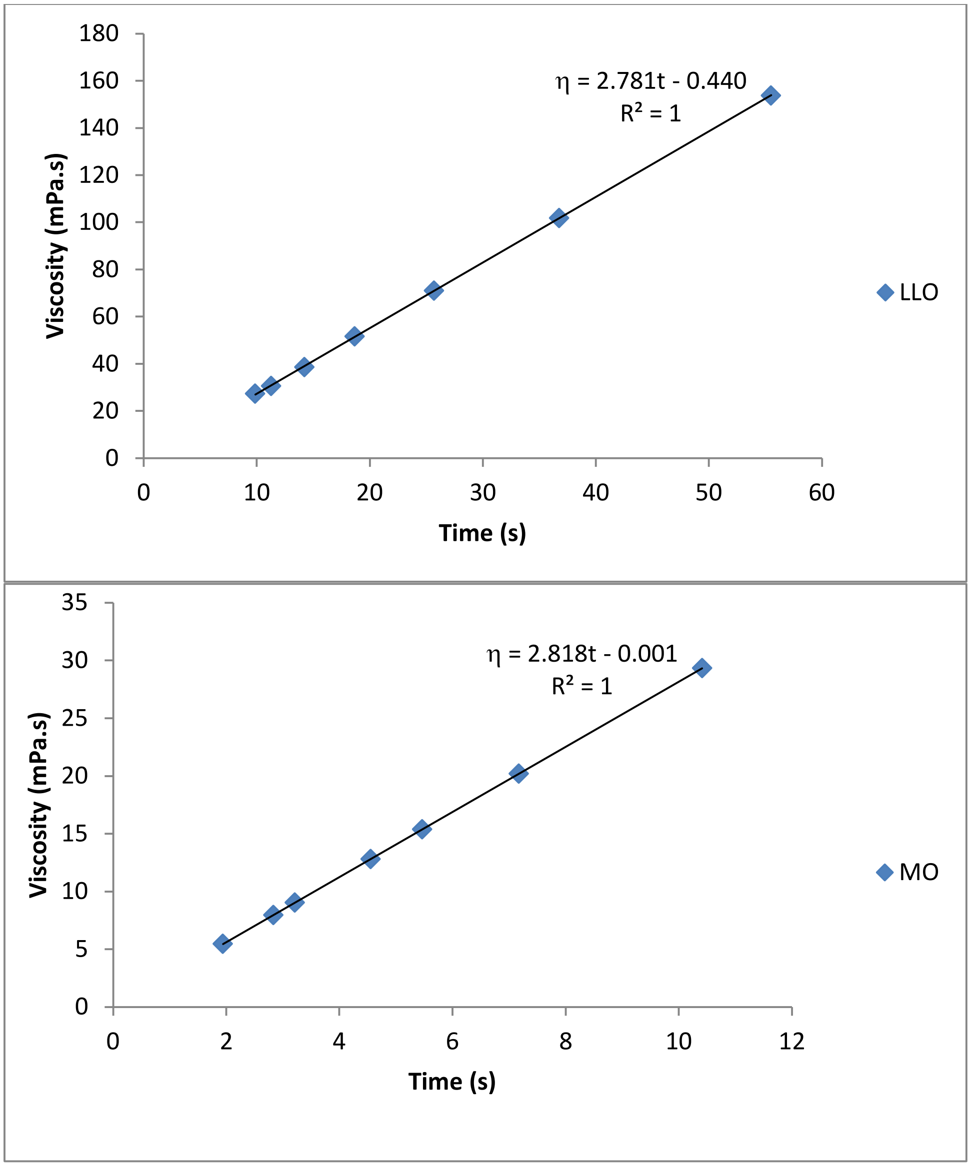

Fig. 4 Variation of viscosities of LLO and MO with time.

Figure 4, shows the viscosity-time curves for MO and LLO which appeared to be straight lines with slopes 2.82 mNm^{-2} and 2.781 mNm^{-2} respectively, which are equivalent to the viscosity indices. The time increases with temperature which is true since viscosity of a liquid decreases with temperature. This means the higher the viscosity, the longer time it takes to tear off the liquid film from the ring.

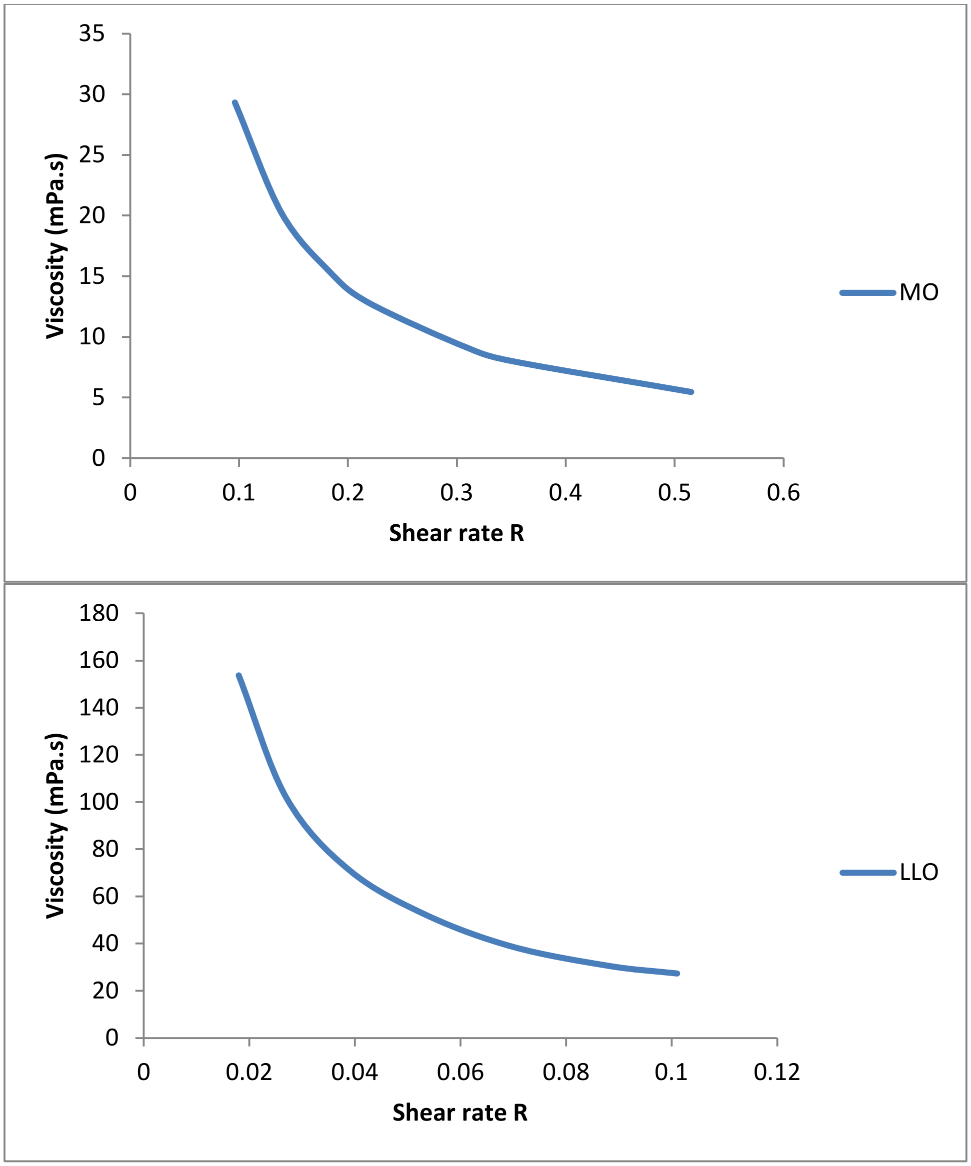

Fig. 5. Variation of viscosity of MO and LLO with shear rate.

Figure 5, shows that the viscosities of both MO and LLO decrease exponentially with shear rates a criterion that the liquids are non-Newtonian in nature. Using observed values of η and R (Table 1) and least squares method according to the relation $\eta = kR^{n-1}$ [15], the viscosity index k, and the shear rate exponent, n were obtained as n=0, k = 2.781 mNm^{-2} and n=0, k = 2.82 mNm^{-2} for MO and LLO respectively. This implies that the relation $\eta = kR^{n-1}$ becomes η = 2.820/R mN/m^2 or η = 2.781/R mN/m^2 for MO and LLO respectively. That is the maximum force required to tear off the oil film from the ring per unit area is 2.820 mN/m^2 and 2.781 mN/m^2 for MO and LLO.

Table 2: Surface Tension of MO, LLO and Water at different temperatures

Temperature (K)	Surface tension (mN/m) MO	LLO	Water *
313	192.6	244.4	69.60

323	186.3	240.6	67.94
333	183.1	238.3	66.24
343	178.4	233.1	64.47
353	172.2	230.6	62.67
363	168.5	225.2	60.82
373	164.7	222.6	58.91

* ***(Source: International Association for Properties of Steam (IAPS, 1985)***

Table 2 shows the experimental values of the surface tensions of MO, LLO and water at various temperatures. The span of the observed values of the temperatures is 60 K and those of the surface tensions of MO, LLO and water are 27.9, 21.8 and 10.7mN/m respectively. These spans are large that any set of three observed values of T (T_1, T_2 T_3) and γ (γ_1, γ_2, γ_3) put in equation (10) cannot yield good results. For better results the averages of T say T_2 and γ say γ_2 were obtained. Then two other values of T say $T_1 < T_2$ and $T_3 > T_2$ were chosen such that the span of T_1, T_2, T_3 is not greater than 2 °C. Also, the other two values of γ say $\gamma_1 > \gamma_2$ and $\gamma_3 > \gamma_2$ were chosen such that the span of γ_1, γ_2, γ_3 is not greater than 2mN/m. Now substituting these new three values of T (T_1, T_2 T_3) and γ(γ_1, γ_2, γ_3) in equation (10) for each liquid we obtained the value of n. Putting this value of n into equation (9) we obtained T_c. Substituting the values of T_c and n in equation (4) we obtained γ^*. Also, the value of the Eotvos constant K was deduced from equation (2) using molar volume from viscosity measurements for all the liquids. The values of these quantities are recorded in Table 3.

Table 3: Thermodynamic Properties of Master oil, Lophira Lanceolata oil and Water.

Liquid	T_c (K)	γ^* (mN/m)	n	V (ml/mol)	K (JK^{-1}Mol$^{-2/3}$)
MO	733.37	327.62	1.030927835	279.0	1.4061625×10^{-7}
LLO	937.33	361.72	1.041666667	165.0	1.2147026×10^{-7}
Water	648.1	152.62	1.143765855	18.9	1.6869851×10^{-7}
	$^{+}$(647.0)			$^{+}$(18.0)	

+ Actual values of T_c and V of water (Adam, 1941 and Gennes *et al.*, 2002).

Table 4: Refractive index of MO, LLO at different temperatures

Temperature (K)	Refractive index M O	LLO
313	9.21	17.15
323	8.10	14.21
333	7.79	12.25
343	6.83	11.38
353	5.32	10.22
363	5.02	8.43
373	3.08	5.26

* ***(Source: International Association for Properties of Steam (IAPS, 1985)***

Table 4 shows the observed values of the refractive indices of MO and LLO at different temperatures. Figure 6, shows that the refractive indices of these liquids linearly decrease with temperature leading to the following regression lines

$$n_{MO} = -0.0965T + 39.578, \quad R^2 = 0.967 \qquad 18$$

$$n_{LLO} = -0.1759T + 71.615, \quad R^2 = 0.968 \qquad 19$$

Equations 18 and 19 show that the rate of decrease of the refractive index of MO (-0.0965 K^{-1}) is higher than that of LLO (-0.1759 K^{-1}), which shows that MO expands faster than LLO. Also, the regression lines reveal that the residual refractive indices as $T \to 0$ are 39.578 and 71.615 for MO and LLO respectively. This implies LLO is expected to have higher pour point than MO. Also, this means that on heating for a fixed angle of incidence in air the increase in the angle of refraction in MO is larger than that of LLO. In other words, on heating, the increase in the velocity of light in MO is larger than that of LLO. This implies on heating the angle of incidence required to produce total internal reflection in MO is smaller than that of LLO which is the determining factor which of the oil is optically preferred in a given particular application. In another perspective, the regression lines reveal that the critical temperatures as the refractive index tends to zero are 410.1 K and 407.1 K for MO and LLO respectively.

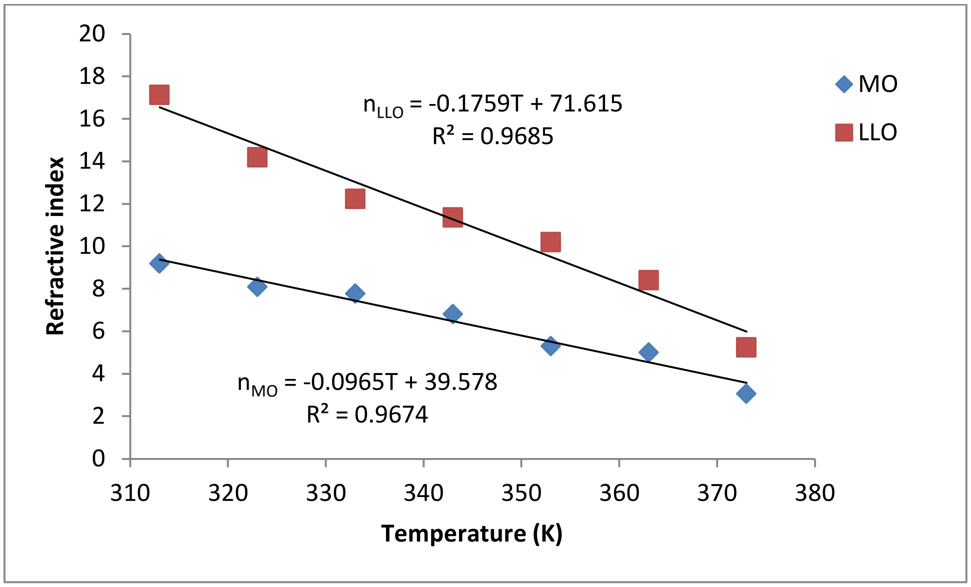

Fig. 6 Refractive index-temperature lines for MO and LLO

Conclusion

In this paper, the viscosities, surface tensions and refractive indices of MO and LLO decrease with temperature. It has been observed that for small spans of temperature and surface tension data say 2°C and 2 mN/m better values of the exponent n, residual surface tension γ^* and the critical temperature T_c were obtained. From the Viscosity-temperature data analysis we obtained the molar volume of water as 18.9 ml with accuracy of 5% above the actual molar volume 18.0 ml. Also, the Eotvos constant K was determined from the relation $\gamma^* = \dfrac{KT_C}{V^{\frac{2}{3}}}$ using the values of γ^* and T_c deduced from Surface tension – temperature data analysis and V deduced from Viscosity – temperature data analysis. All the values of the thermodynamic parameters n, γ^* , T_c ,K and V for LLO are higher than that of MO. The results also show that the viscosities of MO and LLO decrease exponentially with temperature meaning the oils are non-Newtonian liquids. Also, we observed the refractive index of MO decreases faster than that of LLO meaning that on heating the angle of incidence required to produce total internal reflection in MO is smaller than that of LLO. But both the slow and fast decrease in refractive index of liquid are useful signatures in optics depending on the situation at hand.

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