Technical paper

Physico-Chemical and Viscosity Studies in Some Seed Oils from Wild and Cultivated Plants

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Abstract

Physico-chemical properties of *Madhuca longifolia* L, *Sterculia foetida* L and *Hibiscus cannabinus* L seed oils were investigated. *M. longifolia* has significantly high oil content. These determined parameters have been compared with the literature and discussed. The temperature dependence of density and absolute viscosity in these oils has been determined over the temperature range from 303 K to 343 K. The values of density and absolute viscosity in these oils are comparable with that reported for other similar kind of oils. Both density and viscosity decreased monotonically with increase in temperature. Empirical relations which describe the temperature dependence of absolute viscosity were fit to the experimental data and the correlation constants for the best fits are presented and discussed.

Keywords: Oils, wild and cultivated seed oils, physico-chemical properties, density, absolute viscosity, Andrade's equation

1. Introduction

Vegetable oils have a wide range of uses, and whilst many of these involve processes that are too technical for small-scale ventures, there are still many ways in which we can employ them as a food or as a lubricant, a fuel for paraffin lamps and as a wood preservative[1]. More than 95% of lubricants are at present mineral oil based. In view of their high ecotoxicity and low biodegradability, they constitute a considerable threat to the environment. In contrast to mineral oil, base fluids (lubricants and hydraulic fluids) based on vegetable oils are largely, rapidly and completely biodegradable and of low ecotoxicity. They are inherently highly effective lubricants with excellent tribological properties. Also, due to their high viscosity index they are highly suitable for such applications. However their thermal and hydrolytic stabilities are limited and need to be improved by a variety of measures.

Madhuca longifolia (Koenig) (*M longifolia*) and *Sterculia foetida* L (*S foetida*) are large shady, deciduous trees, both wild and cultivated throughout the subtropical region of the Indo-Pak subcontinent, while *Hibiscus cannabinus* L (*H cannabinus*) black and red varieties are cultivated extensively all over India as a source of fiber and forage crop. Recently our group has reported defatted seed cake of *M longifolia* posses' medicinal properties[2]. Ramadan et al.[3] and Mohamed et al.[4] have reported that oil obtained from *M longifolia* and *H cannabinus* respectively is of edible grade. The reason for non-popularity of these oils as edible is due to their unpleasant odour and taste. Previous studies have shown that some plants which grow in wild have seeds whose oil may be of nutritional and industrial values[5]. However, no attempt has yet been made to study their viscosity properties under different temperature conditions. The objective of the present study is to understand the temperature dependence of absolute viscosity and density of the oils. To best of our knowledge the present article is the first on the viscosity parameters of the studied seed oils.

2. Experimental

2. 1. Materials

Seeds of *M. longifolia* and *S. foetida* were collected from Konchavaram forest Gulbarga and local garden Gulbarga, India respectively. A voucher specimen is deposited in dept of Botany, Gulbarga University, Gulbarga herbarium (HGUG No. 723 and HGUG No. 834) respectively. Seeds of *H. cannabinus* black and red variety, purchased from local market, Gulbarga. Seed oils were soxhlet extracted using petroleum ether (40–60 °C) and analyzed by standard methods[6] for oil and fat analysis.

2. 2. Density Measurements

Density, ρ, measurements as a function of temperature on the present oils have been performed by gravimetric method[7] and the specific volumes V_{sp} are estimated by the relation, $V_{sp} = 1/\rho$. Using the density values of the studied oils, the mean molecular weight, M_{wt}, has been estimated using the relation[7],

$$M_{wt} = 3 \times 56108 \times \frac{1}{SV} \quad (1)$$

Where, SV is the saponification value of the oils.

2. 3. Viscosity Measurements

Saybolt's viscometer was employed to determine the viscosity of the oil systems. Oil sample (60 cm^3) was allowed to flow through a capillary tube and the time taken for the flow was counted using a stopwatch. Absolute viscosity, η was calculated using the following relation,[8]

$$\eta = d(at - \frac{b}{t}) \quad (2)$$

Where, a and b are the viscosimeter constants given as 0.0022 and 1.535 respectively, t is the time expressed in seconds for 60 cm^3 of oil to flow through the capillary tube and d is the density of the oil. Measurements were carried out in the temperature range from 303 K to 343 K using a thermometer (accuracy of 0.5 K) in water bath.

3. Results and Discussion

The physico-chemical properties of seed oils are presented in Table 1. The oil content of 58%, 42% and 29.2% (w/w) for *M longifolia* (ML), *S foetida* (SF) and *H cannabinus* black (HCb) respectively, is significantly higher than the ones for some commercial seed oils namely, cotton seed (23–26),[9] soybean (15–24)[10] while it was 21.8% (w/w) for *H cannabinus* red (HCr). The saponification value of all the oils is comparable with that of the values for the common oils, palm oil (196–205), groundnut oil (188–196) and corn oil (187–196)[11] except *H cannabinus* (black). The oils appear to be quite stable based on their peroxide and acid values, as these values are good index for the stability of the oil and its susceptibility to rancidity during storage. Based on the iodine values (Table 1) *M longifolia* and *S foetida* oils could be classified as non-drying oils. The sensitivity to oxidative attack is caused mainly by multiple unsaturated (double) bonds present in the fatty acid moieties of many native oils. Alternatively, the contents of polyunsaturated fatty acids can be reduced by simple chemical modifications such as selective hydrogenation. Ideally all unsaturation should be removed e.g. by catalytic hydrogenation. Yet, this ″hardening″ leads to saturated fatty acid and would turn the (liquid) oil into (solid) fat useless for applications as hydraulic fluids. Thus at least one isolated cis-double bond is required in order to obtain oils with good performance (viscosity, pour point) at low temperatures. Thus, these oil may serve as raw material for various industrial application and thermal stabilization of polyvinyl chloride.[12] The refractive index for *S foetida* at 298 K was 1.466. The observed refractive index value for rest of the oils is higher than the values for some other vegetable oils such as corn (1.4726), soybean (1.4728) or sunflower oil (1.4740).[13] The estimated mean molecular weights were in the range from 948.30 to 681.75 g mol^{-1}. Among the studied oils, *S foetida* oil had the highest mean molecular weight where as *H cannabinus* had lowest. These mean molecular weight values are very much in agreement with the reported values for some other vegetable oils.[7,8]

The densities of four oils were measured at different temperature as shown in Table 2, Fig 1. *S foetida* showed the highest density (0.930 g cm^{-3}) while *M longifolia* has exhibited the lowest density (0.915 g cm^{-3}) at 298 K (Table 1). The density of the latter oil and *H cannabinus* (black) at 303 K is similar to groundnut oil, i.e., 0.912 g cm^{-3}[3,14]. The densities of *S foetida* and *H cannabinus* (black) at 298 K is slightly higher than those published for some other vegetable oils with small or even negligible quantities of polyunsaturated linolenic acid corn oil (0.916 g cm^{-3}), cottonseed oil (0.914 g cm^{-3}), olive oil (0.909 g cm^{-3}), rapeseed oil (0.903–0.907 g cm^{-3}), sunflower oil (0.9178 g cm^{-3}), soybean oil (0.9148 g cm^{-3}).[13] Higher density is quite understandable bearing in mind

Table 1: Physico-chemical properties of seed oils

Physico-chemical properties	***M longifolia***	***S foetida***	***H cannabinus* (black)**	***H cannabinus* (red)**
Oil content % (w/w)	58	42	29.2	21.8
Iodine value (g/100g)	70.2	74.0	96.8	109.4
Peroxide value (mEq kg^{-1})	0.24	1.6	5.9	1.4
Saponification value (mg KOH)	196	177.5	246.9	203.9
Free fatty acid (as oleic acid) (mg KOH)	1.8	1.0	0.15	0.13
Density (g cm^{-3}) at 298 K	0.915	0.930	0.916	0.919
Refractive index at 298 K	1.479	1.466	1.509	1.512
Acid value (mg KOH)	3.5	5.7	2.8	2.1

Table 2: Density and absolute viscosity data of the studied oils at different temperature

Sl. No	Temperature (K)	Density, ρ ($g.cm^{-3}$)	Absolute Viscosity, η (mP)
1	*H cannabinus black*		
	303	0.912	150.44
	308	0.909	124.88
	313	0.905	103.51
	318	0.901	91.15
	323	0.895	83.14
	328	0.892	73.37
	333	0.887	67.39
	338	0.883	65.35
	343	0.879	60.96
2	*H cannabinus red*		
	303	0.916	148.12
	308	0.913	132.43
	313	0.908	113.25
	318	0.906	97.26
	323	0.903	86.49
	328	0.898	78.48
	333	0.897	70.89
	338	0.892	66.95
	343	0.889	62.57
3	*S foetida*		
	303	0.928	361.69
	308	0.923	273.21
	313	0.920	209.95
	318	0.917	169.61
	323	0.913	142.46
	328	0.910	121.68
	333	0.906	105.40
	338	0.902	94.20
	343	0.899	84.89
4	*M longifolia*		
	303	0.911	203.13
	308	0.907	161.48
	313	0.903	131.13
	318	0.898	111.80
	323	0.896	98.13
	328	0.890	86.78
	333	0.885	77.60
	338	0.884	70.16
	343	0.878	66.22

that the density of oil increases as the degree of unsaturation increases.[15] Abramovic and Abram[16] reported a similar density value of 0.918 g cm^{-3} for *Camelina sativa* at 298 K. Furthermore, the reduction in density in the temperature range, 303–343 K for all the oils was not more than 5%.

There is a definite relationship between the structure of the molecules and their properties such as viscosity, low temperature performance such as pour point and the oxidative stability. Base oils based on natural fatty acids in general are known for their high viscosity, they can be considered as multi range oils. The absolute viscosity profiles for the present oils at different temperatures are shown in Table 2, Fig 2. The viscosities of all the oils were much higher with values of up to 361.687 mP for *S foetida* at 303 K, as it showed the highest mean molecular weight amongst the samples. The reduction in viscosity was more or less 30% in the temperature range 323–343 K for all the oils except *S foetida* for which it was 40%. The minimum rate of viscosity variation with temperature is generally desirable in lubricating oils so as to attain better performance over a range of temperature[17] A marked reduction in viscosity at 343 K, by over 60% of the values at 303 K was observed, for all the oils with the highest by 77% for *S foetida*, however the viscosity values obtained

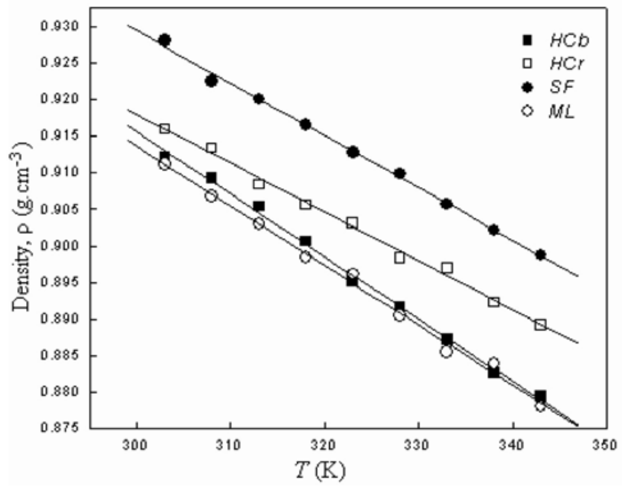

Figure 1. Plots of density, ρ as a function of temperature for the studied oils. Solid lines are the least square linear fits to the data.

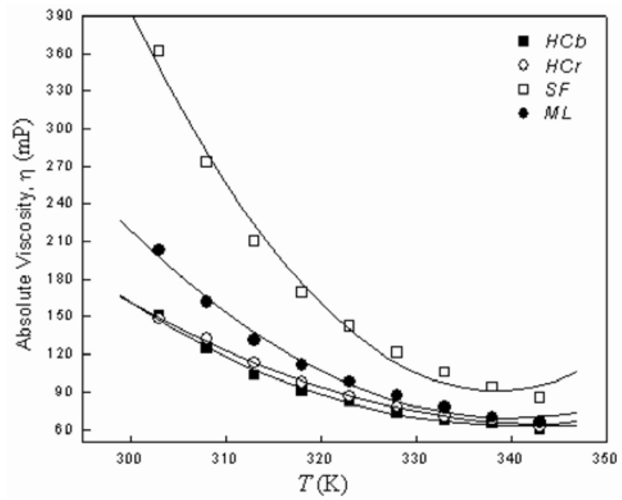

Figure 2. Temperature dependence of absolute viscosity, η for different oil samples. Solid lines are the second order polynomial fits to the data.

for *S foetida* are comparable over the temperature range, 303–343 K with that of castor oil over the temperature range, 298–333 K.[18] Viscosity increases with chain length of carboxylic acid (saponification value) and decreases with unsaturation (iodine value), may be the latter property dominated (regarding *H cannabinus*), since both varieties of *H cannabinus* exhibited low viscosity despite having high saponification value. As *S foetida* oil has the highest viscosity as well as the greatest viscosity variation with temperature, it can be selected for the high temperature operation associated with continuous running of an engine. In general, this type of oil can reduce leakage and blowby. Most of the bonds in the hydrocarbon chains of fatty acids are single bonds. This linear zig-zag organization enables the chains to be lined up close to each other and intermolecular interactions such as van der Waals interactions can take place.[19,8] This system inhibits flow of the fluid, resulting in the relatively high viscosity of the oils.

An attempt has also been made to establish a relationship which describes the variation of viscosity with some structural characteristics (degree of unsaturation i.e. iodine value, *IV* and chain length of the fatty acids i.e. saponification value, *SV*) as per the following relation,[20]

$$\ln\eta = -4.7965 + 2525.92962(1/T) + 1.6144[(SV)^2/T^2] - 101.06\times10^{-7}(IV)^2 \quad (3)$$

where 1nη is the absolute viscosity of the oil. For our samples the proposed equation could not be considered appropriate as it gave substantially higher (about 50%) values of η than those experimentally obtained. In Fig 2 typical viscosity behavior of oil samples as a function of temperature is shown, where the viscosity rapidly decreases with increase in temperature. Many empirical relations have been proposed to predict the temperature dependence of absolute viscosity.[19] For the present oil systems, we have embarked the modified equations of Andrade[21] given by the following relations,

$$\ln\eta = A + \frac{B}{T} + \frac{C}{T^2} \quad (4)$$

$$\ln\eta = A + \frac{B}{T} + CT \quad (5)$$

To elucidate the effect of temperature on the absolute viscosity the following equations have also been used,[19]

$$\log\eta = \frac{A}{T} - B \quad (6)$$

$$\eta = A - B.\log T \quad (7)$$

$$\eta v^{1/2} = Ae^{B/T} \quad (8)$$

and

$$\eta = \frac{A}{v - B} \quad (9)$$

where v is the specific volume of the oil, T is the temperature and A, B and C in the above equations (4) to (9) are correlation constants.

Fig 3 depicts the inverse temperature dependence of absolute viscosity. The modified Andrade Eq. (4) and (5) were fit to the experimental viscosity data. It can be seen from Fig. 3 that the fit lines fall satisfactorily on the experimental data. The fit parameters gave the determination coefficient values to be almost equivalent to unity. However, the experimental data deviate from the fit lines when the Eqs. (6) to (9) was used. This indicates that the Andrade Eq. (4) and (5) successfully explain the temperature dependence of absolute viscosity in the present oils.

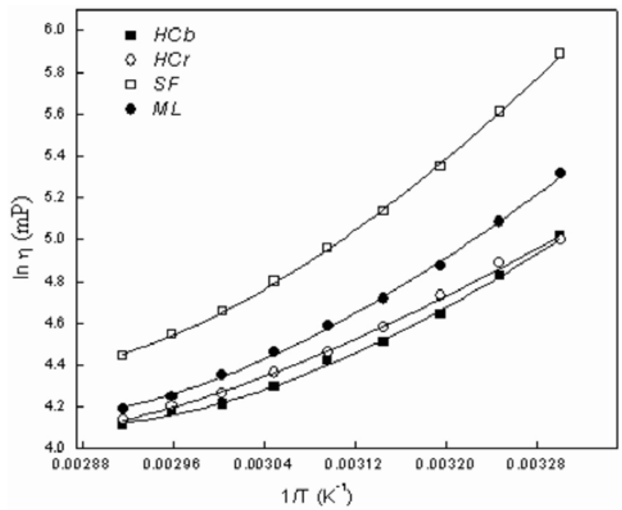

Figure 3. Plots of absolute viscosity, η versus reciprocal of temperature for different oil samples. Solid lines are the best fits to the data as per Andrade's modified Eqs. (4) and (5).

4. Conclusion

Density and absolute viscosity values of studied oils were found to be comparable with the values reported for other similar kind of oils. The density and absolute viscosity exhibited decreasing trend with increase in temperature. The studied oils have shown up relatively higher viscosity as well as the greater viscosity variation with temperature, they can be explored for the high temperature operation generally associated with continuous running of an engine. The temperature dependence of viscosity has been analyzed with the help of Andrade's equations. The determination coefficient values suggest that the Andrade's modified equations adequately explain the temperature dependence of absolute viscosity in the studied oils.

5. References

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Povzetek

Raziskovali smo fizikalno kemijske lastnosti olj, pridobljenih iz semen *Madhuca longifolia* L, *Sterculia foetida* L in *Hibiscus cannabinus* L ter izmerjene parametre primerjali s podatki v literaturi. V temperaturnem območju med 303 in 343 K smo izmerili gostote in viskoznost; vrednosti so primerljive s tistimi za podobna olja. Tako gostota kot viskoznost se z višjo temperaturo enakomerno zmanjšujeta. Njihove temperaturne odvisnosti smo opisali z emiričnimi zvezami.

ERRATA

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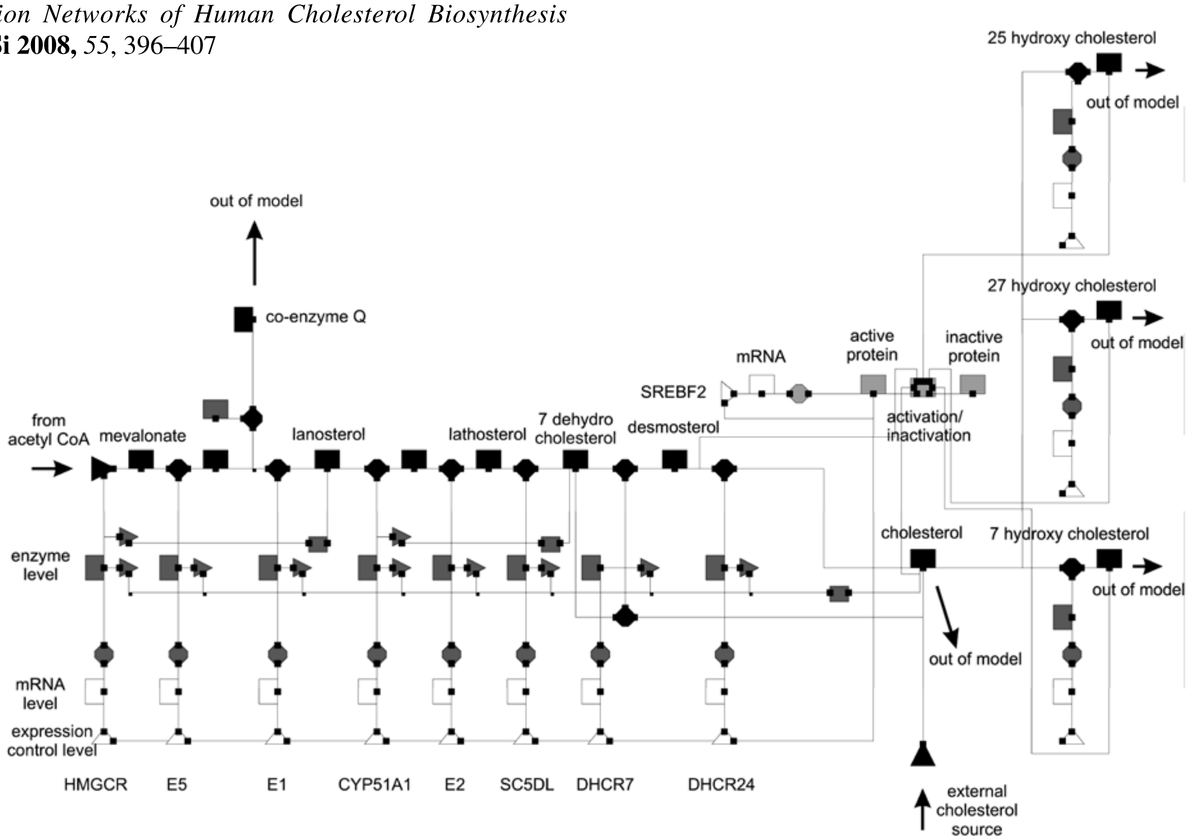

Figure 2. A simplified mathematical model of cholesterol biosynthesis. Black blocks represent metabolites (squares), enzyme reactions (circles) and metabolite sources (triangles). Dark grey blocks represent enzymes (large squares), their biochemical control (triangles and small squares), and enzyme production regarding gene expression (circles). White blocks represent gene expressions (squares) and their control (triangles). Light grey blocks represent transcription factors (squares), their production regarding gene expression (circles), and their activation/inactivation (squares). Gene names are listed in Table 1 in Supplement.