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PRELIMINARY MEASUREMENTS OF FLUIDITY AND ACTIVATION PARAMETERS OF FLOW OF SOME NIGERIAN VEGETABLE OILS IN KEROSENE DILUENT

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The viscosities of cotton seed and walnut seed oils in kerosene diluent have been examined as a function of temperature. The decrease in viscosity values with increase in temperature has been explained in terms of thermal vibration resulting in the weakening of intermolecular forces of the oils. Plots of viscosity versus absolute temperature show curvature whereas the plots of logarithm of viscosity against inverse absolute temperature show linearity for all systems. The activation energy of viscous flow ΔE_v, the latent heat of vapourization L_v and the molar volume of the oil V_m, were evaluated from that plots: ΔE_v and L_v decrease with increase in the volume of kerosene, whilst V_m increases. The fluidity, which is a measure of the degree of entanglement of the oil molecules, is found to be proportional to the volume occupied by kerosene. It appears that the addition of kerosene uncoils the entangled and aggregated oil molecules.

Key words: Fluidity, Activation parameters, Vegetable oils.

Introduction

Previous studies (Gyani and Murari 1956; Barrow 1966; Gyani and Murari 1983) on the viscosity of vegetable oils have provided information relating to the structures of the oils. When the viscosity of pure and mixture of some vegetable oils with liquids of low viscosity was measured as a function of temperature, a linear relationship was observed between the logarithm of the viscosities and the inverse absolute temperatures. The activation energies of viscous flow were then evaluated from that plots.

In the present work, the fluidity of cotton and walnut seed oils of Nigerian origin diluted with kerosene (a paraffinic liquid of low viscosity) was examined over or range of temperatures and the activation parameters, ΔE_v and L_v evaluated. The fluidity parameters and the molecular mass of each oil were also evaluated in an attempt to obtain more knowledge of the structural complexities of those vegetable oils.

Experimental

Oils were extracted from parboiled, dehulled and powered cotton and walnut seeds, bought from the local market in Akure, Nigeria. Extraction was effected in diethyl ether between 60-80°C using soxhlet apparatus. After determination of the cell constant of an appropriate Ostwald viscometer with glycerol, the viscosities of the oils and their mixtures with kerosene (20, 40, 50, 60 and 80% v/v oil) were determined at four temperatures viz. 30, 40, 50, and 60°C. The temperature of the bath was maintained constant within ± 2°C during the measurement. The densities of the oils were also determined with the aid of specific gravity bottle.

Calculation of Parameters

(a) The activation energy of viscous flow ΔE_v and the molar volume, V_m, were evaluated from the Arrhenius equation (Bird *et al* 1960; Barrow 1966; Berry *et al* 1980;Das and Behera 1983; Moore 1986; Atkins 1990).

$$\eta = \frac{hN_o}{V_m} \quad \frac{l\ \Delta E_v}{RT} \quad \ldots\ldots(1)$$

derived from the equation.

$$\theta = \frac{hN_o e}{V_m} - \frac{\Delta E_v}{RT} = \frac{1}{\eta} \quad \ldots\ldots(1)^*$$

On taking logarithms, (1) becomes

$$\log \eta = \log \frac{hN_o}{V_m} \quad \frac{+\Delta E_v}{2.303RT} \quad \ldots\ldots(2)$$

η = Viscosity, h = Plank's constant, N_o = Avogadro's number, R = general gas constant.

T = absolute temperature and V_m = molar volume of the oil.

(b) The latent heat of vapourization L_v was evaluated from the relation (Tabor *et al* 1979; Robert *et al* 1987).

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$$\Delta E_v \Rightarrow = 0.4L_v \quad \text{.........}(3)$$

(c) The intrinsic (Bird *et al* 1960; Das & Behera 1983) viscosity ((η)) defined as

$$(\eta) = \text{Lim}$$

$$V_0 \rightarrow 0\ (1/V_o\ 1\eta\ \eta/\eta_1) \quad \text{.........}(4)$$

(where η = viscosity of oil, η_1 =viscosity of diluent and V_o = % volume of oil in the mixture) was evaluated from the plot of $(1/V_o\ 1\eta\ \eta/\eta_1)$ versus V_o, which gave a straight line that was extrapolated to $V_o \rightarrow 0$. The relative molecular mass (M) of the oil was then evaluated from the equation (Bird *et al* 1960; Das & Behera 1983).

$$(\eta) = 2.0 \times 10^{-4} M^{0.76} \quad \text{.........}(5)$$

(d) The fluidity parameters a, k, α_1, α_2, β & β^*

$$\log \eta = \log k + a \log V_{o.} \quad \text{.........}(6)$$

$$\eta/V_o = \alpha_1 + \beta\,\eta \quad \text{.........}(7)$$

$$\text{and } 1/V_o = \frac{\alpha^2}{\eta} + \beta^* \quad \text{.........}(8)$$

a, k, α_1, α_2, β and β^* are empirical constants as equations 6-8 are being used in those forms for the first time.

Results

The above data are presented in Tables 1 and 2 for the viscosities of cotton seed oils and walnut seed oil respectively and their separate mixtures with kerosene at the four selected temperatures 30, 40, 50 and 60°C. It is observed that viscosity decreases with increase in temperature as expected; this has been attributed (Tabor 1979) to thermal vibrations that weaken intermolecular forces between the molecules of the oils. As the temperature of the oil is increased, thermal vibration would tend to weaken the intermolecular forces between the oil molecules and this reduced molecular cohesion would lead to a decrease in viscosity. Plots of η versus absolute temperature T (Fig 1) for the system show curvature similar to those obtained by Barrow (1966) for some organic liquids. The plots of logη versus I/T show linearity for all systems (Fig 2 and 3), similar to those obtained by Gyani *et al* for some vegetable oils of Indian origin (Gyani and Murari 1956; 1983) and to those obtained for some organic liquids (Atkins 1990). The data fit equation 2. The activation parameters ΔE_v and L_v evaluated from the plots are shown in Table 3. The V_m values evaluated from the plots are also in the same Table. Both ΔE_v and L_v decrease with increase in the volume of kerosene. Although V_m does not show systematic behaviour for cotton seed oil, it shows an increase with increase in the volume of kerosene for walnut seed oil. It appears that the paraffinic kerosene weak-

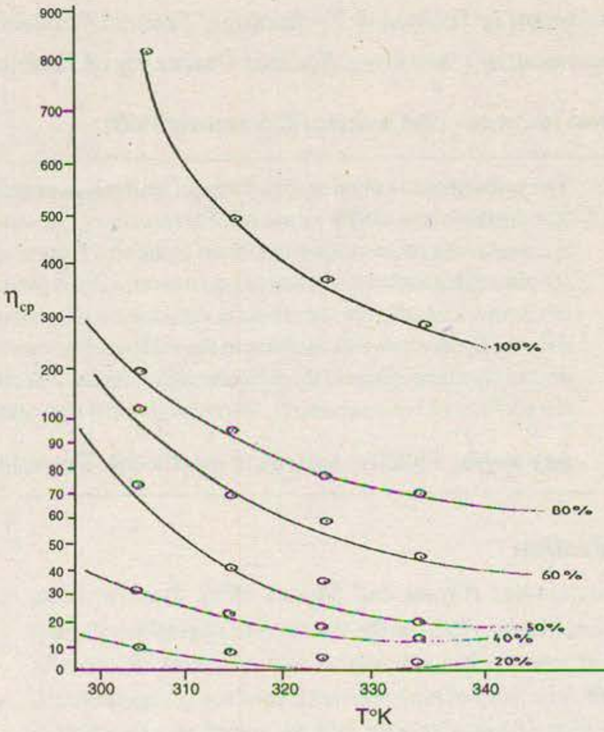

Fig 1. η_{cp} versus T°K for cotton seed oil in kerosene.

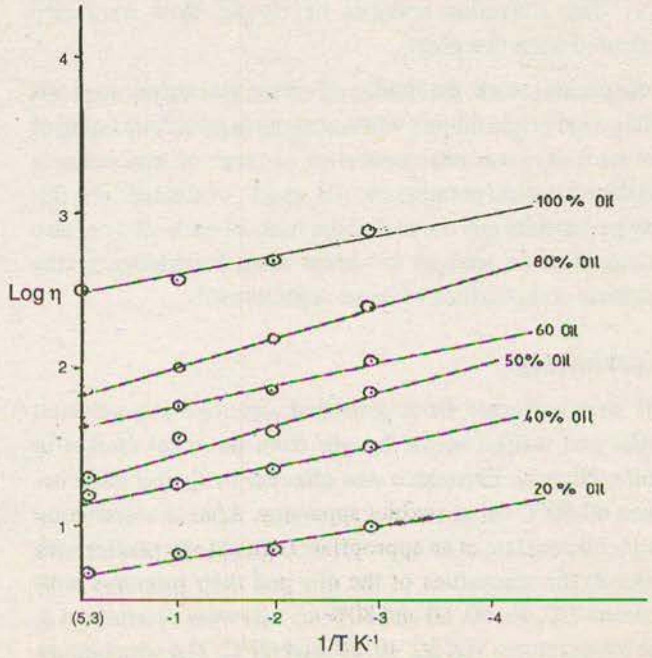

Fig 2. Log η Vs 1/T K^{-1} for cotton seed oil in kerosene.

Table 1

Viscosities of cotton seed oil in mixtures with kerosene

Density kgdm^{-3}					0.978						0.972					0.965					0.959		
Temp. °K					303						313					323					333		
$10^3/T^{k-1}$					3.300						3.195					3.096					3.003		
% Oil					(2.303)/V_o																		
V_o	$1/V_o$	$\log V_o$	$\eta x10(cp)$	$\frac{1}{\eta(cp-1)}$	$\log\eta$	$\log\eta/\eta_1$	η/V_o	$\log\eta/d$	$\eta x10(cp)$	$\frac{1}{\eta(cp-1)}$	$\log\eta$	η/V_o	$\log\eta/d$	$\eta x10(cp)$	$\frac{1}{\eta(cp-1)}$	$\log\eta$	η/V_o	$\log\eta/d$	$\eta x10(cp)$	$\frac{1}{\eta(cp-1)}$	$\log\eta$	η/V_o	$\log\eta/d$
20	.050	1.3010	9.060	.104	.983	.233	0.48	0.992	7.15	.140	0.8543	0.358	0.867	6.10	.164	0.785	0.305	0.801	4.68	.214	0.6703	.234	0.688
40	.025	1.6021	30.50	.033	1.4843	.147	.763	1.494	21.6	.046	1.3345	.540	1.346	18.0	.056	1.2553	.450	1.270	14.8	.068	1.1703	.370	1.188
50	.020	1.699	73.6	.014	1.8669	.134	1.472	1.877	39.7	.025	1.5988	.794	1.611	35.10	.029	1.5453	.702	1.561	19.3	.052	1.2856	.386	1.303
60	.017	1.6682	116.0	.009	2.0645	.118	1.933	2.070	69.0	.015	1.8388	1.15	1.851	57.7	.017	1.7612	.962	1.776	45.1	.022	1.6542	.752	1.672
80	.013	1.9031	185.0	.005	2.2672	.097	2.313	2.270	156.4	.006	2.1942	1.955	2.207	97.6	.010	1.9894	1.22	2.004	69.2	.015	1.8401	.865	1.859
100	.010	2.000	808.2	.001	2.9075	--	8.082	2.9174	494	.002	2.6937	4.94	2.706	367.6	.003	2.5654	3.676	2.581	281.4	.004	2.4493	2.814	2.467

Note: η Kerosene[3], 0.0090.

Table 2

Viscosities of walnut seed oil in mixtures with kerosene

Density kgdm^{-3}					0.978						0.972					0.965					0.959		
Temp. °K					303						313					323					333		
$10^3/T^{k-1}$					3.300						3.195					3.096					3.003		
% Oil					(2.303)/V_o																		
V_o	$1/V_o$	$\log V_o$	$\eta x10(cp)$	$\frac{1}{\eta(cp-1)}$	$\log\eta$	$\log\eta/\eta_1$	η/V_o	$\log\eta/d$	$\eta x10(cp)$	$\frac{1}{\eta(cp-1)}$	$\log\eta$	η/V_o	$\log\eta/d$	$\eta x10(cp)$	$\frac{1}{\eta(cp-1)}$	$\log\eta$	η/V_o	$\log\eta/d$	$\eta x10(cp)$	$\frac{1}{\eta(cp-1)}$	$\log\eta$	η/V_o	$\log\eta/d$
20	.050	1.3010	9.4	.106	.9731	.47	.232	0.999	6.5	.152	0.8129	0.325	0.842	5.0	.20	0.699	0.250	0.731	3.7	.270	0.5682	.185	0.603
40	.025	1.6021	26.5	.038	1.4232	.663	.143	1.449	19.8	.051	1.2856	.495	1.326	16.2	.062	1.2095	.405	1.241	2.3	.081	1.0899	.308	1.123
50	.020	1.6990	36.8	.027	1.5658	.736	.120	1.592	27.2	.037	1.4346	.544	1.464	22.9	.044	1.3598	.458	1.393	16.9	.059	1.2279	.338	1.263
60	.017	1.7782	53.7	.019	1.730	.895	.107	1.756	41.5	.024	1.618	.692	1.647	34.3	.029	1.5253	.570	1.567	23.5	.043	1.3711	.392	1.407
80	.013	1.9031	163	.006	2.2122	2.034	.095	2.238	114	.099	2.057	1.425	2.086	87.4	.012	1.9415	1.093	1.474	63.0	.016	1.7993	.788	1.834

Note: η Kerosene[3], 0.00090.

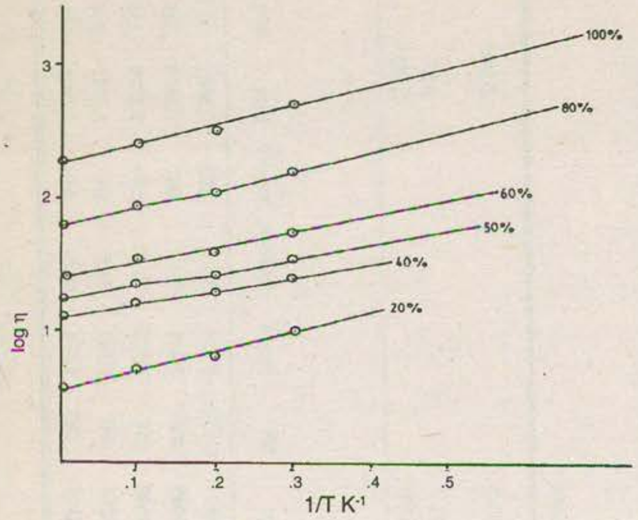

Fig 3. Log η Vs 1/T K^{-1} for walnut seed oil in kerosene.

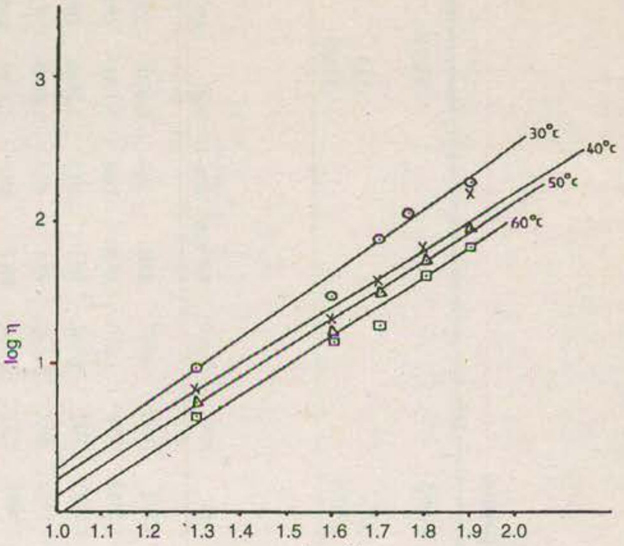

Fig 5. Log η Vs log V$_o$ for cotton seed oil in kerosene.

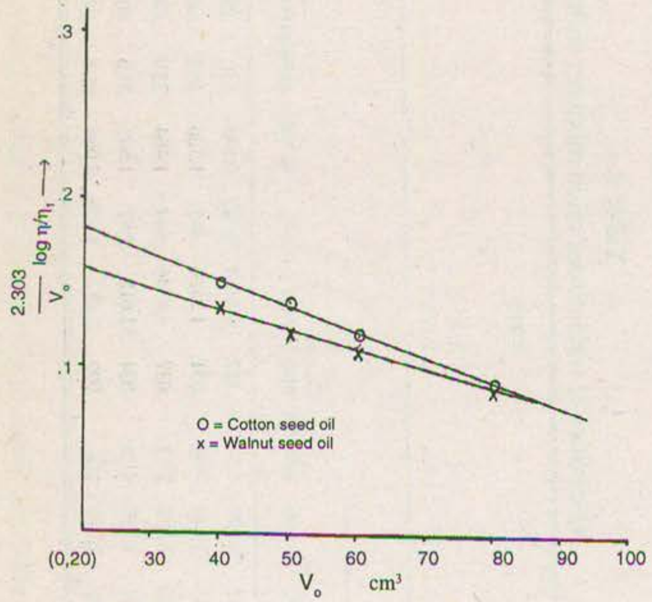

Fig 4. $\frac{2.303}{V_o}$ Log η/η_1 Vs versus V_o cm^3 at 303°K for oil in kerosene.

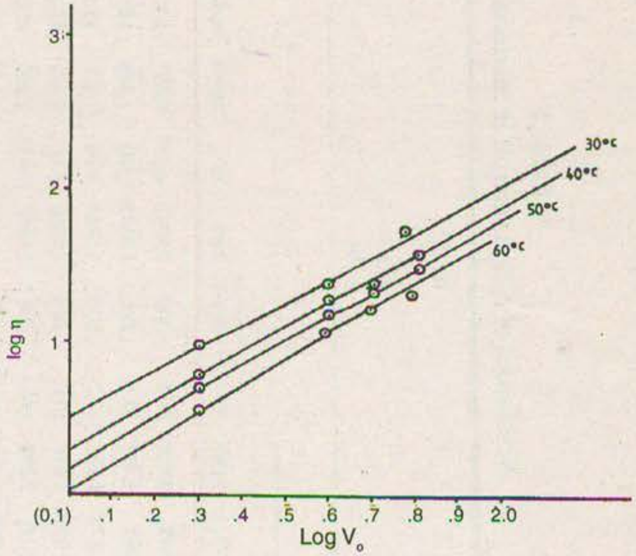

Fig 6. Log η versus Log V$_o$ for walnut seed oil in kerosene.

Table 3

Activation parameters of viscous flow of oils in mixtures with kerosene

V/V	% vegetable oil in the mixture	Cotton seed oil			Walnut seed oil		
		$\Delta E_v \times 10^4$ J/mole	$L_v \times 10^4$ J/mole	$V_m \times 10^4$ cm^3	$\Delta E_v \times 10^4$ J/mole	$L_v \times 10^4$ J/mole	$V_m \times 10^4$ cm^3
20		2.26*	4.88	101.2	2.57*	6.42*	117.40
40		2.04	5.10	35.4	2.06	5.14	54.12
50		3.46	8.65*	Large	2.12	5.29	48.54
60		2.57	6.41	38.3	2.26	5.64	28.39
80		2.83	7.29	184.5	2.65	6.63	89.97*

ens the intermolecular forces between the molecules of the oil by uncoiling the aggregated molecules there by reducing the entanglements (Gyani and Murari 1954; Vovutsky 1975) between them. This would lead to a decrease in ΔE_v and L_v and an increase in V_m as the volume of kerosene increases.

For the pure oils, the evaluated ΔE_v are comparable to those obtained (Gyani and Murari 1954; 1956; 1983) for some other oils (Table 4). That similarities in viscous behaviour suggest some sort of similarities in the structural properties of those oils studied by Gyani and Murari (1954; 1983) the organic liquids reported by Barrow (1979) and the oils now under examination.

The plot of $1/V_o \; 1\eta \; \eta/\eta_1$ versus V_o gave a straight line (Fig 4) whereby the relative molecular mass of cotton seed oil has been evaluated to be 946.4 and that of walnut seed oil 911.5.

Table 4
Activation parameter of some vegetable oils and organic liquids

Oils/organic liquids	ΔE_v J/mole 10^4	L_v J/mole 10^4
Oil		
Karanj	3.54^a	8.86^a
Mahua	3.44^a	8.60^a
Sarguja	3.21^a	8.03^a
Argemone	3.49^a	8.72^a
Cesalpina digyna	3.44^a	8.60^a
++Cotton seed	2.86$^+$	7.16$^+$
++Walnut seed	2.66$^+$	6.65$^+$
Organic liquids		
CCl_4	1.11^b	2.76^b
C_6H_6	1.12^b	2.79^b
$CHCH_3$	1.11^b	2.77^b
$(C_2H_5)O_2$	0.95^b	2.39^b
Acetone	1.07^b	2.68^b

a, Gyani values (converted to J/mole); b, R.H. Ewell and H. Eyring values as reproduced by Barrow (converted to J/mole); ++, Oils under examination; +, Values determined from the present work.

Table 5
Fluidity parameters of oils in mixture with kerosene

Oil	Temp. K°	10^2	a	α_1	α_2	$\beta 10^2$	β'
Cotton seed	303	2.9	2.6	0.51	0.35	1.10	0.01
	313	2.4	2.6	0.22	0.49	0.90	0.02
	323	3.3	2.4	0.29	0.23	0.50	0.01
	333	2.6	2.4	0.22	0.18	0.40	0.01
Valnut seed	303	24.43	0.22	0.28	0.27	0.82	0.01
	313	17.53	0.22	0.22	0.16	0.58	0.02
	325	14.07	0.22	0.19	0.19	0.44	0.01
	333	10.38	0.22	0.15	0.14	0.30	0.01

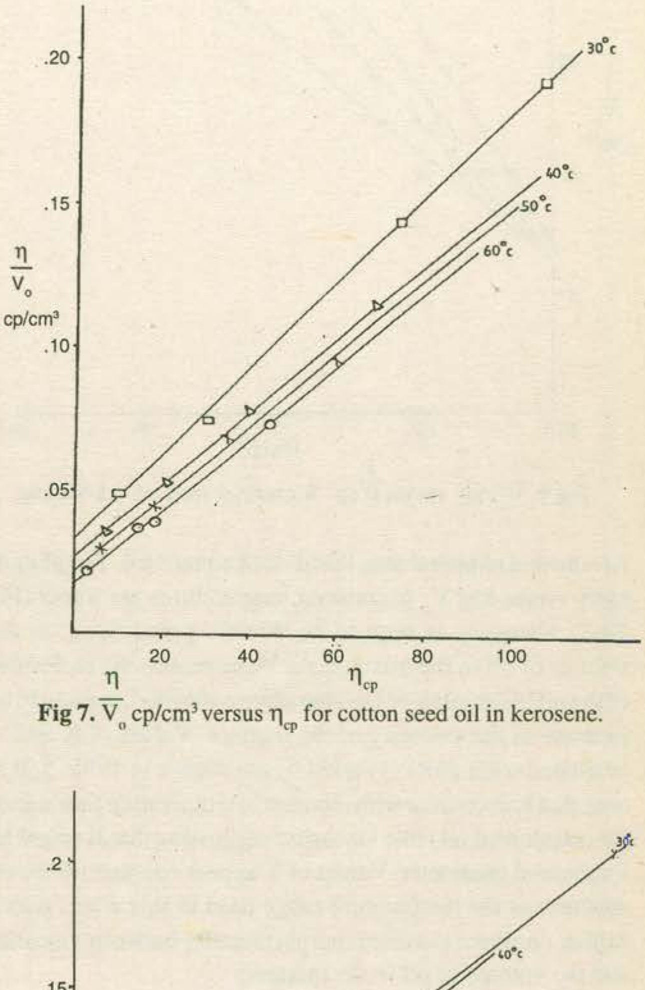

Fig 7. $\frac{\eta}{V_o}$ cp/cm^3 versus η_{cp} for cotton seed oil in kerosene.

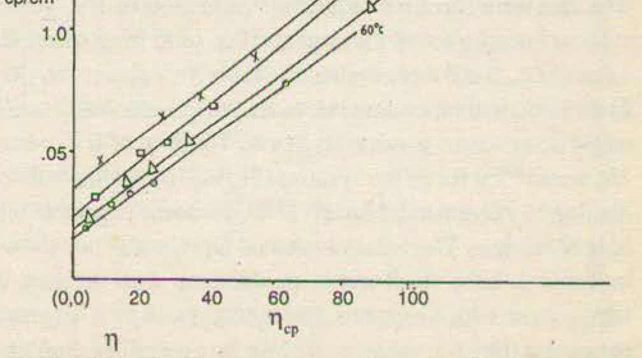

Fig 8. $\frac{\eta}{V_o}$ cp/cm^3 versus η_{cp} for walnut seed oil in kerosene.

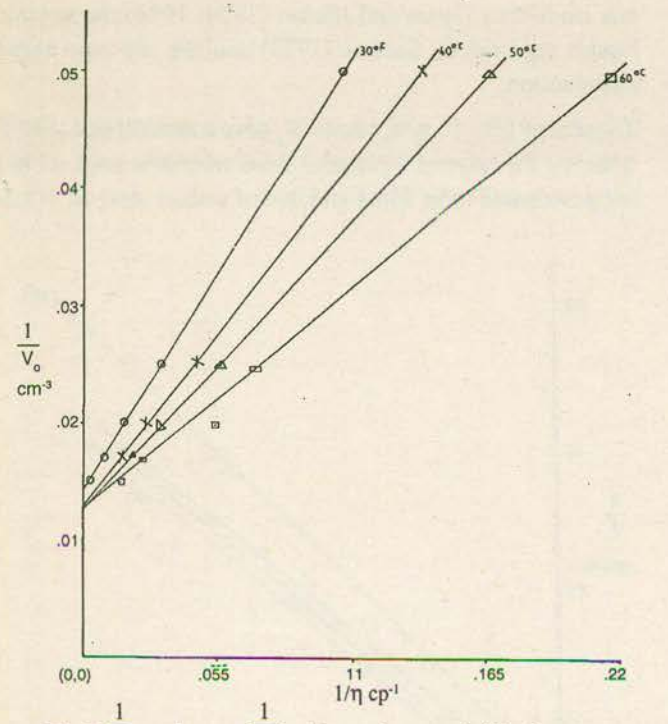

Fig 9. $\frac{1}{V_o}$ cm^{-3} versus $\frac{1}{\eta}$ cp^{-1} for walnut seed oil in kerosene.

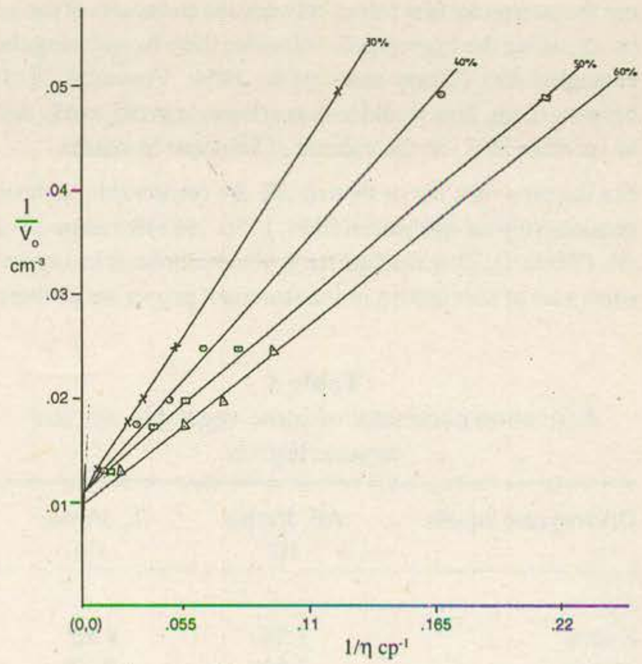

Fig 10. $\frac{1}{V_o}$ versus $\frac{1}{\eta}$ for walnut seed oil in kerosene.

At constant temperatures, that data fit equation 6. The plots of logη versus log V_o at constant temperatures are linear (Fig 5&6). Viscosity is seen to be directly proportional to the volume of oil in the mixture. As V_o increases, the molecules of the oil in the mixture become more entangled, leading to an increase in the viscosity of the mixture. Values of K and 'a' evaluated from plots (v) and (vi) are shown in Table 5. It is seen that K decreases with increase in temperature (not steady for cotton seed oil) like viscosity, suggesting that K might be a structural parameter. Values of 'a' appear constant for the oil mixtures at the temperature range used in this work, which further confirms the direct porportionality between viscosity and the volume of oil in the mixture.

Conclusion

The data were fitted into equation 7, and plots of $1/V_o$ versus η show linearity for all the systems (Fig 7&8) from where the values of α_1 and β were evaluated (Table 5). Values of α_1 (like k) decrease as temperature increases, suggesting that α_1 and β might be structural parameters like K. The plots of $1/V_o$ versus $1/\eta$ were linear for all the systems (Fig 9&10) similar to those obtained by Gyani and Murari (1983) for some vegetable oils of Indian origin. The values evaluated for α_1 and β^* are shown in Table 5. Like α_1, β and k, α_2 decrease with increase in temperature which suggests that α_2 might also be a structural parameter (like K), values of β^* however remained constant. The constancy of β^* and the linearity of the plots indicate that the term $1/V_o$, which is a measure of the volume occupied by kerosene, is proportional to $1/\eta$ which is a measure of the fluidity of the mixture. This tends to lend credence to the view that the addition of kerosene uncoils the molecules of the oil and reduces the entanglements (Gyani and Murari 1954) between them, leading to an increase in fluidity as the volume of kerosene increases.

It might concluded that the structures and flow properties of cotton seed oil and walnut seed oil would be similar to those of the Karanj, Mahua, Sarguja, Argemone and Ceasalpinia digyna oil studied (Gyani and Murari 1954; 1956; 1983) because of the similarities in their viscous parameters coupled with the values of their ΔE_v and L_v. However the structures of the Indian oils might be rather more complex than those under study, with cotton seed oil showing more structural complexity than walnut seed oil. This is based on the fact that the values of ΔE_v and L_v of the Nigerian oils are relatively lower than those of the Indian oils under reference. Activation energy and latent heat of vaporization being dependent on intermolecular forces have been employed in assessing the relative structural complexities of the vegetable oils.

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