

# Anomalous Viscosity Behavior of Fatty Acid Esters in Solution

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Solution viscosity of oils of melonseed (*Colocynthis vulgaris* Schrad.), soyabean [*Glycine max* (L.) Merr], and rubberseed [*Hevea brasiliensis* (Kunth) Muell.] were determined in different solvents at various concentrations. Reduced viscosity ( $\eta_{red}$ ) vs concentration (C) plots showed three types of behavior:  $\eta_{red}$  increased linearly with C (2–30 g/dl);  $\eta_{red}$  levelled off with C (2–1.2 g/dl); and  $\eta_{red}$  rose steeply with decrease in C (below 1.2 g/dl), the latter behavior is anomalous. Similar viscosity behavior was observed for the methyl ester of melonseed oil, methyl palmitate and n-butyl acetate. Molecular cluster formation was believed to cause the observed anomalous viscosity behavior, the extent of which varied, depending on the nature of the fatty acid ester and the solvent.

**KEY WORDS:** Anomalous, behavior, fatty acid esters, molecular cluster, solution, viscosity.

Fats and oils are fatty acid esters of glycerol. They are amphipathic in nature due to the presence of the polar glyceride (ester) group and the nonpolar hydrocarbon chain. Both segments play significant roles in determining the physical and chemical properties of the glycerides, such as degree of unsaturation, molecular weight, density, acidity, etc., which, in turn, influence other oil properties such as melting point and viscosity.

The viscosity of oils in the pure state has been the subject of many studies, particularly in the older literature. These studies have established some of the effects of the physical and chemical properties of oils on their viscosities. For instance, oils containing fatty acids have been found to show decreasing viscosity with increasing degree of unsaturation (1). Also, the viscosity of a fatty oil was found to increase with increasing molecular weight of the oil if saturated acids alone were present (1). A study of the influence of density on viscosity of oils showed that if oils were divided into three groups, namely, drying, semidrying and nondrying (i.e., on the basis of their degree of unsaturation) viscosity increased considerably with density in each group (2).

The study of the solution viscosity of oils has also received attention in the literature. Johnstone *et al.* (3) determined the viscosities of mixtures of soyabean oil and hexane, ethylenedichloride and trichloroethylene, and reported rapid increase in fluidity and the possibility of molecular complex formation in solvents that can form hydrogen bonds. Luck *et al.* (4) determined the apparent specific volume ( $\phi_v$ ) and intrinsic viscosities ( $\eta$ ) for the oils of olive, peanut, soyabean and linseed in  $CS_2$ ,  $Et_2O$ ,  $C_6H_{14}$ ,  $C_6H_{12}$  and  $C_6H_6$ , and found that the  $\phi_v$  of the oils in solution was usually smaller

than that of the pure oils, and that the ( $\eta$ ) in  $C_6H_{12}$  and  $C_6H_6$  and tetralin were greater than those for the other solvents. The latter observation was attributed to the uncoiling of fatty acid chains in the three solvents. More recently, Zymrya *et al.* (5) determined the viscosity of corn oil-ligroine solutions at 0–100% corn oil with a capillary viscometer, and observed that viscosity increased rapidly and nonlinearly with increasing corn oil concentration in solution.

In the course of a study of network formation in drying oils by dilute solution viscometry in our laboratory (6), it was observed that the intrinsic viscosities of both the pure and polymerizing oil showed a steep rise in the dilute concentration range—0.170 to 0.869 g/dl, in toluene. This behavior is anomalous and, to our knowledge, has not been reported for fatty acid esters, including fats and oils. The objective of this work is to examine in detail this anomalous viscosity behavior by extending the concentration range and using other solvents in order to establish its validity and scope, and perhaps attempt to offer a molecular explanation for its occurrence.

## EXPERIMENTAL PROCEDURES

**Materials. Vegetable oils.** The oils of rubberseed [*Hevea brasiliensis* (Kunth) Muell.], soyabean seed [*Glycine max* (L.) Merr] and melonseed [*Colocynthis vulgaris* Schrad.] were solvent extracted and bleached with fuller's earth. Rubber and melonseed oils were alkali refined by Cocks and Reed's method (7) to reduce their acid numbers from 29.12 and 2.38 to 0.78 and 0.31, respectively. Soyabean oil has a low acid number of 0.27. The iodine values of the oils determined by the ASTM method (D1959–69, 1973) are rubber seed oil, 137.56; soyabean oil, 130.45; and melonseed oil, 113.70.

**Solvents.** For viscosity measurements, the following analytical grade solvents were used without further purification: toluene, cyclohexane, xylene and tetrahydrofuran were products of Merck (Darmstadt, Germany); chloroform was purchased from BDH Chemicals Ltd. (Poole, England); and dichloromethane and carbon tetrachloride were products of Vickers Lab. Ltd. (Burley-In-Wharfedale, West Yorks, England).

**Methyl esters of melonseed and palmitic acid.** Both esters were prepared by refluxing 10 g of the oil or acid with 300 cm<sup>3</sup> of 2% methanolic sulphuric acid for 1 hr. The resulting mixture was treated with 500 cm<sup>3</sup> of distilled water in a separatory funnel, and then extracted twice with 250 cm<sup>3</sup> portions of petroleum ether (b.p. 40–60°C). The combined extracts were washed until acid-free. The extract was dried with anhydrous sodium sulphate and the solvent removed under a stream of  $N_2$  on a steam bath. Butyl acetate was also from Merck, and was used as obtained.

**Equipment.** A viscosity bath, a thermoheater and a Cannon-Fenske viscometer, size 50, were used.

*Preparation of ester solutions for viscosity meas-*

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urement. A standard solution (70 g/dl) of each ester was prepared in the required solvent; this solution was then diluted in a 10-cm<sup>3</sup> volumetric flask to the following concentrations for the viscosity measurement: 0.07, 0.21, 0.35, 0.49, 0.70, 0.84, 0.98, 1.19, 1.40, 1.61, 1.82, 2.03, 4.99, 10.01, 14.98, 20.02, 24.99 and 30.03 g/dl.

*Procedure for viscosity measurement.* The viscosity bath was equilibrated at 32°C. Each solvent or solution for viscosity measurement was filtered into the viscometer using a sintered glass funnel and then allowed to equilibrate in the viscosity bath before the efflux time measurement. Three efflux times which agree to within 0.20 seconds were obtained and averaged for each solution or solvent.

## RESULTS AND DISCUSSION

The efflux times (in seconds) of the solvents are: toluene, 180.2; tetrahydrofuran, 152.0; xylene, 193.60; cyclohexane, 314.60; chloroform, 106.50; carbon tetrachloride, 159.20; and dichloromethane, 93.60. Reduced viscosities ( $\eta_{red}$ ) were calculated using the efflux times of the solution ( $t$ ) and those of the solvents ( $t_s$ ) according to the following equations:

$$\eta_{red} = \eta_{sp}/C = (t-t_s)/t_s \cdot C \quad [1]$$

$$\left[ \frac{\eta_{sp}}{c} \right]_{c=0} = (\eta) \quad [2]$$

where  $c$  is solution concentration in g/dl,  $\eta_{sp}$  is the specific viscosity and  $(\eta)$  is the intrinsic viscosity. Plots of reduced viscosity vs concentration of oil solution are given in Figures 1a and 2a (for melonseed oil in hydrocarbon and halogenated solvents, respectively), Figures 3a and 4a (for soyabean oil in hydrocarbon and halogenated solvents, respectively) and Figures 5a and 6a (for rubberseed oil in hydrocarbon and halogenated solvents, respectively).

Each set of (a) curves shows three regions designated as I, II and III on the graphs. Region I (the high concentration region) starting from about 2 g/dl and above, reveals the normal trend in reduced viscosity with concentration—that is, decrease in reduced viscosity with decrease in concentration. In region II (from about 1.2 to about 2 g/dl) reduced viscosity appears to level off with concentration. Region III (below 1.2 g/dl) shows steep rise in reduced viscosity with decrease in concentration. The behavior in region III is anomalous.

To ascertain whether the above viscosity behavior is peculiar to the triglycerides (oils) alone, solution viscosities of three other esters were measured in chloroform at 32°C in the same concentration range. The esters used were methyl ester of melonseed oil (MEMSO), methyl palmitate (MPT) and n-butyl acetate (n-BuA). Plots of their reduced viscosities vs concentration are given in Figure 7a. Trends similar to the behavior of the oils above were observed, suggesting the involvement of a common structural element.

The anomalous viscosity behavior in Region III appears indicative of the occurrence of major structural changes in the system that probably caused significant increases in its size in solution, that is, in its

hydrodynamic volume. And since intrinsic viscosity is a direct measure of hydrodynamic volume, any increase in the latter would cause proportionate increase in the former.

A number of systems are known to exhibit such dramatic changes in solution viscosity as a result of structural changes in the system. For instance, lyotropic liquid crystals exhibit a steep rise in viscosity with dilution following the disruption of the ordered molecules which lead to increase in the hydrodynamic volumes of the affected molecules (9-12). Also, polyelectrolytes have been found to exhibit similar increase in reduced viscosity with decrease in concentration, that is, dilution. In this case, dilution causes increased ionization of the polyelectrolytes and the resulting coulombic repulsion leads to chain expansion and hence, increase in the effective hydrodynamic volume of the system (13,14).

Some other polymeric systems have been reported to show an increase in reduced viscosity at low polymer concentrations. For instance, linear poly(vinyl acetate) in toluene has been reported to exhibit this anomalous viscosity behavior at a critical concentration of 0.05 g/dl (15). This has also been observed for nitrocellulose in various solvents in the concentration range 0.05-0.20 g/dl (16) and for high molecular weight polystyrene between 0.10-0.50 g/dl in various solvents (17,18). Similar behavior was also reported for chloro-

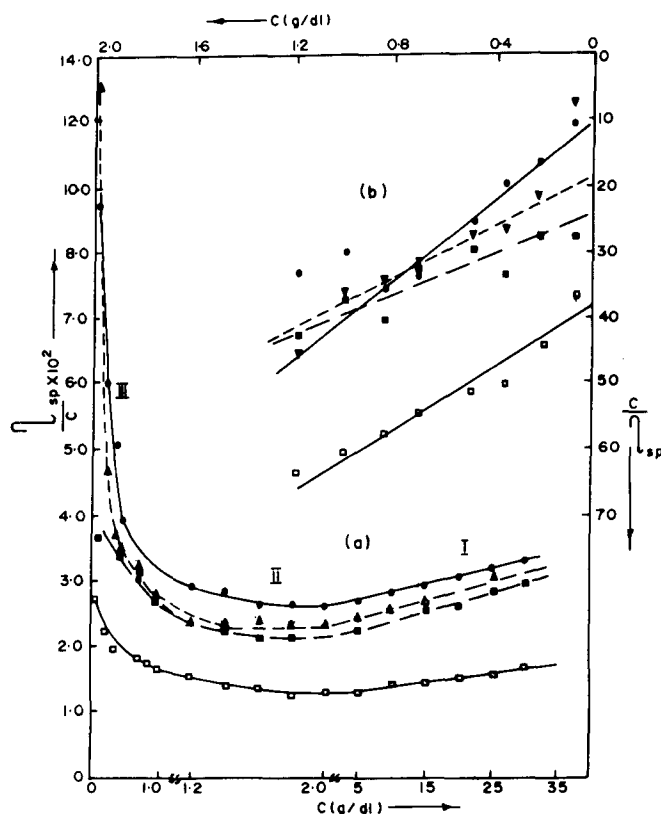


FIG. 1. Reduced viscosity vs concentration (a), and reciprocal reduced viscosity vs concentration (b), for melonseed oil: (●) toluene; (□) cyclohexane (■) xylene; and (▲) tetrahydrofuran.

## ANOMALOUS VISCOSITY BEHAVIOR OF FATTY ACID ESTERS

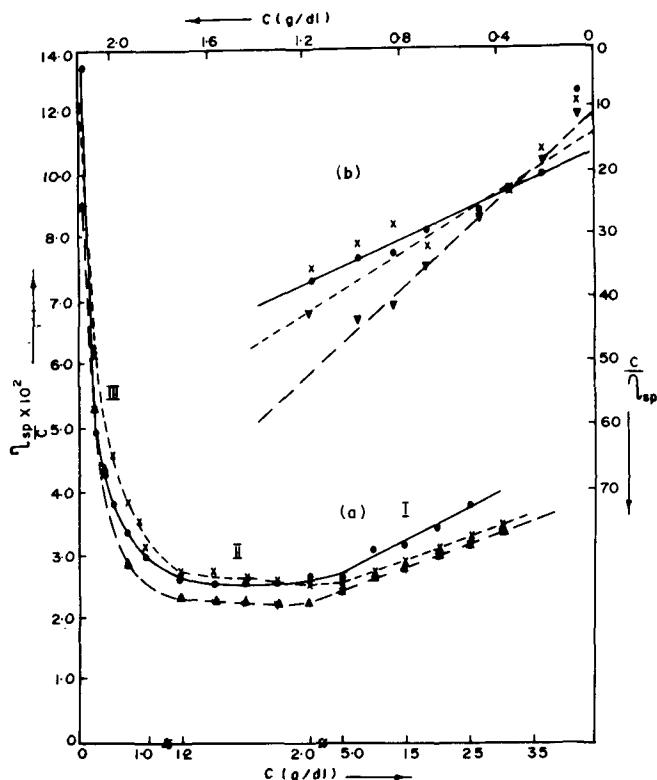


FIG. 2. Reduced viscosity vs concentration (a), and reciprocal reduced viscosity vs concentration (b), for melonseed oil: (●) chloroform; (▲) carbon tetrachloride; and (×) dichloromethane.

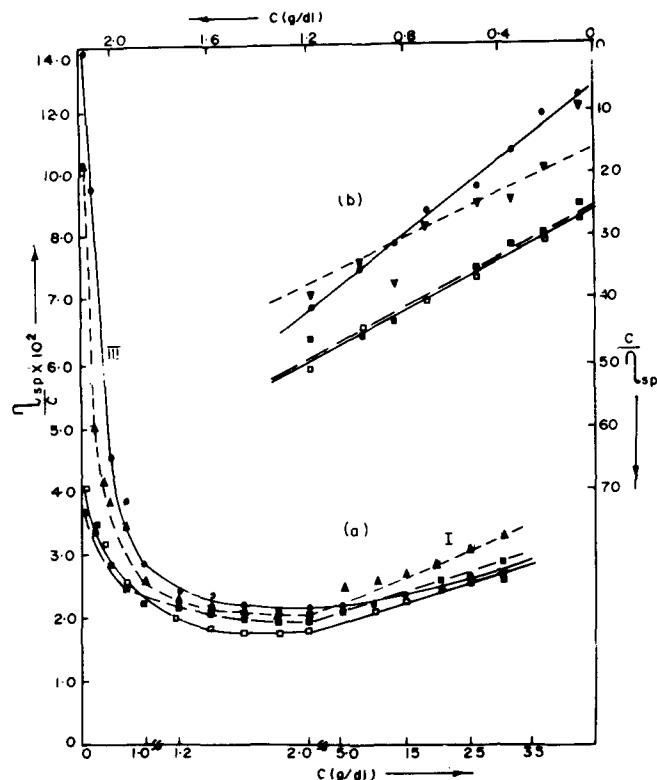


FIG. 3. Reduced viscosity vs concentration (a), and reciprocal reduced viscosity vs concentration (b), for soyabean oil: (●) toluene; (□) cyclohexane; (■) xylene; and (▲) tetrahydrofuran.

phyll (with a long chain fatty acid ester) in benzene, dioxane and methanol at critical concentrations of less than 2 g/dl (19). It should be noted that not all polymers show this anomalous viscosity behavior. For instance, both linear and branched poly(vinyl chloride) have been found to give a linear plot of reduced viscosity vs concentrations down to 0.02 g/dl. A number of reasons have been deduced to explain the observed increase in reduced viscosities at low polymer concentrations, notably, expansion of the individual polymer coil and the final untangling of the whole molecule (16,18), the configurational changes of the polymer molecules with increasing dilution (17) and the formation of network structures (19).

However, for the systems under study (being low molecular weight substances) any molecular expansion would most likely arise from disruption of some form of ordered structure. In the extreme case of liquid crystals, the primary prerequisite for the formation of order is the presence of a rigid, polarizable molecule or segment and that the rigid molecule must be sufficiently soluble. However, the configurational constraints imposed on oil molecules and similar low molecular esters cannot allow for secondary structure necessary to accommodate the long-range orientational order of liquid crystals. Therefore, it seems that some other forms of molecular packing may be present in oil solutions, probably in the form of "molecular clusters",

which are disrupted on dilution leading to an increase in hydrodynamic volume of the oil molecules and, hence, the observed rise in reduced viscosity. These molecular clusters may be micellar in form as shown in Figures 8 and 9 for the triglycerides and mono esters, respectively. The square boxes in Figure 8 represent the ester groups.

It is pertinent to compare the critical solution concentration, CSC (that is, the concentration at which the reduced viscosity starts to increase sharply on dilution) for the vegetable oils and those of various polymeric systems cited above. For the vegetable oils, the rise was observed at CSC of about 1.2 g/dl, while for the polymers this occurred at very low CSC of 0.055 g/dl for poly(vinyl acetate), in toluene, between 0.05–0.20 g/dl for nitrocellulose in various organic solvents, and between 0.05–0.10 g/dl for polystyrene in various solvents. The higher dilution required for polymers is due to their ability to form molecular associates even in solutions as dilute as 0.50 g/dl, as a result of their very large molecular size.

*Curve fitting the anomalous viscosity data of the esters.* As shown in Figures 1a–7a, direct plots of reduced viscosity vs concentration were nonlinear in region III (the anomalous region). The empirical equation (6):

$$c/\eta_{sp} = 1/(\eta) + (B/\eta) \cdot c \quad [3]$$

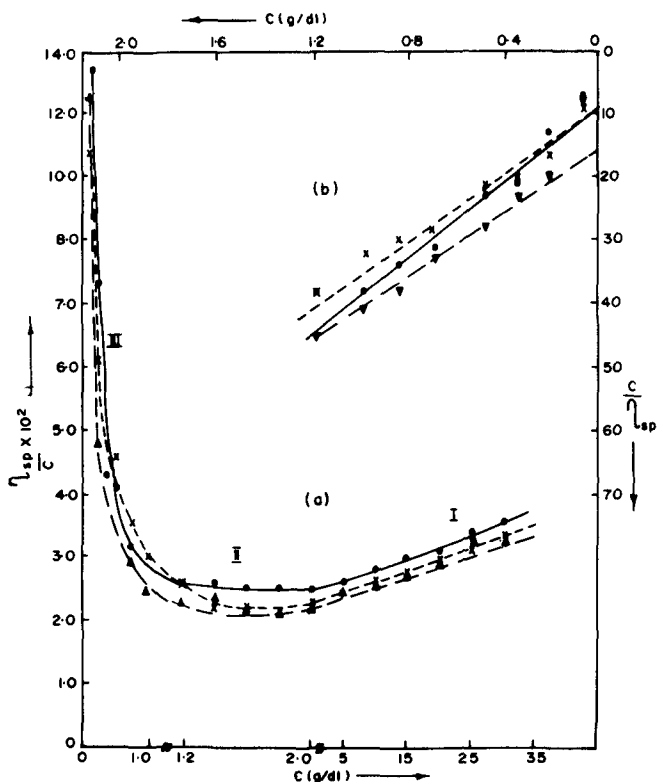


FIG. 4. Reduced viscosity vs concentration (a), and reciprocal reduced viscosity vs concentration (b), for soyabean oil: (●) chloroform; (▲) carbon tetrachloride; and (×) dichloromethane.

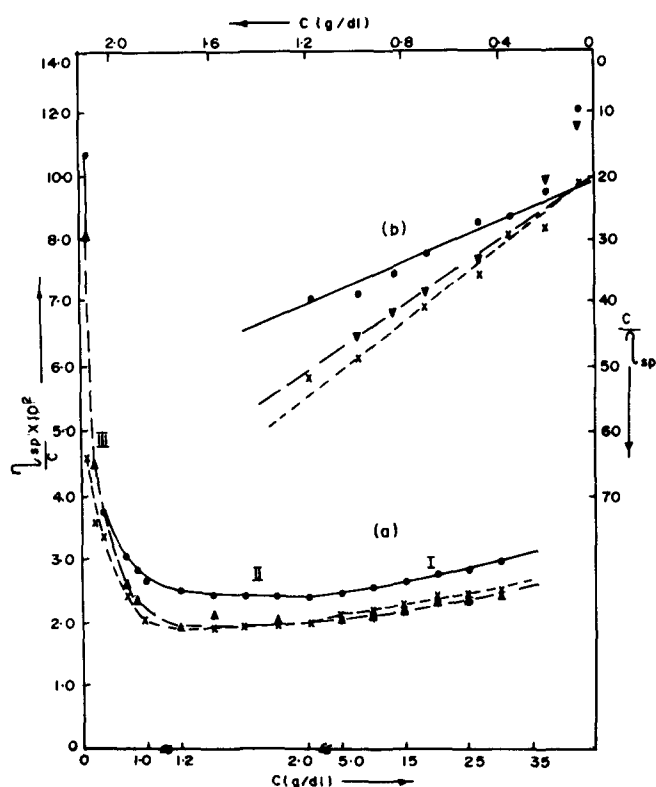


FIG. 6. Reduced viscosity vs concentration (a), and reciprocal reduced viscosity vs concentration (b), for rubberseed oil: (●) chloroform; (▲) carbon tetrachloride; and (×) dichloromethane.

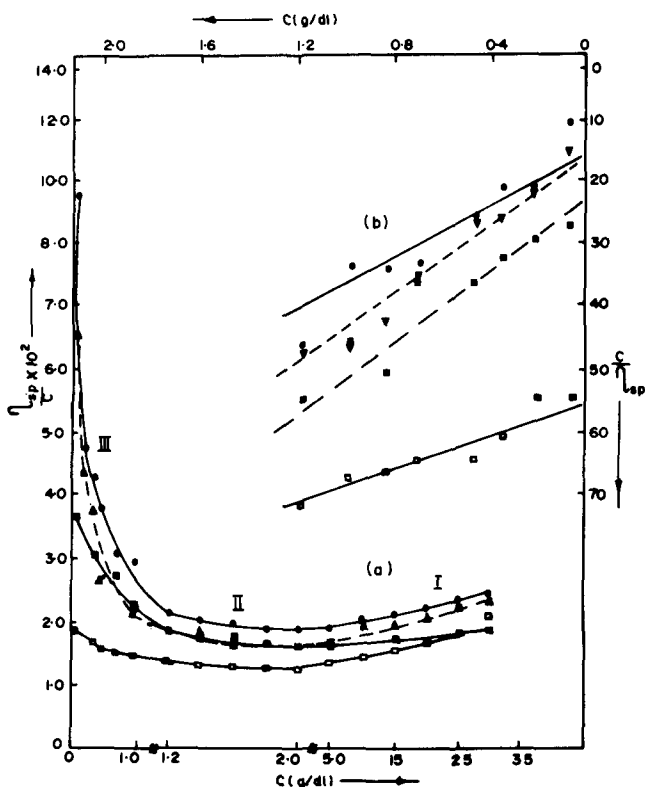


FIG. 5. Reduced viscosity vs concentration (a), and reciprocal reduced viscosity vs concentration (b), for rubberseed oil: (●) chloroform; (□) cyclohexane; (■) xylene; and (▲) tetrahydrofuran.

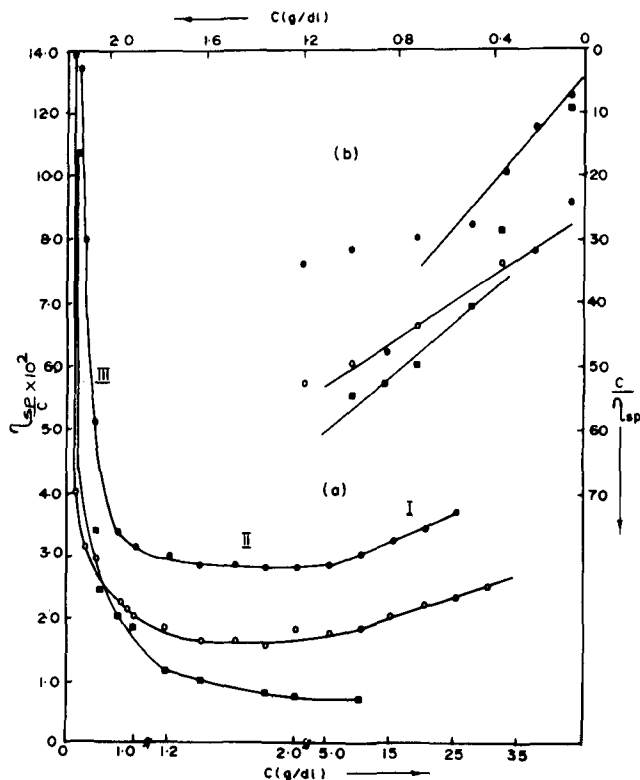


FIG. 7. Reduced viscosity vs concentration (a), and reciprocal reduced viscosity vs concentration (b), for (●) methyl ester of melonseed oil; (○) methyl palmitate; and (■) n-butylacetate in chloroform.

## ANOMALOUS VISCOSITY BEHAVIOR OF FATTY ACID ESTERS

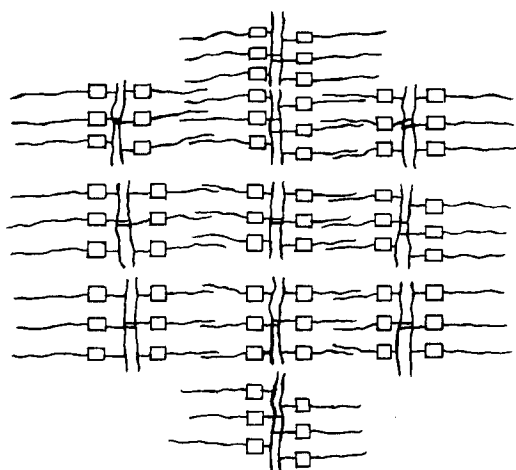


FIG. 8. Schematic representation of molecular cluster formation in solution of vegetable oils.

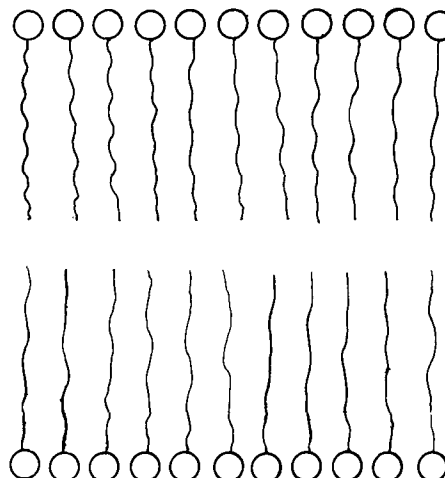


FIG. 9. Schematic representation of molecular cluster formation in solutions of monoesters.

was used to linearize the data by plotting reciprocal reduced viscosity vs concentration as shown in the (b) sets of curves in Figures 1-7 for the oils and the mono esters in different solvents. The plots appear generally linear within the concentration range of 0.98 to 0.21 g/dl. Deviations are observed outside this range. Extrapolation of each curve to zero concentration gives the intrinsic viscosity ( $\eta$ ); extrapolation was effected by the least square method and involved only the points within the above concentration range. The product of ( $\eta$ ) and the slope of each curve gives the factor B. Values of ( $\eta$ ) and B are given in Table 1 for the three oils. The errors in the intrinsic viscosity values are also given in the Table.

Values of both ( $\eta$ ) and B appear to depend on the nature of the oil and solvent. For each oil, the following order in intrinsic viscosity was observed in hydrocarbon solvents: toluene > tetrahydrofuran > xylene > cyclohexane. This order appears to reflect variations in the size and shape of the oil molecule in solution which, in turn, suggests different degrees of molecular clustering, probably arising from solvent steric interference. For instance, cyclohexane in its puckered conformation is less compact than toluene (a planar mole-

cule) and would cause more obstruction in the process of cluster formation. In other words, there seems to be less ordered structure in cyclohexane than in toluene, with less structural expansion on dilution leading to a cumulatively lower intrinsic viscosity. Among the halogenated solvents, there is no clear cut order, with the three solvents showing comparable intrinsic viscosities. This suggests that despite the increasing size as we go from dichloromethane to carbon tetrachloride, the compactness of the molecules appear to be on the same order of magnitude, hence the observed comparable values of intrinsic viscosity of their solute molecules. The factor B appears to be structure-dependent as it varies in the same manner as intrinsic viscosity.

The intrinsic viscosities and the B values in brackets for the mono esters are as follows: methyl ester of melonseed oil, (MEMSO),  $0.247 \pm 0.001$  (8.905); methyl palmitate (MPT),  $0.037 \pm 0.001$  (0.886); and n-butyl acetate (n-BuA),  $0.038 \pm 0.008$  (1.132). The intrinsic viscosity values follow the order: MEMSO  $\gg$  n-BuA  $\approx$  MPT and with MSO in the same solvent, the order is MEMSO  $\gg$  MSO > n-BuA  $\approx$  MPT. The observed order in intrinsic viscosity may be due to differences

TABLE 1

Values of Intrinsic Viscosity ( $\eta$ ) and the Factor B for the Oils in Different Solvents at 32°C

Solvent	Melonseed oil		Soyabean oil		Rubberseed oil	
	( $\eta$ ) $\times 10^2$	B	( $\eta$ ) $\times 10^2$	B	( $\eta$ ) $\times 10^2$	B
Toluene	$9.70 \pm 1.50$	3.01	$16.70 \pm 4.30$	4.88	$6.30 \pm 1.10$	1.56
Tetrahydrofuran	$6.40 \pm 0.30$	1.52	$6.10 \pm 0.40$	1.15	$5.70 \pm 0.90$	1.37
Xylene	$4.10 \pm 0.30$	0.61	$4.10 \pm 0.10$	0.89	$4.30 \pm 0.40$	1.01
Cyclohexane	$2.60 \pm 0.10$	0.56	$4.0 \pm 0.20$	0.79	$1.80 \pm 0.10$	0.27
Chloroform	$5.80 \pm 0.30$	1.02	$11.10 \pm 1.30$	3.38	$4.80 \pm 0.30$	0.99
Dichloromethane	$7.10 \pm 1.10$	1.27	$10.60 \pm 1.40$	2.74	$4.20 \pm 0.40$	0.92
Carbon tetrachloride	$8.80 \pm 0.80$	2.88	$6.60 \pm 0.30$	1.64	$5.0 \pm 0.40$	1.28

in molecular weight, degree of unsaturation and/or the proposed new factor (molecular cluster formation). The molecular weights (MW) or average molecular weights  $\bar{M}_w$  of these esters are MEMSO ( $\bar{M}_w = 293$ ); MSO ( $\bar{M}_w = 289$ ); MPT (MW = 270); and n-BuA (MW = 116). The higher intrinsic viscosity value of MEMSO as compared to that of MSO in the same solvent (chloroform) cannot be attributed to either degree of unsaturation (since it is the same in both compounds) or to difference in their molecular weights, as they are quite close. This leaves molecular cluster formation as the main probable factor. The free nature of the fatty acid segments of MEMSO compared to those of MSO, which are bound in the triglyceride structure, would permit the formation of molecular clusters to a greater degree (probably of the micellar type, shown in Fig. 9) with the resultant greater structural expansion on dilution.

On the basis of the above argument, one would expect methyl palmitate, a linear mono ester like MEMSO, to show equivalent degree of cluster formation. But this is not the case. Besides, on the basis of molecular weight, the viscosity of MPT is expectedly lower; but on the basis of degree of unsaturation, its viscosity should be higher; in other words these two factors make opposite contributions to the viscosity of MPT which may even out. Consequently, the much lower intrinsic viscosity of MPT as compared to that of MEMSO may be largely due to its inability to form thermally-stable molecular clusters due to the comparatively higher flexibility of its saturated fatty acid segments.

From Table 1, it can be seen that there are differences in the intrinsic viscosities of the three oils; these differences are solvent dependent. However, in a given solvent, the order is generally: SBO  $\approx$  MSO  $\gg$  RSO. This order appears to show, to some extent, the effect of degree of unsaturation on the ability of the oil mole-

cule to cluster in solution. For instance, the fatty acid segments of rubber seed oil, being more unsaturated, would have a more bent structure and hence less ability to come together in solution. This observation, however, requires further investigation with a wider range of unsaturated oils.

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