Physical Properties of Fatty Acid Methyl Esters. VI. Viscosity

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Abstract

Kinematic viscosities at 20C, 40C and at 70C have been measured for methyl oleate, linoleate, linolenate, erucate, and for the saturated fatty acid methyl esters acetate through nonadecanoate. Using a recently developed dynamic viscosity-temperature criterion, log $(1.200 + \log \eta) = A - S \log (1 + t/135)$, the viscosity-temperature behavior of the saturated compounds could be characterized by one single parameter.

Introduction

VISCOSITY WAS RECOGNIZED quite early as a significant property of a liquid and there is a considerable number of older investigations on this subject. The work of Thorpe and Rodger (26), who measured the viscosity of the lower fatty acids over the entire liquid range, is a classic in the field. Other measurements on fatty acids, up to stearic acid, were subsequently carried out by Dunstan and co-workers (6,7) in the same period that Gartenmeister (9) reported his work on acetic to caprylic acid.

Data on the low molecular weight esters were obtained much later by Gill and Dexter (10), and also by Shigley and co-workers (21). Of more recent date is the work of Teeter and Cowan (25), who determined the viscometric properties of the higher fatty acids and their derivatives. Viscosities at 75C of the even-numbered fatty acids, their methyl, and their ethyl esters, have been reported by Gros and Feuge (13). Bonhorst et al. (4) measured viscosities in the 20–100C range for the methyl, ethyl, *n*-propyl, and the isopropyl esters of the fatty acids from caproic to stearic acid inclusive.

The number of papers on the viscosities of the unsaturated fatty acids and their esters is more limited. Data on pure oleic acid and some related esters have been reported by Keffler and McLean (15), the viscosities of some unsaturated esters have been obtained at 14C by Teeter and Cowan (25), and the isologous C_{18} fatty acids have been studied by Ravich (19).

Experimental

Products

The compounds investigated are the saturated fatty acid methyl esters from acetate to nonadecanoate, methyl oleate, linoleate, linolenate and erucate. Their preparation, purity, density, refractive index, dispersion, ultrasonic sound velocity, and dielectric constant have been reported in previous communications (11,12).

Measurements

These were carried out with Ostwald viscometers. Both the meters and the auxiliary equipment have been constructed according to the specifications of Sprokel (24), who carried out extensive investigations on this meter type. Careful calibrations were carried out with distilled water and with liquids of known viscosity. These measurements, carried out at 20C, 40C, and at 70C, are estimated to possess a standard deviation of less than 1%.

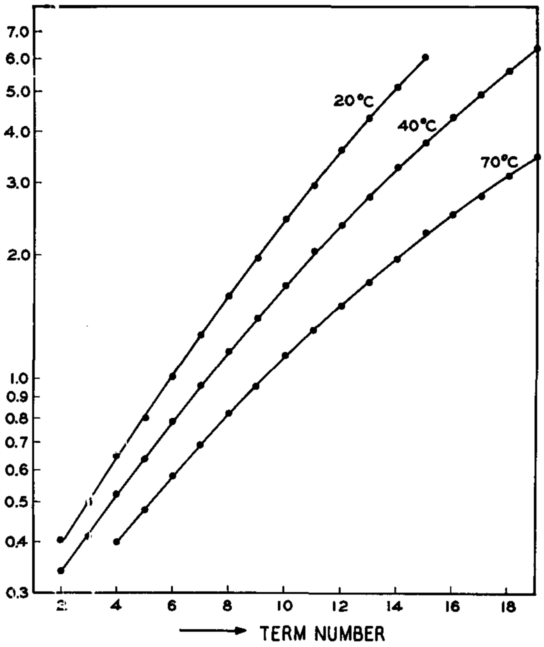

FIG. 1. Kinematic viscosities of saturated fatty acid methyl esters.

Values obtained with an Ostwald viscometer are kinematic viscosities. To obtain dynamic viscosities we refer to our previous communication for data on densities at 20C and at 40C (11).

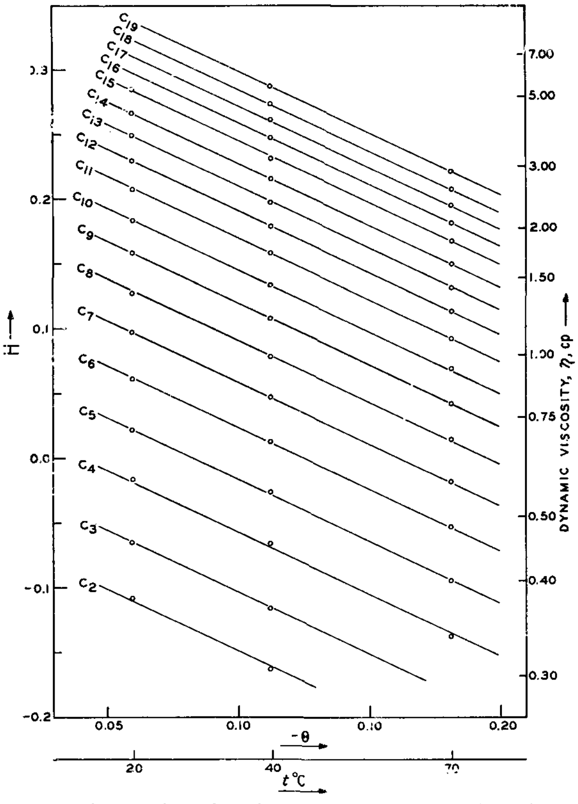

FIG. 2. Dynamic viscosity-temperature relationships for saturated fatty acid methyl esters.

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TABLE I

Kinematic Viscosities of Saturated Fatty Acid Methyl Esters
ν in cs.

Temp, C	Observed			Literature			
	20	40	70	20	40	70	Ref.
Acetate	0.407	0.340		0.412	0.349		(14)
				0.412			(17)
				0.410	0.344	0.276	(23)
				0.408	0.344		(26)
				0.417	0.350		(16)
Propionate	0.500	0.413		0.504	0.420		(14)
				0.501	0.415	0.325	(23)
				0.496	0.413	0.324	(26)
Butyrate	0.646	0.521	0.400	0.645	0.524	0.399	(23)
				0.640	0.517	0.396	(26)
Valerate	0.800	0.634	0.477				
Caproate	1.01	0.785	0.577	1.03	0.780	0.570	(4)
				0.99	0.79		(2)
Oenanthate	1.27	0.96	0.686				
Caprylate	1.58	1.16	0.819	1.59	1.16	0.805	(4)
Pelargonate	1.96	1.40	0.957	1.96			(1)
Caprate	2.42	1.69	1.13	2.44	1.71	1.14	(4)
Undecanoate	2.97	2.02	1.30				
Laurate	3.60	2.38	1.50	3.54	2.40	1.49	(4)
Tridecanoate	4.31	2.78	1.72				
Myristate	5.11	3.23	1.95	5.20	3.29	1.99	(4)
Pentadecanoate	6.09	3.75	2.23				
Palmitate		4.32	2.50	10.1	4.50	2.60	(4)
Heptadecanoate		4.93	2.79				
Stearate		5.61	3.11		5.67	3.10	(4)
Nonadecanoate		6.39	3.48				

Results

The observed kinematic viscosities of the saturated fatty acid methyl esters are presented in Table I. Values reported in the literature are included for comparison.

Dunstan, Hilditch and Thole (7) noted that the lines relating the logarithms of the viscosities of the saturated fatty acids to the molecular weights are approximately linear. We note, however, that the relation, $M = a + b \log \nu$, is not valid over the whole range. Deviations are noted for the lower and for the higher members of the series. This can be observed in Figure 1, where the kinematic viscosities of the investigated esters are plotted against the term number.

We have observed that in a homologous series the Smittenberg (22) relation is very satisfactory to describe the relation between a physical property and the number of C atoms in the chain (12). In the case of the viscosities, however, the inapplicability of this relation is obvious, because the viscosity does not possess a finite value for the limiting homolog.

The kinematic viscosities of the unsaturated fatty acid methyl esters are presented in Table II and compared with one available literature value. Methyl stearate has been included as reference.

The viscosity decreases with increasing unsaturation, but the change is not proportional to the increase in the number of double bonds. The additional double bond in the same chain contributes much less to the fluidity. These findings confirm the data of Teeter and Cowan (25).

Viscosity-Temperature Relationships

An extensive number of theoretical, semiempirical, and empirical viscosity-temperature relationships have been proposed, many of them of only limited and ephemeral interest. A large number of reviews have also been published, of which we will only mention those by Partington (18), Brush (5), Bondi (3) and by Dunstan and Thole (8).

TABLE II

Kinematic Viscosities of Unsaturated Fatty Acid Methyl Esters
ν in cs

Temp, C	Observed			Lit.	
	20	40	70	20	Ref.
Stearate[a]		5.61	3.11		
Oleate	7.23	4.45	2.60	7.79	(1)
Linoleate	5.58	3.64	2.25		
Linolenate	4.84	3.27	2.09		
Erucate	12.5	7.21	3.92		

[a] Included as reference to facilitate comparison.

A new empirical equation, having a number of advantages over existing correlations, has recently been proposed as being successful, over a wide temperature range and within normal viscometric accuracy, to describe the dynamic viscosity-temperature relationships of a large variety of liquids (20), i.e.,

$$H = A + S\,\theta \qquad [1]$$

In this basic equation, $H = \log (1.200 + \log \eta)$ with η being the dynamic viscosity in cp., A = a constant, S = the "slope index," a criterion of the temperature-viscosity behavior of the product, and $\theta = -\log (1 + t/135)$, with t being the temperature in °C.

Figure 2 shows the temperature-viscosity relation of the saturated fatty acid methyl esters as obtained by using equation 1. All the lines are observed to be parallel and the viscosity-temperature behavior of these compounds can, therefore, be characterized by one single slope index, S, which is 0.95 in this particular case.

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