# Viscosity Studies of Some Long-Chain Thiol Esters

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## Abstract

Viscosity studies of thiolaurates, thiomyristates, thiopalmitates and thiostearates of the normal $C_6$, $C_7$, $C_{14}$, $C_{16}$, $C_{18}$; $C_6$, $C_8$, $C_{10}$, $C_{11}$, $C_{13}$, $C_{14}$, $C_{15}$, $C_{16}$, $C_{18}$; $C_9$, $C_{10}$, $C_{11}$, $C_{12}$, $C_{13}$, $C_{14}$, $C_{16}$, $C_{17}$, $C_{18}$ and $C_4$, $C_9$, $C_{10}$, $C_{11}$, $C_{12}$, $C_{14}$, $C_{16}$ and $C_{18}$, respectively, were made. In addition, *n*-propyl and *n*-heptyl thioacetates as well as *n*-heptyl thiohexanoate were studied. Viscosities of thiol esters increase with increasing chain length. These increases are not linear. For each compound, the viscosity decreases with increasing temp. Activation energies for viscous flow were calculated. The activation energies increase as the chains increase. These increases are not linear.

## Experimental

THE SYNTHESIS and the purification of all of the thiol esters with the exception of *n*-propyl and *n*-heptyl thioacetates and *n*-hexyl thiomyristates were described elsewhere (1–3).

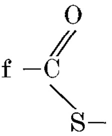
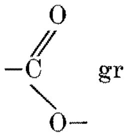
The above mentioned thiol esters were prepared by refluxing 0.1 mole of the appropriate freshly distilled acyl chloride with 0.1 mole of the appropriate alkane thiol for six hr in the presence of 250 ml of dry benzene and 10 ml of dry pyridine. The reaction mixtures were then washed with water and dried over anhydrous sodium sulfate. Benzene was then removed from each reaction mixture by distillation and the crude thiol esters were chromatographed with Florisil and eluted with petroleum ether; after removal of the petroleum ether by distillation, the esters, with the exception of *n*-propyl thioacetate were fractionated under diminished pressure. The *n*-propyl thioacetate was fractionated at atmospheric pressure. The yields, analyses and physical data for these new thiol esters are summarized in Table I.

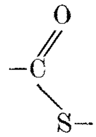
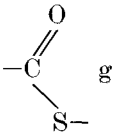
The viscosity measurements were made with Cannon-Fenske type viscometers by the method proposed by ASTM in "Standards on Petroleum Products and Lubricants" (4).

The measurements were made at 60, 75 and 90C, and wherever possible at 30 and 45C. The viscosities in centipoises of all of the compounds at various temperatures were calculated; these values are summarized in Table II.

## Results and Discussion

*Viscosity vs. Chain Length.* Given in Table II are the viscosity and other pertinent data for 34 thiol esters. The number of carbon atoms in the thiol ester chain ranged from 5–36. A plot (Fig. 1) of log viscosity vs. the number of carbon atoms at the four temp studied shows a sharp increase in viscosity for the shorter members of the series. The viscosity increases on the average 1.43 fold/carbon atom at 60C from a chain with 5 carbon atoms to a chain with 12 carbon atoms. In the chains containing between 20 and 27 carbon atoms the average rate of increase in viscosity/carbon atom is 1.24 fold or 87% of that observed in the 5–12 carbon chains at 90C. In the chains containing between 5–12 carbon atoms, the rate of increase of viscosity is 1.36 fold/ carbon atom and 1.22 fold/ carbon atom in the chains containing 20–27 carbon atoms. There is a slight decrease in rates of viscous flow/carbon atom with an increase in temp.

Viscosity data reported in the literature for the aliphatic oxygen (5,6) and for hydrocarbons (7) of comparable chain lengths in the same temp range show the same general type of viscosity-chain length curves as the thiol esters. In most cases, the viscosities of thiol esters are greater than of the corresponding oxygen esters, which in turn are greater than of the corresponding hydrocarbons. This is not surprising, since the intermolecular forces which are holding the molecules together (resisting molecular motion) are greatest for the thiol esters. The contribution to intermolecular interaction of  $-\mathrm{C}(=\mathrm{O})\mathrm{S}-$ group is greater than of  $-\mathrm{C}(=\mathrm{O})\mathrm{O}-$ group which in turn is greater than the $-CH_2-CH_2-$ group.

The effect of the position of the  $-\mathrm{C}(=\mathrm{O})\mathrm{S}-$ group in the chain on the viscosity at a particular temp can be seen by the examination of the data (Table II) obtained for 18 compounds containing an equal number of carbon atoms. These data show the compounds with greatest symmetry about the  $-\mathrm{C}(=\mathrm{O})\mathrm{S}-$ group have the lowest viscosities. This symmetry effect is observed for all thiol esters except those containing 28 and 30 carbon atoms.

*Viscosity-Temperature.* For each compound, the viscosity decreases as the temp increases. Numerous equations relating viscosity and temp can be found in the literature (8). Most of these equations are exponential. One such equation was proposed by Eyring: $\eta = A^{E_{vis}}/RT$. A plot of the logarithm of viscosity vs. the reciprocal of the absolute temp should

TABLE I

Physical Properties of Short-Chain Thiol Esters

| | Mol wt | bp | Press | Density 25C | $n_D^{25}$ | Molar refract calc. | Molar refract found | % calc. | S found |
|---|---|---|---|---|---|---|---|---|---|
| *n*-propyl thioacetate | 118.20 | 139–41C | atm. | 0.9516 | 1.4578 | 33.18 | 33.88 | 27.10 | 27.60 |
| *n*-heptyl thioacetate | 174.30 | 114C | 2 mm Hg | 0.9123 | 1.4638 | 51.87 | 52.71 | 18.37 | 18.21 |
| *n*-hexyl thiohexanoate | 216.39 | 117C | 3 mm Hg | 0.8962 | 1.4645 | 65.65 | 66.68 | 14.80 | 14.84 |

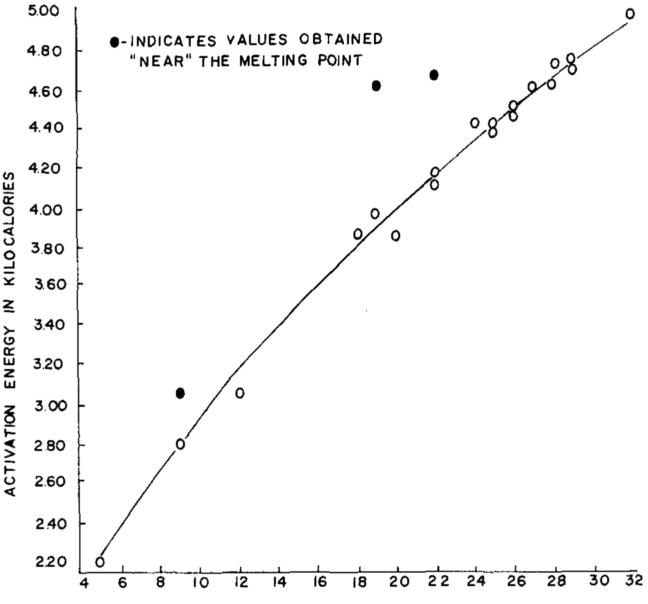


FIG. 1. Activation energy for viscous flow of thiol esters.

yield a straight line if the equation is a valid representation of the data. This treatment of the thiol ester data showed that Eyring's equation represents adequately that data for only *n*-propyl thioacetate, *n*-undecyl thiomyristate, *n*-octadecyl thiomyristate, *n*-nonyl thiopalmitate and *n*-hexyl thiolaurate. For the remaining compounds it was observed that all of the points do not fall on straight lines. In all of the cases, except one, the viscosity shows an abnormal increase with increasing temp.

Deviations in the neighborhood of freezing points would not be entirely unexpected because of a change in liquid structure. As a compound cools, its molar volume contracts and consequently, the number of holes in the liquid decreases. The decrease in the number of holes results in an increase in viscosity; however, this is not the sole factor influencing viscosity.

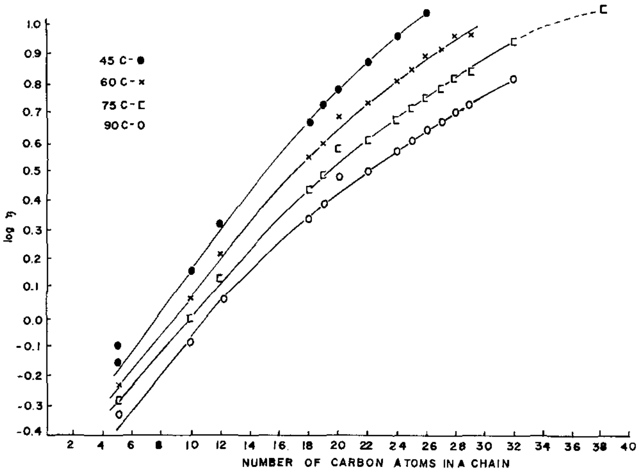


FIG. 2. Viscosity—Chain length relationship of thiol esters at various temp.

Another factor involves the forces which control the orientation of the molecules in the solid state. If these forces become substantial while the material is still in the liquid phase, the structure of the liquid will change. Usually these forces remain inoperative until the liquid solidifies. For thiol esters, there is an apparent alteration of liquid structures slightly above their freezing points.

The temp at which this liquid transition occurs can be determined approximately. Assuming that the viscosity increases linearly for each liquid structure (but not at the same rate), one can project the curve for each structure to a common point from which the temp can be determined for the liquid transition. Table III gives the melting points and liquid transition temp in degrees Kelvin, for *n*-heptyl thiolaurate, *n*-octyl thiomyristate, *n*-decyl thiomyristate, decyl thiopalmitate and *n*-butyl thiostearate. The ratios of transition temp to melting point temp for the above mentioned compounds are 1.09, 1.08, 1.07, 107 and 1.13, respectively. Thus, there is an abnormal increase in viscosity of thiol esters at a temp approx 10% higher

TABLE II

Viscosity in centipoise

| Compound | No. of carbon atoms | (C) mp | 30C | 45C | 60C | 75C | 90C |
|---|---|---|---|---|---|---|---|
| *n*-propyl thioacetate | 5 | | 0.7889 | 0.6669 | 0.5729 | 0.5030 | 0.4432 |
| *n*-heptyl thioacetate | 9 | | 1.792 | 1.411 | 1.151 | 0.9731 | 0.8266 |
| *n*-hexyl thiohexanoate | 12 | | | 1.996 | 1.600 | 1.328 | 1.11 |
| *n*-hexyl thiolaurate | 18 | | | 4.560 | 3.419 | 2.691 | 2.150 |
| *n*-heptyl thiolaurate | 19 | | 7.345 | 5.143 | 3.816 | 2.976 | 2.362 |
| *n*-tetradecyl thiolaurate | 26 | 45.0 | | | 7.444 | 5.477 | 4.216 |
| *n*-hexadecyl thiolaurate | 28 | 49.5 | | | 8.71 | 6.353 | |
| *n*-octadecyl thiolaurate | 30 | 54.0 | | | 10.53 | | 4.846 |
| *n*-hexyl thiomyristate | 20 | | | 5.813 | 4.754 | 3.661 | 2.923 |
| *n*-octyl thiomyristate | 22 | | | 7.205 | 5.193 | 3.915 | 3.076 |
| *n*-decyl thiomyristate | 24 | 38.0 | | 8.80 | 6.249 | 5.045 | 3.595 |
| *n*-undecyl thiomyristate | 25 | 45.5 | | | 6.825 | | 3.895 |
| *n*-tridecyl thiomyristate | 27 | 54.0 | | | | | 4.510 |
| *n*-tetradecyl thiomyristate | 28 | 50.0 | | | 8.75 | 6.361 | 4.850 |
| *n*-pentadecyl thiomyristate | 29 | 57.0 | | | 9.34 | | |
| *n*-hexadecyl thiomyristate | 30 | 53.5 | | | 10.1 | | |
| *n*-octadecyl thiomyristate | 32 | 57.5 | | | 11.94 | 6.38 | 6.377 |
| *n*-nonyl thiopalmitate | 25 | 44.5 | | | 6.849 | 5.063 | 3.917 |
| *n*-decyl thiopalmitate | 26 | 43.5 | | 10.72 | 7.476 | 5.489 | 4.221 |
| *n*-undecyl thiopalmitate | 27 | 51.0 | | | 8.05 | 5.892 | 4.507 |
| *n*-dodecyl thiopalmitate | 28 | 48.5 | | | 9.10 | 6.597 | 5.004 |
| *n*-tridecyl thiopalmitate | 29 | 56.0 | | | 9.45 | 6.844 | 5.187 |
| *n*-tetradecyl thiopalmitate | 30 | 54.5 | | | 10.1 | 7.30 | |
| *n*-hexadecyl thiopalmitate | 32 | 58.5 | | | 11.61 | 8.30 | |
| *n*-heptadecyl thiopalmitate | 33 | 64.5 | | | | 8.93 | |
| *n*-octadecyl thiopalmitate | 34 | 62.5 | | | | 9.62 | 7.158 |
| *n*-butyl thiostearate | 22 | | | 7.67 | 5.531 | 4.166 | 3.266 |
| *n*-nonyl thiostearate | 27 | 50.5 | | | 8.22 | 6.00 | |
| *n*-decyl thiostearate | 28 | 50.0 | | | 8.84 | 6.438 | |
| *n*-undecyl thiostearate | 29 | 55.5 | | | 9.592 | 6.915 | 5.251 |
| *n*-dodecyl thiostearate | 30 | 54.5 | | | | 7.408 | |
| *n*-tetradecyl thiostearate | 32 | 58.5 | | | 11.82 | | |
| *n*-hexadecyl thiostearate | 34 | 65.0 | | | | 9.57 | 7.09 |
| *n*-octadecyl thiostearate | 36 | 65.5 | | | | 10.89 | |

TABLE III

Transition and Melting Point Temp

| | mp K | Transition temp K |
|---|---|---|
| *n*-heptyl thiolaurate | 297 | 308.6 |
| *n*-octyl thiomyristate | 309 | 340.9 |
| *n*-decyl thiomyristate | 311 | 333 |
| *n*-decyl thiopalmitate | 316.5 | 339 |
| *n*-butyl thiostearate | 305 | 341.1 |

than the melting point temp. This explains why *n*-propyl thioacetate, *n*-undecyl thiomyristate, *n*-octadecyl thiomyristate, *n*-nonyl thiopalmitate and *n*-hexyl thiolaurate are adequately represented by Eyring's equation.

This phenomenon also occurs with water (9) and benzene (10). Rossini's viscosity data for hydrocarbons, when treated in the same manner, also shows this property. Because of this non-uniform change in viscosity throughout the entire liquid state, Eyring's equation is not valid for all temp. It does give satisfactory results when a different set of values for $E_{vis}$ and pre-exponential factors are used for each liquid structure. The values are given in Table IV. Because of this alteration of liquid structure, the viscosity has been considered in two regions, one "near" the melting point and the other "far" from the melting point, each of which displays a linear relationship with reciprocal temp. (In this section is is not implied that the liquid structure will change precisely at one given temp. Because of mixing or entropy effects of two types of liquid structures co-existing at the same time, the transition may occur over a temp range of a few degrees or a few hundredths of a degree.)

*Activation Energy.* In the calculation of activation energy for viscous flow, the selected values were from those portions of the viscosity-temperature curves which showed one type of liquid structure.

Figure 2 is a plot of activation energy, $E_{vis}$, vs. the number of carbon atoms in the chain. Treating the data in this manner shows that the activation energy increases as the chain length increases; however, this is not a linear increase.

TABLE IV

Activation Energies for Viscous Flow and Preexponential Factor

| Compound | A | A′ | $E_{vis}$ | $E'_{vis}$ |
|---|---|---|---|---|
| *n*-propyl thioacetate | —1.619 | ........... | 2103 | ....... |
| *n*-heptyl thioacetate | —1.771 | —1.949 | 2733 | 3055 |
| *n*-hexyl thiohexanoate | —1.99 | ........... | 2970 | ....... |
| *n*-hexyl thiolaurate | —1.905 | ........... | 3718 | ....... |
| *n*-heptyl thiolaurate | —1.940 | —2.417 | 3845 | 4555 |
| *n*-tetradecyl thiolaurate | —2.013 | ........... | 4383 | ....... |
| *n*-hexadecyl thiolaurate | —2.04 | ........... | 4536 | ....... |
| *n*-hexyl thiomyristate | —1.880 | ........... | 3898 | ....... |
| *n*-octyl thiomyristate | —1.943 | —2.301 | 4040 | 4599 |
| *n*-decyl thiomyristate | —2.86 | —2.36 | ....... | ....... |
| *n*-tetradecyl thiomyristate | —2.05 | ........... | 4543 | ....... |
| *n*-nonyl thiopalmitate | —1.994 | ........... | 4299 | ....... |
| *n*-decyl thiopalmitate | —2.022 | —2.446 | 4399 | ....... |
| *n*-undecyl thiopalmitate | —2.05 | ........... | 4490 | ....... |
| *n*-dodecyl thiopalmitate | —2.09 | ........... | 4630 | ....... |
| *n*-tridecyl thiopalmitate | —2.08 | ........... | 4640 | ....... |
| *n*-octadecyl thiopalmitate | —2.13 | ........... | 4952 | ....... |
| *n*-butyl thiostearate | —1.94 | —2.01 | 4080 | 4590 |
| *n*-undecyl thiostearate | —2.054 | ........... | 4611 | ....... |
| *n*-hexadecyl thiostearate | —2.17 | ...... | 5020 | ....... |

The prime values refer to that liquid structure "near" the mp.

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# Worksoftening of Margarine and Shortening

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## Abstract

Margarine and butter have a certain yield value which is mainly determined by the fact that the fat crystals do not move in respect of each other but are fixed in a tridimensional network. The permanent network greatly contributes to the total hardness (60–80%). This contribution can be determined by kneading the sample isothermally and by measuring the hardness before and after kneading. The decrease in hardness is called the "structural hardness" and the relative decrease the "worksoftening." These values give a certain impression of the plasticity of the product at a certain hardness, while the Spreadability Index, which can be calculated from the structural hardness and the worksoftening, is a good measure for spreadability.

## Introduction

DETERMINATIONS of the consistency of butter, margarine and shortenings serve mostly to obtain a relative comparative value for hardness or spreadability. It is almost impossible to calculate from these values quantitative data for the internal structure of the samples. The hardness of the products mentioned is, as will be known, for the greater part caused by the presence of a network of fat crystals. Hardness determinations before and after isothermal kneading can give an impression of the nature and strength of the bonds in the crystal lattice. For routine hardness determinations such as are carried out in margarine factories, simple apparatus giving reproducible results is required.

## Procedures and Data

### Network Structure of Crystals

In a rapidly cooled fat, most glyceride crystals are so small that it is often difficult to perceive them microscopically ($<1\ \mu$) (1). The number of crystals/cm$^3$ is so large that their mutual distance is only slight ($0.01\ \mu$). For this reason the mutual attraction (Van der Waals—London attraction) is so strong that the crystals move rapidly towards each other and flocculate. As a result of this flocculation, long chains with many ramifications are formed. This phenomenon has been intensively studied in e.g. clay suspensions and printing inks (2,3).

The attractive forces keeping the network intact are weak and the network can be disturbed by slight stirring. However, the old situation can be re-estab-