Petroleum and Coal

PREPARATION OF SORBITOL PALMITATE BY ORGANIC CATALYSIS AND ITS APPLICATION FOR BASE OIL STABILIZATION

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Abstract

Esters are excellent lubricants and high performance industrial fluids, but they are often costly. We prepared the ester sorbitol palmitate via an inexpensive phase-transfer catalysis method as an additive for the retardation of oil oxidation. The effects of the sorbitan palmitate content on the lubricant properties and oxidation stability of a base oil were determined. The addition of sorbitan palmitate to the oil retarded oxidation and enhanced the pour point depression. A novel method for inhibiting oxidation through the action of micellar cores was suggested. This micellar inhibition offers a new concept for the protection of lubricants against oxidative degradation.

Keywords: *Hydrocarbon; Oxidation; Alkylation; Esterification; Wear.*

1. Introduction

Esters are widely used as lubricants and high performance industrial fluids. They are characterized by good biodegradability, low volatility, good lubricity, good thermal stability, and low pour points [1]. Ester oils are now used in many applications, including as automotive engine oils, hydraulic fluids, and compressor oils [2]. The antiwear and antifriction characteristics of alkyl octadecenoates increase with an increase in the number of polar linkages in the alkyl octadecenoate backbone. This is primarily due to the increase in a number of sites amenable to chemisorption on the surface and, consequently, their reactivity. The antiwear and antifriction characteristics of derivatives of ethyl octadecenoates are inferior to the corresponding methyl 12-hydroxyoctadecenoate derivatives. This can be attributed to the increased reactivity of the latter at surfaces due to the additional hydroxyl moiety [3].

The properties of a non-ionic surfactant are related to its chemical structure. In particular, the structure of its hydrophobic and hydrophilic groups and their interactions are of great importance. The oxidative stability of lubricating oil has a critical influence on its performance during service. In this paper, the non-ionic surfactant sorbitan palmitate (SPT) was prepared by phase-transfer catalysis, and its physicochemical (e.g., cloud point, critical micelle concentration (CMC) [4-5] and performance properties [6] as an antioxidant were investigated.

Ester oils are typically prepared by alcoholysis reactions catalysed by simple inorganic compounds [7]. Transesterification can be catalysed by both acids and bases, with the latter usually proceeding at much faster rates [7]. Aqueous solutions of sodium alkanoates will react with alkyl halides in a second phase provided an amine is added as a catalyst [8-9]. Hennis *et al.* [9] showed that the catalyst must have at least one moderately long alkyl group to function well. The poor nucleophilicity of acetate ion toward various substrates in condensed systems has been attributed to a combination of polarizability, basicity, and solvation factors. Liotta *et al.* [10] reported that the acetate ion, solubilized as the potassium salt in acetonitrile or benzene containing 18-crown-6, becomes sufficiently nucleophilic to react smoothly and quantitatively, even at room temperature, with a wide variety of organic substrates. Because of the cost of

some esterification methods, we explored a phase-transfer catalysis approach for the preparation of SPT.

The aim of this work was to study the preparation and performance of SPT as an additive which can act as an antioxidant and affect the pour and cloud points for a base oil. SPT was added to the base oil in different concentrations, and its antioxidant activity was evaluated as a function of time. The degradation of the oil was monitored by total acid formation. A mechanism of action based on the formation of micelles and micellar inhibition of radical propagation was suggested. The oxidation stability of the lubricating oil was largely affected by the sulfur and aromatic hydrocarbon concentration in the oil, with an increased sulfur content leading to increased oxidative stability. The prepared compounds gave higher oxidation stability than imported compound (IRGANOX® L 135, Ciba) [11].

2. Experimental

2.1. Base oil sample

The physicochemical properties of the base oil are listed in Table 1.

Table 1. Physicochemical properties of the base oil

Property	Base oil	Test
Density (g/mL) at 15.5°C	0.8918	D. 1298
Refractive index (nD20)	1.4945	D. 1218
ASTM colour	4.5	D. 1500
Kinematic viscosity (cSt)		D. 445
at 40°C	18.56	
at 100°C	27.15	
Pour point (°C)	12	ASTM D 97
Molecular weight (g/mol)	450	GPC
Total paraffinic content (wt%)	61.353	Urea adduction [7]
Carbon residue content (wt%)	1.5	ASTM D524
Ash content (wt%)	0.0311	ASTM D482
Naphthenes (wt%)	24.49	ASTM 3238/85
Aromatics (wt%)	9.51	ASTM 3238/85

2.2. Preparation of the additive by phase-transfer catalysis

Method 1. Anhydrous aluminium chloride (1 mol) was added with stirring over 1 h to 1-chloropalmitoyl chloride (1 mol) in CCl_4 (100 mL). The reaction temperature was kept at 20°C, and stirring was continued for another hour to form the aluminium chloride complex. Sorbitan (0.1 mol) was condensed with palmitoyl chloride (0.6 mol) in a three-necked flask in the presence of tetraethylammonium bromide (0.01 g) as a phase-transfer catalyst. The reaction mixture was heated with continuous stirring until the theoretical amount of water was collected. The product was purified by washing with a hot solution of 5% sodium carbonate and was then dissolved in petroleum ether (b.p. 40–60°C). The sorbitol palmitate was completely characterized by IR, ^1H NMR, and mass spectroscopy.

The esters can be also prepared from haloalkanes by phase-transfer catalysis (ptc), as follows: A mixture of 1-bromohexadecane (0.25 mol), sodium acetate trihydrate (0.2 mol), and tetraethylammonium bromide (1 g) was heated at 105°C with vigorous stirring for 1 h. Then, water (300 mL) was added, the organic layer was separated and dried over anhydrous Na_2SO_4, and 1-hexadecyl acetate was recovered in 97% yield.

Method 2. The transesterification of methyl palmitate with 1-sorbiton was catalysed by calcium oxide. The ester was charged with the 1-sorbiton complex in a glass reactor equipped with a Dean-Stark trap. Methanol was removed by azeotropic distillation with isooctane, as per the following equation:

Methyl palmitate + 0.1 Sorbitan → Sorbitan palmitate ($C_{22}H_{42}O_6$) (SPT) + CH_3OH

2.3. Oxidation stability study

The oxidation tests were carried out at 120°C according to the ASTM D 943 standard method. The base stock sample was subjected to oxidation with pure oxygen at a flow rate of 0.1 L/h for a maximum of 70 h. The SPT additive was added in different concentrations (from 1×10^{-6} to 1×10^{-3} mol/L). The viscosity, pour point depression, and total acid number was determined.

3. Results and discussion

The successful preparation of SPT was confirmed by IR and NMR spectroscopy (Fig. 1). In the IR spectrum characteristic CH_2 and CH_3 stretching bands at 2916–2860 cm^{-1} is observed, as is a band at 1750 cm^{-1} typical for a carbonyl group. The molecular weight was confirmed by mass spectroscopy, with the product affording a parent ion at *m/z* 402.5. The melting point is 47°C.
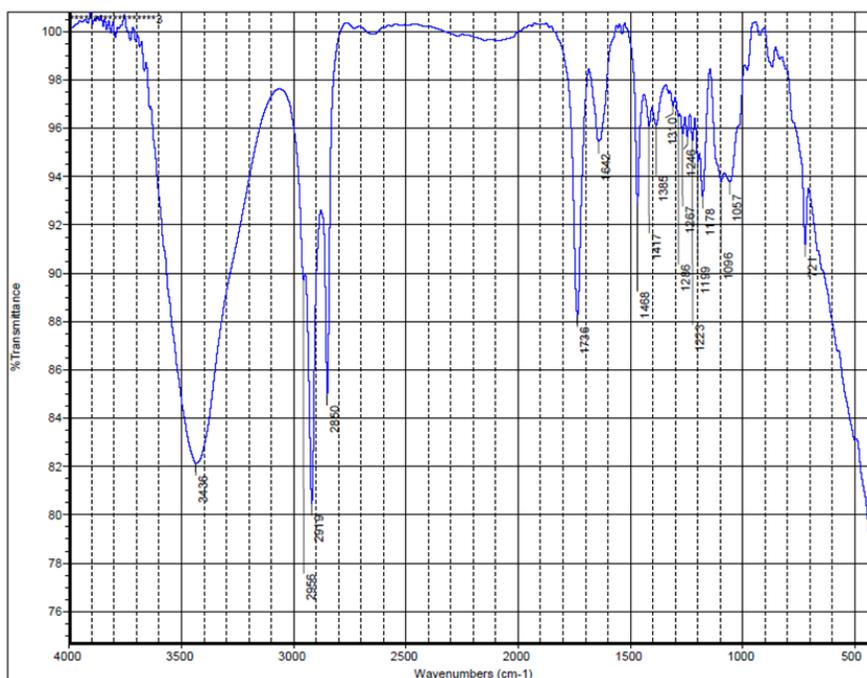

Figure 1. IR spectrum of the prepared compound

The synthesis conditions for SPT were probed by studying the rate of product formation as a function of the catalyst loading. The preparation of SPT from alkyl carboxylates depends on the rate of quaternization relative halides and aqueous sodium (Figure 2).

According to Hennis *et al.* [9], the rate can be determined according to the following:

$$N(Et)_4\, Br \; + \; R\text{-}X \quad \text{--------------}^K\text{---} \quad (Et)_3N^+RX^-$$
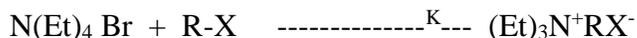
$$(Et)_3N^+RX^-/dt = \; K[(Et)_3N/RX]$$

3.1. Evaluation of SPT as a pour and cloud point depressant and a flow improver for the base oil

Figures 3 and 4 present the data for the changes in the pour and cloud points as a function of the SPT additive concentration. The additive clearly depresses both the pour and cloud points. This indicates that SPT prevents aggregation of the wax nuclei, but the value is nearly equal to the critical micelle concentration (CMC) in the oil phase (5×10^{-5} mol/L). Thus, the additive disperses the wax molecules and disrupts the formation of aggregates, in accordance

with the findings in a previous report [11]. The onset of the effect is observed at a concentration below the critical micelle concentration (CMC) and reaches a maximum at the CMC. Further increases in the concentration of the additive lead to the reversal of its adsorption orientation, as confirmed by Omar and Khidr [12].
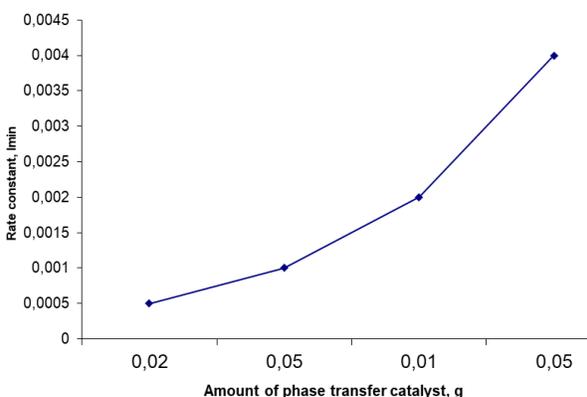
Figure 2. Relationship between the esterification rate and concentration of the phase transfer catalyst
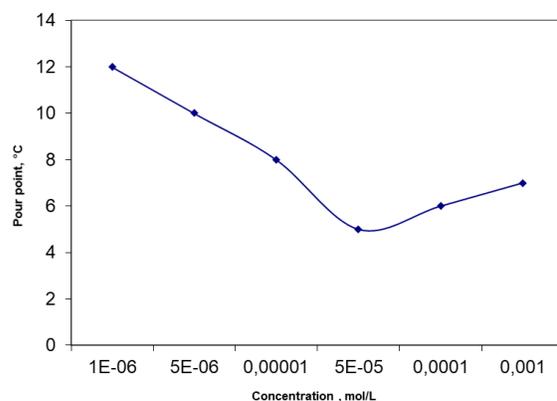
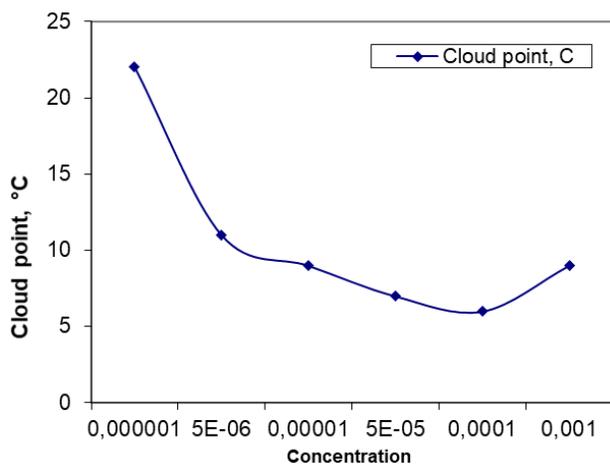Figure 3. Effect of SPT concentration on pour point (°C)

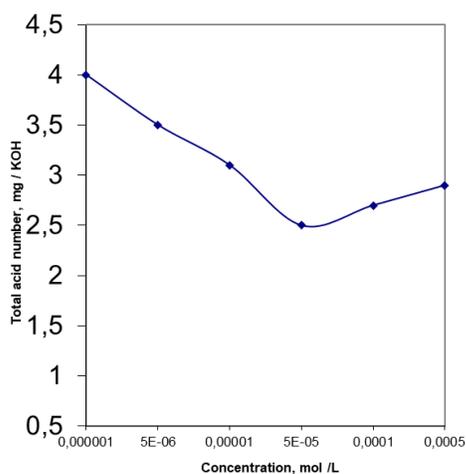Figure 4. Effect of SPT concentration on cloud point (°C)

Figure 5. Effect of SPT concentration on total acid number after 72 h

There is a good relationship between the oxidation stability of an oil and its viscosity. The oxidation behaviour of the oil was studied by oxidizing it at 120°C and determining the total acid number at different times, whereas the viscosity was determined at 100°C. The results in Table 1 show that the viscosity and total acid number increase slightly over time during oxidation. These data confirm that the addition of SPT retards hydrocarbon degradation and the increasing of the oil viscosity with time. Thus, SPT increases the oil's stability toward oxidation and extends its lifetime. These results can be clearly observed in Figure 5. From this diagram, the addition of the additive to the oil retards the increase in the total acid number through oxidation. The best results are obtained at 5×10^{-5} mol/L (the CMC of the additive).

To explain these results, the author suggests a concept of revised micelle formation during hydrocarbon oxidation. The formation of micelles and their aggregation may take part in the oxidation process by inhibiting the chain propagation of the alkoxy free radicals R−O˙. The author believes that the micelles have cores in which the alkoxy free radicals are trapped. This means that the radicals that form oxidatively lose their ability to attack other species. Moreover, increasing the concentration of the additive does not change the degree of oxidation stability. It can be suggested that the possibility of micelle to aggregates or destruct of micelle lead to a free molecule of this additive tend to adsorbed at oil interface. This mechanism

implies that before an additive is added into oil, the critical value of micellization must be determined. This work agrees with early research by the author [11].

To elaborate on this concept, further work will be needed to calculate the aggregation number of the micelles and their geometry at the oil interface. Moreover, the effects of non-ionic polymers on the degree of stability of the micelles, which can have a predominant role in oxidation processes, should be studied.

4. Conclusion

The mechanism of action for sorbitan palmitate as a multifunctional additive for the modification of the pour and cloud points and viscosity improver for a base oil was examined. The efficiency of this additive depends on its critical micelle concentration. The micelle cores act as traps for hydrocarbon oxide radicals in which to terminate hydrocarbon oxidation chains. The micellar inhibition depends on the incorporation of hydroperoxide or other polar oxygen-containing molecules in the reversed micelle, as the results revealed the increased oxidation stability of the oil. This information may be useful in further efficiency improvements for antioxidant additives.

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