LINEAR SULFONATE DETERGENTS AS POUR POINT DEPRESSANTS

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SUMMARY
Oil-soluble metallic sulfonate detergents have been extensively used in automobile lubricants to keep engines clean and extend their useful life. Calcium alkylbenzene sulfonate is widely used in the lubricant industry as a detergent. However, we discovered that only linear sulfonate detergents have the ability to play another role in lubricants, i.e., to depress the pour point of mineral oils. We have studied the relationship between the molecular structures of sulfonate detergents and pour point depression ability and found that in order for a sulfonate detergent to be a pour point depressant, it must have a linear hydrocarbon tail. Other factors, such as the metal type, e.g. Ca or Mg, and the degree of overbasing, are not critical for pour point depression activity. We propose a model to explain why sulfonate detergents with linear hydrocarbon tails can function as pour point depressants.

Keywords: sulfonate detergent, pour point depression, engine lubrication, oscillatory rheometry

1 INTRODUCTION
Oil-soluble metallic sulfonate detergents have been extensively used in automobile lubricants to keep engines clean and extend their useful life [1]. Calcium alkylbenzene sulfonate (ABS), like most other lubricant additives, contains a polar, hydrophilic head and a long, non-polar, hydrophobic tail. They form reversed micelles in oil and are capable of solving oil-insoluble polar degradation products, which would otherwise form deposits in the engine. The non-polar, hydrophobic tail is usually an alkyl group ranging from C10 to C24. ABS can be considered either “branched” or “linear”, depending upon the linearity of the alkyl side chain. The polar head group consists of a metal salt of a sulfonic acid. The most common metals are calcium and magnesium. If metal hydroxide, carbonate, or similar species are associated with the sulfonate portion of the molecule, the sulfonate is said to be “overbased”. Otherwise it is “neutral” or “low base”. Overbased detergents are able to neutralize acidic combustion and oxidation products in the motor oil, and hence, control rust, corrosion, and resinous build-up in the engine [2, 3].

In addition to the traditional application of ABS as a lubricant detergent, its ability to play another role in lubricants has been explored. For example, it has been shown that olefinic sulfonate with a C20–C30 alkyl chain can be used as a pour point depressant [4]. However, the investigation of a sulfonate’s ability as a pour point depressant was limited to alkaline salt and simple base oil mixtures. During the course of a study to determine how various alkylbenzene sulfonate detergents interact with other lubricant additive components, we discovered that alkylbenzene sulfonate detergents’ pour point depression property is not limited only to alkaline sulfonate. Certain alkaline earth sulfonate detergents also possess the ability to depress the pour point of mineral oils. The pour point depression ability is maintained even in the complex fully formulated lubricants.

Using the ASTM D 97 [5] method of pour point determination and oscillatory rheometry (OR), we have studied the pour point depression activity of different types of sulfonate detergents and investigated how the pour point depression activity is affected by the metal type, the level of overbasing, and the structure of the hydrocarbon tail.

2 EXPERIMENTAL
The detergents used in this study are commercial ABS and their molecular structures are shown in Table 1. The table includes (1) Detergent A, an overbased calcium sulfonate detergent with a linear R1 group derived from α-olefin, (2) Detergent B, a neutral version of Detergent A, (3) Detergent C, an overbased magnesium version of Detergent A, (4) Detergent D, an overbased calcium sulfonate detergent with a branched R2 group made from polypropene, (5) Detergent E, a neutral calcium sulfonate detergent with branched R3 group derived from a natural petroleum fraction, and (6) Compound F, the linear alkylbenzene, which, after sulfonated, is used to make “linear” Detergents A, B and C.

![Table 1. The detergents and the precursor compound](image)

R1: \( \underset{n}{\overset{\text{linear}}{\underset{\text{n}=10\ to\ 24}{\text{C}}}} \)
R2: \( \underset{n}{\overset{\text{branched}}{\underset{\text{n}=10\ to\ 24}{\text{C}}}} \)
R3: “branched” alkyl group
The pour point depression performance of sulfonate detergents was evaluated by pour point measurement to the nearest 3°C according to ASTM D 97 and by oscillatory rheometry (OR). Oscillatory rheometry is a well-established tool in rheology science [6]. Application of OR to characterize engine oil has been demonstrated in the literature [7,8], and we have found that OR could be used to differentiate wax networks from polymer gel [9]. The measurements were carried out with a Paar Physica UDS-200 rheometer at a constant cooling rate of 1 °C/min. All measurements were made using parallel-plate geometry in oscillatory mode with angular frequency 2s⁻¹.

3 RESULTS

3.1 Assessment of PPD performance with oscillatory rheometry

Oscillatory rheometry provides a unique view of pour point depression, as illustrated in Figure 1. The figure shows temperature sweeps for two different oils blended with a Group I base oil. The two oils are Shell 60AL alone and Shell 60AL base oil with 0.2 % PPD (a derivatized alkylmethacrylate/acrylate copolymer). For the Shell 60AL base oil itself, there is a very sharp transition in both G' (elastic modulus) and G” (viscous modulus) curves in a very narrow temperature range (−15 °C to −20 °C). In this sharp transition temperature range G’ and G” increase more than two orders of magnitude. The transition marks the formation of a three-dimensional wax network. On the other hand, the oil system consisting of the base oil with a PPD also shows a similar transition in the same narrow temperature range. However, both G’ and G” are much lower in magnitude at temperatures below the transition temperature compared to the G’ and G” of the pure base oil. The G’ and G” curves remain relatively flat until a second transition that occurs as the base oil treated with a PPD is cooled below −40 °C. The small transition between −15 °C and −20 °C is believed to be the formation of small paraffin crystals. In the absence of PPD, these small paraffin crystals will quickly interact with each other to form a three-dimensional wax network producing high viscous and elastic moduli.

In the presence of a suitable PPD, wax network formation is inhibited and the oil remains in a liquid state with lower viscous and elastic moduli. Below −40 °C, even the oil treated with PPD eventually becomes immobile and both G’ and G” increase sharply. This solidification defines the pour point of the oil. ASTM D 97 pour point measurement indicated that adding 0.2 % PPD to Shell 60AL oil drops the pour point to −45 °C, which is 30 °C lower than the pour point of the base oil itself (−15 °C).

3.2 The pour point depression property of sulfonate detergents

The ability of certain sulfonate detergents to act as pour point depressants was studied by oscillatory rheometry and ASTM D 97 pour point measurements. Each of the detergents listed in Table 1 was blended at 4.43 %wt with RLOP 100N, a Group II base oil. Figure 2a shows that adding Detergent A to a RLOP base oil significantly lowers G’ and G” moduli at temperatures below −10 °C as much as a pour point depressant would, meaning that Detergent A shows the ability to prevent the formation of wax networks. Pour point measurements confirmed the finding shown in Figure 2a. The pour point of the RLOP 100N base oil itself was −18 °C. Adding Detergent A to the RLOP base oil significantly lowers the pour point of the oil. The pour points of the detergent-treated oils become −45 °C.

To test whether the level of overbasing plays a role in pour point depression, we compared the viscoelasticities of the blends containing Detergent A and Detergent B in RLOP 100N base oil. Both Detergent A and Detergent B are linear calcium ABS detergents differing only in their levels of overbasing; Detergent A is highly over-based and Detergent B is neutral. Both oscillatory rheometry and pour point measurements indicate that Detergent B, just like Detergent A, can lower the pour point of base oil.

Detergent C is the magnesium version of Detergent A. It is used in this study to determine the effect of metal type on pour point depressancy. We find that the type of metal of the detergent does not influence the pour point depression ability of ABS. The findings from oscillatory rheometry, again, are consistent with pour point data. The pour point of the oil blend of the RLOP base oil with magnesium ABS is −45 °C, the same as the pour point of the RLOP 100N blended with the Detergent A.
Having shown that the level of overbasing and the type of metal in the sulphonate detergent are not important for the detergent to act as a pour point depressant, we turned our attention to the molecular structure of the non-polar, hydrocarbon tail (R-group). Detergents A, B and C are derived from linear α-olefins, and thus can be expected to be predominantly linear alkylates. On the other hand, the R-group in the Detergent D is derived from polypropene and the R-group in Detergent E is from a natural petroleum fraction, which is known as a “branched” alkyl chain, so both Detergents D and E have non-linear, or “branched” side chains. Figure 2b shows the oscillatory results from the oils blended with “branched” Detergent -D in the RLOP base oil. The RLOP base oil serves as the base line. As the highly overbased, “branched” Detergent D is added to the RLOP base oil, the viscoelasticities of the blends behave like the base oil itself. That means branched sulphonates do not show pour point depression properties. On the other hand, adding linear sulfonate, such as Detergent A to RLOP 100N base oil, significantly improves the low temperature flow properties of the base oil, as though a PPD had been used (see Figure 2a). Therefore, it is the linear structure of the R-group in the sulphonates that allows the detergent molecules to act as pour point depressants. Again, the finding from OR is confirmed by pour point measurement. The pour points of the RLOP base oil plus “branched” detergents D and E are –18 °C and –15 °C, respectively, similar to the pour point of the base oil itself, meaning “branched” detergents are not able to depress the pour point of a mineral oil.

Finally, we should point out that the linear structure of the ABS alkyl group itself, although necessary, is not sufficient to confer pour point depression properties on the component. There is no pour point depression observed when the linear alkylbenzene, the compound F in Table 1, which is the precursor of the linear ABS detergents A, B, and C, is blended into a RLOP base oil. The linear alkylbenzene is not able to prevent three-dimensional wax network formation. The pour point of RLOP blended with the compound F is –15 °C.

### Table 2: The pour point data

<table>
<thead>
<tr>
<th>Oil system</th>
<th>Pour Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grp-I BO</td>
<td>-18</td>
</tr>
<tr>
<td>Grp-I BO + 0.2%PPD</td>
<td>-45</td>
</tr>
<tr>
<td>Grp-II BO</td>
<td>-18</td>
</tr>
<tr>
<td>Grp-II + Det A</td>
<td>-45</td>
</tr>
<tr>
<td>Grp-II + Det B</td>
<td>-48</td>
</tr>
<tr>
<td>Grp-II + Det C</td>
<td>-45</td>
</tr>
<tr>
<td>Grp-II + Det D</td>
<td>-18</td>
</tr>
<tr>
<td>Grp-II + Det E</td>
<td>-15</td>
</tr>
<tr>
<td>Grp-II + Compound F</td>
<td>-15</td>
</tr>
</tbody>
</table>

3.3 The linear ABS detergents used as a PPD in fully formulated oils

The “linear” ABS detergents also depress the pour point of a fully formulated oil, as demonstrated below. Here we blended two SAE 5W-30 oils with same base oils, viscosity index improver and detergent inhibitor (DI) package. The DI package contains “linear” calcium sulphonate detergents (Detergent-A and -B). However, oil-1 contains no PPD and oil-2 contains 0.1 %wt of a polymethacrylate-type PPD. The oscillatory rheometry results of oil-1 (without any PPD) and oil-2 (with a PPD) are shown in Figure 3.

The oscillatory rheometry results reveal that the two blends show very similar temperature-dependent viscous (G") and elastic (G’) moduli. This indicates that without adding a PPD, the oil-1 is still able to achieve good low temperature flow properties like those of oil-2 with a PPD.

The findings here are further confirmed by data from Mini Rotary Viscometer (MRV) measurements [10]. The TP-1 pumping viscosity of the oil-1 is remarkably low at 31,000 mP/s (-35 °C) with no yield stress, considering that it has no PPD. On the other hand, the MRV TP-1 viscosity of oil-2 is 29,400 mP/s at –35 °C with no yield stress. It is normally impossible for oil to achieve such low MRV TP-1 viscosity without a PPD.

It is noteworthy that the pour point depressant property of ABS detergents with a linear alkyl group is relatively robust across base oil groups. A DI package was prepared incorporating detergents A and B. The MRV TP-1, pour point measurement and oscillatory rheometry results reveal good low temperature properties for the blends of the DI in Group I and Group II base oils.

4 DISCUSSION

Base oil produced from petroleum refining processes contains small amounts of paraffin molecules. At low temperatures, these paraffins (n-alkanes) are relatively insoluble and come out of solution as wax crystals [11]. Under undisturbed conditions, the paraffin crystals grow into three-dimensional interlocking networks, which can trap a substantial amount of oil in the interstices and inhibit oil flow [2, 3]. Wax formation can cause oil to be unpumpable on startup in the automobile engine, resulting in a catastrophic engine failure.

Pour point depressants act to lower the pour point of a mineral oil through interfering with the formation of
three-dimensional wax networks [2]. As the temperature of the oil decreases below the paraffin saturation temperature, supersaturated paraffin molecules form crystal nuclei. In the absence of a PPD, other molecules of paraffin will accumulate on the nuclei, building large, irregular structures that entangle with each other, trapping oil into an ever more rigid matrix. Eventually the mixture solidifies into a wax state. There is evidence that PPDs can lower the temperature at which nuclei are formed [12], reduce the amount of crystalline wax [13], and finally, prevent the nuclei from growing and aggregating. The activity of a PPD depends on having part of its linear, non-polar structure interact or co-crystallize with the wax molecules, while the polar or otherwise non-wax like portion disrupts the building of aggregates. Commercial pour point depressants (PPDs) include derivatized alkyl methacrylate/acrylate copolymers, olefin copolymers, vinyl ester copolymers, alkylated polystyrene, esters from maleic anhydride copolymers, and finally, prevent the nuclei from growing and aggregating. The activity of a PPD depends on having part of its linear, non-polar structure interact or co-crystallize with the wax molecules, while the polar or otherwise non-wax like portion disrupts the building of aggregates. Commercial pour point depressants (PPDs) include derivatized alkyl methacrylate/acrylate copolymers, olefin copolymers, vinyl ester copolymers, alkylated polystyrene, esters from maleic anhydride copolymers with styrene and alkylated naphthalenes. Polymethacrylates (PMA) are the most commonly used pour point depressants in the lubricant industry [2, 3]. All pour point depressants have common structural features: they are polymers with a broad molecular weight distribution. They contain a mixture of linear alkyl chains 4 to 25 carbon atoms long with a polar component, through which they are attached to a polymer backbone [14]. Figure 4 compares the structure of ABS detergents with a typical polymethacrylate PPD. It is not unreasonable to envision that the linear alkyl group of the ABS has the capability to interact with wax molecules in the oil, in a manner similar to the side chains of a polymethacrylate PPD. The “soap” structure of the detergent, then, prevents the formation of three-dimensional wax networks in the oil. The ABS with a branched side chain, however, cannot interact with the wax molecules.

5 CONCLUSIONS

We report that alkylbenzene sulfonate detergents having linear hydrocarbon side chains can act as pour point depressants in oils. The type of metal cation and level of overbasing do not affect the pour-point depressing ability. The structure of the non-polar hydrocarbon tail is, however, a critical factor. A linear hydrocarbon group is necessary for the ABS detergents to associate with wax molecules in the oil. The sulfonate functional group and incorporated CaCO₃ then serve to disrupt the aggregation of wax molecules into three-dimensional networks that cause the oil to solidify. The ABS detergents can be thought of as structurally analogous to PMA PPDs. Linear ABS detergents can depress the pour points of both Group I and Group II oils alone and also in the presence of the other DI components that make up of a fully formulated SAE multi-grade oil.

6 REFERENCES


