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Simulated aging of lubricant oils by chemometric treatment of infrared spectra: Potential antioxidant properties of sulfur structures

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ABSTRACT

Lubricant oils are complex mixtures of base oils and additives. The evolution of their performance over time strongly depends on its resistance to thermal oxidation. Sulfur compounds revealed interesting antioxidant properties. This study presents a method to evaluate the lubricant oil oxidation. Two samples, a synthetic and a paraffinic base oils, were tested pure and supplemented with seven different sulfur compounds. An aging cell adapted to a Fourier Transform InfraRed (FT-IR) spectrometer allows the continuous and direct analysis of the oxidative aging of base oils. Two approaches were applied to study the oxidation/anti-oxidation phenomena.

The first one leads to define a new oxidative spectroscopic index based on a reduced spectral range where the modifications have been noticed (from 3050 to 2750 cm^{-1}). The second method is based on chemometric treatments of whole spectra (from 4000 to 400 cm^{-1}) to extract underlying information. A SIMPLe-to-use Interactive Self Modeling Analysis (SIMPLISMA) method has been used to identify more precisely the chemical species produced or degraded during the thermal treatment and to follow their evolution. Pure spectra of different species present in oil were obtained without prior information of their existence. The interest of this tool is to supply relative quantitative information reflecting evolution of the relative abundance of the different products over thermal aging. Results obtained by these two ways have been compared to estimate their concordance.

1. Introduction

Among many requirements, car manufacturers aim to space the engine oil drain interval. Lubricating oils are composed of base oils supplemented with 1–30% of additives to improve their quality. They protect against corrosion, reduce damages of moving parts in engine and ease their actuation. To insure the performance and an appropriate lifetime of engines, lubricants have to be protected against aging, which is one of the major causes of oil degradation.

The stability of a lubricant regarding to the thermal and mechanic tension is mainly due to the stability of base oil [1]. Their resistance to oxidation is influenced by the nature of their hydrocarbon constituents and non-hydrocarbon ones [2]. Very small internal and environmental variations may cause major modifications in physicochemical behavior of lubricant. The influence of each component on lubricant stability is fundamental for the formulation of this lubricant. For example, the oxidation of paraffinic compounds begins slowly during the induction period then the oxidation rate increases autocatalytically [3], while aromatics compounds decrease the hydrocarbon oxidation. Their ramifications increase their resistance to oxidation. Burn and Greig [4] have shown that when the aromatic and heterocyclic (A+H) fraction in a lubricant increases a minimum amount of natural sulfur compounds is required to conduce an antioxidant action of the aromatic compounds.

In addition, Ahmad et al. [5] have shown that sulfides (as dialkylsulfides, alkylarylsulfide and diarylsulfide) were better antioxidants than mercaptans, themselves better than thiophenes. Moreover, at 0.5% (w/w) of sulfide, the resistance to oxidation of lubricant increases between 0.5 and 3% the oil inhibition level is constant.

Several researches have highlighted the natural antioxidant character of sulfur compounds naturally present in base oils [6–9]. However, the structures of these antioxidants are not well known.

The aim of this study is to determine the antioxidant behavior of several sulfur compounds on two base oils. This study was

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achieved with an original Fourier Transform Infrared method using a simulating aging cell. Many kinetics of aging were carried out using different sulfur compounds at several concentrations in order to determine which compounds could be responsible for a natural inhibition of base oils and limits of inhibition with increasing concentration were defined.

A SIMPLe-to-use Interactive Self Modeling Analysis (SIMPLISMA) approach has been used to define chemical species involved during the aging treatment and to follow their evolution [10–12]. Pure spectra of some species were identified without prior information of their existence. The aim of this method is to get relative quantitative information explaining the evolution in time of the relative concentration of the different species during the thermal process.

2. Material and methods

2.1. Sampling

2.1.1. Base oils

Two base oils were chosen among samples available in the laboratory, according to their composition. The first one, oil A, which is synthetic poly-α-olefin base oil containing only paraffinic compounds, was used to study the action of sulfur compounds on paraffins, i.e., long aliphatic chains.

The second one, oil B, is a hydrotreated base oil without aromatic compounds containing paraffinic compounds and about 30% of naphtenic compounds, was selected to reveal the role of naphtenic compounds in the phenomenon of oil inhibition by sulfur compounds. This base oil presents a density of 0.854, a vicosity index (VI) equal to 98 and contains 5 ppm of sulfur.

2.1.2. Sulfur structures

Seven compounds (Sigma-Aldrich) were chosen as sulfur structures susceptible to be present in mineral base oils as following [4]:

- hexadecyl mercaptan (M), with a long aliphatic chain,
- dibutyl sulfide (DBut) with a short aliphatic chain, and didodecyl sulfide (DD), with long chain, were chosen to determine the effect of the chain length on antioxidant effect,
- two aromatic structures: diphenyl sulfide (DPh) and dibenzyl sulfide (DBZ), to study the influence of a methylene group in steric hindrance between aromatic groups.
- thiophene (T) and dibenzothiophene (DBT) chosen to evaluate the effect of the hydrogen in the α position and the influence of the stabilization resonance of aromatic groups.

2.2. Infrared spectroscopy

FTIR spectra were performed on a Nicolet Protégé 460 spectrometer coupled with a Nicolet Nic-Plan infrared microscope fitted with a MCT detector cooled with liquid nitrogen. The standard analytical conditions were, 15 × infrared objective, beam size of $100 \times 100\ \mu m^2$. The spectra were acquired using Omnic Nicolet software. 64 scans of symmetrical interferograms were averaged and the spectrum was calculated from 2000 to 850 cm^{-1} at 4 cm^{-1} spectral resolution.

Ageing tests were performed with an ageing cell that had been initially developed in our laboratory to study the structural evolution of liquid fossil organic material [13] during ageing. It allows working in a horizontal geometry decreasing crop of fluids under regulated thermo-oxidizing conditions. To study the resistance to oxidation of base oils of different groups, this cell has been used with some modifications.

The oil sample was “trapped” in a 1 mm deep cavity (diameter 0.5 mm) in a NaCl window (13 mm × 2 mm) machined so that it was possible to collect a background spectrum at any time in a smaller cavity (diameter: 0.5 mm) that did not contain the sample.

6 mg of oil was placed in the 5 mm diameter cavity of the NaCl window and heated from 22 °C up to 170 °C under neutral gas at 11 °C min^{-1}. Then, heating was maintained at 170 °C under oxidant gas (synthetic air) during all the experiment. Spectra were collected every 2 min during the oxidation process.

Aging of samples was followed by calculating a spectroscopic index, from band areas measured from valley to valley [14–17]. The band areas were considered rather than the band heights in order to obtain a finer index.

The following areas were defined (Fig. 1a):

- A1: from 1850 to 1685 cm^{-1} (multiple C=O bands.)
- A2: from 1502 to 1419 cm^{-1} (bands at 1467 and 1450 cm^{-1}.)
- A3: from 1396 to 1369 cm^{-1} (band at 1378 cm^{-1}.)

The carbonyl index is given by the following Eq. (1):

$$I_{C=O} = A1/(A1+A2+A3) \tag{1}$$

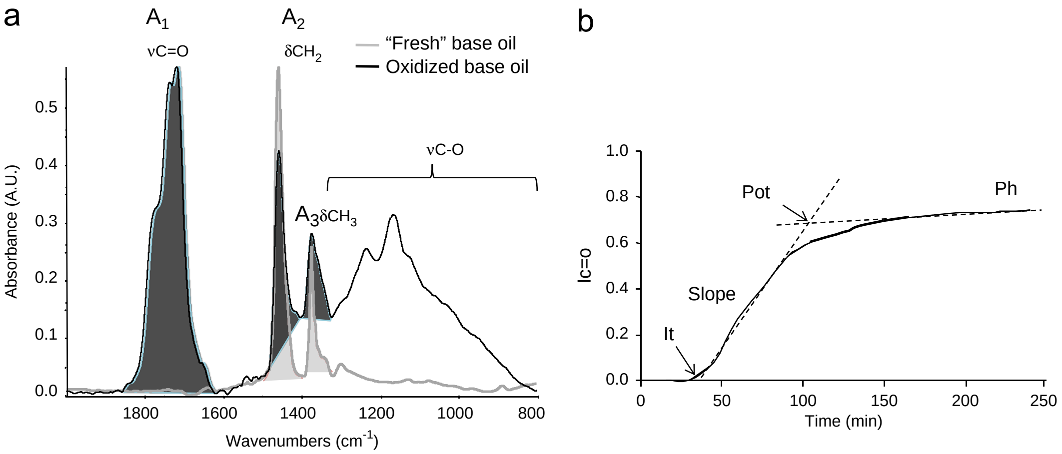

Fig. 1. (a) FTIR spectrum of base oil A before and after oxidation (2000 to 800 cm^{-1}); (b) graphic representation carbonyl index ($I_{C=O}$) versus time of oxidation and the oxidation kinetics parameters. It: induction time; Pot: plateau onset time; Ph: plateau height.

The use of the carbonyl index eliminates the constraints due to the sample thickness and thus to the spectrum intensity. It makes comparing the different tests on the same scale possible.

Kinetics can be interpreted according to four parameters (Fig. 1b):

- Induction time (It): time corresponding to the beginning of the oxidation process.
- Slope: representative of the rate of the oxidation reaction.
- Plateau onset time (Pot): time corresponding to the end of the oxidation.
- Plateau height (Ph): maximum oxidation rate.

2.3. Chemometrics

The method used for self-modeling mixture analysis is the SIMPLISMA approach described in the literature. This interactive method [18,19] is used for self-modeling mixture analysis by resolving mixture data in pure component spectra and concentrations profiles without prior information about the mixture. When overlapping spectral features are present in spectroscopic data, this tool is unable to resolve broad spectral components and separates spectral absorption bands characterizing one component. Its concept is based on the determination of pure variables (e.g., a wavelength or a wavenumber in spectroscopic terms) that have contributions from only one component. In mathematical terms, pure variable is a variable with the maximum ratio of the standard deviation to the mean. This ratio, called as purity, is given by the following expression:

$$P_{ij} = W_{ij}\left(\sigma_i / (\mu_i + \alpha)\right) \tag{2}$$

P_{ij} is the purity value of the variable (i is the variable index), from which the jth pure variable will be selected. μ_i and σ_i represent the mean and the standard deviation of the variable i respectively. The constant α is added to give pure variables with a low mean value (i.e., in the noise range) a lower purity value P_{ij}. The weight factor W_{ij} is a determinant-based function that corrects for previously chosen pure variables. The value of W_{ij} also depends on the value of α. The purity values are represented in the form of spectra. Along with the purity spectrum, the standard deviation spectrum is available, described by:

$$S_{ij} = W_{ij} \times \sigma_i \tag{3}$$

This spectrum has more similarities with the original spectra and is used to facilitate the validation of pure variables. The interactive process enables to guide the pure variable selection by changing the value of α in combination with the option to exclude some spectral ranges for the selection of pure variables. This ability is especially useful since pure variables may describe unwanted features in the dataset. As a result, intensity of the pure variable can be considered as proportional to a contribution or a relative “concentration” of that component in the mixture. When pure variables have been determined by iterations procedure with the maximum ratio (called purity) of standard deviation to mean intensity of each spectrum, the original dataset can be resolved into pure components and their contributions in the original mixture spectra. The task of the mixture analysis is to express the dataset as a product of a matrix containing relative concentrations and a matrix with spectra of pure components:

$$\mathrm{D} = \mathrm{C} \times \mathrm{P}^T + E \tag{4}$$

D is the matrix with the original data with spectra in rows. Its size is cv, where c is the number of case (spectra) and v the number of variables (wavenumbers). The matrix C (size cn, where n is the number of pure components) contains concentrations of the pure components in the mixture. The matrix P (size nv) contains the resolved spectra. P^T represents the transpose of P and E, the residual error. Typically, D exists, but C and P are not known. When matrices D and C are known through the SIMPLISMA algorithm, the estimate of the pure spectra $\hat{\mathrm{P}}$ can be calculated by standard matrix algebra.

$$\hat{\mathrm{P}} = \mathrm{D}^T C (C^T C)^{-1} \tag{5}$$

In the next step, contributions are calculated from $\hat{\mathrm{P}}$, which is basically a projection of original pure variable intensities in the original dataset. This step reduces the noise in contributions. The equation is

$$C^{*} = \mathrm{D}\hat{P}(\hat{P}^T \hat{P})^{-1}, \tag{6}$$

where C^{*} stands for the projected C.

For more information, Gemperline [20] and Hamilton and Gemperline [21] wrote excellent articles about factor analysis based on mixture analysis. In order to obtain the proper resolution of the mixture data, user interaction is necessary. This requirement is important in order to deal properly with features such as noise, peak shift, and instrument drift [22]. Some applications of SIMPLISMA have already been reported in the literature, i.e., on Fourier transformed Raman spectra of a time-resolved reaction of hydrogen peroxide activation by nitriles [23], analysis of oil petroleum [24], FT-IR microscopy spectra of a polymer laminate, and pyrolysis mass spectra of biomaterials (feedstocks) [25,26].

3. Results and discussion

3.1. Kinetics of pure lubricating oils ageing

The aging cell limits, by the choice of windows used, the spectral range of study, between 2000 and 800 cm^{-1}. Indeed, the upper spectral zone presents a saturated signal while the lower one is very noisy. Fig. 2 shows the spectral evolution during oxidation kinetics of B base oil. Similar profiles are observed after MIR spectra collection of A and B base oils, from the beginning to the end of the aging process. Two bands are characteristic, the first at 1460 cm^{-1} corresponding to $\delta_{as}(CH_3)$ and $\delta_s(CH_2)$, and the second at 1376 cm^{-1} relative to $\delta_s(CH_3)$. Carbonyl area grows up with the aging process around 1700 cm^{-1}, in the same time than another area, corresponding to ν(C–O) around 1100 cm^{-1}. Carbonyl absorption zone is complex, with different characteristic wavenumbers around 1710, 1730 and 1760 cm^{-1}. In their study, [14] highlighted specific absorption of different species that could be observed in carbonyl zone, after spectral deconvolution (acid: 1710 cm^{-1}; ketone: 1718 cm^{-1}; ester: 1735 cm^{-1}; acid anhydrid: 1660 cm^{-1}; lactone: 1770 cm^{-1}). In this study, neither the acid form nor the lactone and anhydrid ones could be properly

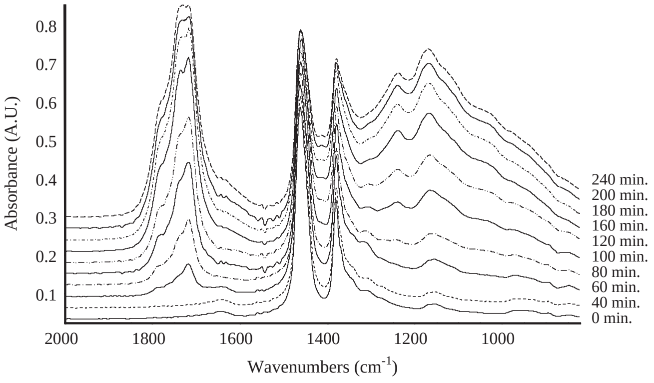

Fig. 2. Spectral superposition from 2000 to 800 cm^{-1} versus time for base oil A.

identified, whereas other species could be observed after spectral deconvolution.

3.2. Results with base oil A

The base oil A was first studied at 170 °C, under an oxidative atmosphere. Graphically, differences between spectra (Fig. 2) appear about 1 h after the beginning of the aging process. The same simulated aging treatment was then applied for each sulfured structure oil added at 0.5% (*w*/*w*) into oil A. To properly compare results, carbonyl index was calculated for each kinetics. Except for sample containing didodecyl sulfide, all curves plotted are similar and oxidation parameters defined were close to those observed during aging of pure oil A.

In the presence of didodecyl sulfide, no oxidation phenomenon occurred, so no oxidation parameter could be defined. Thus, didodecyl sulfide appeared as the only sulfur structure tested acting as an antioxidant, when added at only 0.5% (*w*/*w*) in this synthetic base oil. This is consistent with the results of Qiu et al. [27], which show that that sulfide with long chain has good antioxidant activity, and the antioxidant activity of cyclic sulfides is poor. This compound presents a free radical inhibitor behavior with paraffinic compounds since no increase of baseline was observed during the induction period as described by Maleville et al. [1].

3.3. Results with base oil B

3.3.1. Study with all sulfur compounds

Kinetic parameters of base oil B doped with 0.5% (*w*/*w*) of sulfur compounds are noted in Table 1. Some slight differences are noticeable between results of all kinetics, but are not significant and so hardly interpretable. To confirm these observations, the same study was performed with 3% (*w*/*w*) sulfur compounds added into base oil B. Fig. 3 presents the evolution of *I*c=o index over time for each sample. At this concentration, it is obvious that didodecyl sulfide presents an antioxidant effect, but less important than the one observed when added into base oil A. This is not surprising since synthetic oils are already more resistant to oxidation than mineral oils [28]. Mercaptan also seems to have an antioxidant effect, even if it is lower than the didodecyl one. The other sulfured compounds did not provide any antioxidant effect on base oil B.

3.3.2. Effect of didodecyl sulfide content

Didodecyl sulfide presents a strong antioxidant effect on synthetic base oil (A) and shows an interesting effect, more significant at 3% (*w*/*w*) than at 0.5% (*w*/*w*) on mineral base oil (B). An additional study was carried out on samples containing different contents of didodecyl sulfide (0.5, 1.5, 3, 3.75 and 4.4% (*w*/*w*)) into oil B. Fig. 4 highlights the evolution of the antioxidant effect of didodecyl during aging kinetics. The higher the sulfur content is in oil B, the more the slope decreases and the longer the plateau onset is. Up to a content of 3%, variations of induction time and plateau height seem to be negligible and nonrepresentative of an antioxidant. These parameters are not measurable beyond 3.75% since the oil has not been oxidized. However, for a didodecyl sulfide content equal to 3% and a fortiori beyond, its behavior looks like a hydroperoxide decomposer. Indeed, the induction time remains nearly unchanged, but the slope is reduced. This behavior seems to have been caused by the result from the presence of naphtenics. In base oil A, 0.5% of didodecyl sulfide protects oil from oxidation. By extrapolation, and by assuming that the variation in the composition of paraffins does not influence the reactivity of the sulfur compound, it is possible to consider that 70% of the paraffins composing base oil B were also protected. The only oxidation substrate would therefore be the naphtenics which, by oxidizing, form peroxyl radicals that initiate a free radical chain reaction whose substrate can include paraffins. This can occur either by breaking the cycle or not. Since the latter protected by the sulfur structures, two types of phenomena come into competition: oxidation and inhibition. The consequence of this competition is the reduction of oxidation speed and thus the reduction of slope. Therefore naphtenics play a role of oxidation initiators in presence of sulfur compounds.

Table 1
Oxidation kinetics parameters of oil B with 0.5% (w/w) of sulfur compounds.

Sample	It (min)	Slope	Pot (min)	Ph
B	42	0.0089	122	0.770
M	34	0.0075	124	0.716
DBut	34	0.0077	131	0.784
DD	29	0.0086	113	0.782
DPh	36	0.0069	141	0.753
DBZ	30	0.0095	105	0.775
T	35	0.0100	106	0.790
DBT	12	0.0065	132	0.830

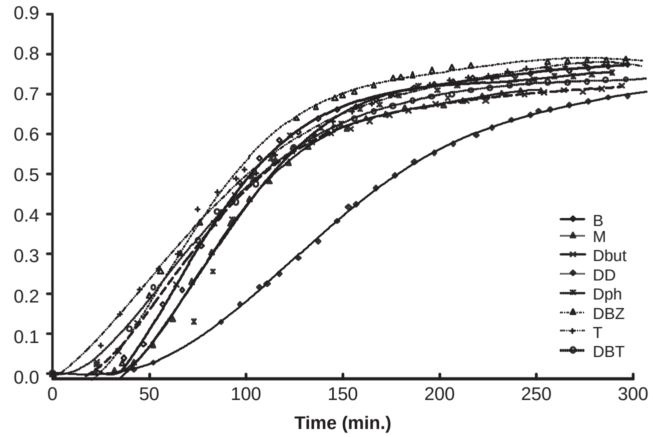

Fig. 3. Progression of Ic=o indexes of oil B with 3% mass of sulfur compounds.

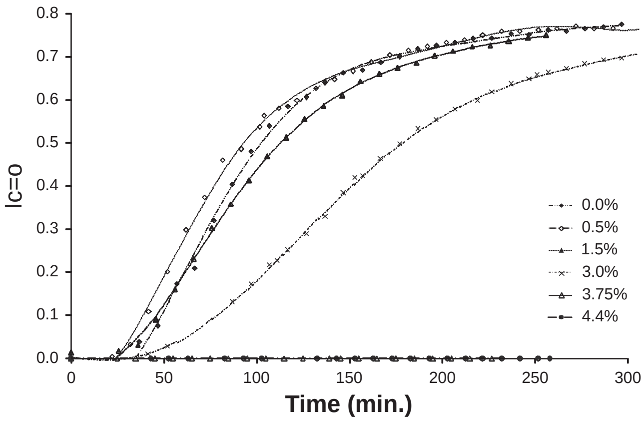

Fig. 4. Progression of Ic=o indexes of oil B with different rates (% w/w) of didodecyl sulfide.

The comparison, one by one of all kinetics, was not sufficient to explain all phenomena, so chemometric treatment of infrared data was performed.

3.4. SIMPLISMA results

Four aging kinetics were chosen to apply the SIMPLISMA method to data collected. Thus, infrared spectra collected during oxidation of base oils A and B, and mixtures with B added with 3%

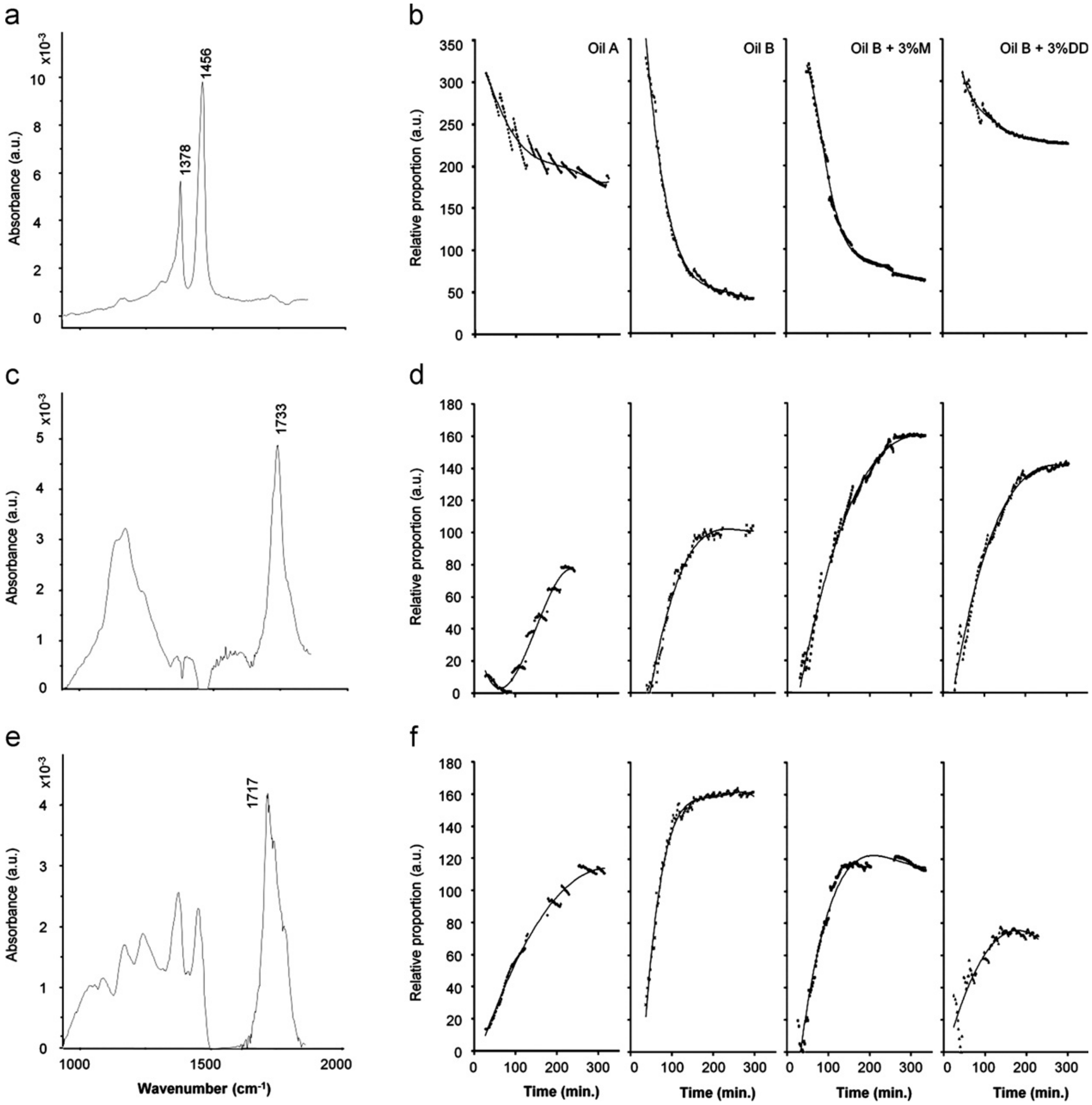

Fig. 5. SIMPLISMA results.

(*w*/*w*) mercaptan and didodecyl sulfide, that seem to have an antioxidant effect, were placed into the same data matrix. All data were considered simultaneously in order to study if degradation products are the same for all kinetics or not and if they present a similar behavior. SIMPLISMA highlighted three different species, with their own concentration profile (Fig. 5).

The first spectrum extracted (Fig. 5a) corresponds to base oil A before any oxidation, with two bands well defined, at 1376 and 1455 cm^{-1}. Its concentration profile (Fig. 5b) shows a decrease of the presence of this specie, which is logical as base oil is present at the beginning and is then oxidized and so become chemically different over time. If plots relative to both pure base oils kinetics are compared, a higher intensity and slope for B results are notable, what means that oxidation is stronger and faster on B than on A.

The second spectrum extracted (Fig. 5c) presents an intense peak at 1732 cm^{-1} and a large absorption band between 1000 and 1300 cm^{-1}, it is attributed to an ester form. Two negative peaks are also specific on this spectrum, located at 1376 and 1455 cm^{-1}, characteristic of the disappearance of base oil along the ageing. Concentration profile relative to this second specie (Fig. 5d) shows that kinetics on samples containing sulfur have a lower rate of oxidation, both with mercaptan and didodecyl sulfide.

The third spectrum (Fig. 5e) presents many peaks of absorption between 1100 cm^{-1} and 1500 cm^{-1} and an intense peak at 1716 cm^{-1} corresponding to an acid form of the structure. Its concentration profile (Fig. 5f) provides many information. First, by comparing the relative abundance of the specie, which is an oxidized product, into the four kinetics studied, it appears that aging is less severe in presence of sulfur compound, in particular with didodecyl sulfide. The appearance of this product seems faster in oil B than in A when they are oxidized and produced in larger amounts.

The addition of didodecyl sulfide induced a slowing down of the oxidation process. Ratio of the species found by SIMPLISMA is different from the one relative to B base oil, with the ester form preferred to the acid one. So, as expected, didodecyl sulfide acts as a hydroperoxide decomposer.

4. Conclusions

Many kinetics were achieved with samples containing different sulfur compounds, in order to highlight those who are responsible for an inhibition effect on base oils.

Two compounds presented an interesting effect, namely sulfur aliphatic compounds, mercaptan and didodecyl sulfide. Added into base oils, mercaptan enables a slower oxidation of lubricant, significant from 3% (*w*/*w*). The most effective sulfur structure among those tested in this study is the didodecyl sulfide. This one makes it possible to considerably slow down the ageing of oil, and even to prevent it during a certain lapse of time, according to the composition of the oil into which it is added. Into base oil A, which is purely paraffinic, it showed an efficient antioxidant effect, since it already prevents oil from any aging degradation when added into oil at 0.5% (*w*/*w*). With base oil B, such a similar effect was visible once didodecyl sulfide concentration reached at least 3.75% (*w*/*w*). This highlighted the effect of the structure on antioxidant activity or not of the compounds. Thus, the presence of hydrogen atoms carried by carbon of sulfur appeared as a determining parameter so that the sulfur compound was antioxidant toward oils, except if this carbon atom belongs to an aromatic cycle. According to the experimental conditions, we can propose two phenomena. Firstly, the maximum concentration used, 4.5% (*w*/*w*), of didodecyl corresponds to the limits of inhibition being able to be brought to oil. Between 3.75 and 4%, the maximum threshold of inhibition is reached.

SIMPLISMA approach highlighted three different species, and their concentration profiles, that are involved into oxidation process of base oils, with or without sulfur compounds. This method has lead to a better understanding of successive steps of the samples aging, from the beginning to the end.

Didodecyl sulfide seems to be able to react on the one hand as an inhibitor of radicals, since it delays the induction time, and on the other hand as a hydroperoxide decomposer, by lowering the slope.

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