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Cyclic voltametry and differential scanning calorimetry of lubricating oils: amine antioxidants

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Abstract

The use of cyclic voltametry for the determination of dioctyldiphenylamine in three different types of lubricating oils has been investigated. The electrochemical measurements were made using a three-electrode configuration with the oils dissolved in a mixture of methylene chloride and tetrabutylammonium perchlorate. The analytical results are obtained from the experimental data using a convolution procedure in which the concentration of the antioxidant is determined from the limiting value of the convoluted current. The results are compared with those obtained from differential scanning calorimetry where the overall oxidative stability is measured.

INTRODUCTION

Both cyclic voltametry (CV) and differential scanning calorimetry (DSC) have been used in the testing of lubricating oils. DSC is particularly well established and refs. 1–5 are representative of the many papers published on its use for assessing oxidative stability. Two techniques have been employed, one is dynamic and the other isothermal. In the former the oil is subjected to a linear programmed temperature rise and the temperature at which oxidation commences is recorded. In the isothermal technique the temperature of the oil is held constant and the time taken for rapid oxidation to commence is measured. In both tests the atmosphere in the apparatus may be air or oxygen either flowing or static. Both tests have their advocates. Vaporisation of volatile components is minimised by the high pressure atmosphere used in the isothermal procedure but no one fixed temperature is suitable for all oils. The presence of a thin film of oil in the typical DSC test has been regarded as a positive advantage bearing in mind the presence of such thin films in the engine. The addition of a catalyst package to the oil under test has been recommended [2] as a further move to reproduce the typical engine environment.

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The emphasis in CV is on the direct determination of the amount of antioxidant present in the oil. This information may be used to obtain an estimate of the useful remaining life of an oil. In this respect it offers an approach complementary to DSC but one in which the determination is specific to a particular type of antioxidant. Substantially less work has been reported using CV compared with that from DSC. Furthermore, little attempt has been made to link the results with those from other test procedures: a feature which has marked much of the early use of thermal analysis. Even so, there are sufficient results [6–11] to indicate the promise of electrochemical technique.

The purpose of the present work is to investigate the use of CV in the determination of the amine antioxidant dioctyldiphenylamine (DODPA) in three types of lubricating oil. Initially the work was directed at establishing a trouble-free procedure. Subsequently the results have been compared with those obtained from DSC. Both techniques are low cost compared with engine tests. The advent of multiple sample equipment has provided a further impetus to the use of DSC. However, in spite of the apparent simplicity of the DSC test the associated chemistry is far from simple. The difficulty encountered with DSC in obtaining reproducible results in interlaboratory testing [12] lends added attraction to the possible use of CV as a technique for oil analysis.

EXPERIMENTAL

Materials

Three base stocks have been used, selected for their different compositions: a synthetic base stock (RTS-9745) made by oligomerisation of dec-1-ene followed by hydrogenation of the product; a mineral oil (BSM-150N) containing a low sulphur North Sea distillate blended with a Middle East cut; a pentaerythritol ester aviation grade base stock (LPE-504). Mixtures of each of the base stocks and the antioxidant DODPA (0.05–2% by weight DODPA) were prepared by shaking the weighed components vigorously for about 1 h. The mixtures were stored in glass bottles in the dark and showed no significant change over the period of the work (about 6 months). The volatility of the base stocks determined by thermogravimetry (TG) was mineral oil $>$ oligomer oil $\gg$ ester oil.

Differential scanning calorimetry

Measurements were made using Du Pont equipment incorporating the DSC cell with base (model 910) and controller (model 990). The instrument signals were captured using a computer (Amstrad PC1640 HD20). The DSC cell was housed in a purpose-built high pressure vessel made of steel, with an integral water-cooled jacket. The base of the vessel was fitted with insulated pins for electrical connections and entry and exit ports for gases. The pipe work for the gases incorporated a safety valve (Nupro type R3A) set at 8350 kPa (1200 lbf in^{-2}) and a connection to a gauge (Matheson calibrated test gauge) which allowed pressure measurements to be made with a resolution of about 20 kPa. The equipment was calibrated in the conventional way using samples of indium, tin, lead and zinc ($>$ 99.999% pure, Goodfellow). The fusion peaks were recorded with an atmosphere of nitrogen in the cell at 3500 kPa (500 lbf in^{-2}) and atmospheric pressure (the pressures used in the subsequent measurements on the oils).

Measurements on the oil samples were made using both the isothermal and dynamic test procedures with an atmosphere of oxygen in the DSC cell. The samples were contained in bright aluminium crucibles (6 mm diameter), pressed to ensure flat bases. The mass of the samples was 2.00 ± 0.05 mg in the isothermal experiments, reduced to 1.00 ± 0.05 mg in the dynamic experiments to avoid ignition of the samples. The samples were added to the crucibles using a narrow glass rod and allowed to spread evenly over the base of the crucible. In the isothermal experiments the samples were heated at 100 K min^{-1} to the fixed temperature and the pressure of oxygen adjusted to maintain 3500 kPa. The induction time was measured from the instant when the sample attained the fixed temperature. In the dynamic experiments the samples were heated at 10 K min^{-1} in flowing oxygen (50 cm^3 min^{-1}) at atmospheric pressure. The onset of oxidation was identified as the point of intersection of the leading edge of the oxidation peak and the base line.

Cyclic voltametry

The apparatus was a jacketed glass vessel fitted with a wide diameter inert plastic lid which accommodated three electrodes, a gas bleed, a water cooled condenser and a thermometer. Water from a thermostat was passed through the jacket. The three electrodes were a reference electrode consisting of a silver wire in a saturated solution of lithium chloride in the electrolyte/solvent mixture, a planar glassy carbon working electrode and a counter electrode consisting of a 1 cm^2 platinum foil. The potential–current–time sweeps were controlled by a potentiostat/galvanostat (model 363) and universal programmer (model 175) made by Princeton Applied Research Corp. The programmer allowed a series of programmes to be specified with single or multiple sweeps at sweep rates from 1 mV s^{-1} to 1000 V s^{-1}. The galvanostat provided a current range from 1 μA to 1 A and was triggered by the programmer to give a triangular wave form. The potential–current–time data were captured as 2000 data points using the Amstrad computer. The maximum rate of data acquisition was 10^4 data points per second.

The successful application of CV requires the closest attention to the experimental technique. Of considerable concern is the choice of solvent. Various mixtures of the following solvents were investigated: acetone; benzene; cyclohexane; dimethylformamide; methylene chloride; pentane; tetrahydrofuran. Methylene chloride was judged to be the most suitable: it readily dissolved the antioxidant and oil; it gave a highly conducting mixture with the electrolyte and had a sufficiently wide voltage window (-1.8 to 1.8 V). The electrolyte was tetrabutylammonium perchlorate and the electrolyte/solvent mixture contained 0.1 mol dm^{-3} in methylene chloride. Solutions containing 2.5–3.5% by weight of the oils in the electrolyte/solvent mixture were used in the experiments, although solutions containing up to 10% oil gave satisfactory results.

Measurements on the electrolyte/solvent mixture identified the potential at which no current passed. This was approximately 0.1 V. Subsequent measurements were made between this potential and $+1.3$ V at 0.5 V s^{-1} both on the electrolyte/solvent mixture and solutions of the oils. It was essential that the apparatus was clean and dry before use if reproducible results were to be obtained. The methylene chloride was dried before use by passing down a column of silica gel. The working electrode was ground with silica paste and washed with solvent before each measurement. Similarly the platinum foil of the counter electrode was heated to red heat to remove adsorbed impurities and washed with solvent. The electrolyte/solvent mixture was deoxygenated before each measurement by passing oxygen-free nitrogen (15 cm^3 min^{-1}) through the mixture in the cell for about 10 min. Vaporisation of the solvent was minimised by passing cold water through the condenser. Measurements were made on freshly prepared solutions of the oils in the electrolyte/solvent mixture: some degradation of the antioxidant occurred in solutions kept for long periods (usually several hours).

RESULTS AND DISCUSSION

A typical cyclic voltamogram for an oil after correcting for the background signal from the electrolyte/solvent mixture is shown in Fig. 1. The peaks represent the electrochemical oxidation of the antioxidant followed by reduction of the product on the return sweep. The mean potential of the peaks is 0.83 V which is approximately the half-wave potential. The concentration of the antioxidant may be derived from the current height of the oxidation peak but the peak height is also a function of the sweep rate, the area of the working electrode and the number of electrons transferred in the electrode process. An alternative procedure is to use a convolution transform of the current i [13] with the function $(\pi t)^{-1/2}$

$$I(t) = i(\pi t)^{-1/2} = \int_0^\infty \frac{i(u)}{\sqrt{\pi(t-u)}}\,\mathrm{d}u \tag{1}$$

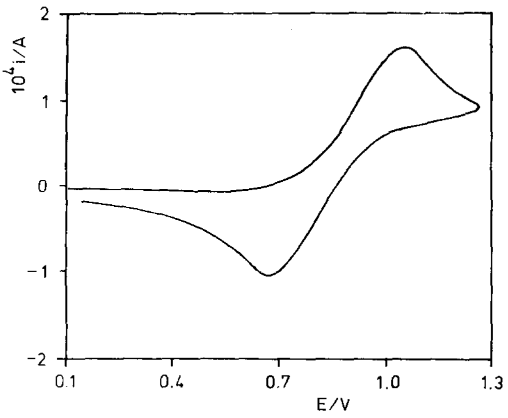

Fig. 1. Cyclic voltamogram for 1.9 wt.% DODPA in the oligomer oil.

where $I(t)$ is the convoluted current at time t. The convolution procedure has the advantage that all the previous data are used in the analysis rather than a single point. Figure 2 shows the transform obtained from the cyclic voltamogram in Fig. 1. The presence of the plateau region in the convoluted current is indicative of a simple electron transfer process but does not preclude subsequent chemical reaction of the products of the electrochemical oxidation. The failure of the convoluted current to return to zero on the return sweep is an indication of such chemical reaction within the time scale of the experiment (5 s). Deconvolution of the data (dI_t/dt) shows that the separation between the peaks representing electrochemical oxidation and reduction is less than 50 mV in keeping with a moderately fast electron transfer process ($k \approx 10^{-4}$ m s^{-1} at 290 K). The width of the oxidation peak at half-height is 105–112 mV which together with the peak

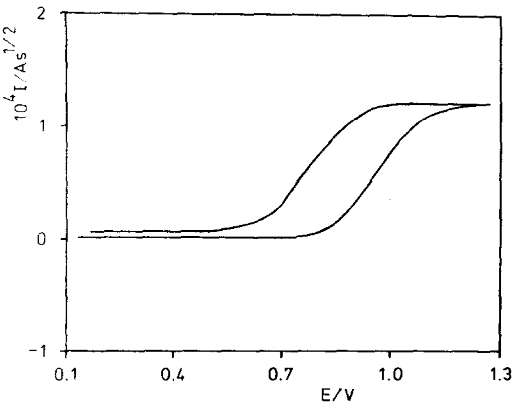

Fig. 2. Transform of the voltamogram shown in Fig. 1.

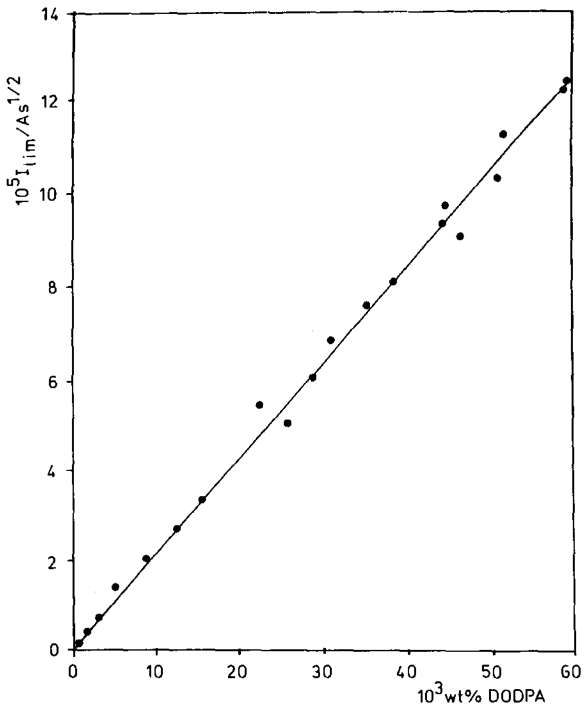

Fig. 3. Relationship between I_{lim} and DODPA (wt.%) in electrolyte/solvent mixture for the mineral oil.

displacement is consistent with a single electron involved in the electrochemical oxidation.

The limiting value of the convoluted current I_{lim} (A $s^{1/2}$) is proportional to the concentration of antioxidant (in the bulk phase) [A] (mol m^{-3})

$$I_{lim} = nFSD^{1/2} [A] \tag{2}$$

where n is the number of electrons in electrode process and F is the Faraday constant (C mol^{-1}), S (m^2) is the surface area of the working electrode and D (m^2 s^{-1}) is the diffusion coefficient of the antioxidant. This relationship is valid even when the products of the electrochemical oxidation undergo chemical reaction. Figure 3 shows the expected linear relationship between I_{lim} and [A] for the mineral oil. For convenience [A] has been expressed as weight per cent in the electrolyte/solvent mixture. Similar results were obtained for the antioxidant dissolved in the other base stocks. The results are summarised in Table 1 and are for measurements at 290 K. The measurements for the three oils (70 determinations) have been combined to give the relationship

$$I_{lim} = (2.05 \pm 0.02) \times 10^{-3} [A] + (1.5 \pm 4.7) \times 10^{-6} \tag{3}$$

TABLE 1

Calibration equations for the determination of DODPA in the base stocks for measurements at 290 K, $I_{\mathrm{lim}} = a[\mathrm{A}] + c$

Base stock	$10^3 a$ (A $s^{1/2}$ wt.%)	$10^6 c$ (A $s^{1/2}$)
Ester	1.95 ± 0.08	2.7 ± 3.2
Mineral	2.07 ± 0.03	2.6 ± 1.2
Oligomer	2.14 ± 0.02	-0.7 ± 3.9

where [A] is in weight per cent, which is the calibration equation for the determination of DODPA in the three base stocks. The calibration is valid for antioxidant concentration ranges 0–0.06 wt.% in the electrolyte/solvent mixture and 0–2.5 wt.% in the oil. The diffusion coefficient calculated from equation (2) assuming n to be unity is $(1.0 \pm 0.1) \times 10^{-9}$ m^2 s^{-1}. The mechanism of the chemical reaction which follows the electrochemical oxidation is likely to be free radical diffusion controlled. The activation energy 11–12 kJ mol^{-1} derived from rate constants measured in experiments at different sweep rates and temperatures is consistent with such a mechanism.

The results for the isothermal DSC experiments are shown in Fig. 4. The temperature of the measurements was ester oil 493 K, mineral oil 483 K and oligomer oil 467 K. The results from the dynamic test showed similar trends with the oxidation temperature reflecting both the relative stability of the base stocks and the enhanced stability afforded by the presence of the antioxidant. The oxidation temperatures for the base stocks were 499 ± 2 K ester, 490 ± 1 K mineral oil and 470 ± 2 K oligomer oil. The oxidation peaks recorded with the oligomer oil and ester oil were well formed whereas those for the mineral oil showed shoulders which in mixtures containing more than 0.3% antioxidant often separated to form pre-peaks. This may reflect the greater complexity of the mineral oil base stock but the shoulders and pre-peaks were irreproducible and induction times and oxidation temperatures were estimated from the onset of the main peak. Simultaneous TG–DTA showed that in the dynamic test a significant fraction of the sample (10% by weight) was vaporised before the onset temperature of the oxidation peak was reached. We found that with the careful choice of temperature the isothermal test gave a better discrimination between samples than the dynamic test. The gradient of the leading edge of the oxidation peak recorded in the isothermal test showed an increase with the addition of antioxidant to the base stocks although overall the peaks became broader. We observed no monatonic relationship between peak area and composition and a substantial but varying amount (50–75% of the initial weight) of a dark brown viscous residue remained at the end of the experiment. In contrast the residue from the dynamic test

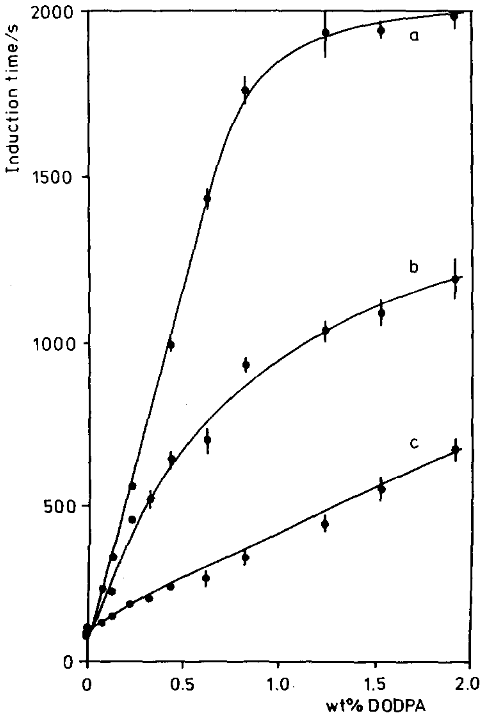

Fig. 4. Induction times measured by isothermal DSC for DODPA (wt.%) in (curve a) ester oil 493 K), (curve b) mineral oil (483 K), (curve c) oligomer oil (467 K).

was a dark brown or black lacquer and weighed less than 10% of the initial weight of the sample. The intrinsic oxidative stability of the base stocks was ester > mineral oil > oligomer, which was reflected in the temperatures used for the isothermal analyses (Fig. 4). The ester base stock showed the most marked increase in stability with the addition of antioxidant.

The temperature–induction-time relationship has been explored for the three base stocks and their mixtures with DODPA. The results show the expected decrease in the induction time as the temperature is increased. Those for the ester base stock are shown in Fig. 5. An alternative approach adopted by a number of authors [3,14,15] is to plot ln t_{ind} against $1/T$ on the grounds that t_{ind}^{-1} is a measure of the rate of reaction during the induction period. Zeman et al. [3] have used such plots to relate ageing times and temperatures. Other authors have derived activation energies from the gradient $\mathrm{d}\ln t_{\text{ind}}/\mathrm{d}T^{-1} = E/R$. If we adopt this approach we obtain the activation energies (kJ mol^{-1}) 170 ± 12 (mineral oil base stock); 70 ± 10 (oligomer base stock); 103 ± 11 (ester base stock). Even with the large experimental errors there is a distinct difference between the results for the three base stocks. The value 170 kJ mol^{-1} for the mineral oil base stock may relate to radical initiation reaction $RH + O_2 = R + HO_2$ and

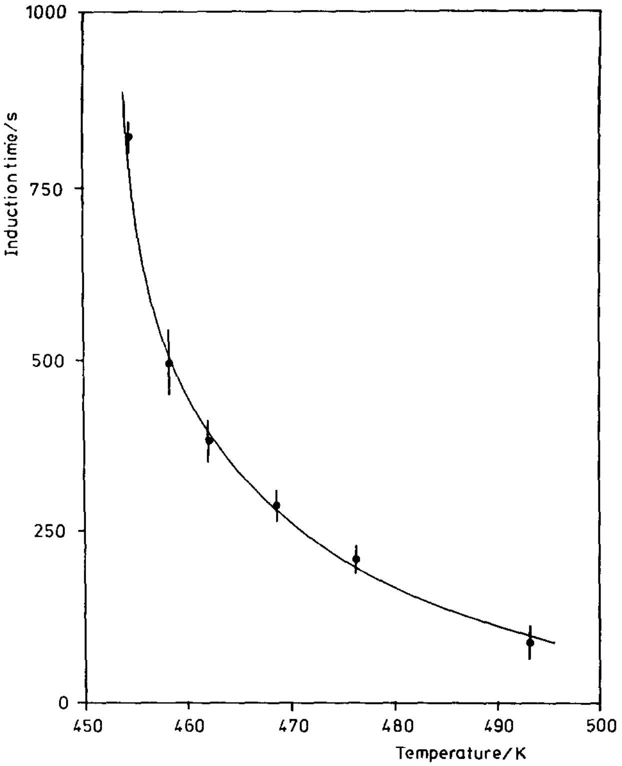

Fig. 5. Dependence of induction time on temperature for the ester base stock.

$RO_2 = RO + OH$ [15]. Whether or not the results for the other base stocks have a straightforward mechanistic significance is open to question. A similar uncertainty exists about the results obtained for mixtures of the base stocks and DODPA (1.5 wt.%). The activation energy obtained for both the mineral oil and oligomer oil was about 130 kJ mol^{-1} whereas the value for the ester oil was unchanged from that of the base stock. Brown et al. [14] have attempted to model the DSC results for a paraffin oil using a simple reaction scheme in which an activation energy of 159 kJ mol^{-1} was derived from the induction time.

The results obtained by DSC underline the singular advantage of the technique in indicating the overall oxidative stability. Differences between the results from DSC and CV emerge in tests on partially oxidised samples of the synthetic oil containing 1.9% DODPA. The partially oxidised samples were prepared by heating the samples in air and daylight at 415 K for up to 168 h. The results from DSC and CV are compared in Fig. 6. The oxidative stability measured by DSC has been expressed as an apparent concentration of DODPA. It initially remains unchanged whereas CV indicates the consumption of antioxidant. Both techniques indicate an eventual levelling off in which the oxidative stability and antioxidant

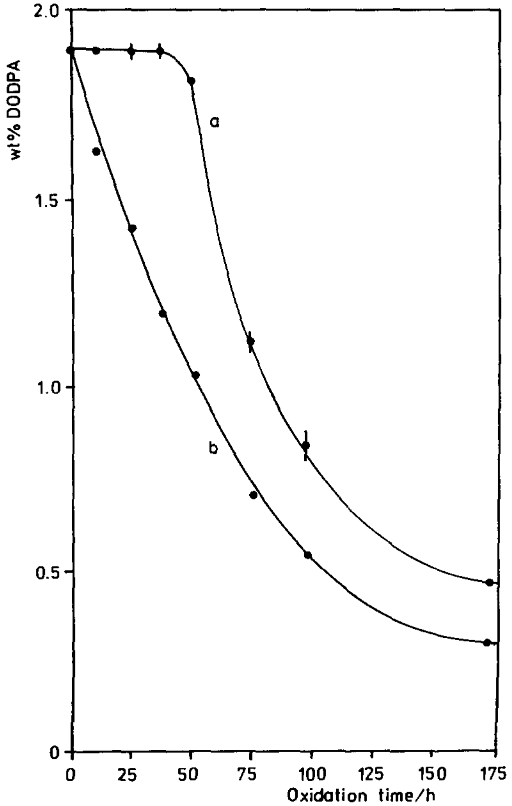

Fig. 6. Comparison between the results obtained by (curve a) DSC and (curve b) CV for partially oxidised samples of the oligomer oil containing initially 1.9 wt.% DODPA.

concentration scarcely change over the period of the tests. The initial oxidative stability was much less marked with the other base stocks. We have also compared the results from the two techniques when known amounts of antioxidant were added to the partially oxidied samples. CV correctly accounted for total amount of antioxidant present whereas DSC indicated an increase in oxidative stability considerably greater than that expected. This "extra" oxidative stability has also been observed by Massey and Wilson [16] in transformer oils but no entirely satisfactory explanation has been offered.

SUMMARY

CV and DSC both require close attention to experimental procedure if reproducible results are to be obtained. With the recognition of the importance of excluding moisture, the technique developed for CV proved to be trouble free. Each analysis takes about 15 min. This includes the time taken to clean and dry the apparatus but there is also the time needed to prepare the various solutions. DSC is a more direct technique, because it uses the oil without further preparation. The isothermal test may take longer than CV depending on the temperature used in the experiments. Our measurements rarely took longer than 30 min. The dynamic test has the disadvantage that extensive vaporisation of the sample may lead to an erroneous result. The results from CV are routed in the theory of the technique but in practise a calibration is needed since the bulk phase diffusion coefficients are not known a priori. CV leads to the amount of antioxidant whereas DSC gives a measurement of the overall oxidative stability. The difference between the two techniques is exemplified in the results both for the base stocks themselves which show inherent oxidative stability and for the addition of antioxidant to partially oxidised oils. The effect of temperature on the induction time measured by DSC prompts a discussion of the reaction kinetics. The extent to which the results are likely to influence the design of additive packages is modest in view of the crude nature of the reaction schemes and our incomplete knowledge of the kinetic parameters under the conditions prevailing in an engine.

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