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Lability of zinc dialkyldithiophosphates under reversed-phase high-performance liquid chromatography conditions

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Abstract

Investigations of the behaviour of zinc dialkyldithiophosphates in aqueous-based media indicate that the species retained in reversed-phase HPLC on a C_{18} column is not the zinc complex. Electrospray mass spectrometric (ES-MS) studies on collected chromatographic peaks show no evidence for the presence of zinc in these samples in the negative and positive ion modes. Electrochemical studies support the mass spectral data by indicating that the zinc complexes dissociate in aqueous-based media to yield free ligand.

Keywords: Oil additives; Zinc dithiophosphates

1. Introduction

Zinc dialkyldithiophosphates (ZDDPs) have been used for many years as multifunctional additives in lubricants, particularly in engine oils. They have the ability to combine anti-wear, anti-oxidation and corrosion-inhibiting properties to protect the engine against deterioration. The mode of action of zinc dialkyldithiophosphates is believed to be in the decomposition products that react with the metal surface to form a protective surface coating [1].

Previous reports have indicated that mixtures of zinc dialkyldithiophosphates can be separated in reversed-phase HPLC on C_{18} columns using methanol–1 m*M* sodium acetate or alcohol–aqueous mobile phases under gradient elution [2–4]. In a recent paper, we reported that several problems were encountered when we attempted to carry out the reversed-phase HPLC of ZDDPs [5]. The initial problem encountered was the low solubility of ZDDPs in the aqueous eluents required for reversed-phase HPLC. At flow-rates of approximately 1 ml min^{-1} on a 25-cm column, back pressures in excess of 3000 p.s.i. developed after a few injections of solutions containing ZDDP, consistent with the high pressures quoted by Ohnishi et al. [2]. Column performance deteriorates over a period of time as indicated by a loss in sensitivity and peak broadening. Peak fractions were collected and addition of dithizone to test for the presence of zinc gave negative results indicating that the species being eluted under reversed-phase conditions did not appear to be the zinc dialkyldithiophosphate.

In this paper, we provide additional new evidence from analysis of the collected chromatographic peaks by electrospray mass spectrometry (ES-MS) and

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from cyclic voltammetric investigations of solutions of the ZDDPs in aqueous-acetonitrile media which suggests strongly that the zinc dialkyldithiophosphates are not eluted as intact chelates under reversed-phase HPLC conditions.

2. Experimental

2.1. Preparation and characterisation of zinc dialkyldithiophosphates

Zinc di-isopropyl- and di-isobutyldithiophosphates and their corresponding ligand salts were prepared by slight variations of standard methods [6–9] in which phosphorus pentasulphide (Sigma, Steinheim, Germany) was added to a stoichiometric amount of the desired alcohol (BDH, Darmstadt, Germany). The dithiophosphoric acid ligand was used immediately for the preparation of the metal complexes by reaction with excess zinc acetate (Sigma). The solution was gently heated and the metal complex precipitated out of solution on cooling. The precipitate was recrystallised from chloroform (BDH), followed by acetone (BDH). As the ligand is unstable, its ammonium salt was prepared by bubbling dry ammonia through the dithiophosphoric acid ligand solution to yield a crystalline product [8]. The zinc complexes were characterised by metal analysis using flame atomic absorption spectrometry and their identities confirmed by infrared studies.

2.2. Instrumentation

Chromatographic system A: the chromatographic system for the separation of ZDDPs was a GBC Instruments HPLC system (GBC Scientific Equipment P/L, Dandenong, Victoria, Australia) consisting of an LC 1150 HPLC pump, LC 1210 UV–Vis detector and LC 1610 autosampler. The analytical column was a 5-μm Spherisorb reversed-phase column (15×0.46 cm, ODS, ICI, Australia). The GBC system was coupled to an IBM compatible computer and the GBC 'Winchrom' chromatography data management system was used to collect and process results. Gradient elution was used to effect the separation of the ZDDPs. Flow was maintained at 1 ml min^{-1}, the volume injected was 10 μl and detection was carried out at 254 nm.

Chromatographic system B: the chromatographic system used for fraction collection consisted of a Knauer 40 HPLC pump (Berlin, Germany), a Rheodyne 7125 injector fitted with a 200-μl sample loop (Cotati, CA, USA), an Altex Ultrasphere reversed-phase column (25×0.46 cm, ODS), a Model D1000 variable wavelength detector (Knauer, Berlin, Germany) and a BAS dual-pen recorder. Flow was maintained at 1 ml min^{-1} with detection at 254 nm. Conductivity detection was performed using an Alltech Model 350 detector.

Electrospray mass spectra were recorded using a VG Bio-Q triple quadrupole mass spectrometer (VG Bio-Tech, Altrincham) with a propanol–water (50:50, v/v) mobile phase. The diluted sample was injected into the spectrometer via a Rheodyne 7125 injector and a Phoenix 20 micro LC syringe pump delivered the carrier solution to the vaporization nozzle of the electrospray ion source at a flow-rate of 5 μl min^{-1}. Voltages at the first skimming electrode (B1) were varied between 80 V and 30 V.

All cyclic voltammograms were acquired using a Cypress Systems Model CYSY-1 computer controlled electroanalysis system (Cypress Systems, Lawrence, KS, USA). A single compartment cell with a conventional three electrode arrangement was used: glassy carbon working electrode (1 mm diameter), platinum wire counter electrode and a Ag/AgCl reference electrode [internal filling solution: 0.01 *M* $AgNO_3$ and 0.1 *M* tetrabutylammonium perchlorate (Southwestern Analytical, Austin, TX, USA) in acetonitrile].

Metal analyses of ZDDPs were performed using a Varian Model AA-275 atomic absorption spectrophotometer (Varian Techtron P/L, Springvale, Australia) with an air/acetylene flame, a lamp current of 5 mA at a wavelength of 213.9 nm. IR studies were carried out on a 1430 ratio recording infrared spectrophotometer (Perkin-Elmer, Buckinghamshire, UK).

2.3. Preparation of chromatographic mobile phases and samples

Water (17.8 MΩ cm) for the preparation of the mobile phases was from a Barnstead NANOpure

de-ionized water purification unit. All solvents used were of HPLC grade. The mobile phase used for the separation of ZDDPs was as follows: mobile phase A consisted of a 5:95 ratio of MeOH (Mallinckrodt)–1 m*M* NaOAc (Sigma), and mobile phase B consisted of a 50:50 ratio of MeOH–1 m*M* NaOAc. Both mobile phases were filtered prior to use with a Millipore filtering system fitted with a 0.2-μm nylon filter membrane. The gradient elution program used to separate the metal chelates was: 100% A from 0 to 3 min, 100% A to 100% B from 3 to 8 min, 100% B for 4 min and then a declining gradient to return to 100% A. For chromatographic studies ZDDP samples (0.001 *M*) were prepared by dissolution in methanol, followed by 50% dilution with 1 m*M* NaOAc. ES-MS samples were prepared by dilution of the collected chromatographic fraction with an equal volume of propanol. ZDDP samples and their corresponding ligands were prepared for cyclic voltammetric studies by dissolving the appropriate amount of sample in a 0.1 *M* tetrabutylammonium perchlorate (TBAP) acetonitrile electrolyte solution. Aqueous-based solutions were prepared by adding aliquots of water to the acetonitrile electrolyte solution. Solutions were degassed with N_2 for 10 min prior to electrochemical experiments. A 0.001 *M* ferrocene solution in acetonitrile containing TBAP (0.1 *M*) gave an E_p value of 416 mV in the above voltammetric cell.

3. Results and discussion

3.1. Reversed-phase high-performance liquid chromatography

The separation and identification of ZDDPs has been achieved successfully by normal-phase HPLC [5], however separation of ZDDPs under reversed-phase conditions has proven to be more complicated mainly because of the low solubility of ZDDPs in the aqueous-based solvent system required for reversed-phase studies and the high back pressures generated by the column.

The reversed-phase chromatographic method for the separation of ZDDPs developed by Ohnishi et al. [2] was investigated to determine if their results could be repeated. Isocratic separation of ZDDPs was not realistic because of the impractical time period required for elution of the second component in a mixture of ZDDPs, therefore non-linear gradient elution using a methanol–sodium acetate eluent was employed. After equilibration of the column with the desired eluent, the chromatogram of a mixture of di-isopropyl and di-isobutyldithiophosphates of zinc showed two peaks as expected (Fig. 1). These results are consistent with those reported by Ohnishi with the complexes eluting in order of increasing carbon number on the alkyl chain.

Although it appeared that good separation of the ZDDPs was achieved, injection of these species on to the reversed-phase column created problems. Excessive back pressures (>3000 p.s.i.) were induced, column efficiency deteriorated with time as indicated by peak broadening and this was accompanied by a loss in sensitivity with successive injections. It was found to be essential to condition the column with methanol at regular intervals (approx. every 10 injections) in order to regenerate the column and hence re-establish a sensitive response. If the mobile phase flow in the chromatographic system was stopped for any reason during a series of analyses, it was also necessary to flush the system with methanol. In order to obtain the chromatographic results shown in Fig. 1, it was found to be essential to dissolve the ZDDP samples in methanol first before dilution with 1 m*M* sodium acetate. Samples not prepared in this manner produced unreliable and unrepeatable peak profiles and responses. The problems encountered with column

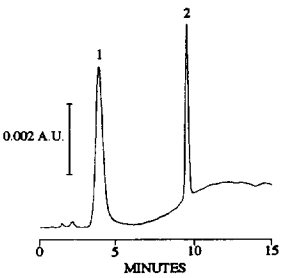

Fig. 1. Liquid chromatogram of a mixture of zinc di-isopropyl and di-isobutyldithiophosphates. Eluent: methanol–sodium acetate (1 m*M*) varied from 5:95 to 50:50 (v/v) over 15 min using gradient elution at 1 ml min^{-1}. Column: 15×0.46 cm I.D, ODS. Wavelength: 254 nm. Peak identities: 1=$Zn[(i\text{-}C_3H_7O)_2PS_2]_2$; 2=$Zn[(i\text{-}C_4H_9O)_2PS_2]_2$.

performance and reproducibility led us to investigate the possibility that the zinc complexes were dissociating in aqueous solution and that the intact ZDDP was not being detected.

In one attempt to identify the eluting species, the chromatography of the di-isopropyl- and di-isobutyldithiophosphate ligands (ammonium salts) were investigated under the same conditions as the zinc complexes. The chromatogram indicates (Fig. 2) that each ligand elutes at approximately the same retention time as its related zinc complex. To establish the "nature" of the eluting species, the spectrophotometric detector was replaced by a conductivity detector. Injections of solutions of the di-isopropyl ZDDP and ligand resulted in both species being detected at the same retention time, which implied that in the case of the ZDDP the retained species was not the neutral metal complex as previously thought. In a further attempt to identify the retained species, samples from injections of zinc di-isopropyl- and di-isobutyldithiophosphates were collected and analyzed by electrospray mass spectrometry.

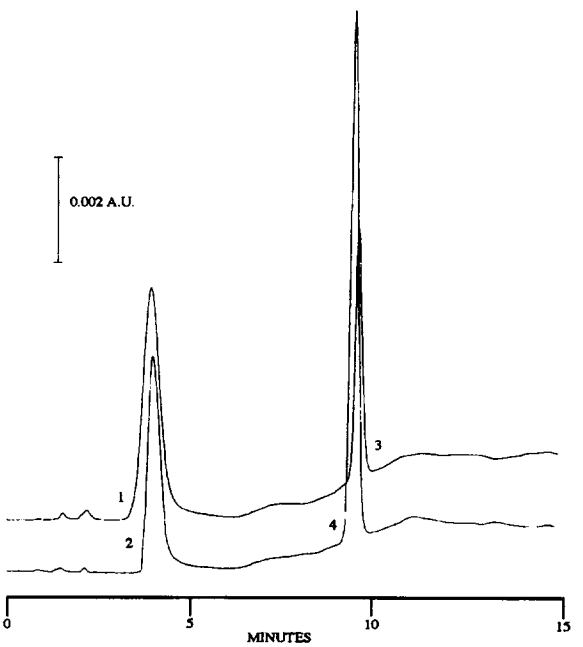

Fig. 2. Liquid chromatograms of two ZDDPs and the corresponding ligand salts. Conditions: as in Fig. 1. Peak identities: 1=$NH_4[(i\text{-}C_3H_7O)_2PS_2]$; 2=$Zn[(i\text{-}C_3H_7O)_2PS_2]_2$; 3=$NH_4[(i\text{-}C_4H_9O)_2PS_2]$; 4=$Zn[(i\text{-}C_4H_9O)_2PS_2]_2$.

3.2. Electrospray mass spectrometry

In a previous paper, it was demonstrated that ES-MS could be used to analyse ZDDPs [10]. Although the neutral zinc chelates cannot be observed by ES-MS, reactions with excess dithiophosphate ligand or dimethylsulphoxide (DMSO) generate ionic products which can be observed by this technique. In the following discussion, all peaks in the mass spectra are identified by the m/z value of the most abundant peak in the characteristic isotopic mass distribution of samples containing zinc. In all cases, the agreement between experimental and calculated isotopic mass distributions was excellent.

The negative ion mass spectra of solutions of $Zn(Pr_2dtp)_2$ and $Zn(Bu_2dtp)_2$, where dtp= dithiophosphate, in the presence of excess of their corresponding ligands show the expected principal ions at m/z of 703 $(Zn(Pr_2dtp)_3]^-$ and 787 $[Zn(Bu_2dtp)_3]^-$, respectively [10], and the isotopic mass distributions are consistent with zinc-containing species. After injection of solutions containing dissolved $Zn(Pr_2dtp)_2$ and $Zn(Bu_2dtp)_2$, fractions collected from the eluted chromatographic peaks were analyzed by ES-MS in the presence of excess ligand, however these samples showed no trace of the ZnL_3^- anion species. The collected chromatographic fraction without the addition of ligand gave a negative ion spectrum with a very intense signal for the free dithiophosphate ligand, arising from dissociation of the neutral complex in aqueous-based media. The results obtained from the negative ion mass spectra indicate that it is highly unlikely that zinc is present in the components retained in the chromatogram in Fig. 1.

When ZDDP is reacted with DMSO in propanol at room temperature, the neutral complex undergoes ligand exchange and zinc-containing cations are observed in the positive ion mode. At a low B1 voltage of 30 V the mass spectrum is dominated by the principal ion $[Zn(Pr_2dtp)(DMSO)_2]^+$ (m/z 433). Further fragmentation of the ion can be induced by increasing the B1 voltage which causes collisionally

activated decompositions with solvent molecules, e.g. when the B1 voltage is 50 V, the dominant species in the mass spectrum is the ion $[Zn(Pr_2dtp)(DMSO)]^+$, and again when the voltage is increased to 80 V the principal ion $[Zn(Pr_2dtp)]^+$ is observed.

The collected chromatographic fraction from injection of $Zn(Pr_2dtp)_2$ gave no indication of the characteristic mixed-ligand DMSO complexes that form from ligand exchange reactions with the zinc dithiophosphate compounds.

3.3. Cyclic voltammetry

The cyclic voltammograms of $NH_4(Pr_2dtp)$ in 100% acetonitrile and acetonitrile–water (80:20) containing 0.1 *M* TBAP show one irreversible oxidation wave at a potential of 0.57 V (vs. Ag/AgCl), as shown in Fig. 3 (curve b). In the potential range −1.0 V to 1.0 V, a solution of zinc diisopropyldithiophosphate in acetonitrile (0.1 *M* TBAP) showed no oxidation around 0.6 V. In contrast to the voltammogram of the zinc dithiophosphate in acetonitrile, the voltammograms of the zinc complexes in aqueous–acetonitrile media gave an irreversible oxidation wave at a potential of 0.58 V comparable to that of the free ligand. Stepwise addition of water aliquots indicated that at a composition of acetonitrile–water (80:20) maximum current was obtained (Fig. 3, curve c). These voltammograms provide strong evidence that the complex appears to dissociate in aqueous media to form free ligand.

4. Conclusions

Reversed-phase HPLC is unsuitable for identification and analysis of zinc dialkyldithiophosphates because of the lability of these complexes in aqueous-based media. Electrospray mass spectra of fractions of the retained chromatographic peaks are void of characteristic anions and cations observed in spectra of the zinc dialkyldithiophosphate in the presence of excess ligand or dimethylsulphoxide. Electrochemical studies confirm that the zinc dialkyldithiophosphates dissociate in an aqueous environment to release free ligand.

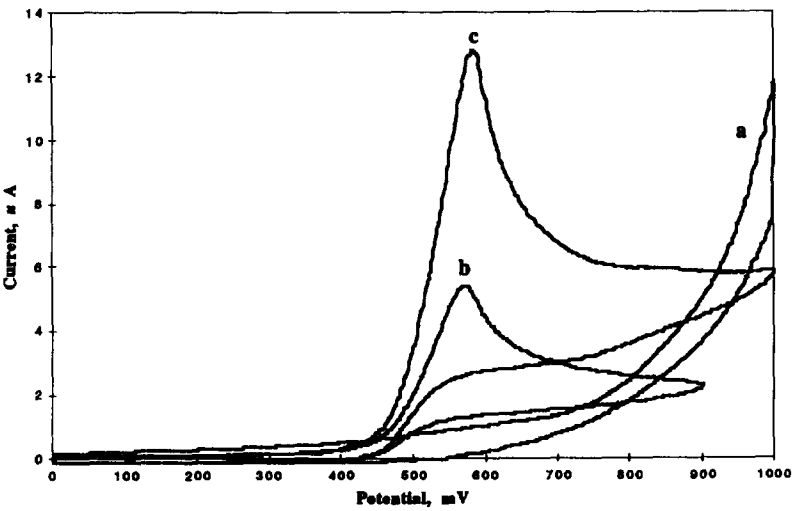

Fig. 3. Cyclic voltammograms of (a) 0.005 *M* $Zn(Pr_2dtp)_2$ in acetonitrile (0.1 *M* TBAP), (b) 0.002 *M* $NH_4(Pr_2dtp)$ in acetonitrile (0.1 *M* TBAP) and (c) 0.0025 *M* $Zn(Pr_2dtp)_2$ in acetonitrile–water (80:20, v/v) (0.1 *M* TBAP). Potential vs. Ag/AgCl; scan rate 100 mV s^{-1}; working electrode, 1 mm diameter glassy carbon disk.

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