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THE HEATS OF ADSORPTION OF ZINC DI n-ALKYL DITHIO PHOSPHATES ONTO PURE IRON, CAST IRON AND FERRIC OXIDE SURFACES

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ABSTRACT

Zinc dialkyl dithio phosphates are used as anti-oxidant and anti-wear additives in lubricating oils.

The synthesis of a homologous series of zinc di n-alkyl dithio phosphates (ZDDPs), ranging from propyl to octyl, is described. Heats of adsorption of these compounds from n-heptane solution on to pure iron, cast iron and ferric oxide have been determined by flow microcalorimetry. Negligible adsorption was observed on high purity iron; cast iron containing 2.8% carbon and ferric oxide both behaved in a similar manner, maximum heat of monolayer formation occurring with the n-butyl ZDDP. All the isotherms were of the high affinity type.

It appears that the heat evolved due to the formation of an adsorbed monolayer initially increases with increasing hydrocarbon chain length, reflecting the increased molar mass. Then at longer chain lengths steric hindrance progressively reduces the number of zinc dithio phosphate groups that can interact with the adsorbent surface, thereby causing less heat to be evolved.

INTRODUCTION

Zinc dialkyl dithio phosphates (ZDDPs) have been used extensively as lubricating oil additives since the nineteen thirties [1]. Originally their main purpose was to act as oxidation inhibitors for the hydrocarbon oil, but their performance in reducing engine wear has become increasingly important as engine compression ratios and power output per unit capacity has risen progressively. Today multi-grade engine oils generally contain ZDDP concentrations approaching one percent. The importance of ZDDPs as an oil additive lie in the fact that they combine in a single compound both anti-oxidant and anti-wear characteristics. They also show no interaction [2] with the other main additives in lubricating oil compositions.

However, even after fifty years of use the way in which ZDDPs achieve these desirable effects seems to be little understood, despite numerous studies. It would be expected that the ZDDP first adsorbs physically on to

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the iron surface, possibly followed by chemisorption as a result of reaction with the iron [3]. Indeed, work by Larson [1] using a radio-tracer technique appeared to show that a monolayer of ZDDP formed very rapidly on iron from a solution in hydrocarbon oil. Similar results have been obtained by Dacre and Bovington [4], again using a tracer technique; the ZDDP was found to chemisorb on iron, or steel, over the range 25–80 ° C. Above 80 ° C, the original ZDDP appeared to decompose; tests were conducted up to 121° C.

Conversely, Rounds [5] could find very little evidence of adsorption of a ZDDP on iron below about 150° C, a result which is in accord with our own measurements.

Controversy also exists as to whether it is the ZDDP itself which displays the anti-oxidant and anti-wear properties, or if these are due to decomposition products of the original material. Larson [1] concluded that the more easily decomposed ZDDPs are the better anti-oxidants; therefore branched chain ZDDPs are generally better than those with linear hydrocarbon chains. More recent work [6] with n-octyl ZDDP suggested that the decomposition products did not make good anti-wear agents.

Ming-Feng et al. [7] found that evolution of hydrogen sulphide from secondary butyl and n-hexyl ZDDP could be detected at temperatures as low as 42 and 45° C, respectively. This however conflicts with other studies [8,9], which suggest that ZDDPs are generally thermally stable at least up to 180° C.

Hence, because of the confusion surrounding the adsorption of ZDDPs on to iron surfaces and the stability of the adsorbed film (if any), we have set out to investigate the adsorption from n-heptane solution of ZDDPs ranging from n-propyl to n-octyl onto pure iron, cast iron and ferric oxide surfaces. We have chosen to employ the technique of flow microcalorimetry (FMC) so that we can determine not only the extent of adsorption of the ZDDPs, but also from the magnitude of the heat evolved we should be able to ascertain whether physical or chemisorption has occurred. From the magnitude of the heat of adsorption it should be possible to estimate if the resulting rise in temperature could be sufficient to initiate decomposition of the ZDDP.

EXPERIMENTAL

The flow microcalorimeter and the experimental procedure used in this work have already been described in two previous papers [10,11]. Adsorption isotherms of ZDDPs, with alkyl chains ranging from n-propyl to n-octyl, were determined from n-heptane solution at concentrations up to ca. 0.5wt%, at 20° C. ZDDP additive packages used commercially are generally of unknown composition and difficult if not impossible to purify.

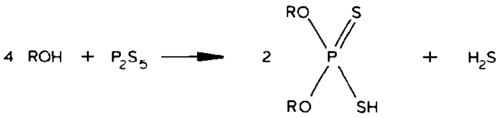
TABLE 1

Preparation of ZDDPs

Alcohol	Mass (g)	P_2S_5 (g)	T_R (°C)	T_{max} (°C)
Ethyl	45	60	40	50
n-Propyl	60	60	46	70
n-Butyl	75	60	70	96
n-Pentyl	85	60	70	100
n-Hexyl	100	60	70	110
n-Heptyl	115	60	70	110
n-Octyl	130	60	70	140

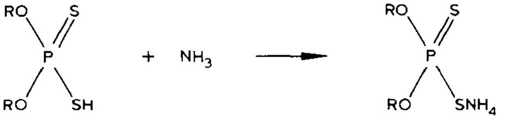
It was therefore decided to synthesize our own ZDDPs using the following procedure, based on the work of Paddy and Waters at Brunel University [12].

The first step is to prepare the dialkyl dithio phosphoric acid (DDPA) by reacting the selected alcohol with phosphorus pentasulphide



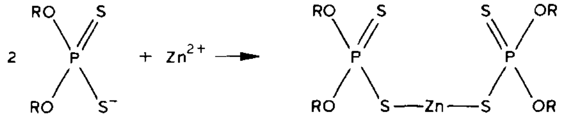
The alcohol contained in a three neck flask was heated to the reaction temperature (T_R) and phosphorus pentasulphide, held as suspension in toluene, added from a dropping funnel. The other two necks carried a thermometer and a reflux condenser. During the addition, the temperature was not allowed to exceed T_{max}, values of which are given in Table 1. The reaction mixture was then heated for 90 min at a temperature 10–15 °C below T_{max}. After cooling, excess phosphorus pentasulphide was filtered off and the filtrate treated with active carbon, which was in turn separated by filtration. The resulting DDPA was a viscous oily liquid.

Next the ammonium salt, ADDP was formed by bubbling ammonia gas through the acid; the solid salt was separated by filtration and purified by recrystallization from double distilled 60–80 °C petroleum ether



Further purification was achieved by dissolving 3-g portions of ADDP in 5 cm^3 distilled water, adding 2 g ice, followed by excess concentrated sulphuric acid. The free DDPA was then extracted with petroleum ether and the ammonium salt again precipitated by passage of ammonia gas.

The final ZDDP product was prepared by dissolving 0.025 mole portions of the ADDP in 50 cm^3 water and adding 50 cm^3 of an aqueous solution containing 0.025 moles zinc nitrate. This resulted in formation of a white emulsion, from which the ZDDP was extracted with 60–80 °C petroleum ether; the ether was then removed by vacuum distillation to leave the pure, liquid ZDDP



In the case of ethyl ZDDP, the product was a solid at room temperature. All the ADDP and ZDDP compounds were characterized by their infra-red and NMR spectra.

MATERIALS

The phosphorus pentasulphide and straight chain alcohols used in the work were supplied by Fisons plc as SLR grade, except that n-propanol was obtained from BDH Ltd, and n-octanol from Aldrich Chemical Co. Ltd.

Adsorbents were pure iron, cast iron and ferric oxide powders. The iron powder was supplied by Hoganas AB of Sweden to specification NC 100-24; the iron was 99.99% pure with a carbon content of < 0.01% and the particle size range was between 20 and 175 μm. Cast iron powder was supplied by BDH Ltd; analysis carried out by the British Steel Corporation, Port Talbot Works, gave a carbon content of 2.8%, silicon 2.2% and phosporus 0.24%; the particle size was not specified, but appeared relatively large. Ferric oxide with a stable, homogeneous surface, free from adsorbed ionic impurities, was prepared by heating ferrous oxalate in flowing oxygen for 2 h at 500 °C [10].

RESULTS AND DISCUSSION

The heat of adsorption isotherms of n-butanol from n-heptane solution at 20 °C were first determined to characterize the surfaces of the ferric oxide, cast iron and pure iron adsorbents. Normal butanol was chosen for this purpose for the reasons discussed in a previous paper [10]; again all the Langmuir plots showed excellent linearity. Calculation of the heat of adsorption corresponding to monolayer formation for our sample of ferric oxide gave a value of 735 mJ g^{-1}, equivalent to a specific surface area [13] of 8.4 m^2 g^{-1}.

Adsorption of n-butanol on this (and other) specimens of pure iron proved to be extremely small; the calculated heat of monolayer formation of 1.08 mJ g^{-1} leads, using the same conversion factor (1 J $g^{-1} \equiv 11.475$ m^2 g^{-1}), to a specific surface area of only 0.0124 m^2 g^{-1}. In case this result

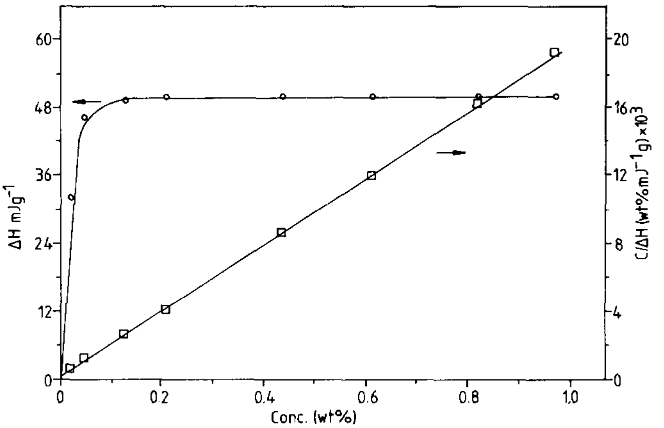


Fig. 1. The adsorption of n-butanol from n-heptane solution on to cast iron, showing (○) the heat evolution isotherm at 20 ° C and (□) the corresponding Langmuir plot.

should have been due to surface contamination, the sample was repeatedly solvent extracted, but without any effect on the specific surface area as measured by adsorption of n-butanol. However, Groszek [14] has also reported very low surface areas for sponge iron samples measured in the same way, and concluded that "clean" iron surfaces have a very low surface free energy. It appears [15] that adsorption from n-heptane solution on to iron depends very markedly on the carbon content of the iron. Accordingly we selected a sample of cast iron as being a more realistic adsorbent for studying the interaction of oil additives with ferrous engine components. This cast iron sample had a carbon content of 2.8% and, as predicted by Groszek, showed a much greater affinity for n-butanol. The adsorption isotherm and corresponding Langmuir plot are shown in Fig. 1; the heat of monolayer formation of 51.3 mJ g^{-1} corresponds to a specific surface area of 0.58 m^2 g^{-1}.

Adsorption isotherms of the ZDDPs on to ferric oxide from n-heptane solution were all of the high affinity type [16]. Saturation adsorption occurred at a concentration of only 0.25wt% for the n-butyl ZDDP, falling progressively to < 0.1wt% for the n-octyl compound.

The ethyl ZDDP was insufficiently soluble in n-heptane for its adsorption isotherm to be determined.

Heats of monolayer formation for the n-alkyl ZDDPs on ferric oxide are shown in Fig. 2. A maximum value is recorded for the n-butyl ZDDP at 337 mJ g^{-1}; thereafter the heat evolved decreases with increasing hydrocarbon chain length, falling to 91 mJ g^{-1} for the n-octyl ZDDP. It is surprising that despite the high affinity type of adsorption isotherm, the maximum heat of monolayer formation of any of the ZDDPs was found to be less than half the corresponding value for n-butanol. However, it must be remembered that one n-butanol molecule occupies only [14] some 0.25 nm^2, while the

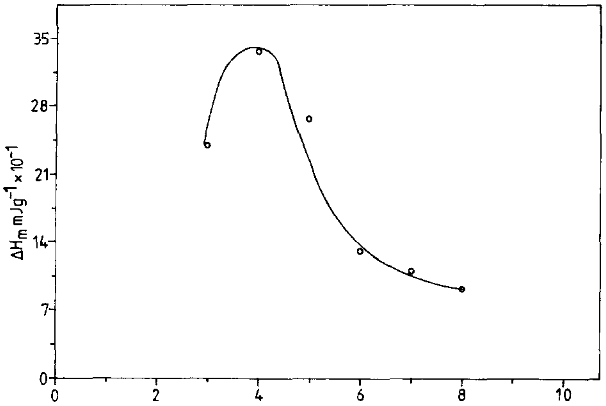


Fig. 2. Heat of monolayer formation of n-alkyl ZDDPs on ferric oxide, plotted against the number of methylene groups in the hydrocarbon chain.

molecular area of n-butyl ZDDP has been calculated from liquid density measurements to be approximately 0.98 nm^2. Hence four times as many butanol molecules are required to cover the ferric oxide surface.

Estimates of the area occupied by ZDDP molecules were obtained by measuring the liquid density of each compound. Then, assuming the molecule to be spherical and knowing the volume of an individual molecule, the area of an equivalent circle can readily be obtained (see Table 2). These figures appear reasonable, since Dacre and Bovington [4] using a radio tracer technique, calculated the area occupied by iso-propyl ZDDP molecules to be 0.89 nm^2, while the figure based on molecular models was 0.94 nm^2.

The sorption data for ferric oxide (Fig. 2) can therefore be seen to be the result of two conflicting effects. Increasing molecular mass increases the tendency for ZDDP molecules to adsorb on the solid surface. However, increasing mass is accompanied by an increase in the area occupied by each ZDDP molecule, so that fewer molecules are needed to form a monolayer. Maximum heat of monolayer formation was observed with n-butyl ZDDP;

TABLE 2

Molecular area A_m of ZDDPs

Alcohol	Molar mass (g)	Liquid density (g cm^{-3})	A_m (nm^2)
n-Propyl	491.5	1.168	0.954
n-Butyl	547.5	1.242	0.984
n-Pentyl	603.5	1.108	1.133
n-Hexyl	675.5	1.058	1.238
n-Hepyl	715.5	1.036	1.328
n-Octyl	771.5	1.048	1.385

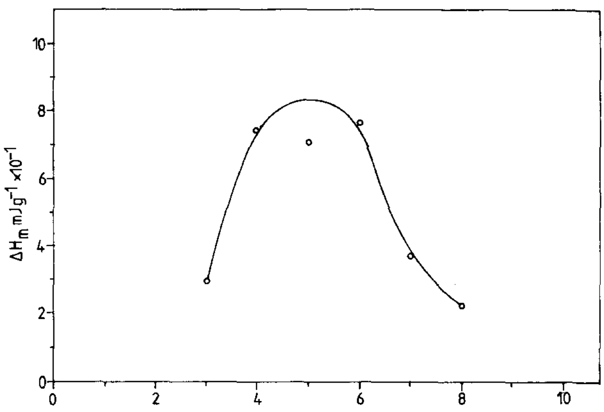


Fig. 3. Heat of monolayer formation of n-alkyl ZDDPs on a cast iron powder, plotted against the number of methylene groups in the hydrocarbon chain.

with increasing hydrocarbon chain length, the monolayer heat of adsorption declines as fewer zinc dithio phosphate groups are able to interact with the oxide surface, due to steric hindrance.

As with n-butanol, the ZDDPs showed a negligible tendency to adsorb on the pure iron samples. All the results obtained were too small for any significance to be attached to them.

However, adsorption on the cast iron powder showed a generally similar trend to that observed with ferric oxide (Fig. 3). The maximum in the curve is now much broader, while the heats of monolayer formation are an order of magnitude lower. The latter is only to be expected, since the specific surface areas, as determined by adsorption of n-butanol, were 8.4 m^2 g^{-1} for the ferric oxide sample and only 0.58 m^2 g^{-1} for the cast iron.

In fact the ratio of the heats of monolayer formation of the n-butyl to that of the n-octyl ZDDP on ferric oxide and on the cast iron are remarkably similar being 3.7 and 3.4, respectively. Hence a similar explanation probably applies to both sets of data. The broadness of the maximum in Fig. 3 is probably due to adsorption of the ZDDPs occurring not on the iron itself, but on active sites resulting from the impurity elements deliberately introduced to form cast iron. These active sites would be expected to be more widely spaced, due to the low impurity concentrations, than the sites available for adsorption on the homogeneous ferric oxide surface. Because of this wider spacing, steric hindrance between adsorbed ZDDP molecules would be expected to be less significant at lower hydrocarbon chain lengths.

Laser Raman spectroscopy, carried out at the Royal Arsenal East, Woolwich, showed that spectral lines due to the n-alkyl chains were displaced as a result of adsorption. Since these groups would not be expected to be involved in bond formation with the adsorbent, the most likely explanation of the spectral shift is that re-orientation has been caused by steric hindrance between adjacent adsorbed molecules.

CONCLUSION

The adsorption of a homogeneous series of zinc di n-alkyl dithio phosphates from n-heptane solution shows a similar trend on both ferric oxide and cast iron surfaces. Surprisingly, adsorption of these compounds on high purity iron appeared to be negligible.

As the molar mass of the ZDDPs increases with increasing length of the hydrocarbon chains, so the heat of monolayer formation rises to a maximum. Further increases in the hydrocarbon chain length reduce the number of individual molecules that can be accommodated on the adsorbent surface. Hence fewer zinc dithio phosphate groups are able to interact with the adsorbent, so that the heat of monolayer formation falls progressively. Maximum heat of adsorption was observed with the n-butyl ZDDP on ferric oxide; but viewed as a lubricating oil additive, much less of the n-octyl ZDDP would be needed for monolayer formation, the property necessary for it to function as an anti-wear reagent.

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