THE INFLUENCE OF WATER CONTENT ON THE ADSORPTION OF LUBRICATING OIL BASE STOCKS ONTO FERRIC OXIDE, STUDIED BY FLOW-MICROCALORIMETRY

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ABSTRACT

Heats of adsorption of lubricating oil base stocks from n-heptane solution onto a ferric oxide surface have been determined by flow microcalorimetry. Results show that the heat evolved is due almost entirely to the chemisorption of water present in the hydrocarbon oils, even though the water content of the original oils was always less than 50 ppm. Removal of most of the dissolved water by vacuum evaporation caused the heat of adsorption to fall by a factor of at least ten in all cases studied. Since lubricating oils are always exposed to water vapour under normal operational conditions, it must be very difficult to make meaningful studies of the adsorption of chemical additives from lubricating oils onto ferric oxide by calorimetric methods. The significance of chemisorbed water present on engine components in affecting lubrication performance may not have been considered sufficiently.

INTRODUCTION

Modern lubricating oils for use in conjunction with internal combustion engines are complex formulations, in which numerous additives are incorporated in the hydrocarbon base stock. These additives are required for a number of distinct purposes, and include (i) detergents or dispersants, (ii) viscosity index improvers, (iii) pour point depressants, (iv) antioxidants, (v) anti-foaming agents, (vi) rust inhibitors, (vii) other corrosion inhibitors and (viii) load-bearing additives. The purpose of the work here reported was to investigate the mode of action of the last mentioned substances.

Load-bearing additives are present in very dilute solution in the hydrocarbon base stock. It seems reasonable to suppose [1] that their effect is due to chemisorption on the metallic components of the internal combustion engine. In order to chemisorb, such additives must first displace the surface layer of hydrocarbon, or other constituent of the lubricating oil, already present. Even base stocks themselves are in fact complex solutions, containing detectable amounts of sulphur, halogen and various compounds, including trace amounts of water.

Hence before attempting to study the behaviour of load-bearing additives, it is essential first to understand the sorption characteristics of the lubricating oil base stocks themselves. Base stocks meeting a given specification often originate from widely different sources and accordingly show significant variations in their chemical composition. The adsorption of a range of base stocks from n-heptane solution onto a ferric oxide surface has therefore been determined by flow microcalorimetry.

Ferric oxide was chosen as the substrate because exposed iron of the engine components will necessarily be subjected to high temperatures, in the presence of a humid oxidising atmosphere. Such surfaces will therefore almost certainly be covered with a monomolecular layer of hydroxyl groups, and not consist of exposed metal atoms.

The advantage of using flow microcalorimetry to study the adsorption behaviour of lubricating oil base stocks is that it is not necessary to know the chemical nature of the species being adsorbed. Most techniques for studying adsorption from solution onto a solid surface rely on determination of the concentration of the solute [2] before and after adsorption has occurred, the difference giving the mass of solute adsorbed. Others, such as DTA [3], or infra-red spectroscopy [4], estimate the amount of solute present on the surface of the solid, as a result of adsorption. Any of these techniques will give rise to misleading information in circumstances where an impurity, present in the supposed adsorbate, interacts very strongly with the solid surface, as is the case if chemisorption occurs.

Flow microcalorimetry (hereafter referred to as FMC) measures the total heat evolved due to the removal of solvent molecules from the solid surface, and their replacement by adsorbed species derived from the solute. Previous studies of the interaction of hydrocarbons or lubricating oils with metal or oxide surfaces, by heat of adsorption measurements, have been carried out by several workers [5,6]. In particular, Groszek has used FMC to investigate chemisorption of boundary lubrication additives at both iron [7,8] and ferric oxide [9] surfaces.

EXPERIMENTAL

The main apparatus used was a "Microscal" mark 2 flow calorimeter, modified so as to bring its performance up to that of the current mark 3 model. Operation was controlled by means of a computer program, which inter alia provided base line compensation and slope determination, peak onset and termination detection, together with peak area integration.

Approximately 0.2 g of the ferric oxide was used as the adsorbent, with n-heptane as the carrier fluid, flowing through the calorimeter at a rate controlled between 0.1 and 0.2 cm^3 min^{-1}. The calorimeter was used in the equilibrium, rather than the pulse mode; the former involves passing solu-
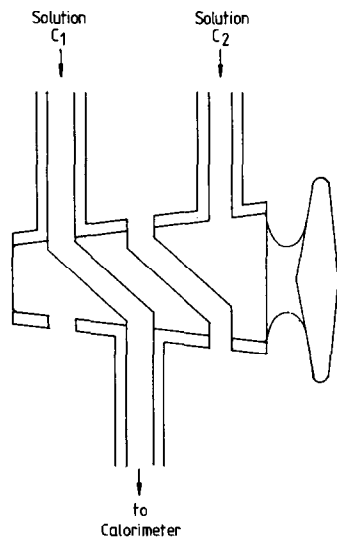
Fig. 1. The two-way tap used to select adsorbate solutions of increasing concentration, showing the essential drain holes.

tions of increasing concentration over the adsorbent and determining the additional heat evolved with every increase in concentration of the adsorbate. In the pulse mode, known volumes of solution are injected into the flowing carrier liquid, and the heats evolved and absorbed during the adsorption/desorption process are recorded. In this latter technique, the equilibrium concentration corresponding to the adsorption process is not known accurately.

An essential modification for operation in the equilibrium mode involved drilling holes in the two way tap, as shown in Fig. 1; this allows the bores to drain freely. Without such an arrangement, solution trapped in the bores of the tap was found to blur the onset of the calorimetric peak, when one adsorbate solution was changed to another of a higher concentration.

Typical response peaks for the adsorption of n-butanol from n-heptane solution onto ferric oxide are shown in Fig. 2.

Factors affecting the calculation of physicochemical data from the calorimetric measurement of solution adsorption isotherms have been reviewed by Parfitt and Rochester [2]. It is assumed that solvent is displaced from the solid/liquid interface by adsorption of solute molecules, and that the rate of displacement is proportional to the concentration of the solution. Also it is assumed that a dynamic equilibrium is set up, such that solute molecules are leaving the surface at the same rate as they are being adsorbed. On this basis, Allen and Patel [10] have shown that a Langmuir type of equation will apply

$$C/H = C/H_m + 1/k_h H_m$$

where C is the concentration of the solute under equilibrium conditions, H
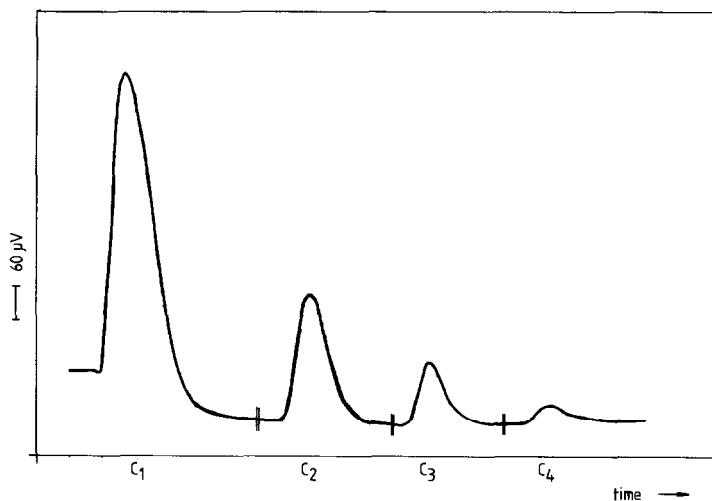
Fig. 2. Typical response curves obtained by flow microcalorimetry for the adsorption of n-butanol from n-heptane solution on to ferric oxide. Ordinate: temperature rise due to adsorption, expressed in mV; abscissa: time; each peak corresponds to passage of solutions of increasing concentration. $C_4 > C_3 > C_2 > C_1$.

the total heat evolved due to adsorption, H_m the heat evolved when the surface is completely covered by a monomolecular layer of adsorbed molecules and k_h is a constant. Hence a plot of C/H against C should yield a rectilinear graph, of slope $1/H_m$, from which H_m can be evaluated.

This equation has been shown [11] to hold for the adsorption of n-alcohols from n-heptane solution onto a ferric oxide surface, and for several other systems [12,13]. If the nature of the adsorbing species and the extent of adsorption are known, then the differential heat of adsorption can be calculated. However, this is not the case with lubricating oil base stocks, which are themselves dilute solutions of various trace components. Some of these may be expected to adsorb much more strongly than the hydrocarbon molecules; one component of particular interest is water present in the oil.

Water contents have been determined using the Karl Fischer method, as specified in I.P. Standard 356/82. A 10 cm³ sample of oil was weighed accurately and added to 10 cm³ of xylene, and the mixture shaken vigorously. 10 cm³ of this mixture was titrated with Karl Fischer Reagent, following the prescribed procedure; pure xylene (10 cm³) was also titrated, to correct for any water introduced by the xylene solvent.

Vacuum evaporation treatment of the lubricating oil base stocks yielded a distillate thought to consist largely of water. The composition of this liquid was investigated by measurement of refractive index, using an Abbé model 60 refractometer (Bellingham and Stanley); the infrared absorption spectra of both oils and distillate were determined by means of a Perkin-Elmer 683 spectrophotometer.

Having established that the distillate was almost entirely water, its purity was determined from the DTA endothermic peak due to melting, using the well-known method described elsewhere [14]. Differential thermal analysis was carried out using the Standata 671B (Stanton-Redcroft Ltd.). 1.0×10^{-3} cm^3 samples of distillate were measured out using a microsyringe and encapsulated in aluminium pans. They were then cooled rapidly to $-20°C$, using an empty pan in the reference position, followed by heating at $2°C$ min^{-1} until melting was complete. The instrument was set to give 100 μV f.s.d. on a 10 inch chart recorder.

MATERIALS

The n-butanol and n-heptane were supplied by Fisons, the former being AR and the latter SLR grade.

Ferric oxide was prepared by the thermal decomposition of ferrous oxalate at 450°C in a flowing oxygen atmosphere. This method was used, since previous studies [15–17] had demonstrated that ferric oxide formed in this way was free from surface ionic impurities, had a homogeneous surface and showed long-term stability.

Karl Fischer Reagents A and B were supplied by British Drug Houses; equal volumes of solutions A and B were mixed to give the reagent, 1 cm^3 of which is equivalent to approximately 3 mg of water.

The lubricating oil base stocks used in this work were supplied by the Procurement Executive, Ministry of Defence, Harefield. These samples were selected because a considerable amount of analytical data already existed (see Table 1) and to facilitate comparison of our results with those from other research projects. Details of their origins are given below.

Laboratory identification numbers	Source
(1)	Middle East base oil
(2)	Middle East base oil
(3)	Kuwait base oil
(4)	North Sea base oil
(5)	North Sea base oil
(6)	Venezualan base oil
(7)	Synthetic hydrocarbon mixture

RESULTS AND DISCUSSION

The heat of adsorption isotherm of n-butanol in n-heptane solution was first determined on ferric oxide at 20°C to act as a standard, against which

TABLE 1

Some chemical and physical properties of the base oils used

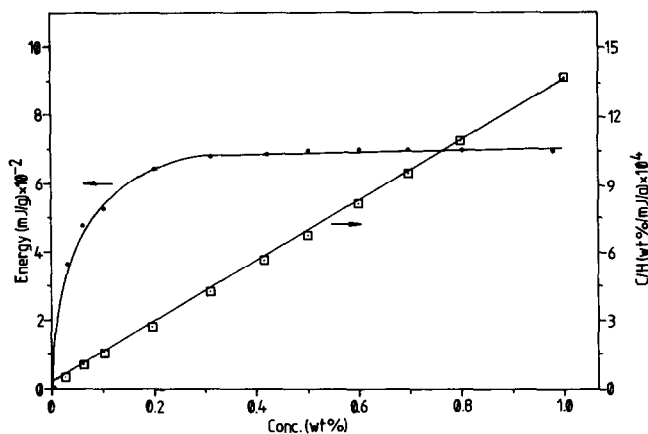| Adsorbate No.	Sulphur NDX RFS (wt%)	Hydrocarbon type			Kinematic viscosity cSt at 20°C	Viscosity index	H_m m J g^{-1} at 20°C before evacuation	H_m m J g^{-1} at 20°C after evacuation	Water content as received (ppm)
		Aromatic (wt%)	Paraffinic (wt%)	Naphthenic (wt%)					
1	0.53	9.5	66.5	24.0	81	103	8.45	0.75	22.5
2	1.47	12.5	61.0	26.5	345	77	51.06	1.03	32.6
3	1.28	6.9	69.5	23.6	304	103	62.72	0.32	34.6
4	0.27	6.5	63.0	30.5	77	102	24.76	1.13	20.9
5	0.30	9.2	63.7	27.1	536	100	151.60	1.45	46.5
6	0.74	6.2	66.7	27.1	344	94	43.64	0.56	33.2
7	0.0001	0.0	> 70	–	41	118	3.61	0.32	15.4

Fig. 3. The adsorption of n-butanol from n-heptane solution onto ferric oxide, showing (a) the heat evolution isotherm at 20°C and (b) the corresponding Langmuir plot.

sorption data for the oil base stocks could be compared. Normal butanol was chosen because extensive studies already exist [9,18–21] on the sorption characteristics of this compound.

The isotherm (Fig. 3) corresponds to L2 of the classification of Giles [22]; the resulting Langmuir plot shows excellent linearity, giving a linear coefficient of correlation of 1.0.

Calculation of the heat of adsorption corresponding to monolayer formation (H_m) gives a value of 756 m J g^{-1}, equivalent [23] to a specific surface area of 8.6 m^2 g^{-1}.
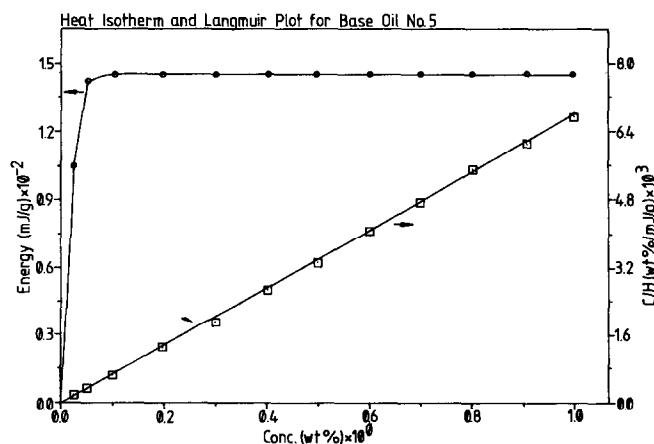

Fig. 4. The adsorption of lubricating oil base stock No. 5 (see Table 1) from n-heptane solution on to ferric oxide at 20°C: (a) the heat evolution isotherm; (b) the corresponding Langmuir plot. The other oils gave very similar results.

Corresponding isotherms were then determined for the lubricating oil base stocks, again using n-heptane as the solvent. The concentrations studied covered the range from 0.025 to 1.0 wt% of the oil, but of course the actual concentration of the species being adsorbed was not known. All of the heat of adsorption isotherms obtained again corresponded to type L2 of the classification of Giles. Langmuir plots were used to evaluate H_m for each of the oils, giving figures ranging from 3.61 to 152 m J g^{-1}. These results are recorded in Table 1, together with all the analytical data then available for the oils used. Figure 4 illustrates the excellent linearity of the Langmuir plots derived from the sorption data.

It had been expected that the H_m values would show some correlation with the chemical composition of the base stocks, but in fact no such relationship could be established. The relatively pure synthetic oil (7), having the lowest sulphur content, also gave the lowest H_m value. However, results for the other base stocks gave no indication of any dependence of H_m values on sulphur content.

Further study of the data appeared to suggest a totally unexpected trend, in that the highest H_m value corresponded to the oil having the highest viscosity (5); conversely the oil of lowest viscosity (7) also had the lowest H_m value. Now viscosity is also known to bear a semi-quantitative proportionality to the water content of lubricating oil base stocks, although the total water contents of all such oils is, of course, very low. Water contents of our oil base stocks were therefore determined by the Karl Fischer method and the data plotted against kinematic viscosity at 20°C; this was calculated from experimental measurements made at 40°C and 100°C, using the procedure set out in A.S.T.M. publication D341. The results (Fig. 5) confirm the approximately rectilinear relationship.

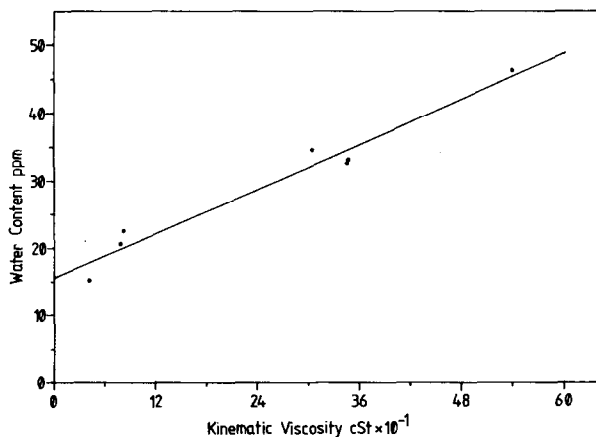In order to verify that the observed heats of adsorption were primarily

Fig. 5. Ambient water content of the lubricating oil base stocks plotted against their kinematic viscosity at 20°C.
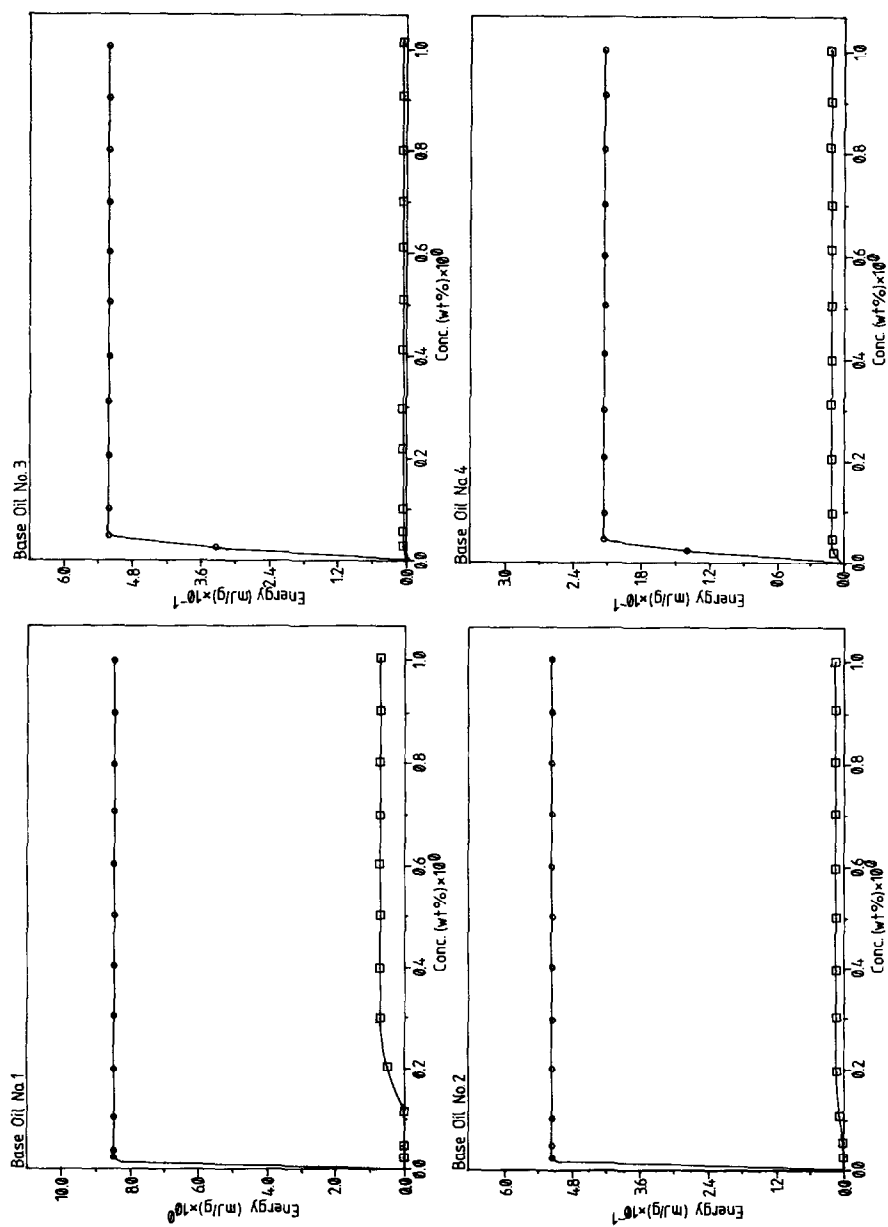
Fig. 6. Heat evolution isotherms obtained for the adsorption of the lubricating oil base stocks from n-heptane solution on to ferric oxide at 20°C. (O———O) Oils stored under ambient conditions, (□———□) after degassing at room temperature.
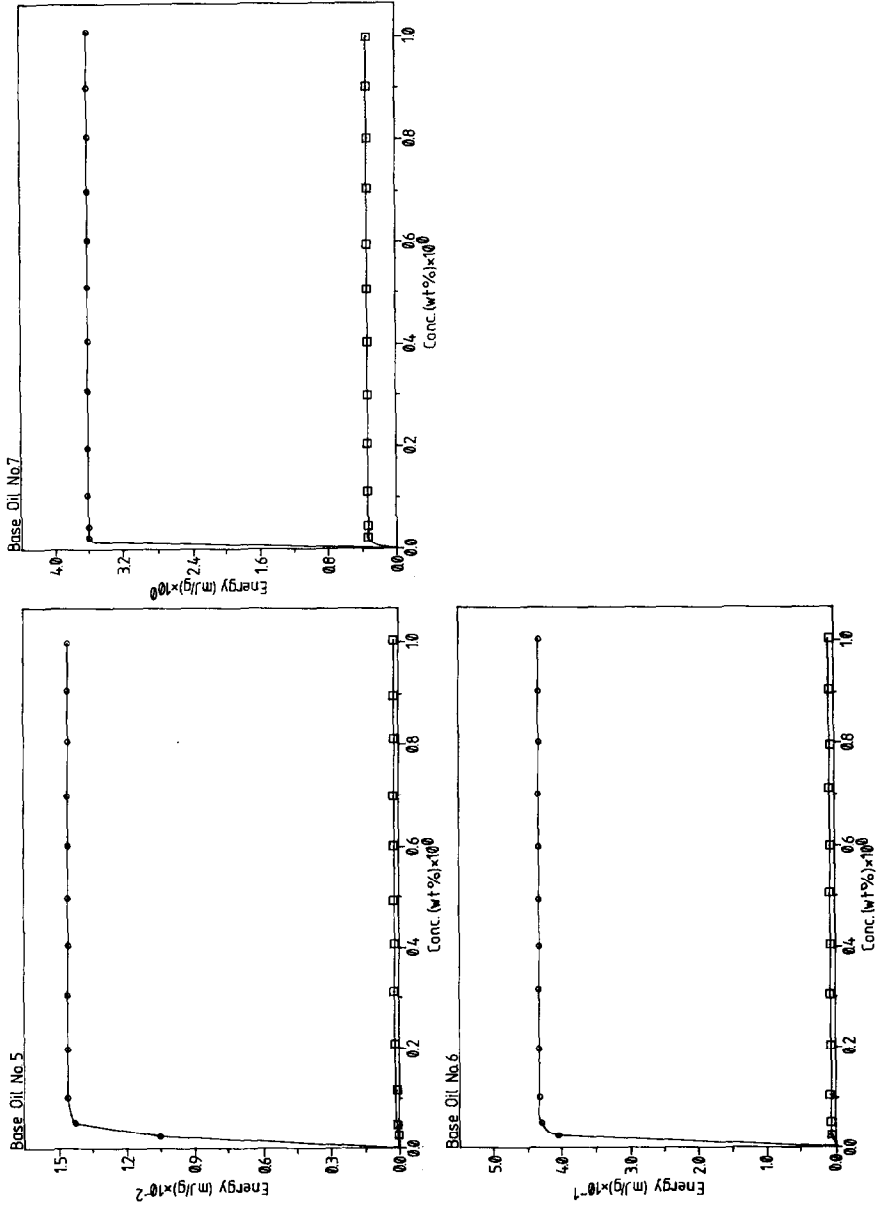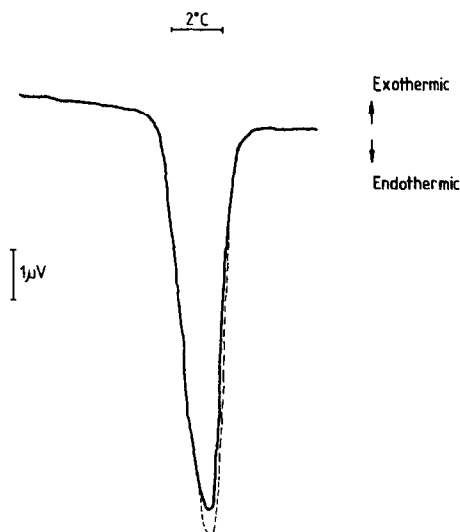
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Fig. 6 (continued).

Fig. 7. Melting endothermic peaks obtained by DTA using 1.0×10^{-3} cm^3 samples, under identical conditions: the solid line is for volatile matter from the degassed oils and the broken line for freshly distilled water.

due to chemisorption of the trace amounts of water present in the oil base stocks, all the oil samples were subjected to treatment under vacuum for 48 h at room temperature, in the presence of a liquid nitrogen trap to condense any evolved volatile matter. The contents of the trap were subsequently analysed, using the techniques previously described. Heat of adsorption isotherms were then redetermined on the degassed oils, giving the striking results shown in Fig. 6. In every case the heat of monolayer formation, calculated from the Langmuir plot, had fallen by a factor of at least ten. With oil (5) the value of H_m had actually fallen by two orders of magnitude.

Confirmation that the volatile matter removed from the oil base stocks consisted of virtually pure water was demonstrated as follows. Measurement of refractive index of the distillate gave a figure of 1.33196 at 30°C, identical to that obtained from freshly distilled water. Melting of the distillate was investigated by DTA, using a 1.0×10^{-3} cm^3 sample; the resulting endothermic peak was absolutely reproducible (Fig. 7). A corresponding endothermic peak obtained under identical conditions, using a sample of freshly-distilled water, is also illustrated. The two peaks can almost be superimposed; the small difference observable in peak height can be ascribed to irreproducibility in the microsyringe used to measure out such small samples. Mathematical analysis of the melting endotherm of the distillate indicated that it consisted of > 99 mol% pure water.

The quantities of water present in the lubricating oil base stocks proved to be too small to give rise to characteristic peaks in the infrared absorption spectra.

CONCLUSION

Our results show that the heat evolved when our lubricating oil base stocks came into contact with a ferric oxide surface was due almost entirely to water present in the oils. With all our oil samples, very little additional heat was evolved when the concentration of oil in n-heptane exceeded 0.5 wt%. Since the total water content of any of our oil base stocks was less than 50 ppm, the maximum concentration of water in the adsorbate solution, corresponding to 0.5 wt% oil, must have been less than 2.5×10^{-7}, expressed as a weight fraction.

Hence any study of the adsorption of lubricating oil additives onto ferric oxide surfaces by means of flow microcalorimetry faces a formidable problem. Traces of water will always be present in lubricating oils under operational conditions, and chemisorption of that water is likely to mask any heat effects due to the additives. If the water content of the base stocks is first minimised, in order to determine the heat of adsorption of oil additives, then the data will be obtained under artificial conditions, not representative of those existing in an internal combustion engine (or anywhere else exposed to the atmosphere).

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