

PHYSICAL AND CHEMICAL ADSORPTION

IN BOUNDARY LUBRICATION

by

HUGH ALEXANDER SPIKES

A thesis submitted for the degree of

DOCTOR OF PHILOSOPHY

of the University of London

and also for the

DIPLOMA OF MEMBERSHIP of the IMPERIAL COLLEGE

DECEMBER 1971

Lubrication Laboratory, Department of Mechanical Engineering,
Imperial College of Science and Technology,
London, SW7 2BX.

ABSTRACT

This thesis examines the mechanisms of various boundary friction systems by comparing surface chemical and lubricated test results.

Three aspects of boundary lubrication are investigated, oiliness using long chain amine solutions, extreme pressure activity using dibenzylidisedisulphide and surfactant-extreme pressure additive interference. In each case a short literature survey is presented, followed by experimental results measuring the change in surface chemistry and friction with temperature.

For long chain amines on stainless steel, adsorption and slow speed friction results show that lubrication is provided by a predominantly reversible adsorbed amine monolayer. Lubricant action fails when this film is critically depleted which, under conditions of Langmuir adsorption, occurs at constant adsorbed amine excess for a given load.

A simple analysis of certain published results has shown that this adsorption-scuffing model may also be applicable at high speeds.

The reaction of radioactively tagged dibenzylidisedisulphide on steels has been investigated and a reaction mechanism proposed. A comparison of chemical and frictional results for similar systems indicates that an anti-seizure extreme pressure film may be fully effective when only a few monolayers deep. Differences in extreme pressure lubrication at low temperatures for different steels have been noted and an explanation proffered.

In additive interference experiments it has been shown that surfactants can suppress the reaction of dibenzylidisedisulphide with steel. However, whereas long chain amine is most antagonistic at low temperatures it has been found that calcium sulphonate detergent solution interferes up to high temperatures. The importance of this calcium sulphonate antagonism has been demonstrated in lubricated tests, where it is shown to suppress extreme pressure activity.

ACKNOWLEDGEMENTS

I am most grateful to Dr. Kitchener and Dr. Cameron for their kind help and advice, and also to all the members of both their laboratories for providing such a comfortable milieu in which to work.

I should also like to thank Mr. R. Dohson for instructing and aiding me in many technical problems and Caterpillar Tractor Company for providing the funds which made this study possible.

CONTENTS

Title page		1
Abstract		2
Acknowledgements		3
Contents		4
List of figures		10
Symbols		13
<u>Chapter One</u>	<u>General Introduction</u>	14
1.10	Boundary lubrication	14
1.20	Oiliness and e.p. activity	15
1.30	Lubricant chemical composition	17
1.31	Base stock	19
1.32	Lubricant additives	20
1.40	Additive interference	21
1.50	Introduction to the project	22
1.60	Scope of research	23
<u>Chapter Two</u>	<u>Adsorption of Long Chain Amines on Steel</u>	24
2.10	Introduction	24
2.20	Review	25
2.21	Surface oxide layers and cleanliness	25
2.22	Effect of solvent on adsorption	27
2.23	The thickness of adsorbed films	27
2.24	Adsorption of long chain surfactants on metals	28
2.25	Reversibility of adsorption	30
2.26	Orientation and packing	31

2.27	Variation of adsorption with temperature	32
2.28	Summary of review	32
2.30	Experimental work	33
2.31	Experimental aims and design	33
2.32	Adsorption measurement technique	34
2.33	Materials and apparatus	38
2.34	Experimental procedure	42
2.35	Cleanliness and adsorption	44
2.36	Accuracy	46
2.40	Results and discussion	50
2.41	Kinetics of adsorption	50
2.42	Effect of chain length on adsorption	53
2.43	Reversibility of adsorption	56
2.44	Effect of temperature on adsorption	59
2.45	Thermodynamic analysis	62
2.46	Adsorption area and orientation	72
2.50	Conclusions	75
<u>Chapter Three</u>	<u>Boundary Lubrication using Long Chain Amine</u>	<u>76</u>
	<u>Solutions</u>	
3.10	Introduction	76
3.20	Review	77
3.21	Adsorption in boundary lubrication	77
3.22	Relationship between adsorption	81
3.23	Other solid-surfactant adsorption systems	86
3.24	Scuffing	87
3.25	Summary	88
3.30	Experimental	89

3.31	Experimental aims and design	89
3.32	Bowden-Leben apparatus	90
3.33	Materials	93
3.34	Experimental technique	93
3.35	Cleaning procedures	94
3.36	Stick-slip and friction	95
3.37	Accuracy	98
3.40	Results	99
3.41	Effect of immersion time on friction	99
3.42	Reversibility of lubricant breakdown	99
3.43	Concentration effect on friction (dry systems)	100
3.44	Concentration effect on friction (wet systems)	104
3.45	Oleophobic monolayer effects	105
3.46	Effect of load on friction	107
3.50	Discussion	108
3.51	Effect of concentration and temperature on scuffing	108
3.52	Correlation between scuffing and adsorption	109
3.53	Chain matching	114
3.60	Conclusions	117
<u>Chapter four</u>	<u>Adsorption Theory Applied to High Speed Scuffing Systems</u>	118
4.10	Introduction	118
4.20	Adsorption theory at medium speeds	118

4.21.	Assumptions	124
4.30	Lubrication at very high sliding speeds	125
4.31	Assumptions	131
4.40	Conclusions	132
<u>Chapter Five</u>	<u>The Reaction of Dibenzylidisulphide on Steel</u>	133
	<u>Surfaces from Hexadecane Solution</u>	
5.10	Introduction	133
5.20	Literature review	134
5.21	Use of sulphur e.p.'s	134
5.22	Methods of investigating e.p. activity	135
5.23	Effect of temperature on e.p. films	136
5.24	Effect of load and sliding speed on e.p. films	138
5.25	Anti-wear and anti-seizure	139
5.26	Mechanisms of e.p. action	140
5.27	Summary	144
5.30	Experimental	145
5.31	Experimental aims and design	145
5.32	Materials	146
5.33	Apparatus	147
5.34	Experimental technique	148
5.35	Calibration	150
5.36	Accuracy	150
5.40	Results and Discussion	152
5.41	Effect of stirring on e.p. reaction	152
5.42	Effect of temperature on e.p. reaction	152
5.43	Reaction rates of dibenzylidisulphide on steel	157

5.44	Effect of steel type on e.p. reaction	157
5.45	Effect of oxide film	159
5.46	Electron-probe results	161
5.50	Conclusions	162
<u>Chapter six</u>	<u>Lubrication of Steel with Dibenzylidissulphide</u>	163
6.10	Introduction	163
6.20	Experimental	163
6.21	Experimental aims and design	163
6.22	Ball on triplane apparatus	163
6.23	Materials	166
6.24	Experimental technique	167
6.25	Accuracy	169
6.30	Results	169
6.31	Dibenzylidissulphide-stainless steel lubrication results	169
6.32	Reversibility of lubrication	169
6.33	Effect of dibenzylidissulphide concentration	169
6.34	Effect of metal type on e.p. lubrication	173
6.40	Discussion	173
6.50	Conclusions	176
<u>Chapter seven</u>	<u>Interference Effects in Boundary Lubrication</u>	179
7.10	Introduction	179
7.20	Literature review	179
7.30	Experimental	182
7.40	Results	183
7.41	Interference in radioactive reaction tests	183
7.42	Interference in lubricating tests	183

7.50	Discussion	187
7.51	Interference in radioactive reaction tests	187
7.52	Interference in lubrication tests	193
7.60	Conclusions	195
<u>Chapter eight</u>	<u>Conclusions and Suggestion for Future Work</u>	196
8.10	Oily boundary lubrication	196
8.20	Extreme pressure lubrication	198
8.30	Additive interference	200
<u>Appendices</u>		
Appendix A	Solvent purification	202
Appendix B	Amine-stainless steel adsorption results	208
Appendix C	Thermodynamics of adsorption	212
<u>References</u>		218

LIST OF FIGURES

Chapter one

Fig. (1.1)	Lubricating film thickness	18
------------	----------------------------	----

Chapter two

Fig. (2.1)	Colorimetric adsorption curve	37
Fig. (2.2)	Calibration of spectrophotometer	39
Fig. (2.3)	Photographs of steel powder	41
Fig. (2.4)	Adsorption apparatus	43
Fig. (2.5)	Effect of cleaning on adsorption	45
Fig. (2.6)	Adsorption of octadecylamine at 22°C	49
Fig. (2.7)	Adsorption rates of octadecylamine	51
Fig. (2.8)	Adsorption rates for different chain length amines	52
Fig. (2.9)	Adsorption isotherms: different chain length amines	54
Fig. (2.10)	Logarithm of adsorption isotherms	55
Fig. (2.11)	Reversibility of adsorption	57
Fig. (2.12)	Adsorption isotherms for n-octadecylamine	60
Fig. (2.13)	Adsorption isotherms for n-hexadecylamine	61
Fig. (2.14)	$\log_{10} C$ vs $1/T$ for octadecylamine	64
Fig. (2.15)	Variation of ΔH with coverage.	65
Fig. (2.16)	Concentration/adsorption vs. concentration plot for octadecylamine	67

Chapter three

Fig. (3.1)	Models of boundary lubrication	78
Fig. (3.2)	Diagram of Bowden-Leben apparatus	91
Fig. (3.3)	Photograph of Bowden-Leben apparatus	92
Fig. (3.4)	Ionic bombardment apparatus	96
Fig. (3.5)	Reversibility of lubricant breakdown	101

Fig. (3.6)	Friction change with concentration. 22°C, 55°C and 90°C.	102
Fig. (3.7)	Friction change with concentration. 35°C and 68°C.	103
Fig. (3.8)	Effect of water on friction	106
Fig. (3.9)	$\log_{10} C$ vs. $1/T$ for lubricant breakdown	109
Fig. (3.10)	Comparison of scuffing and adsorption for octadecylamine	110
Fig. (3.11)	Comparison of scuffing and adsorption for hexadecylamine	115
Chapter four		
Fig. (4.1)	Scuffing results taken from ref.(81)	119
Fig. (4.2)	$\log_{10} C$ vs. $1/T$ for scuffing	123
Fig. (4.3)	Gear tests results from refs. (102).(105).	126
Chapter five		
Fig. (5.1)	Reaction of dibenzyl disulphide with stainless steel	153
Fig. (5.2)	Reaction of dibenzyl disulphide with mild steel	154
Fig. (5.3)	Suggested dibenzyl disulphide reaction sequence	156
Fig. (5.4)	Reaction kinetics of dibenzyl disulphide	158
Fig. (5.5)	Effect of steel composition on reaction with dibenzyl disulphide	160
Chapter six		
Fig. (6.1)	Photograph of ball on triplane apparatus	164
Fig. (6.2)	Friction traces of ball on triplane apparatus	168
Fig. (6.3)	Friction variation with temperature. Dibenzyl disulphide on stainless steel	170
Fig. (6.4)	Reversibility of e.p. activity with temperature	171
Fig. (6.5)	Effect of dibenzyl disulphide concentration on lubrication	172
Fig. (6.6)	Friction curve for EN 31 steel	174
Fig. (6.7)	Photograph showing wear tracks on EN 58 and EN 31 steel	177

Chapter seven

Fig. (7.1)	Effect of added amine on reaction of disulphide on steel.	185
Fig. (7.2)	Effect of added calcium sulphonate on reaction of disulphide on steel.	186
Fig. (7.3)	Friction curve of amine solution	188
Fig. (7.4)	Friction curve of sulphonate solution	189
Fig. (7.5)	Friction curve for amine + disulphide	190
Fig. (7.6)	Friction curve for sulphonate + disulphide	191

Appendices

Fig. (A.1)	Drop-volume apparatus.	204
------------	------------------------	-----

MAIN SYMBOLS AND ABBREVIATIONS

B.E.T.	Brunauer, Emmett and Teller adsorption model.
C_i	concentration of component i.
D.B.D.S.	dibenzylidisedisulphide.
e.p.	extreme pressure.
K	equilibrium constant for adsorption process..
ln	logarithm to the base e.
m, mol	moles.
n_o	initial total number of moles of liquid.
n_i^α	number of moles of component i in phase α at equilibrium.
n^s	total possible molar adsorption.
nm	nanometer.
N	newton.
$\frac{n_o \Delta x 1^L}{m}$	composite adsorption isotherm parameter.
q_{st}	isosteric differential heat of adsorption.
R	gas constant.
R.H.	relative humidity.
T	Temperature, in $^{\circ}\text{K}$ unless otherwise stated. $(-_B)$ lubricant breakdown temperature. $(-_w)$ wetting temperature. $(-_amb)$ ambient temperature $(-_film)$ film temperature. $(-_t)$ temperature at time t.
ΔT_f	flash temperature. $(-_fm)$ maximum flash temperature $(-_f.t.)$ flash temperature at time t.
V	velocity of sliding.
W	applied load.
x_i^α	concentration of component i in phase α (mole fraction).
Γ_i	surface concentration of component i.
μ	coefficient of friction $(-_s)$ static coefficient.
μ_i^α	chemical potential of component i in phase α

CHAPTER ONE

GENERAL INTRODUCTION

This chapter introduces the subject of lubrication and some of the chemical problems involved.

1.10. Boundary Lubrication

Rubbing two clean metal surfaces together generally gives rise to considerable friction. The contact points seize and tear, and high temperatures are generated at the interface. The normal outcome is both extremely damaged surfaces and an erratic and rough sliding motion.

Two effects are responsible for this phenomenon. The first is that the two surfaces are probably very uneven on the atomic scale, so that they interlock to resist sliding. As Herschel (1) put it in 1845;

"A surface artificially polished must bear somewhat the same kind of relation to the surface of a liquid or crystal, that a ploughed field does to the most delicately polished mirror".

The second contribution to the high coefficient of friction arises because it is energetically more favourable for clean metals to coalesce and reduce their overall surface area than to remain apart. Extra work is thus continually required to shear newly formed areas of metal contact. Lubrication is concerned with mitigating these two effects so as to reduce the friction between sliding metal surfaces.

The most effective solution available is to separate the two surfaces entirely by a film of fluid. If the film is thicker than the combined surface roughness, then metal-metal shear is replaced entirely by fluid shear. In this case the coefficient of friction is usually low and depends on the fluid viscosity rather than on the surface properties of the rubbing solids. This is the state of affairs in a correctly designed journal bearing. The

oil, a classical hydrodynamic fluid, obeys the laws developed by Reynolds in 1886 (2). The lubrication occurring under these conditions is thus termed "hydrodynamic lubrication".

For high loads, between surfaces with a high elasticity modulus, the viscosity of the oil increases with pressure. This is the regime of "elastohydrodynamic lubrication", first introduced by Ertel-Grubin in 1947 (3). It occurs, for example, between a ball and flat surface at moderate speeds, as in a ball-bearing race. The film thickness in this region is generally several hundred nanometers so that solid-solid contact makes only a very minor contribution to the frictional coefficient.

Unfortunately it is not always possible to have a complete fluid film between rubbing metal surfaces. At very high loads and low speeds a coherent oil film cannot be maintained and it is only "boundary lubrication" that prevents the system reverting to dry, unlubricated conditions. The function of a boundary lubricant is to modify the solid surfaces in some way, by adsorption or reaction, so as to provide a surface film which is more easily sheared than the bulk metal itself. It has been found that such films need often be only one or two molecules in depth to lower the coefficient of friction between two quite rough metal surfaces (see Chapter 3).

Although boundary lubrication is most common where high loading exists, such as in hypoid gears, it occurs in almost all machines on stopping and starting before hydrodynamic lubrication is established. It is thus normal practice to include some boundary lubricant even in oils expected to function primarily as hydrodynamic fluids.

1.20. Oiliness and Extreme Pressure Activity

Two forms of boundary lubricating action can be distinguished. These tend to operate under different conditions and are often known, respectively,

as oiliness and extreme pressure (e.p.) activity.

Oiliness is a low temperature lubricating property which, it has been shown, is related to the adsorption of very thin films on metal surfaces. These provide a plane of low shear strength between the two rubbing solids and give, characteristically, coefficients of friction of 0.05 - 0.15. Because the adsorbed films are quite thin, metal-metal contact is not completely prevented and a "wear-track" is produced due to limited tearing in the contact region.

Typical oiliness additives are long chain acids, esters and amines, and these are sometimes added to commercial oils to improve their low temperature boundary lubricating properties. Since adsorption is the key to this type of lubrication, however, many large polar molecules are effective to some degree. For most purposes the natural polar oxidation products of mineral oils provide the required oiliness properties. This can be seen by noting the marked decrease in boundary lubricating action of a crude oil as it is progressively refined.

It is a characteristic of oiliness additives that they modify only the immediate metal surface. This is not the case with extreme pressure additives, which are designed to provide boundary lubrication above the breakdown temperature of the oily adsorbed layer, at about 150°C. Extreme pressure additives are generally organic compounds containing a reactive element such as sulphur, chlorine or phosphorus. These combine chemically with the metal surfaces at high temperatures to give either a low shear chemical film or a film upon which further polar adsorption can occur, but more strongly than on the metal itself (see chapter 5).

The action of an e.p. additive is a controlled corrosion process (4). An uneasy compromise often has to be reached between an efficient extreme pressure agent, which corrodes the surface rapidly causing heavy wear, and

a less reactive e.p. additive which is not such an effective lubricant in preventing seizure. To limit corrosion, extreme pressure agents are designed to begin reaction only at high temperatures where they are actually needed. Sometimes powerful extreme pressure additives are used during the running-in of a machine, with a milder one being substituted for normal use.

This simple picture of two types of boundary lubrication is not an exact one. There is evidence that some e.p. additives behave as oiliness agents at low temperatures. It has also been suggested that lubrication at temperatures higher than the usual oiliness breakdown range can be provided by a polymerised film of surface active material produced at the contact region (5).

Both oiliness and extreme pressure activity are subject to investigation in this thesis. Much fuller descriptions of both these types of boundary lubrication are therefore given later in the text. A diagram showing the range of action of the various lubricating regions, which illustrate the difference between oiliness and e.p. activity, is shown in Figure (1.1).

1.30. Lubricant chemical composition

Many fluids serve as lubricants including water, molten glass and metals, air and both vegetable and mineral oils. Animal and vegetable fats were probably the first to be widely used, since although simple refining methods were available in the 5th century B.C. (6), it was only in the 19th century that these were developed sufficiently to produce reasonably pure hydrocarbon mineral oils. Nowadays hydrocarbon petroleum products are the most widely used of all lubricating fluids.

An important feature in lubrication is the addition of chemical compounds to improve the various properties of an oil. This can be traced back to the middle of the 19th century when Little (7) proposed the mixing

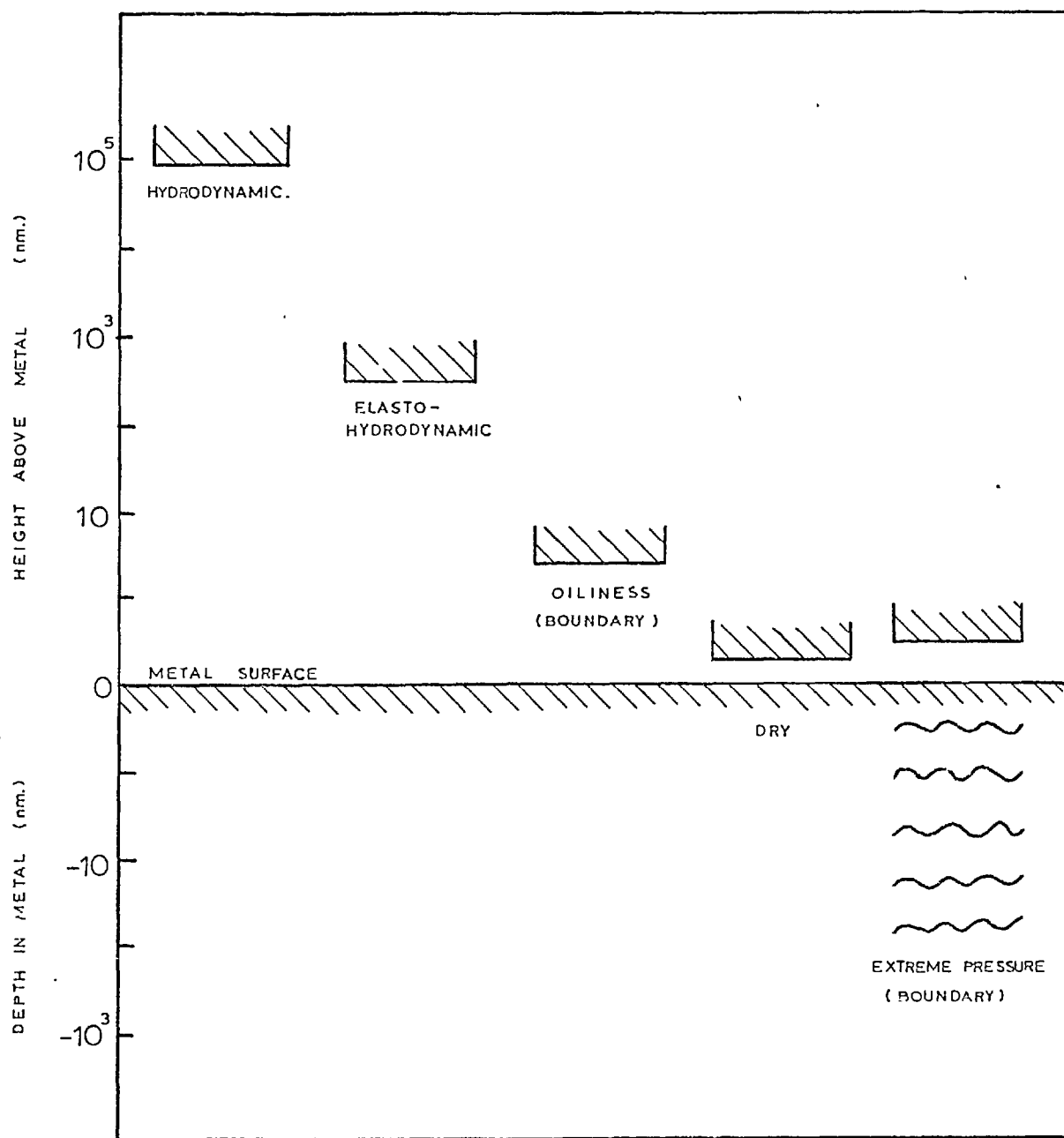


Figure 1.1. Film thicknesses in Lubrication.

(The unloaded asperity height is approximately 10^2 - 10^3 nm., so that elasto- and hydrodynamic lubrication have only minimal metal-metal contact. In the other three regimes considerable metal contact occurs and the asperities will be heavily deformed).

of fatty acid soap with mineral oils to produce lubricating greases. It was in the 1930's, however, that such chemical addition really became popular, and by 1945 most of the present day additive types were already in use. Many of these are not concerned with the lubricating properties of the oil directly, but with its ancillary characteristics, its cleanliness, pouring properties, temperature stability and so on. All these additives make the modern lubricating oil a very complex mixture. It may be useful, therefore, to summarize the chemical composition of typical oils.

1.31. Base stock

The most common bulk fluid or "base stock" used today is a hydrogenated and refined petroleum oil. This, even after refining, is by no means simple. It generally consists of a mixture of aliphatic or saturated ring hydrocarbons chosen to have particular viscosity properties. Small concentrations of organic nitrogen and sulphur-containing compounds are also present as well as poorly defined oxidation products. As was mentioned earlier, these polar impurities act as oiliness agents and can make the base stock itself a reasonable lubricant under mild conditions.

The complexity of a mineral oil and its impurities is a source of difficulty in standardising lubricant behaviour. Even quite highly refined base stock can vary from batch to batch enough to make its properties hard to maintain without using large quantities of chemical additives.

Where performance is of overriding importance with respect to cost, synthetic base stocks can be used. These have special properties such as high temperature stability and also the advantage, especially useful to scientists, of a well defined chemical structure. Thus, for example, diester base stocks are used in gas turbine lubrication where reliability and high temperature performance are essential. Silicone hydrocarbons are

also sometimes used as base fluids. They have very high temperature stability but only poor boundary lubricating properties. Often some thermal stability has to be sacrificed by including chlorine in the silicone molecules to improve oiliness.

1.32. Lubricant additives

Oiliness and e.p. agents, the main lubricating additives, have already been considered in section (1.20). The other principal oil additives are now considered in turn.

Detergents and dispersants are chemicals designed to prevent solid deposits forming in a lubricating oil. Detergents generally denote those which function at high temperatures, whereas dispersants are added to disperse sludge forming in the cold. Innumerable detergents have been used in oils since their first application in 1936 (8). Commercially the most important today are long chain alkyl substituted sulphonates, phosphates, phenates and salicylates. These are all metal salts, the metal usually being barium, calcium or zinc. Almost always there is more metal present than is needed just to neutralise the acid so that the salt is basic. The basicity is valuable in neutralising acid contamination produced by oil oxidation and fuel combustion. Dispersants also have a varied chemical structure. They generally consist of a hydrocarbon base with added polar functional groups such as amides or carboxyls. Fowkes (9) has shown that dispersants function by adsorbing on particles of contaminant.

Corrosion and rust inhibitors are added to lubricating oils to protect, respectively, non-ferrous and ferrous engine components against chemical attack. Corrosion inhibitors are usually metal dithiophosphates, and sulphurised terpenes. Typical rust inhibitors are amine phosphates and alkylthioacetic acid. Both of these additive types work by adsorption on

the metal surface to give a protective film.

Two additives which are used to alter the bulk properties of oils are viscosity index improvers and pour-point depressants. Organic polymers are added to some base stocks to improve their viscosity properties. They exert a greater thickening effect on the oil at high temperatures than at low ones and so limit the overall viscosity change. Pour-point depressants are also organic polymers. They modify crystal growth in cold oils to limit the formation of interlocking wax crystals (10).

The final important additive type is the antioxidant group. Oils at high temperatures and in the presence of metals and complex organic chemicals are normally very prone to oxidation. This results in increased acid content, carbon impurities and a higher viscosity. Additives are therefore employed to inhibit this oxidation either by adsorbing on the metal to suppress catalysis or by directly quenching oxidation chain reaction. The chemicals which have been used as antioxidants are legion. Disulphides, amines and phenols are just a few typical examples.

This has been only a brief summary of lubricant additives. More thorough reviews are to be found in references (11) and (8).

1.40. Additive Interference

It can be seen that a lubricating oil may be quite a melange of chemicals. All are important and are there for a specific purpose. With so many different components great care has to be taken to ensure that they do not interfere with each other. Obvious possible interference effects are straightforward chemical reaction in solution between different additives, either cold or under hot running conditions. Such reactions are quite easy to identify and eliminate by chemical methods. More subtle solution interactions are possible, however, such as the formation of association

complexes retaining the simple chemical properties of both constituents but lowering the activity of each.

Much more important are interference effects in specific chemical functions. Almost all boundary additives are designed to act at the metal surface, albeit in different ways and at different times. Since most of these additives are polar surface-active compounds the likelihood of interference as different additives compete for the surface of the metal is very great.

Indications that such interference or "antagonistic" effects do occur have been appearing more and more frequently in recent literature. These will be reviewed in chapter 7 where experimental work in additive interference is described.

1.50. Introduction to the Project

The practical use of boundary additives has outstripped research. The mechanism even of the simplest boundary lubricant is not yet fully understood whereas new and ever more complex lubricating mixtures are continuously being developed.

Much lubricant test work is done on complex systems and, from these, conclusions are drawn as to the basic lubricating mechanism of the various additives. This is arguing from the complex to the simple, an approach that is rarely very satisfactory. The work in this thesis tries to move the other way by investigating the simple so as to find out about, and understand, the complex.

A very simple lubricating system is considered. Hexadecane is the base stock, long chain amine the polar material and dibenzylidisedulphide the extreme pressure additive. By using pure chemicals the number of extraneous variables is minimized. The lubricating properties of this system are

examined in detail with especial reference to the surface chemistry of each component. From these experiments it is hoped to gain insight into the action of much more complex lubricating oils.

The use of this type of "model" lubricating system is not new in lubrication. A recent example is provided by Rudston and co-workers (12). It is, however, a valuable technique for studying the mechanism of action of lubricating oils which, since they are often natural products, normally have only a statistically defined structure.

1.60. Scope of Research

The work described in this thesis investigates and correlates the chemical reaction and lubricating properties of two simple additives with stainless steel. The experiments divide into three sections.

- a) The adsorption and lubrication of long chain aliphatic amines in hexadecane solution.
- b) The adsorption, reaction and lubricating properties of dibenzyl-disulphide in hexadecane.
- c) Interference effects of polar additives on the reaction and lubricating properties of dibenzyl-disulphide.

CHAPTER TWO

ADSORPTION OF LONG CHAIN AMINES ON STEEL

2.10. Introduction

In 1925 Sir William Hardy (13) demonstrated that some forms of boundary lubrication could be explained by the adsorption of long chain polar surfactants. He suggested that the hydrocarbon molecules of such adsorbed films lowered the field of force between rubbing surfaces and thus reduced friction.

Many experimenters have subsequently developed this theory. The general method has been to correlate the change in a surfactant's lubricating property with its changing surface adsorption. Thus, for example, Frewing (14) and Grew and Cameron (15) postulated that the fall in lubricating capability of fatty acid solutions at a particular temperature was due to physical desorption.

A major deficiency in most correlations has been that both adsorption and friction studies have rarely been done by the same worker, using the same system. The notable exception to this is the work by Hutchinson and Rideal (16) who, in 1946, carried out adsorption and friction experiments for long chain surfactant solutions on sodium nitrate crystals. They observed quite good correlation between the concentration at which significant polar adsorption took place and the concentration where boundary lubrication started to become effective. Unfortunately the work was limited to one temperature so that full thermodynamic analysis was not possible.

This chapter concerns an investigation into the adsorption of long chain amines on steel powder. An important feature of the work is that the adsorption is measured at several different temperatures. The study is of intrinsic interest as a non-aqueous adsorption system. However, the results

will be used primarily for correlation with friction experiments (chapter 3) and with additive interference tests (chapter 7).

2.20. Review

Adsorption from solution on to solid surfaces has been a flourishing branch of surface chemistry ever since the pioneer work of Freundlich (17). This is partly because of its great practical importance in a number of industrial fields, such as flotation and detergency. However the solid-liquid adsorption involved in lubrication is slightly different from these as it is concerned with adsorption from a non-aqueous, non-polar solvent. In this case the simplification can be made that double layer effects and other electrical surface phenomena are absent. This survey will concentrate on non-aqueous work on metals and metal oxides.

Only certain specific aspects of non-aqueous adsorption are considered, effect of oxide layer, effect of solvent, adsorbed film thickness, etc. Each aspect has considerable bearing on the work presented in this chapter and together they provide a framework in which to view both the experimental technique and the new results obtained in this thesis.

2.21. Surface oxide layers and cleanliness

An important feature of working in adsorption and lubrication is that many metals quickly acquire a thin layer of oxide or hydroxide (18). Most experimental work has thus been done on metal oxide layers rather than the metals themselves. This creates great difficulties since an oxide layer is not very reproducible, its thickness and porosity both being variable.

Some adsorption work has been carried out on clean metals. Smith and collaborators (19) (20) and Groszek (21) have prepared surfaces by machining metals under inert solvents. One disadvantage of this technique is the

danger of the metals reacting with the solvent itself under the violent preparative conditions involved. Similarly Greenhill (22) outgassed metal powders and then reduced them in a stream of hydrogen to try to produce clean, non-oxidised surfaces. The powders were then plunged directly into solution. None of these authors reported higher adsorption on clean metal than on oxidised surfaces although Groszek (21) suggested that the heat of adsorption of octadecanoic acid on ground iron was higher than it was on iron oxides.

Platinum and gold surfaces have often been used in adsorption studies to minimise the oxide-film problem. They have been extensively studied by Greenhill (22) Zisman et al. (23) (24), Smith and Fusak (25), and many other investigators. With these unreactive surfaces no mention could be found of adsorption of more than one monolayer.

There is still controversy over the relative importance of oxidised and non-oxidised adsorption in boundary lubrication. The persistence of an oxide film between metal surfaces after repeated rubbing has not been assessed. Groszek (21) suggests that it is important to consider adsorption on both iron oxide and freshly prepared iron surface in order to understand lubrication. Apart from oxidation effect on the adsorption of polar material on surfaces, Roberts et al. (26) have suggested that the converse is important and have shown that adsorbed films inhibit the formation of metal oxide on aluminum.

Cleanliness is also a critical factor in adsorption and boundary lubrication work. Very small quantities of adsorbed water and grease contaminants can greatly alter the properties of surfaces (18). Most metal surfaces quickly adsorb at least one monolayer of water shortly after preparation if exposed to damp air (27). This water can have a marked effect on the surface energy of the metal (28). Bascom (29) has obtained

different results for the adsorption of polar compounds on metal oxide surfaces dependent on the extent of pre-heating of the metal. He associated this with the changing quantity of adsorbed water on the metal.

2.22. Effect of solvent on adsorption

The effect of solvent on adsorption is very marked. Both competitive adsorption of solvent on the metal and solubility of solute in the solvent are important. Groszek (21) has shown that the heat of adsorption of octadecanoic acid on iron oxide differs depending on whether heptane or hexadecane is the solvent.

Bewing and Zisman (24) measured contact potential and contact angles to prove that polished metal surfaces are covered by an adsorbed hydrocarbon layer on withdrawal from alkanes. From contact angle measurements they deduced that the alkane was adsorbed parallel to the surface rather than vertical. A similar orientation has been suggested by Davidson and Kipling (30) for the adsorption of alkanes on graphon.

2.23. The thickness of adsorbed films

A considerable amount of work has been devoted in recent years to determining the thickness of adsorbed films on metal surface. There are two major schools of thought. Sometimes adsorption seems to be in the form of a monomolecular layer (21), (25), (31), (32). On the other hand evidence has accumulated, particularly from Russian sources, of the existence of a thicker film, sometimes hundreds of nanometers deep. Thus Deryagin and co-workers (33) have studied the viscosity variation, with distance from the surface, of thin layers of solutions on polished metal substrates. They report structural layers 10 to 100 n.m. deep. Gaines (34) investigated the adsorption of radioactive polar solutes on metal plates and found an

equivalent of six monolayers of octadecanoic acid on aluminium and copper. A recent review of thick films is given by Allen and Draughlis (35).

Sherwood and Rybicka (36) and Smith and co-workers (19) (20) both showed that the presence of moisture was necessary for the formation of a thick film of fatty acid. Harding (31) studied the adsorption of long chain acids on iron by several techniques but was unable to detect films more than one or two monolayers thick.

Recent work by Smith (37) has made the whole situation much clearer. He investigated the formation of thick films of octadecanoic acid from hexadecane on to steel. The film thickness was calculated by displacing hexadecane solution with mercury and measuring the remaining film's capacitance. Smith found that ionically bombarded, and thus very clean and dry surfaces, adsorbed only a monolayer of octadecanoic acid. When moisture was present a film several hundreds of nanometers thick was formed. He observed this thick film under a scanning electron microscope and showed that it had a fibrillous grease structure. With amines no thick film was formed even in the presence of moisture.

From this it seems likely that thick film formation is more a corrosion than an adsorption phenomenon. It is not yet clear how great a part such thick films play in lubrication with boundary additives such as fatty acids. Certainly amines and alcohols lubricate despite the fact that they do not appear to form more than a monolayer.

2.24. Adsorption of long chain surfactants on metals.

The most common additives used in polar adsorption experiments have been fatty acids. Bowden (38), Hirst (39), Cook (40), Walker (41), Doyle (42), Greenhill (22), Daniel (32) and many others have carried out adsorption tests of acids on various metal surfaces. Generally speaking they reported

monomolecular films. Exceptions are Hirst, who obtained thicker films on zinc and copper when moisture was deliberately introduced, and Cook who found rather more than a monolayer of octadecanoic acid on iron after five days. Both Bowden and Moore (38) and Daniel (32) showed that a group of metals, cadmium, copper and zinc were much more prone to chemical attack by fatty acids than iron, chromium or nickel.

Some adsorption work has also been done using esters and alcohols. Bowden and Moore (38) showed that octadecylalcohol, unlike the corresponding acid, did not react chemically with zinc, cadmium or copper at room temperature. Alcohols and esters adsorb less strongly than acids and a characteristic feature of their adsorption is the existence of a step in the isotherm. This step has been observed by Daniel (32) and Groszek (21) and has been explained in terms of an orientation change in the adsorbed phase as concentration increases.

Investigations of amine adsorption are somewhat scarce. Cook and Hackermann (40) studied octadecylamine adsorption on steel powder from benzene by a direct weighing method. Measuring the powder surface area by B.E.T. methods, they decided that total adsorption did not exceed two monolayers over the concentration range studied. Their adsorption did not reach a limiting value with concentration but seemed to rise linearly. This may result from their experimental technique since they tried to correct for solution evaporation from the powder surface after extraction from benzene solution. A consistent evaporation error would account for the steady rise in the adsorption they noted with increasing amine concentration.

Block and Simms (43) also investigated the adsorption of octadecylamine from bicyclohexyl on steel and glass. They used radioactive measuring techniques and found adsorption rather less than a close-packed, vertically oriented monolayer. Haydon (44) obtained isotherms for adsorption of

n-hexadecylamine on steel and other metals using surface potential measurements.

Bewig and Zisman (24) have carried out a thorough investigation of adsorption of primary amines on platinum from alkanes at room temperature. Using contact potential and contact angle measurements they studied the rate of adsorption of amines and also the amount of alkane included in the adsorbed layer. The alkane content of the film dropped gradually to zero for most solutions. When the chain lengths (number of carbon atoms) of both amine and alkane were the same, however, such as with hexadecylamine and hexadecane, about 15% of the alkane was retained indefinitely in the adsorbed film.

2.25. Reversibility of adsorption

Daniel (32) observed reversibility in the adsorption of fatty acids and alcohols on metal powders. He noted that some desorption took place when the ambient temperature was increased, and also on dilution.

In polar adsorption from non-aqueous solvent there is often a mixture of reversible and irreversible reaction. Timmons (45) found that 60% of the total monolayer of octadecanoic acid adsorbed on iron was removed by heating to 100°C. He concluded that the other 40% was chemically adsorbed in some way. Cook and Hackermann (40) investigated the adsorption of octadecylamine on to steel from benzene and found a similar result. About a quarter to a third of the total amount adsorbed could not be removed by washing in pure solvent.

Cook and Ries (46) carried out experiments on the adsorption of octadecanoic acid on iron from hexadecane. About one third of the total was absorbed very quickly with the remainder taking much longer. They showed that a ratio of octadecanoic acid to hexadecane of 1 to 2 would be

particularly stable from a lattice point of view and postulated that such a monolayer was formed rapidly and that further adsorption took place as a slow hexadecane, acid exchange. (This does not explain, however, why Cook and Hackermann should find a similar ratio for benzene).

The most detailed reversibility tests were carried out by Block and Simms (43). They investigated the adsorption of radioactive octadecylamine from bicyclohexyl on steel and measured both desorption by dilution and exchange of amine by adding more concentrated, non-radioactive solution. They found that the amount desorbed was about 55% of the total, but 60% could be exchanged. They suggested that strong, non-exchangeable adsorption took place on the metal itself. The exchangeable fraction, they thought, might be adsorption on a film of water and the easily desorbed fraction could be molecules filling in the spaces between the rest, held mainly by weak, lateral forces.

2.26. Orientation and molecular packing of adsorbed molecules

Many of the early adsorption experiments were done using powders whose surface areas were unknown. In such cases it is difficult to draw any firm conclusions as to orientation on the area of surface occupied by each adsorbed molecule. Some indication can be obtained from Daniel's work (32). He showed that a similar adsorption plateau, in terms of number of adsorbed molecules, could be obtained for different chain length fatty acids on nickel, and suggested that this indicated a vertical rather than a horizontal orientation. The break in adsorption isotherms observed by Daniel (32) and Groszek (21) also points to the orientation involved. The ratio of limiting adsorption values above and below the step region corresponds well with the ratio of the areas of upright and flat adsorbed molecules.

More recent work has tended to include a B.E.T. surface area evaluation

so that conclusions about molecular packing can be drawn. Generally speaking polar molecules adsorb vertically at high concentrations whereas alkanes are horizontally oriented.

There is not very much information available on the packing density of amines for adsorption on solids. Block and Simms (43) for octadecylamine on mild steel found that a 0.003% solution in bicyclohexyl did not exceed 0.54 of a close-packed, vertically oriented monolayer even after seven days. Adsorption on glass reached 0.86 monolayers in the same time. Cook and Hackermann (40) found that there was between 0.3 and 1.5 monolayers of octadecylamine adsorbed on steel in the range of concentration studied; the 0.3 being irreversibly bound.

2.27. Variation of adsorption with temperature

References to the effect of temperature on adsorption are very scanty. Daniel (32) carried out experiments with octadecanol and fatty acid solutions at two temperatures. Sakurai and Baba (47) showed that as temperature increased so did the chemical reaction of long chain fatty acids on steel and iron. They detected appreciable amounts of iron in solution after steel had been immersed in fatty acid for over two hours at 100°C. No work on the effect of temperature on adsorption of amines in non-aqueous systems could be found.

2.28. Summary of review

A survey of the literature suggests that adsorption of long chain surfactants on to metal-oxide surfaces at room temperature is generally only in the order of monolayers. This is certainly the case for esters, alcohols and amines. Long chain acids can behave exceptionally in two instances. A small group of metals, copper, calcium, lead and zinc seem to

react chemically with fatty acids under most conditions. Fatty acid will also react corrosively with other metals if these are damp before immersion in solution.

The effect of increasing temperature is to reduce adsorption although in some instances more chemical reaction can occur.

Adsorption is partially reversible but there is strong evidence that an irreversible fraction of about one third is often found.

The literature shows that amines and fatty acids are more strongly adsorbed than esters or alcohols.

This review mentions only a selection of the papers published in the field. More thorough reviews of non-aqueous adsorption on solids can be found in references (31) and (48).

2.30. Experimental work

2.31. Experimental aims and design

One of the main points of this work was to make a comparison between adsorption and friction. For this a simple and controlled system was desirable, amenable to theoretical adsorption analysis. This precluded the use of long chain fatty acids, which the survey has shown, can attack metals corrosively. It was decided to use long chain amines which were less reactive chemically. Alcohols and esters were not suitable since the literature has demonstrated that their adsorption on metals is only weak: it was thought that unacceptably high concentrations would be necessary to observe appreciable adsorption at high temperatures.

In designing these experiments a balance had to be reached between a very pure and well-defined system such as the sodium nitrate adsorbate used by Hutchinson and Rideal (16), and a more complex and reactive metal adsorbate which had some practical application in boundary lubrication. Unreactive

stainless steel was chosen as a compromise which, it was considered, would minimise the chemical reaction occurring, whilst still being relevant to lubrication. It was assumed that some water would inevitably contaminate the steel and, instead of trying to eliminate adsorbed water as much as possible, the contamination was controlled by maintaining a constant absolute humidity throughout the experiments.

The choice of solvent was quite straightforward. A temperature stable and non-volatile compound was needed. n-Hexadecane fulfils both these requirements and it also has similarities to a lubricating base stock. It was the most commonly employed solvent in the literature and thus useful for comparison purposes.

There was a notable gap in the literature for adsorption above 25°C, which indicated that work done in this field would be valuable in its own right, apart from its application to friction. The rest of this chapter therefore describes studies at several temperatures into the adsorption of long chain amines on to stainless steel from hexadecane solution.

2.32. Adsorption measurement technique

Two general methods are available for measuring adsorption on solids from liquids. The most common consists of mixing a solid powder and liquid in known proportions, allowing equilibrium to be established, and then determining the resultant change in the composition of the liquid.

The second method is not limited to powders but can be used with bulk solid surfaces. The solid is removed from the liquid after equilibration and the solute remaining on the surface is determined after removing excess liquid clinging to the solid. The difficulty in this method is in the treatment to remove supernatant liquid. The assumption has to be made that adsorbed surfactant is not removed whereas excess liquid is. Many other-

wise valuable pieces of work have lost credibility by making this assumption.

The first method also has a disadvantage. The change in relative concentration of one component is measured as it adsorbs on the solid. Unless the area of the solid is very great, or the adsorption many monolayers thick, changes in concentration become very hard to distinguish at high concentrations. A small difference between two large quantities has to be measured - always an unsatisfactory procedure.

Fortunately the concentrations to be studied in these experiments were quite low and it was possible to use a solution monitoring technique. (The second method of determination, direct measurement on solid surfaces, is used in chapter 5 of this thesis where irreversible reaction is specifically studied). The solution measuring technique enforced an upper limit in equilibrium concentration of $\sim 50 \times 10^{-5}$ moles amine/mole hexadecane, which was rather unsatisfactory at very high temperatures.

At low concentrations the exact amount of solute adsorbed on the surface can be worked out from the relative change in concentration using the formula: ref. (48)

$$n_1^S = \frac{n_o \Delta x_1^L}{m} \quad \dots\dots\dots 2.1$$

n_1^S = moles of solute (component 1) in the adsorbed phase/gram after equilibration.

n_o = initial total number of moles of liquid.

Δx_1^L = difference between mole fraction of component 1 in liquid before and after adsorption.

m = wt. of solid (grams).

n_o , Δx_1^L and m are all measurable so that solute adsorption can be calculated. (At high concentrations the system is more complicated).

To measure amine concentration a spectrophotometric method was adopted. The amine was complexed with an acidified solution of a sulphanaphthalein indicator, and then this coloured complex was extracted into chloroform. The intensity of colour in the chloroform gave a measure of the initial amine concentration. The indicator solution was prepared by dissolving 0.1 gms. of bromocresol green (a sulphanaphthalein indicator) in 10 cm³ of ethanol, adding 0.5 cm³ of conc. sulphuric acid and finally diluting to 100 cm³ with distilled water.

The analytical procedure was as follows:- In each determination a small quantity of amine solution was extracted with a micropipette and weighed in a 20 cm³ ground glass stoppered test-tube. To this was added 5 cm³ of 0.2N HCl, 4 cm³ of chloroform and 1 cm³ of the indicator solution. The whole mixture was shaken for one minute and then centrifuged. Some of the clear yellow chloroform layer was then extracted from underneath the aqueous layer with a hypodermic syringe and placed in a 10 mm cell in an H700 Hilger-Watts spectrophotometer.

This method is a modification of one described by Pearce and Streatfield (49). The procedure has been simplified to determine amine from hexadecane rather than from an aqueous solution.

By varying the initial weight of amine extracted, a wide range of concentration could be measured. The actual weight chosen in each case was adjusted so that the final optical density of the chloroform with respect to the standard lay between 0.2 and 0.4, which is the most accurate measuring region.

A percentage transmittance against wavelength plot for the complex is shown in Figure (2.1). The adsorption peak at 416 nm. varied with concentration and was used in all subsequent work.

Calibration tests, where different amine concentrations were used,

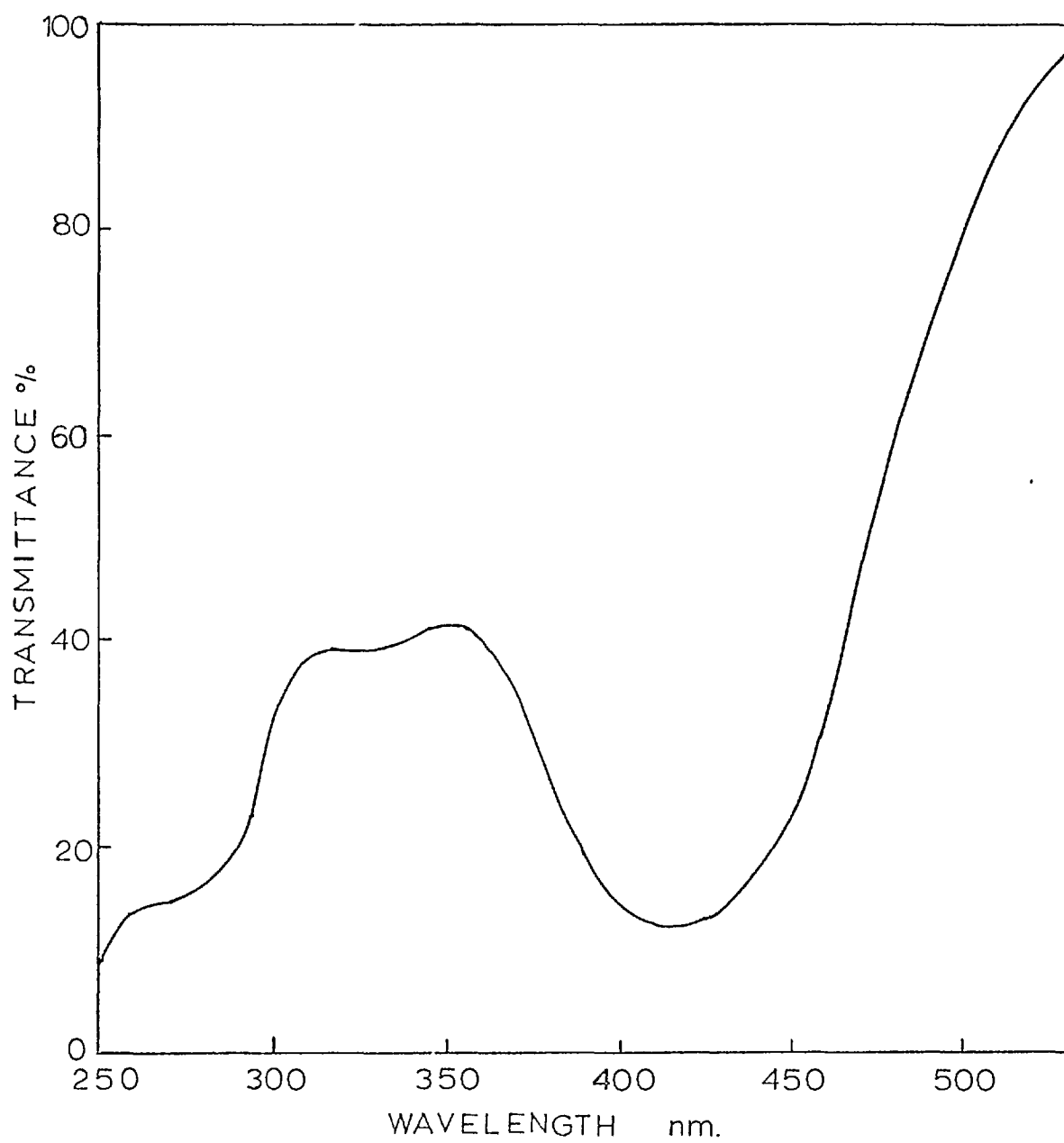


Figure 2.1. Variation of transmittance with wavelength for n-hexadecylamine, bromocresol green complex.

showed that Beer's law was obeyed over a wide optical density range. These are shown in Figure (2.2). The abscissa in this graph has a scale of concentration which is calculated by:-

$$\text{Scale concentration} = \frac{C_1 \cdot V_{\text{hex}}}{V_{\text{hex}} + V_{\text{chl}}}$$

C_1 = concentration of amine in hexadecane (moles/1000 cm³)

V_{hex} = volume of hexadecane extracted (cm³)

V_{chl} = volume of chloroform added (cm³)

It is important to make this correction for the hexadecane solution volume since it is entirely miscible with the chloroform rather than the aqueous phase.

In early experiments a special chloroform standard was prepared by shaking pure hexadecane with hydrochloric acid, indicator and chloroform. It was soon found, however, that the optical density of this chloroform with respect to pure chloroform was always less than 0.01. Thereafter pure chloroform was used as a standard in the spectrophotometer although every few days the original method was repeated as a purity check. (It was found that if the chloroform were shaken with distilled water rather than 0.2 N HCl a higher optical density was obtained).

This determination method was found not to be significantly dependent on temperature. The amount of hexadecane mixed with the chloroform did not change the optical density noticeably nor were measurable differences found when small quantities of steel powder were carried over into the chloroform mixture.

2.33. Materials and apparatus

Metal powder was obtained from B.S.A. Metal Powders Ltd., Birmingham. It was prepared by an atomisation process and its composition and main properties are shown in Table (2.1). Also given here is the surface area of

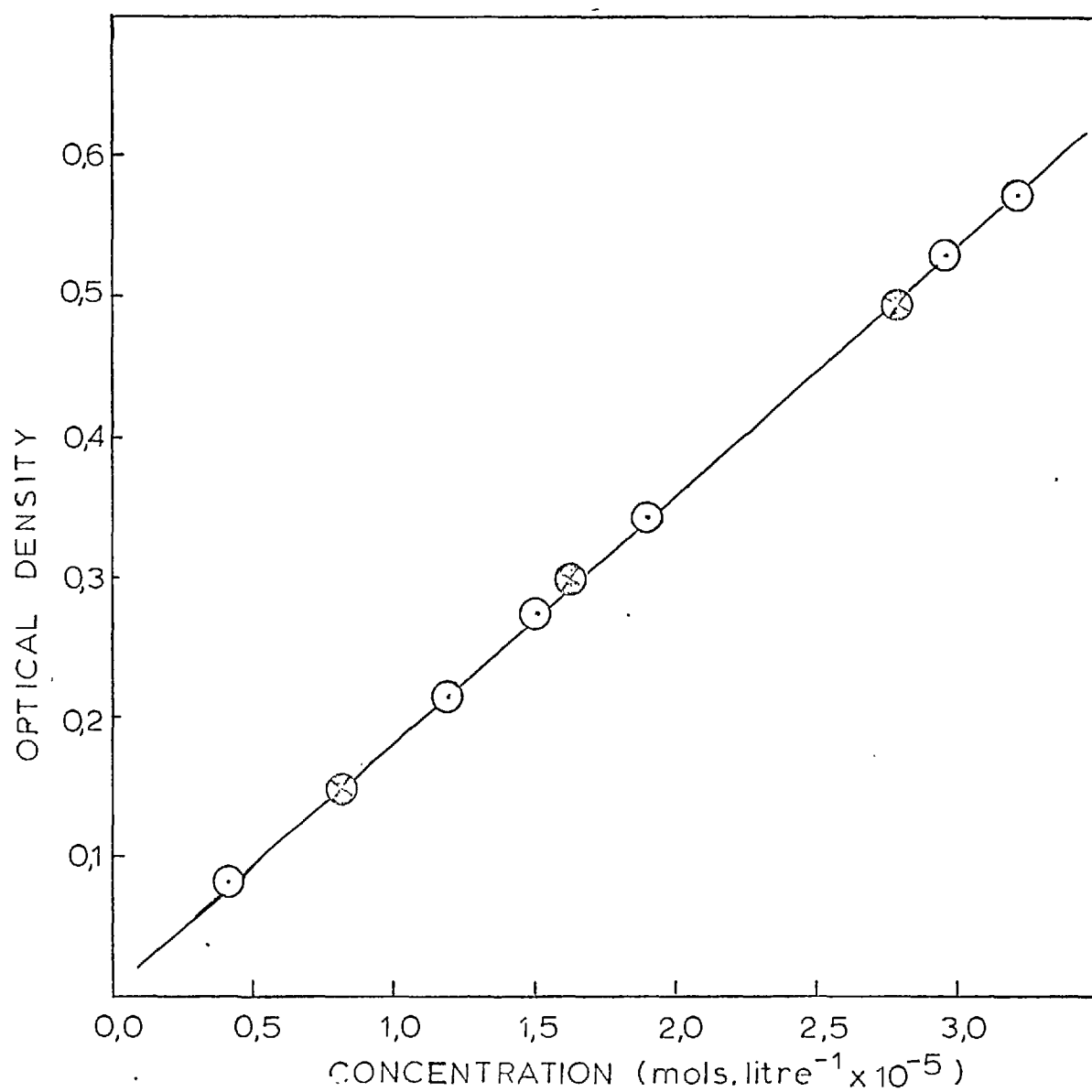


Figure 2.2. Calibration of spectrophotometer for the determination of amines

- octadecylamine
- ⊗ dodecylamine

the powder measured by krypton B.E.T., with the cross-sectional area of a krypton atom taken as 0.185 nm^2 .

Table (2.1)

SPECIFICATION				
AISI 302B. This is an "18/8" stainless steel similar to EN58B				
COMPOSITION				
Fe%	Ni	Cr	Si	C
70	9.7	18.2	2.43	0.16
B.E.T. surface area = $0.060 \text{ m}^2/\text{gram}$ 250 - 400 mesh grade Mainly austenitic (non-magnetic)				

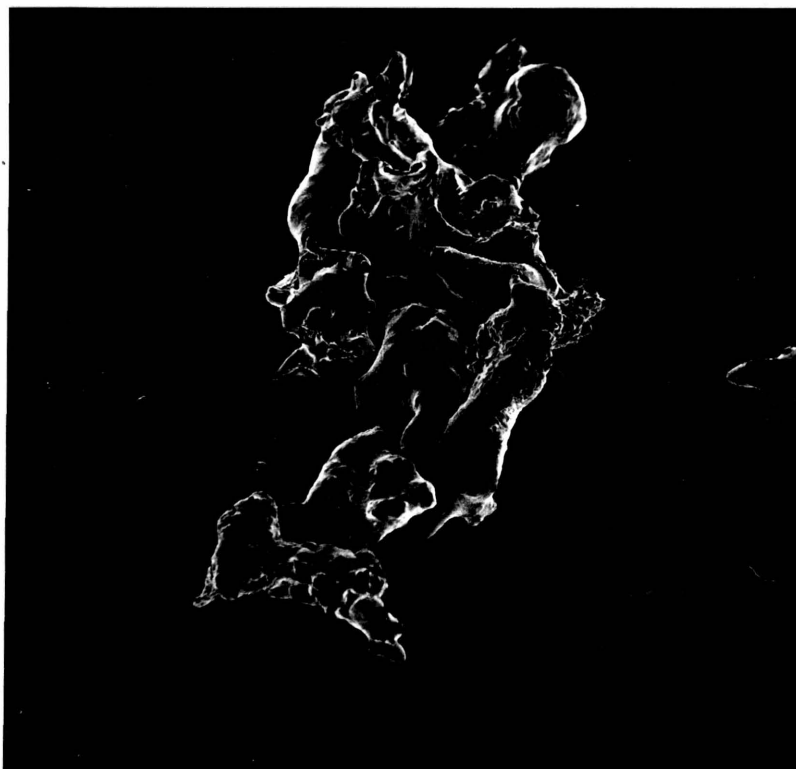
Scanning electron micrographs of the powder are shown in fig. (2.3). It can be seen that the individual particles are non-spherical but that the actual surface is quite smooth.

Hexadecane was obtained from Koch Light Ltd., and was "puriss grade". It was necessary to purify this further, however. Since solvent purity was very important in all the experiments described in this thesis, some time was devoted to determining just how much surface active material was present in the hexadecane. These experiments are described in appendix A.

n-Octadecylamine, n-hexadecylamine and n-dodecylamine were obtained from Liljenholmens Stearinfabriks A.B. Stockholm, Sweden. They were "pur"



Stainless steel powder. Magnification X 1800



Stainless steel powder. Magnification X 324

Figure 2.3. Scanning electron micrographs of the stainless steel powder

and were used without further treatment.

Two slightly different experimental methods were used. For preliminary tests, and investigations at high temperatures, the apparatus shown in Figure (2.4) was employed. The reaction vessel was a 50 cm³ flask with a detachable lid having four ground glass sockets. The metal powder was mixed with a two-bladed stirrer which entered the top, central socket through a mercury seal. The stirrer was shaped so as to fit neatly against the bottom of the flask. Temperature was maintained by an enclosing heating mantle controlled by feedback from a thermocouple immersed in the solution. Temperature was held steady within $\pm 1^{\circ}\text{C}$ up to 100°C and $\pm 2^{\circ}\text{C}$ up to 170°C .

In later experiments the apparatus was simplified. Powder and solution were placed in a series of 50 cm³ ground glass stoppered test-tubes. These were two-thirds immersed in a water bath and automatically shaken. This apparatus could be used satisfactorily up to 75°C . Again temperature was constant to $\pm 1^{\circ}\text{C}$.

2.34. Experimental procedure

A suitable concentration of amine in hexadecane was prepared and a weighed quantity transferred to the reaction vessel. This solution was then purged for 15 minutes with white spot nitrogen, which had passed through a series of MgCl_2 bubblers and finally cotton wool. This controlled the initial humidity of the experiment to a humidity corresponding to 25% R.H. at 25°C .

The required temperature was then established, which generally took less than five minutes. After this, solution samples were withdrawn to check the initial concentration, and a known weight of powder was added.

The solution was then sampled periodically to check the concentration. Each time, the stirrer was halted five minutes before a sample was taken to

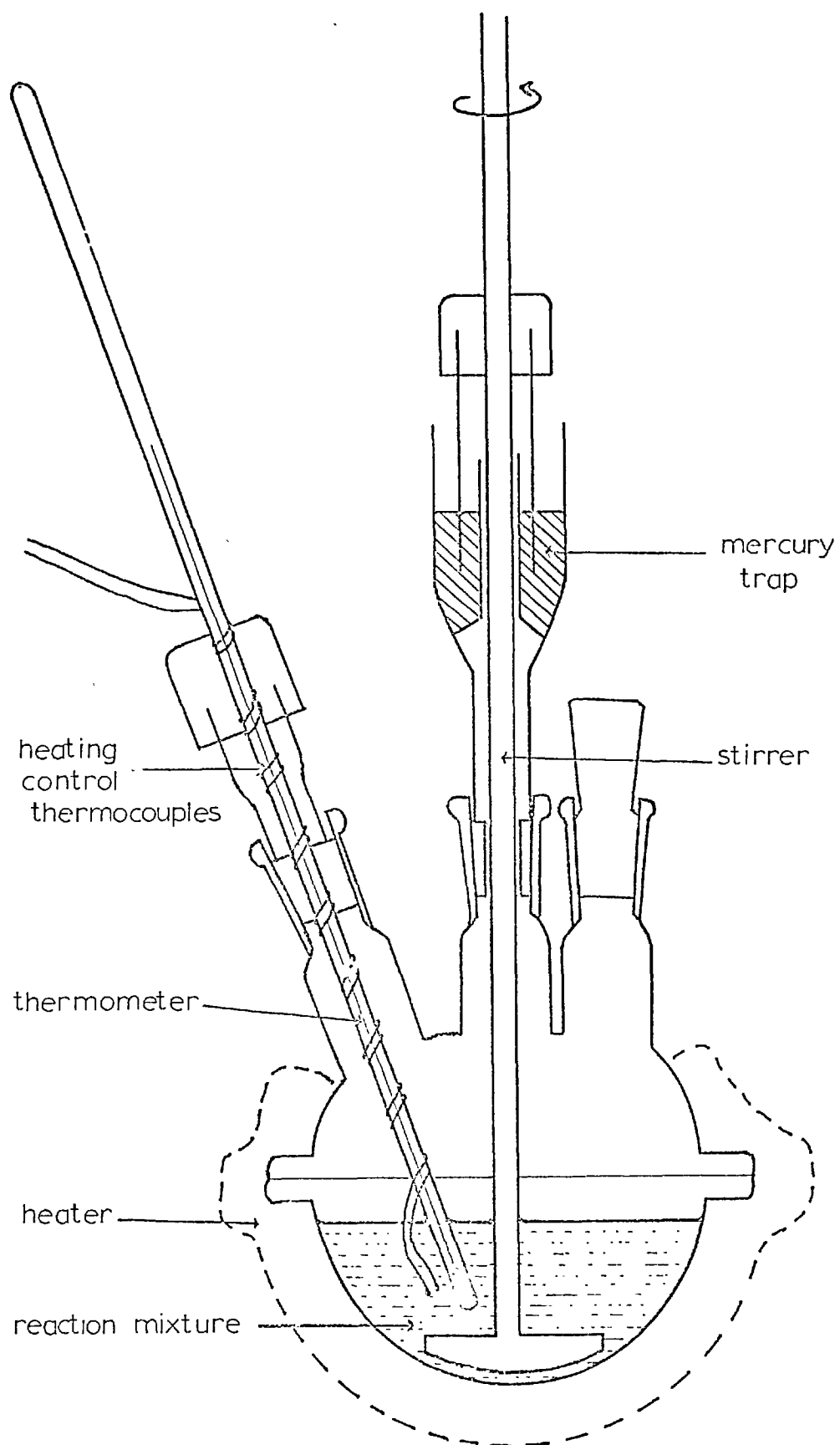


Figure 2.4. Adsorption apparatus

allow the powder to settle. The amount of adsorption could be calculated from the initial and final concentrations using equation 2.1, allowance being made for the solution removed during sampling.

Points further up the isotherm were obtained by adding small volumes of more concentrated amine solution and determining the new equilibrium concentration. As successive points were measured in this way the accuracy was reduced, since allowance had to be made for all the solution removed during previous sampling.

When the kinetics of adsorption had been established, the second, simpler type of apparatus was used. In this case the powder and solution were shaken together, without intermediate sampling, until equilibrium was reached, after which the final concentration was measured. Using this apparatus it was possible to do batches of five to ten runs simultaneously.

2.35. Cleanliness and adsorption

Using powders it was obviously not possible to remove any surface contamination by rubbing or ionic bombardment. Therefore a washing procedure had to be adopted. A sample of stainless steel powder was Soxhletted with benzene in a cellulose thimble for two days. It was then dried in an oven at 50°C and an octadecylamine adsorption isotherm measured. This was compared with the adsorption isotherm using unwashed steel powder. The results are shown in Figure (2.5). Each point represents a reading taken after at least four hours equilibration (see section 2.31). As can be seen there was negligible difference between adsorption on treated and untreated steel over the concentration range studied.

This indicates that grease and oil (which would be removed by benzene) were not serious contaminants. Further evidence of this is shown by the fact that when the steel powder was placed on a surfactant-free, distilled

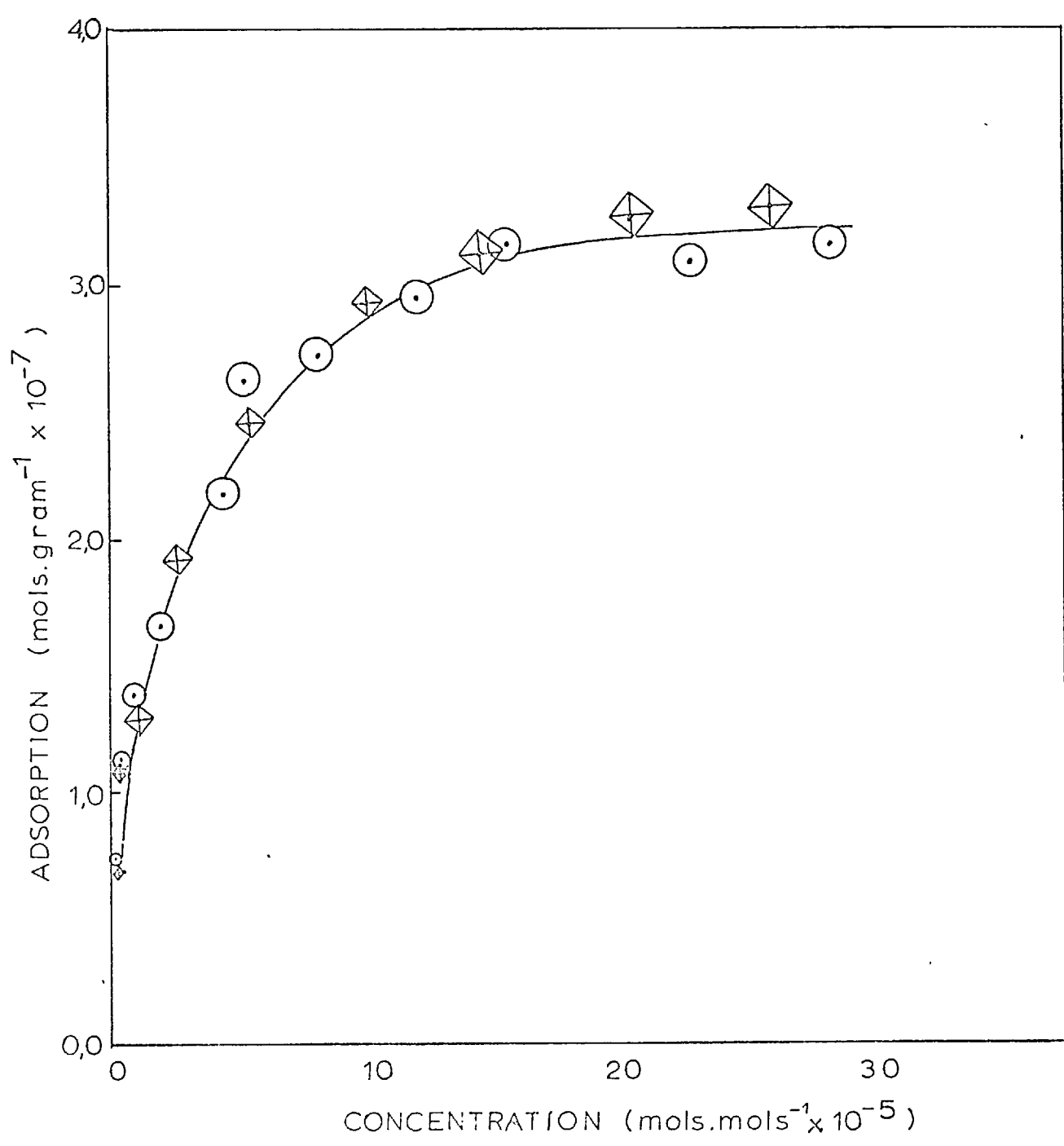


Figure 2.5. Effect of cleaning on the adsorption of n-octadecylamine on steel powder at 22°C.

- untreated steel
- ◈ steel soxhletted in benzene for two days

water surface, all the particles sank rather than floating at the air-liquid interface. Since washing seemed to have no effect on adsorption further work was carried out on untreated steel powder.

It is important to note that only the absence of surfactant contaminant has been demonstrated. There was almost certainly an adsorbed water layer on the oxide surface which could not be removed by washing.

2.36. Accuracy

Before considering the results in detail the factors determining the accuracy of the adsorption experiments need to be discussed.

The preparation of initial amine solution, the addition of steel powder and the extraction of samples for analysis all used a weighing technique, and their combined errors were less than 1%. The greatest uncertainty arose from the measurement of concentration which almost always controlled the overall experimental accuracy. The concentration measurement error was compounded of experimental inaccuracy in preparing the chloroform samples and intrinsic scatter from the spectrophotometric apparatus itself. The former was usually about 2% and the latter, within the optical density range 0.2 - 0.4, was 1-2% (50).

An indication of the typical reproducibility of concentration measurements using a series of samples from the same solution can be seen in Table (2.2).

A difference between two concentrations gave the adsorption so the accuracy of this is rather less than the accuracy of the concentration measurements themselves.

For the concentration range $2 \times 10^{-6} \rightarrow 3 \times 10^{-4}$ moles/mole the largest error was in the adsorption value and was $\pm 4\%$. At higher final concent-

rations, as the change in concentration with adsorption dropped, this accuracy decreased to reach $\pm 7\%$ at 5×10^{-4} moles/mole. At very low

Table (2.2).

Sample	wt. extracted gms.	vol. extracted cm ³	Vol CHCl ₃ cm ³	Adsorbance	conc. m/1000cm ³
1	0.0535	0.0696	4	0.313	1.01×10^{-3}
2	0.0540	0.0702	4	0.320	1.04×10^{-3}
3	0.0529	0.0688	4	0.320	1.05×10^{-3}
4	0.0524	0.0681	4	0.303	1.00×10^{-3}
5	0.0528	0.0687	4	0.315	1.04×10^{-3}
6	0.0540	0.0702	4	0.312	1.00×10^{-3}
				Mean = 1.02×10^{-3} σ = 0.02×10^{-3}	

concentration the limiting accuracy was in the equilibrium concentration rather than the adsorption value and large ratios of hexadecane solution to chloroform were needed to obtain a measurable optical density. Thus although the accuracy of the equilibrium concentration fell to $\pm 30\%$ at 1.5×10^{-7} moles/mole, the adsorption, which was almost entirely dependent on the initial concentration could still be measured to $\pm 4\%$.

This measurement of concentration with sufficient accuracy was a paramount limitation in all the adsorption experiments. A way over the problem would have been to have used a higher surface area solid. This would have ensured larger concentration changes on adsorption, giving more

accurate adsorption determination. The use of a higher surface area steel powder, however, would have resulted in a less well characterised steel surface which would have detracted from subsequent comparison with friction experiments.

Another possible inaccuracy arose from the effect of adsorbed water. It was impossible to remove all the water contaminant from the metal, so instead the humidity was controlled to 25% R.H. at 25°C, which could be paralleled in the later friction work. In a few early experiments carried out without this humidity control no differences were observed in adsorption behaviour.

The temperature control was generally $\pm 1^\circ\text{C}$. This was entirely adequate above 35°C, where the accuracy of measurement was less than the adsorption response to 1°C variation. At 22°C and 30°C there was a slight problem, however. An isotherm for adsorption of n-octadecylamine from n-hexadecane on to stainless steel powder at 22°C is shown in Fig. (2.6) (This system was used as a proving test for the various trial procedures tried out during the experiments, which explains the large number of points on the curve). The calculated accuracy is shown for each point as the standard deviation. As can be seen there is quite wide scatter in the middle concentration range, which is probably due to the effect of temperature variation.

There were one or two other possible sources of error. The optical calibration was tested with each newly prepared amine solution. This checked both the original calibration and the newly prepared solution. Experiments were also carried out to monitor amine adsorption on the glass. Slight adsorption could be detected at very low concentrations. This was not considered to be significant, however, since the ratio of metal area to exposed glass area was always greater than 50 to 1, and very low metal

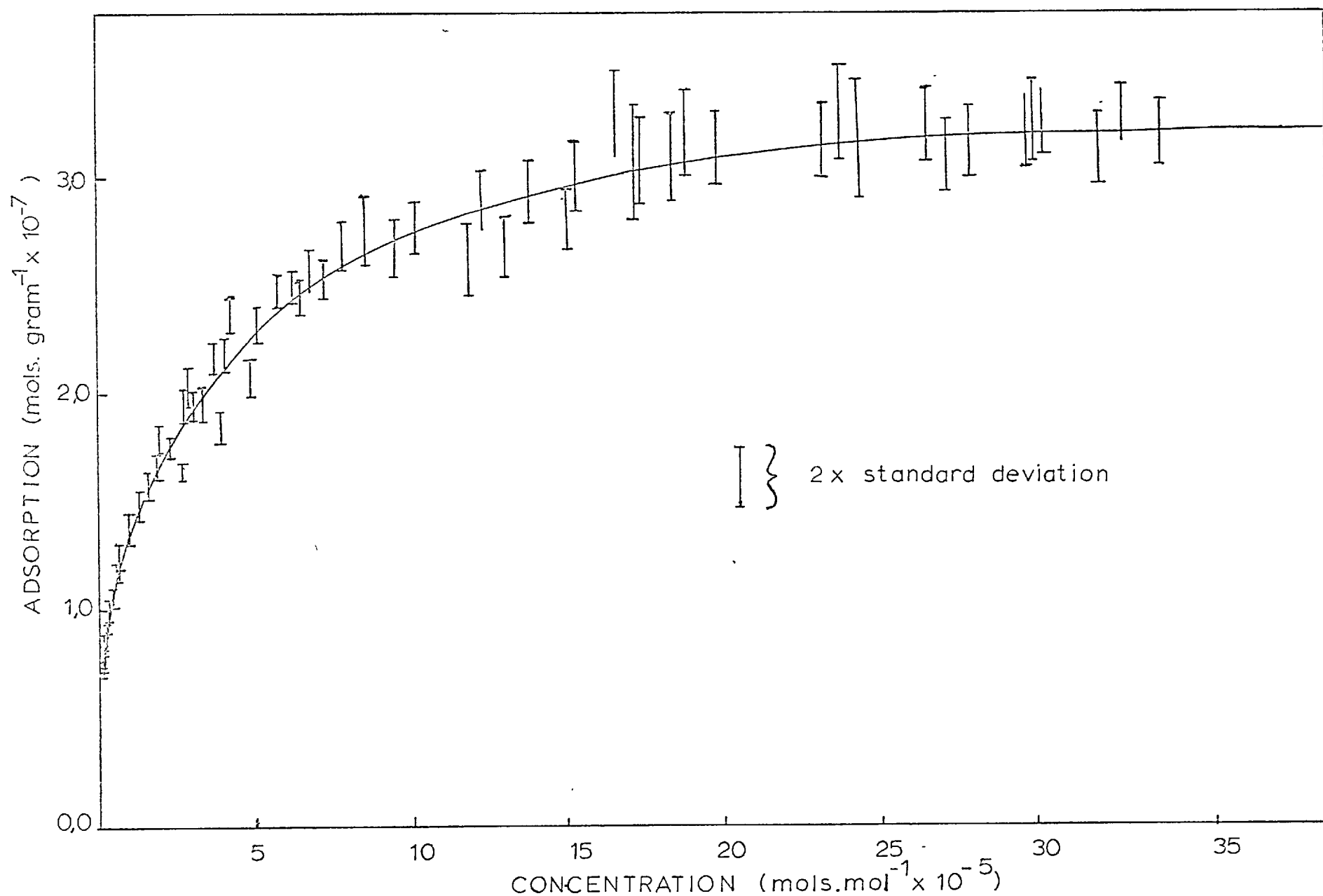


Figure 2.6. Adsorption of octadecylamine at 22°C

coverages were not to be investigated.

2.40 Results and Discussion

2.41 Kinetics of adsorption

The kinetics of amine adsorption on stainless steel was investigated. Most of the experimental work involved octadecylamine in hexadecane, and its rate of adsorption on steel was calculated at several temperatures over a wide concentration range.

Some kinetic results are shown in Figure (2.7). Below 60°C an equilibrium was reached after four to six hours, but ninety percent of the adsorption occurred in the first ten minutes. Above 50°C there was a comparatively slow, secondary reaction superimposed on the fast adsorption. This was time-dependent and increased with temperature and so was probably chemical in nature. Below 90°C this slow, secondary reaction contributed only a minor fraction of the total adsorption, even after several hours. It was thus relatively unimportant in lubrication tests where high temperatures are rarely maintained for more than thirty minutes. Attention was therefore concentrated on the fast, primary adsorption and experiments were designed to limit the effect of the slow, secondary reaction.

No attempt was made to analyse the kinetics of adsorption quantitatively. The time lag required for the powder to settle before a reading could be taken made this impractical. It was noted, however, that concentration differences above a very low concentration level made little difference to the reaction rate. A comparison was made between the rates of adsorption of n-octadecylamine and n-hexadecylamine on stainless steel. This can be seen in Figure (2.8). The two curves are of the same form which suggests the same kinetic process occurred for both the matching and non-matching amine-solvent adsorption systems.

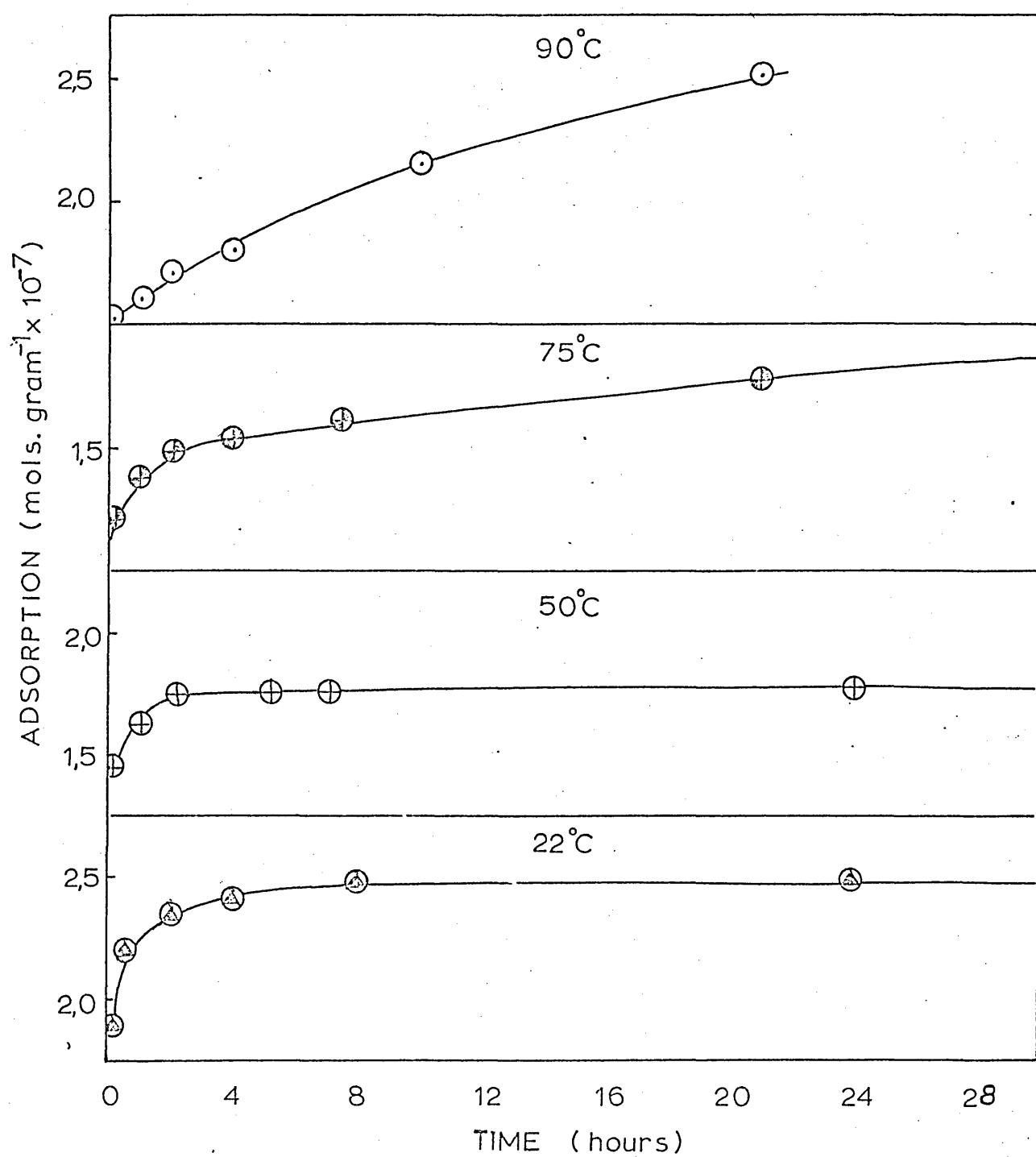
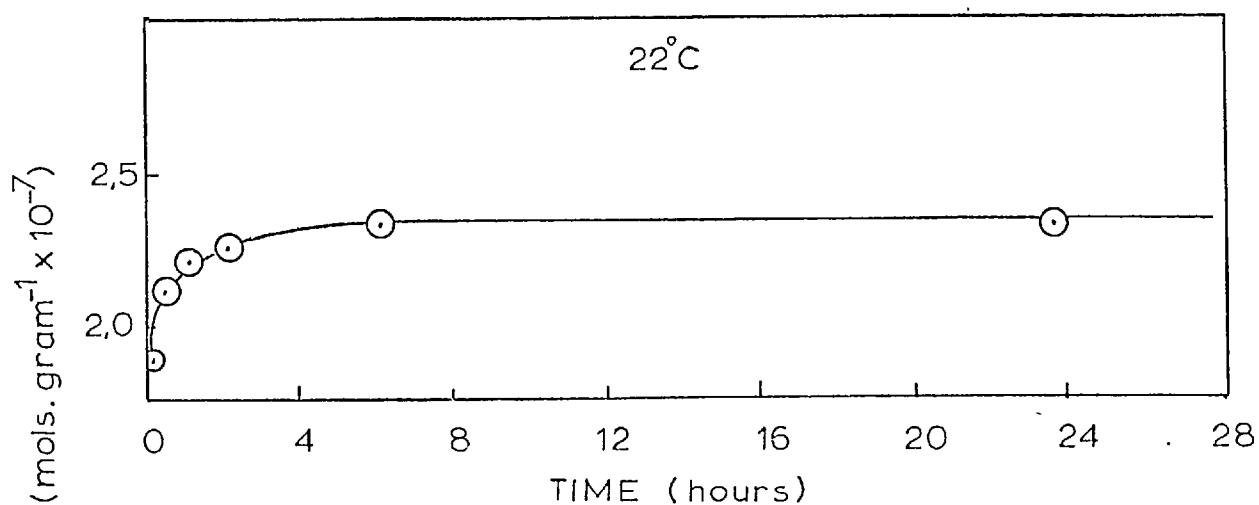
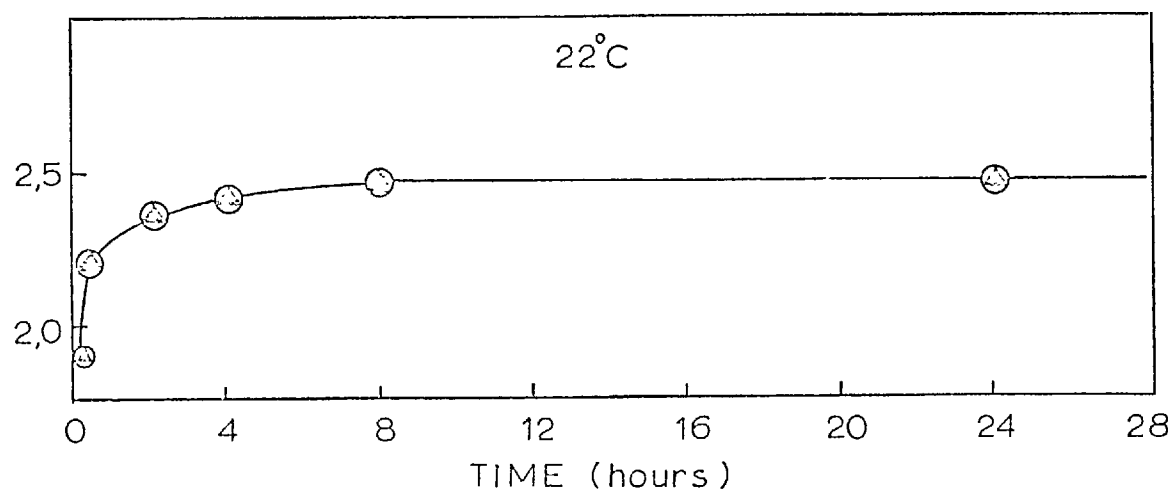


Figure 2.7. Adsorption rates of octadecylamine on stainless steel at different temperatures

temperature	22°C	50°C	75°C	90°C
concentration (mols/mol x 10 ⁻⁵)	5.4	8.6	8.0	14.3
(after one hour)				



Adsorption of n-hexadecylamine on stainless steel



Adsorption of n-octadecylamine on stainless steel

Figure 2.8. Adsorption results for different chain length amines

- ⊙ concentration 6.5×10^{-5} mol/mol (1 hour)
- ⊙ concentration 5.4×10^{-5} mol/mol (1 hour)

The results compare well with the only adsorption rates available for an approximately similar system, those of Daniel (32) and Greenhill (22) for stearic acid on iron powder. Daniel found 90% of the adsorption occurred within five minutes and equilibrium was reached in one or two hours. Greenhill, for the same system, showed that equilibrium was attained after four hours.

2.42. Effect of chain length on adsorption

Although most tests were carried out on the octadecylamine-hexadecane system, some experiments were also done using hexadecylamine and dodecylamine. These were in order to determine the effect of chain length on adsorption, with particular attention to any differences occurring when both solute and solvent had the same number of carbon atoms.

Adsorption isotherms for octadecylamine, hexadecylamine and dodecylamine on stainless steel from hexadecane at 22°C are shown in Figure (2.9). These results are replotted in Figure (2.10) where concentration is represented on a logarithmic scale. There are three main adsorption regions:-

a) At very low concentrations adsorption is the same in moles/gram regardless of chain length. This can be seen most clearly in Figure (2.10) where the three isotherms are clearly superimposed at low values.

b) At intermediate concentrations adsorption is dependent on chain length such that the amount of amine adsorbed at a given concentration increases with increasing chain length.

c) At very high concentrations the adsorption reaches the same constant plateau value for all amines, independent of chain length.

These results are similar to those of Daniel (32) who studied adsorption of fatty acids from benzene on to nickel powder. He also noted that increasing chain length increased the strength of adsorption and that a constant

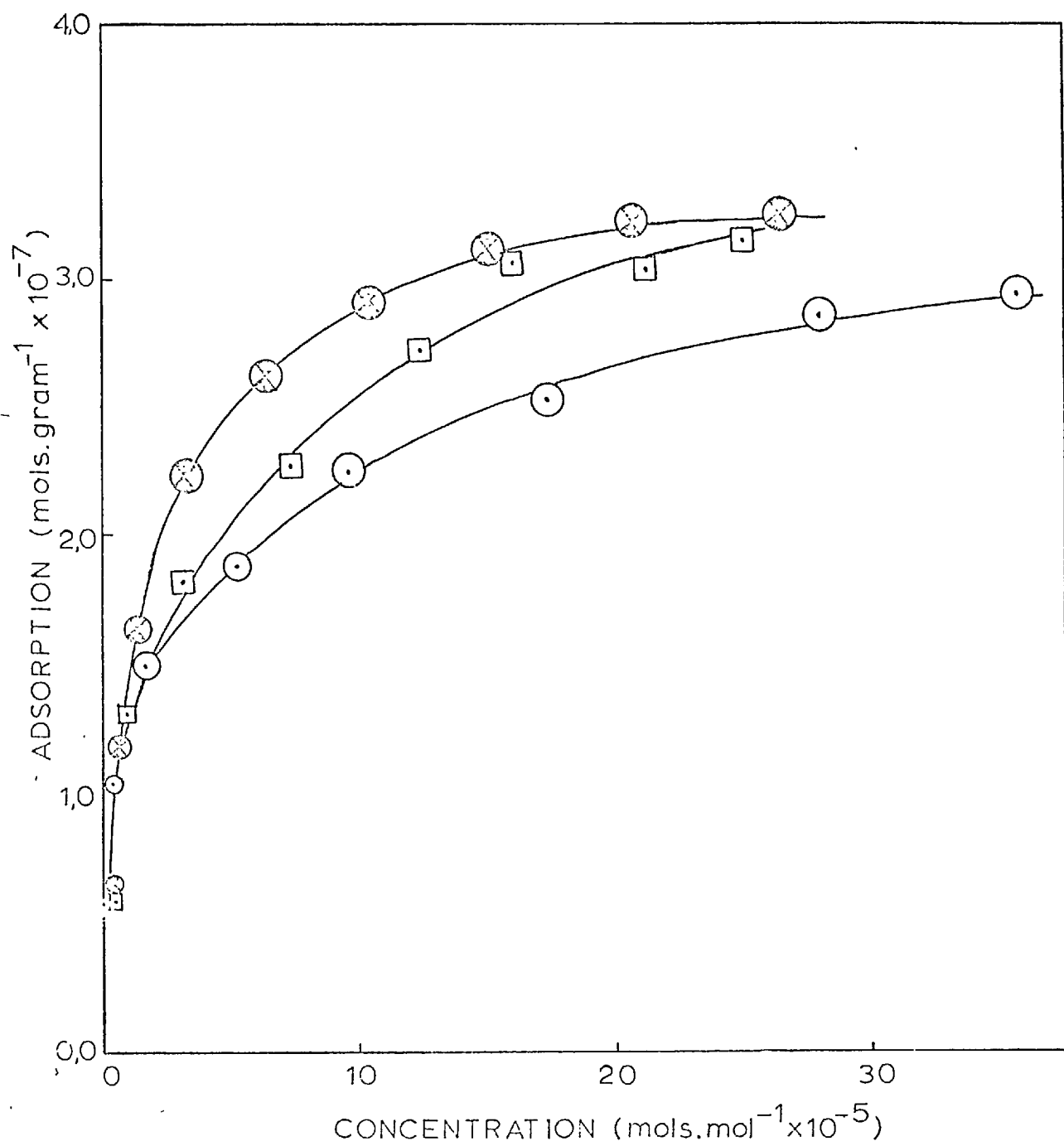


Figure 2.9. Adsorption isotherms for different chain length amines at 22°C and 25% R.H.

- octadecylamine
- hexadecylamine
- ⊙ dodecylamine

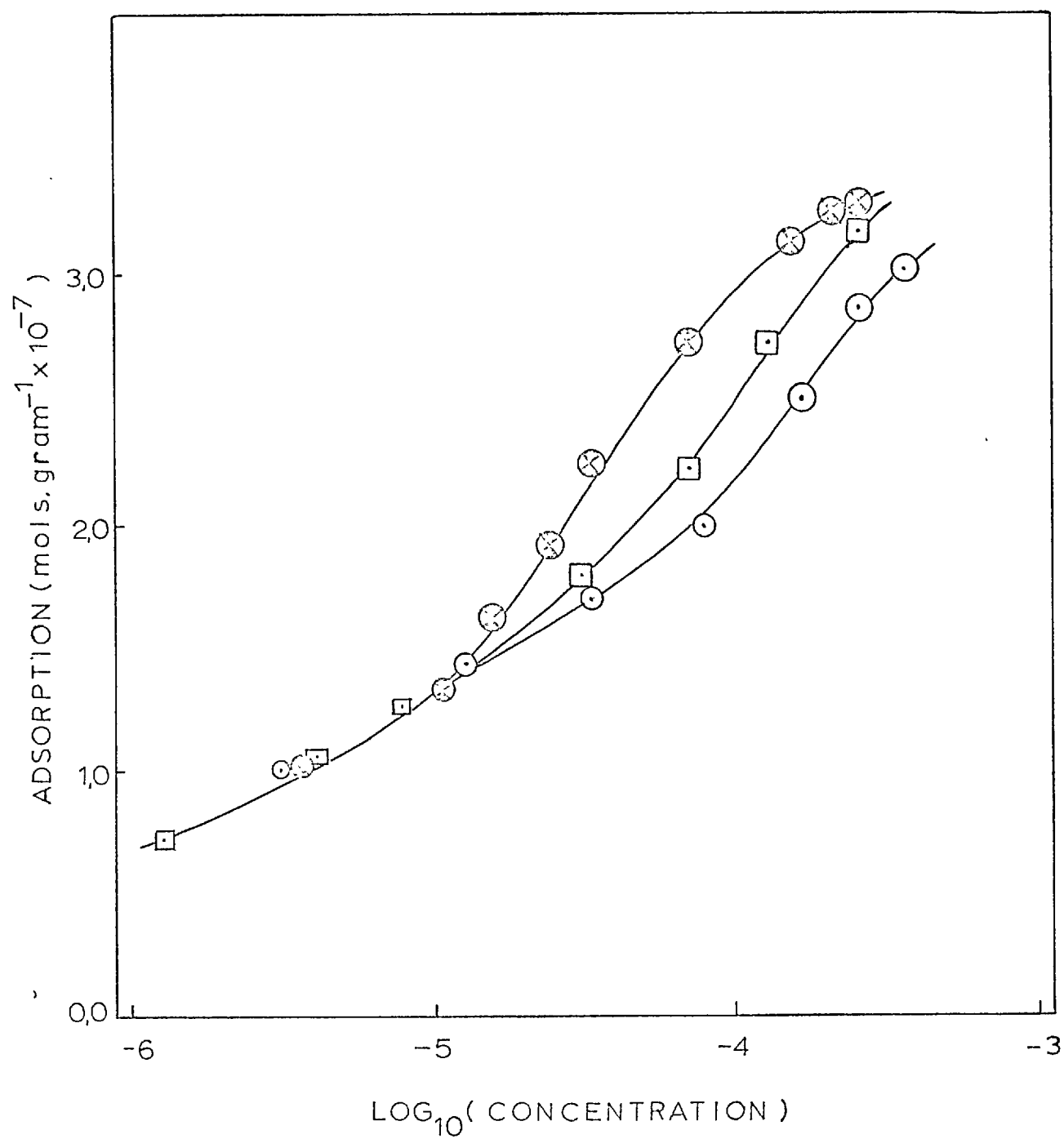


Figure 2.10. Adsorption plotted against $\log_{10} C$ for different chain length amines (results from Fig. 2.9)

molar plateau value was reached. Unfortunately he did not measure the surface area of the nickel and thus could not determine the area/adsorbed molecule.

It is interesting to note from Figure (2.9) that the total adsorption of hexadecylamine from hexadecane is similar to that for octadecylamine at high concentrations. This, combined with the kinetic data in Figure (2.8) suggests that hexadecylamine in hexadecane behaves normally in the sequence dodecylamine, hexadecylamine, octadecylamine.

Several authors have observed atypical adsorption effects when the chain lengths of solute and solvent match. Bewig and Zisman (24), in particular, found that adsorption of long chain amines from alkanes on platinum generally gave a complete amine monolayer after six hours. If solvent and solute matched, however, a residual 15% of alkane was retained in the adsorbed film even after twenty-four hours.

Many of the adsorption points on the hexadecylamine curve in Figure (2.9) were measured after the system had been left at least twenty-four hours. Thus it seems clear that for the hexadecylamine-hexadecane-stainless steel system at 22°C there is no such obvious chain matching effect as was observed by Zisman on platinum.

The general topic of chain matching will be considered in more detail in chapter 3.

2.43. Reversibility of adsorption

The result of a simple experimental run to demonstrate that the adsorption was, at least in part, reversible is shown in Fig. (2.11). The temperature was raised periodically and the concentration monitored whilst equilibrium stabilised. Temperature responded fully to change after four minutes. This figure also shows the slow, time-dependent reaction occurring

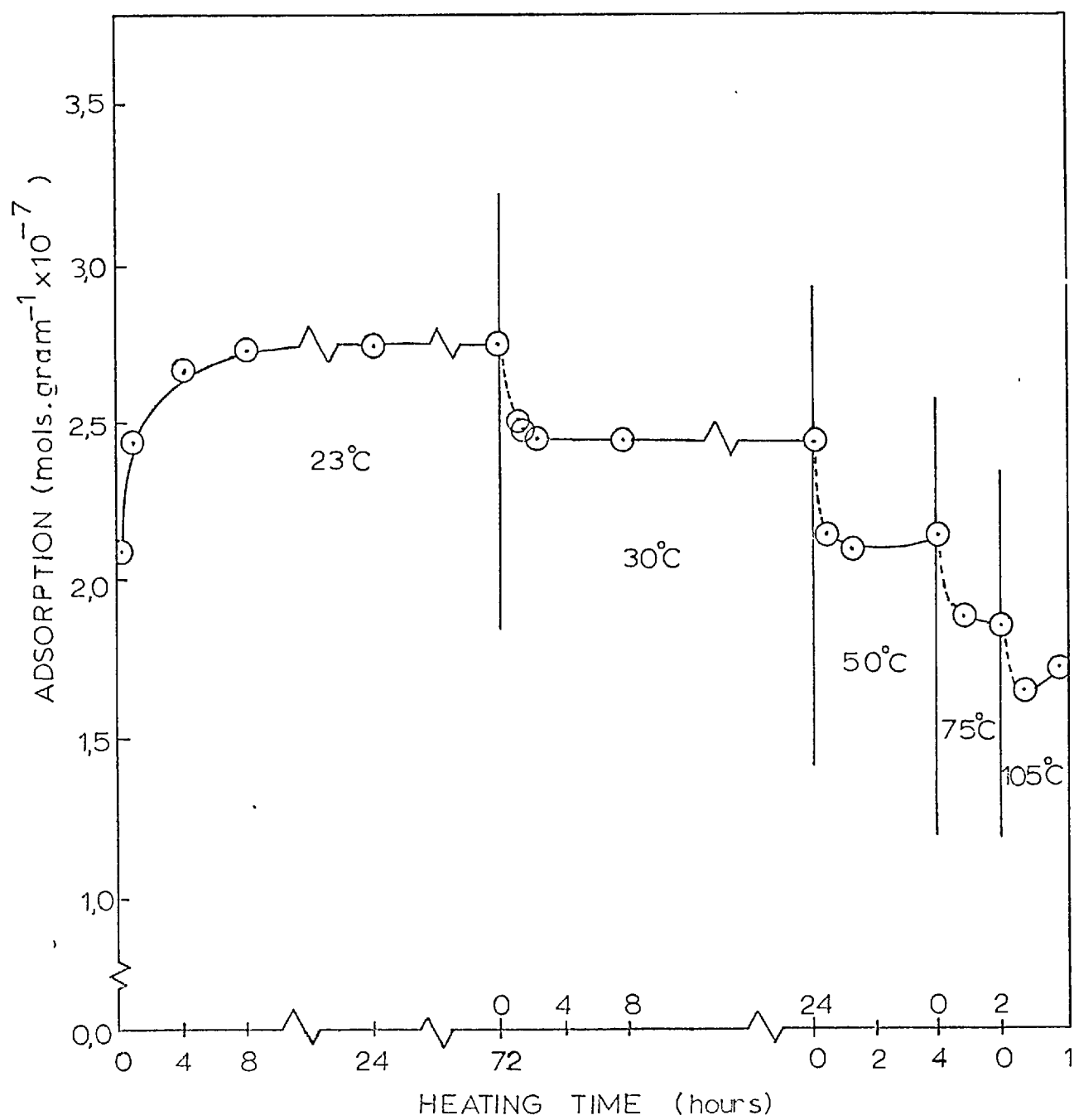


Figure 2.11. Reversibility of octadecylamine adsorption with temperature

at high temperatures.

A few experiments were also carried out which showed that the adsorption was not entirely reversible. After adsorption of hexadecylamine, some of the metal powder, (carrying with it a little supernatant liquid), was weighed into a cellulose thimble. This was then soxhletted in n-hexane for twenty-four hours and the concentration of amine in hexane measured. From the drop in weight of the metal powder during the washing process, a correction could be made for the excess amine which had been carried over in solution. At low concentrations of less than 10^{-4} moles/mole it was thus possible to obtain approximate values ($\pm 10\%$) of the quantity of amine desorbed by hexane.

These desorption results showed that for hexadecylamine on stainless steel a residual $(0.9 \pm 0.2) \times 10^{-7}$ moles/gram, or about one third of the total adsorbed amine was not easily removed. This agrees well with the lower portion of the adsorption curves in Figure (2.10). Here the three isotherms for different chain length amines were observed to coincide below 1.0×10^{-7} moles/gram, so that only above this was the adsorption dependent on chain length. As will be seen in the next section, one third of the total adsorbed molecules is removed by increasing temperature. This gives three pieces of evidence for a fraction, more strongly adsorbed, probably irreversibly.

- a) One third of the adsorption is not removed by boiling hexane (B.Pt. = 68°C).
- b) Increase of temperature produces a limiting adsorption of about one third of the total.
- c) One third of the total amine is adsorbed at very low concentrations and the adsorption tends only very slowly to zero as concentration drops. Below this one third, the amount adsorbed is independent of chain length.

Exchange of adsorbed amine on the surface was not attempted, so the observation of Block and Simms (43) that some of the irreversibly bound amine may be exchangeable was not verified.

The approximate ratios of one third strongly and two thirds weakly adsorbed often feature in the literature and seem to be characteristic of several metal adsorption systems. It has been found by Timmons (45) Cook and Ries (46), Cook and Hackermann (40) and Block and Simms (43). Their findings have been discussed in the review, section (2.25).

2.44 The effect of temperature on adsorption

A major part of the experimental work discussed in this chapter was devoted to measuring the change in adsorption of amines with temperature. This has already been considered briefly in section (2.41), where two types of adsorption were identified. The first was a fast, semi-reversible adsorption which attained equilibrium within four hours at 22°C and more quickly still at higher temperatures. The second, which below 90°C comprised only a small percentage of the total was slow and time dependent, increasing with temperature and having all the characteristics of a chemical adsorption. The results presented in this section concentrate on the primary, rapid reaction.

Figure (2.12) shows isotherms at five temperatures for the adsorption of n-octadecylamine from n-hexadecane on to stainless steel. The adsorption fell with temperature over most of the concentration range. Similar results for n-hexadecylamine on stainless steel are shown in figure (2.13). The actual experimental results from which figures (2.12) and (2.13) were obtained are given in appendix B.

For both amines, the amount adsorbed at very low concentrations was independent of temperature and apparently irreversible (see section 2.43).

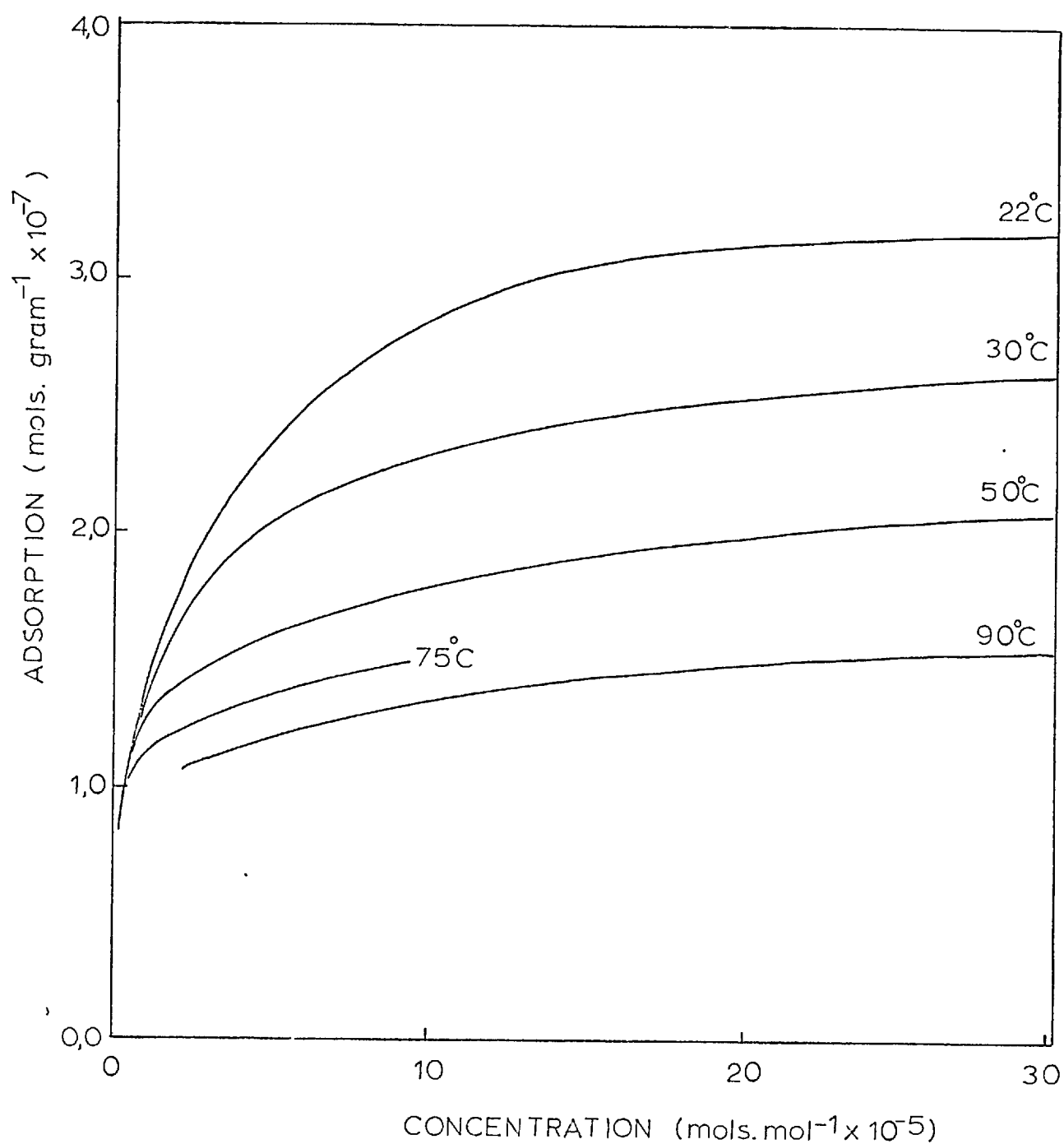


Figure 2.12. Adsorption isotherms for n-octadecylamine on stainless steel from hexadecane solution at a series of temperatures and 25% R.H. (numerical results in Appendix B)

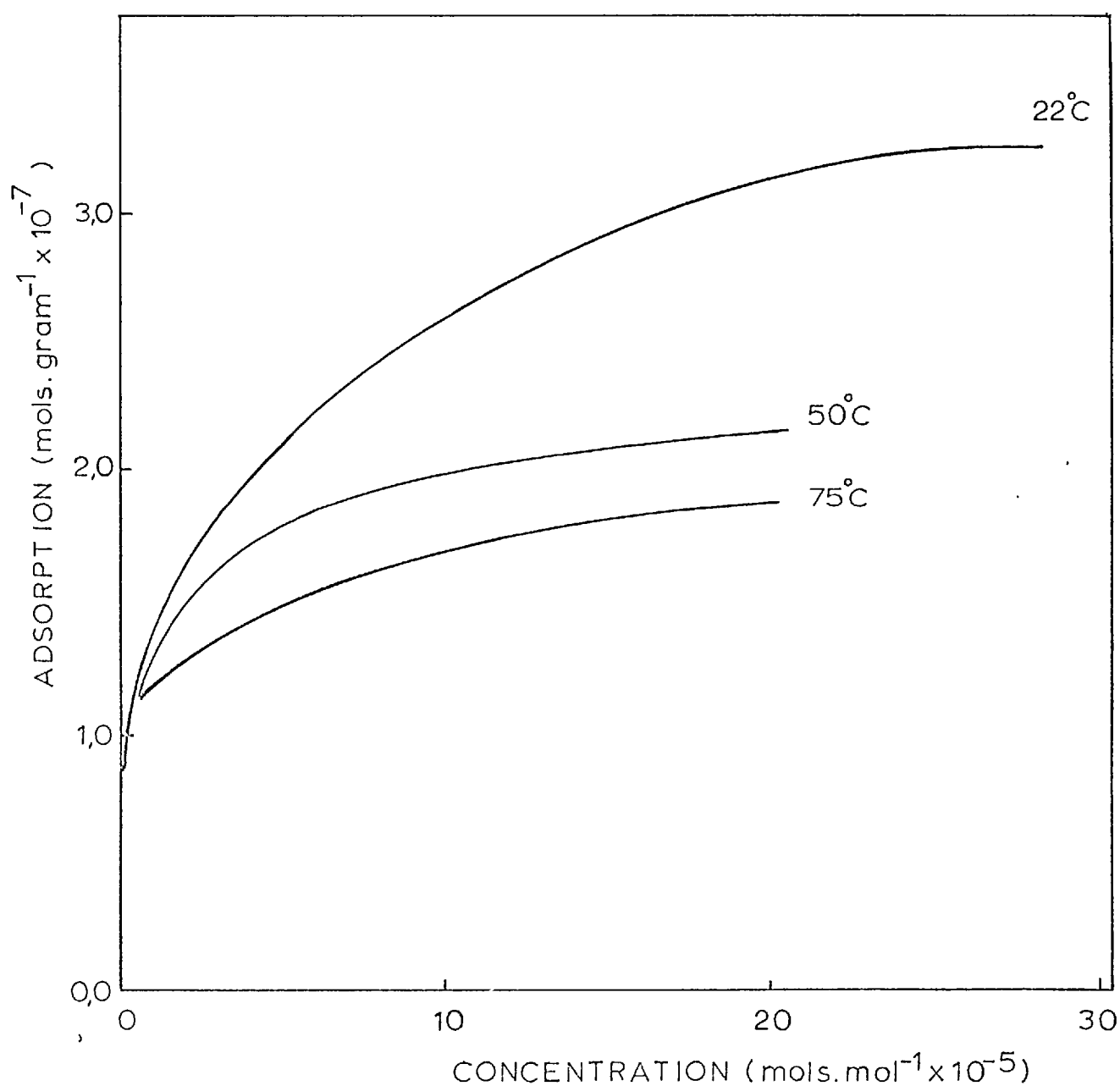


Figure 2.13. Adsorption isotherms for n-hexadecylamine on stainless steel from hexadecane solution at a series of temperatures and 25% R.H. (numerical results in Appendix B)

At very high temperatures, 75°C and 90°C, true equilibrium was never reached because of the slow secondary reaction. Fortunately the main adsorption was so much faster than this, that equilibration could be assumed within a time interval for which the slow reaction contribution was negligible.

2.45. Thermodynamic analysis of adsorption results

Some caution is necessary in applying thermodynamics to the experimental adsorption results. The adsorbing surface was only poorly defined and heterogeneous, so that quite a sophisticated adsorption model would be necessary to describe the system adequately. The results were not accurate enough for this, however, so a simple model was used which enabled general trends to be discerned.

It has been demonstrated in sections (2.41) and (2.43) that adsorption reaches equilibrium and is at least partially reversible. This is important since equilibrium and reversibility are pre-requisites for classical thermodynamics. The slow, secondary reaction mentioned in section (2.41) is neglected. This is considered justifiable since this reaction was minor compared to the main adsorption, superimposed on it and easily separable.

Of the main adsorption only the two thirds reversible fraction can be considered thermodynamically. This leaves a constant adsorbed fraction of about one third about which no information is available, which leads to difficulties in working out the total adsorption energy of the system (see appendix C). The thermodynamic bases of the formulae used in this section are derived in appendix C.

The thermodynamics of adsorption gives the following formula for the isosteric heat of adsorption.

$$\left[\frac{d \ln C_1}{d(1/T)} \right]_1 = - \frac{\Delta \bar{H}_{ads}}{R} = \frac{q_{st}}{R} \quad \dots\dots\dots 2.2$$

- c_1 = equilibrium concentration (moles/mole solvent)
 Γ_1 = adsorption coverage of adsorbate (constant)
 $\Delta \bar{H}_{\text{ads}}$ = differential enthalpy change on adsorption
 q_{st} = isosteric heat of adsorption (defined as positive for heat evolved).

This equation is applicable generally to monolayers, multilayers or reversible chemisorption (51) so that no specific model needs to be assumed. The basic assumptions inherent in equation 2.2 are:-

a) That some of the measured adsorption is reversible; q_{st} then applies to this part.

b) That the solution is ideal within the range studied, (otherwise activity coefficients must be introduced).

The standard state of the solution is taken to be a concentration of one mole/mole solvent. The "coverage" is defined as excess moles of adsorbate per unit area of surface. This definition does not involve any serious ambiguity in the case of a strongly adsorbed solute, although difficulties do arise in defining adsorption from very concentrated solutions, which were not used here.

q_{st} is the molar heat of transfer of molecules from the standard state to an infinite surface contained adsorbed molecules at a surface excess Γ_1 . It is, of course, the difference between the heats of adsorption of amine and hexadecane on the bare metal, since in all cases amine was displacing hexadecane rather than adsorbing directly on the metal.

Equation 2.2 is applied in Figure (2.14) to the adsorption data from Figure (2.12); $\log_{10} C$ is plotted against $1/T^{\circ}\text{K}$ for a series of different amine coverages. From this equation it is possible to calculate the different isosteric heats of adsorption at various coverages in a given temperature range. These are shown in Figure (2.15). It can be seen from

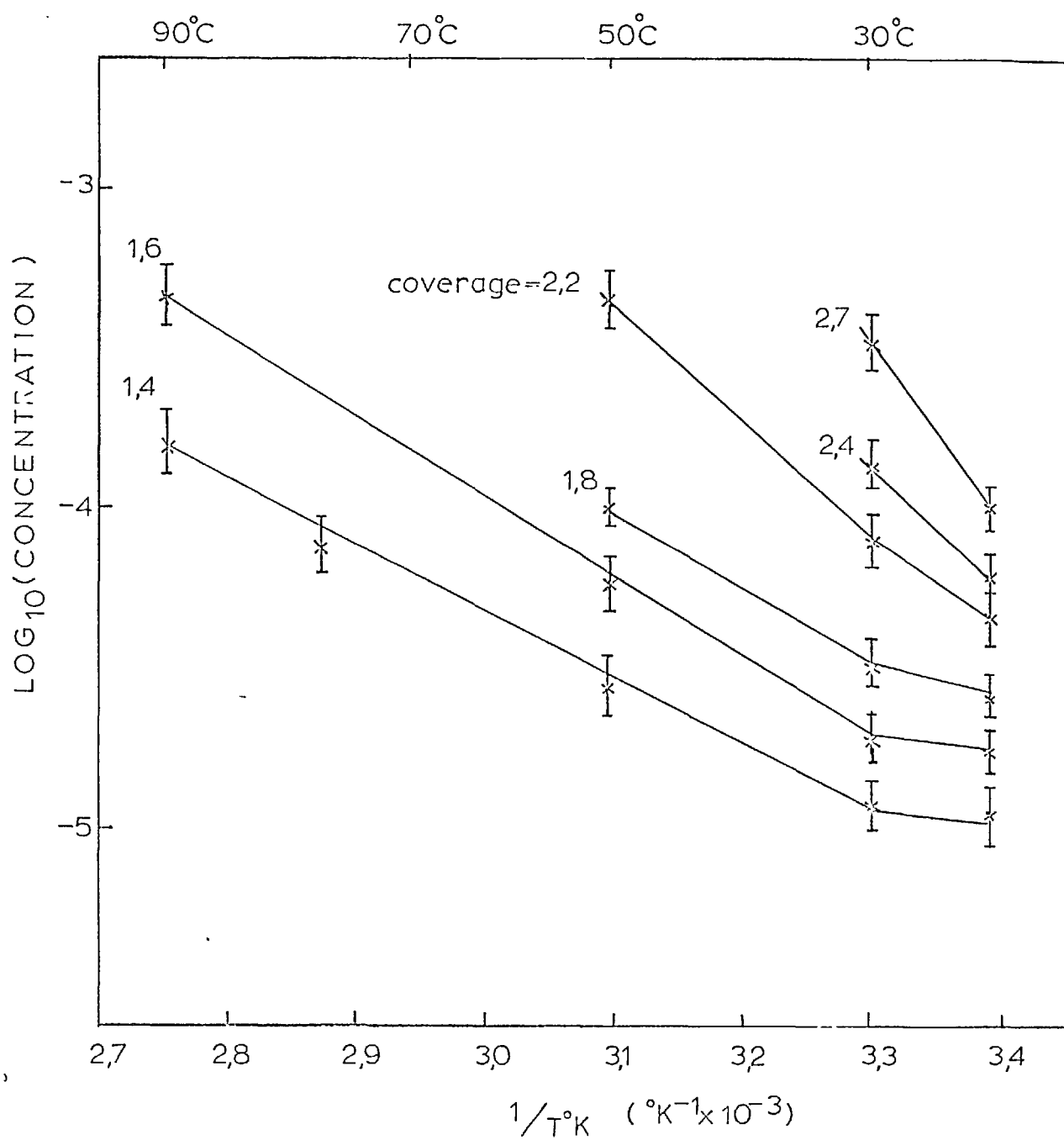


Figure 2.14. $\text{Log}_{10} C$ plotted against $1/T$ at several constant octadecylamine coverages. Coverage in (mols $\times 10^{-7}$ /gram)

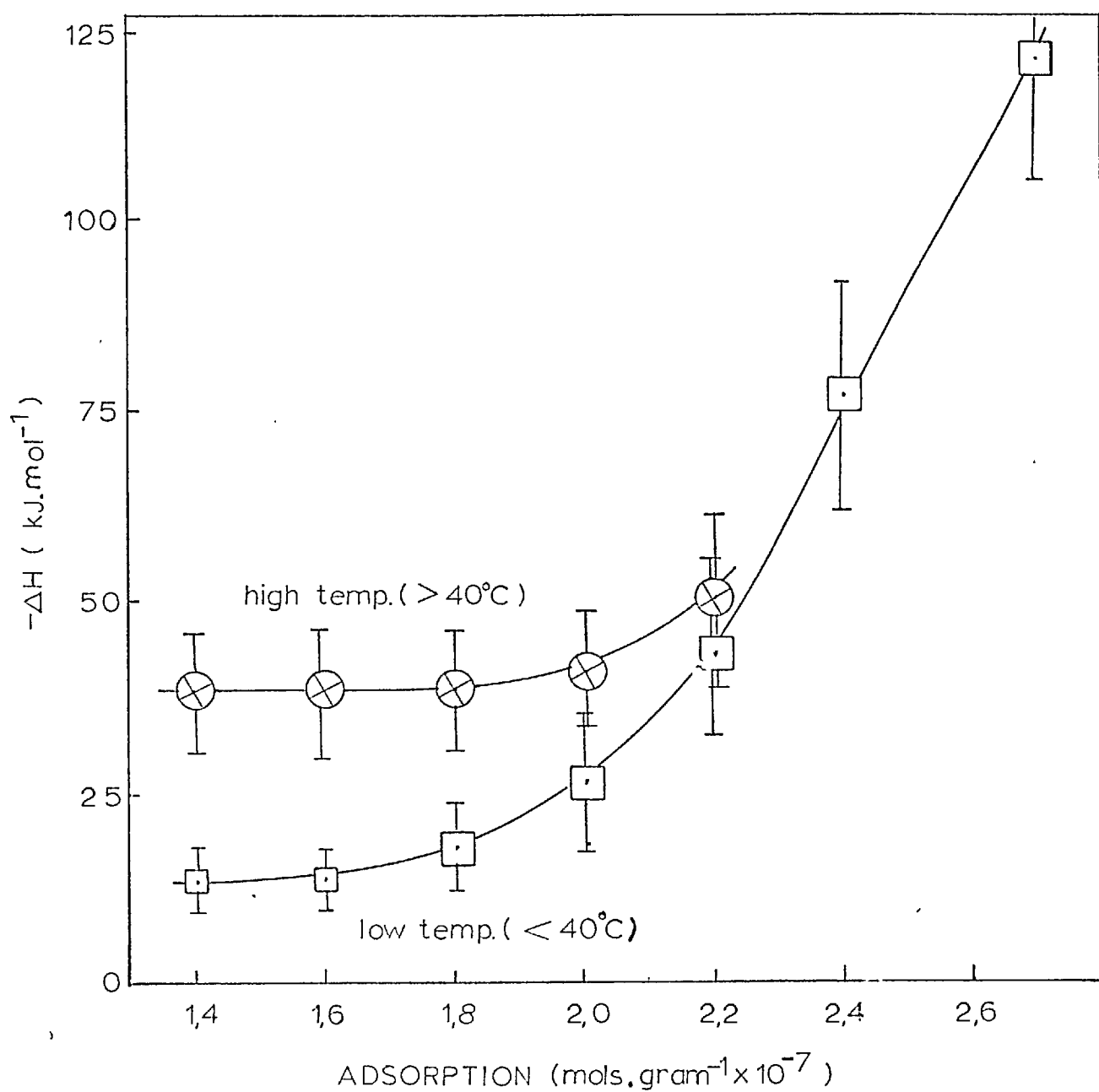


Figure 2.15. Variation of differential enthalpy of adsorption, ΔH , with octadecylamine coverage.

Figures (2.14) and (2.15) that there are three main regions of reversible adsorption.

a) At high temperatures q_{st} is 35–50 kJ/mole. This is in line with values other authors have obtained for similar systems. Zisman and co-workers (52) found that heats of wetting for long chain amines on platinum lay between 35 and 55 kJ/mole when they plotted $\log_{10} C$ against $1/T_w$, T_w being the temperature needed for wetting. Frewing (14) also plotted $\log_{10} C$ against $1/T_B$ where T_B was the temperature of breakdown of a lubricant film on steel. He used fatty acids dissolved in white oil and found heats of adsorption of 45–55 kJ/mole.

b) At low temperatures and coverages, much lower values of q_{st} , between 12 and 20 kJ/mole, were observed. A likely explanation for this is that at these low temperatures the heat of adsorption of the solvent plays a significant part in determining the overall adsorption equilibrium. It must be remembered that, for a given coverage,

$$q_{st} = \overline{\Delta H}_{ads.amine} - \overline{\Delta H}_{ads.hexadecane}$$

It seems likely that at temperatures of less than approximately 40°C, the enthalpy of adsorption of hexadecane on the metal may be progressively increased by a pre-freezing effect, the freezing point of hexadecane being 18°C. Some evidence for this can be found in ref. (53).

c) The third region of q_{st} occurs at high amine coverages, where the isosteric heat starts to increase with coverage. Thus despite the fact that in the low temperature range q_{st} is especially small at low coverages, at high coverages it increases, to reach 100 kJ/mol at an area per amine molecule of 0.38 nm².

Only one reference to a large increase in heat of adsorption at high coverages for a similar non-aqueous system could be found in the literature. Daniel (32) noted that the differential heat of adsorption rose from 50 to

100 kJ/mol as the saturation adsorption level was reached, for octadecanoic acid from benzene on to nickel. He could not identify the exact significance of this but suggested that it was possibly due to experimental inaccuracies. This explanation seems unlikely in view of the similarity between Daniel's results and those found in this chapter.

One possible explanation for this phenomenon is that the heat of adsorption increases with coverage as a result of lateral interaction forces. The sideways attraction between octadecylamine molecules might be expected to be particularly large because of their long chain length. Isirikyen and Kiselev (54) have reported an increase in differential enthalpy of adsorption with coverage for the adsorption of hexane on carbon. They noted a rise in enthalpy of adsorption of 20% as coverage increased to a monolayer, and ascribed this to lateral interaction forces. Such lateral interactions have even been found for the adsorption of the spherical atom, krypton, on solids (55).

The effect can be analysed quantitatively from an equation by Salem (56), which relates the dispersive energy of interaction ($W_{\text{disp.}}$) between two hydrocarbon chains to their distance apart. Salem derives the expression:

$$W_{\text{disp.}} = - 5.2 \times 10^{-2} \left(\frac{N_C}{D_{\text{nm}}^5} \right) \text{ kJ/mol}$$

N_C = number of carbon atoms in one of the chains (18 for octadecylamine).

D_{nm} = distance between chains (nanometers).

By assuming a hexagonal adsorption structure the total interaction energy can be worked out for different packing densities. It is found that such interactions are negligible for an area per molecule of 0.5 nm^2 but rise to reach 80 kJ/mol when the area is just under 0.3 nm^2 per molecule.

This expected increase agrees with the rise in q_{st} at high coverages, noted for octadecylamine.

Salem's equation calculates the total Van der Waals energy for a close-packed monolayer and does not take into account the fact that the molecules, even before adsorption, will have some Van der Waal's interaction with the solvent. It can be demonstrated, however, that this initial interaction is quite small, by considering the latent heat of fusion of octadecane. This will result purely from the difference in hydrocarbon chain interactions between the liquid and solid state and has a value of > 60 kJ/mol. It can therefore be assumed that most of the dispersive energy of Salem's equation is, in fact, released during adsorption, so that his formula is applicable.

It thus seems likely that a basic 40 kJ/mol represents the heat of adsorption of the polar amine heads on the metal surface. This is then augmented, as the film becomes close-packed, by lateral interactions forces between the long hydrocarbon chains.

An implication of this increasing lateral interaction at high coverages is that hexadecane is not close-packed within an adsorbed amine framework at low coverages. If it were then there would be no increasing heat of adsorption with amine coverage, since laterally interacting amine would merely be replacing laterally interacting hexadecane.

For further thermodynamic analysis it is useful to apply a model to the adsorption system. By correlating the model with the observed experimental results it is then possible to derive values for the various thermodynamic parameters. This is discussed in appendix C.

Thermodynamics could only be applied to the reversible part of the adsorption. A constant, irreversible fraction was therefore assumed and this was subtracted from the total adsorption, before analysis. This irreversible adsorption was taken as 0.9×10^{-7} moles/gram (see section

(2.44)).

In this analysis the simplest model was used, one due to Everett (57), which gives the same equation as the Langmuir model applied to solution-solid systems. This model should suffice to give a rough estimate of the free energy and limiting adsorption value. (The accuracy of the results hardly warranted the application of a more sophisticated and detailed analysis).

Everett assumed a perfect adsorption system with similarly sized solvent and solute molecules and derived an equation relating concentration and adsorption, (appendix C). The equation is:-

$$\frac{x_1^L x_2^L}{(n_0 \Delta x_1^L / m)} = \frac{1}{n^S} \left(x_1^L + \frac{1}{(K-1)} \right) \quad \dots\dots\dots - 2.3$$

x_1^L = concentration of component 1 in solution (mole fraction)

x_2^L = concentration of component 2 in solution (mole fraction)

$n_0 \Delta x_1^L / m$ = apparent adsorption of component 1 per gram of solid
(as derived from analysis of solution)

n^S = total adsorption of components 1 and 2 per gram of
solid

K = equilibrium adsorption constant.

For a very dilute solution, with component 1 much more strongly adsorbed than the solvent, this simplified to

$$\frac{x_1^L}{n_1^S} = \frac{x_1^L}{n^S} + \frac{1}{Kn^S} \quad \dots\dots\dots - 2.4$$

$$n_1^S = \frac{n_0 \Delta x_1^L}{m} \quad (\text{see equation 2.1})$$

(for a strongly adsorbed component 1, K is large so that $(K-1)$ can be taken

as effectively equal to K .)

A plot of x_1^L/n_1^S against x_1^L thus enables values of n^S , the total possible adsorption, and K , to be estimated from the slope and intercept of the line obtained. Deviations from linearity indicate the deviations from the perfect adsorption system.

From the equilibrium constant, K , the standard free energy of adsorption ΔG° can be calculated using the equation

$$\Delta G^\circ = - RT \ln K \quad \text{..... -2.5}$$

ΔG° is the standard free energy change in adsorbing one mole of amine and desorbing a mole of hexadecane between standard solution and standard surface. Standard solution for equation (2.4) is one mole/mole of component 1 and standard surface can be taken as one half coverage. (Everett's model actually gives the Helmholtz rather than the Gibbs free energy but the two can be taken as identical for a condensed system).

Equation (2.4) is applied in figure (2.16) using adsorption results, at two temperatures, taken from figure (2.12). From each value has been subtracted 0.9×10^{-7} moles/gram as representing the constant irreversible adsorption (see section 2.43). In this way the analysis concentrates on the reversible adsorption system only.

Figure (2.16) shows straight lines plots almost down to zero concentration, which indicated that Everett's model may be valid for the system studied. Using equation (2.4), ΔG° becomes -24 kJ/mol, and the total amine coverage, after the irreversible fraction has been added on, gives $0.27 \text{ nm}^2/\text{molecule}$ of octadecylamine at 22°C .

If the values for adsorption from figure (2.12) are plotted directly using equation (2.4), without modification by the removal of the irreversible fraction, the curve obtained falls below a straight line at lower concentrations,

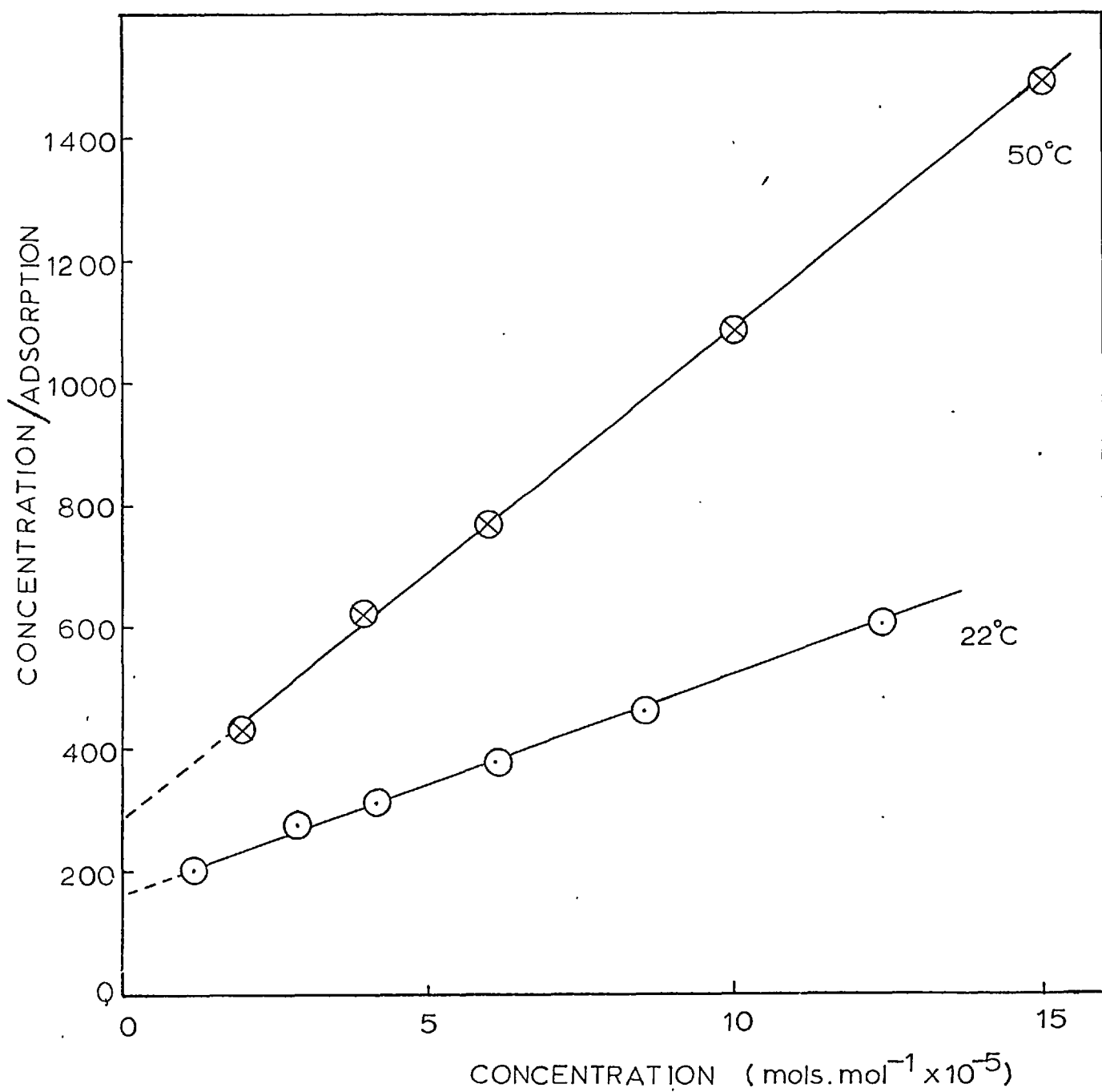


Figure 2.16. Concentration/Adsorption plotted against concentration for octadecylamine

indicating that the Everett model is not obeyed. This suggests that splitting up of irreversible and reversible adsorption before analysis was valuable. The fact that experimental results fit the graphical requirements of the simple model used does not mean that the adsorption is perfect, although the converse is true. Kitchener (58) has stressed the risk attached to assuming an adsorption model from a straight line fit. This is particularly true for the experimental data shown since it has already been demonstrated that the enthalpy of adsorption varies with coverage. This makes a perfect adsorption system unlikely.

The values ΔG^0 and n^S do, however, represent basic constants of the system and serve to give the general shape of the monotonic adsorption curve.

2.46. Area of adsorption and molecular orientation

Before discussing orientation and area of adsorption of amines on steel it is necessary to consider the dimensions of the various molecules involved.

If the n-hexadecane molecule is taken to be extended as a flattened zig-zag, it can be likened, for packing purposes to a cylinder of length 2.3 nm and cross-sectional area 0.19 nm^2 . Thus it would occupy an area of approximately 1.00 nm^2 if laid flat and 0.19 nm^2 if perpendicular. In solution the alkane is almost certainly convoluted most of the time. There is evidence (30), however, that it is extended on adsorption, and it is certainly a linear zig-zag in the crystalline solid.

The three amines, n-dodecylamine, n-hexadecylamine and n-octadecylamine all have a shape similar to n-hexadecane with approximately the same cross-sectional area of 0.19 nm^2 . n-Dodecylamine is 1.9 nm. long, n-hexadecylamine 2.4 nm and n-octadecylamine 2.65 nm. Thus the areas of these molecules if adsorbed horizontally are approximately 0.84 nm^2 , 1.05 nm^2 and 1.17 nm^2 respectively.

An approximate estimate of the limiting area of adsorption can be obtained by extrapolating the isotherms in figures (2.12) and (2.13). For 22°C, in both cases, there is a plateau at about 3.3×10^{-7} moles/gram of powder. Since the area of the powder (Krypton B.E.T. - area per krypton atom = 0.185 nm^2) was $0.06 \text{ m}^2/\text{gram}$, then, no. of adsorbed molecules/ m^2

$$= \frac{(3.3 \times 10^{-7}) \times (6 \times 10^{+23})}{6 \times 10^{-2}} \quad \text{molecules}/\text{m}^2$$

$$= 3.3 \times 10^{18} \quad \text{molecules}/\text{m}^2$$

This gives an area/molecule of

$$\text{Area} = \underline{\underline{0.3 \text{ nm}^2/\text{molecule}}}$$

This value can be improved by applying the Everett-Langmuir adsorption model (equation (2.4)). The area then works out as $0.27 \text{ nm}^2/\text{molecule}$.

Whatever the exact value it seems likely, both from the area occupied and from the fact that different length molecules reach the same molar adsorption plateau, that adsorption is roughly a monolayer and adsorbed vertically rather than horizontally. The main alternative is that the strongly bound layer is attached horizontally to the metal with an incomplete vertically oriented monolayer on top of this.

The molecular area of 0.27 nm^2 is high compared to the theoretical consensed area which Fox (59) has found to be 0.205 nm^2 , for octadecylamine on an aqueous substrate at pH 8.2. Several values of around $0.30 \text{ nm}^2/\text{molecule}$ have, however, been reported in the literature for adsorption on solids rather than liquids. Bigelow, Pickett and Zisman (23) adsorbed octadecylamine on to platinum from dicyclohexyl solution using a multiple dip technique. They calculated an area/molecule of 0.30 nm^2 . Similarly Bornung and Martin (60) found a coverage of only 0.7 of the theoretical condensed value for octadecylamine on chromium, and Block and Simms (43) mention a similar

fraction for the same amine on steel.

Changes in temperature apparently alter the limiting adsorption value. Applying the Langmuir analysis to curves in Figure (2.12), the final adsorption drops from $0.27 \text{ nm}^2/\text{molecule}$ at 22°C to $0.48 \text{ nm}^2/\text{molecule}$ at 50°C . This suggests that the most stable film density under given conditions decreases with increasing temperature and there is no reason why 22°C should be the temperature at which the closest packed monolayer occurs. At lower temperature a denser film still may be obtained.

There are two explanations of why the area/molecule should be greater than the condensed monolayer area on a liquid and why it should also be temperature dependent.

a) The molecules may be tilted permanently, or vibrate around their vertical position. They would, in either case, occupy more than the theoretical limiting area, and if they vibrated they would also occupy a larger area at higher temperatures. Evidence of tilting has been found, using electron diffraction measurements, by Brockway and Karle (61) and Bigelow and Brockway (62).

b) The molecules may be close packed, but in separate micellar clusters on the surface. These clusters would become smaller or more widely spaced with temperature. This sort of configuration has been proposed by Epstein (63).

Yet a third possibility exists for the area per adsorbed amine molecule being higher than the liquid condensed area. This may arise from the B.E.T. surface measurement technique. It has been assumed that the area of metal available to every adsorbing krypton atom is also available to amine molecules. Both species do have very similar cross-sectional area, but if there were any narrow pores in the metal these might adsorb more krypton than amine because krypton is, overall, so much smaller. In this case the adsorbed area

per molecule of the amine would have to be recalculated over the concentration range based on a limiting adsorption of $0.205 \text{ nm}^2/\text{molecule}$. This discrepancy could only overestimate the area of the metal since it is unlikely that amine could adsorb where krypton could not.

2.50. Conclusions

These experiments were designed to provide adsorption data for a comparison with friction results, to be described in the next chapter. Several facts have been demonstrated, however, concerning the amine-hexadecane-stainless steel adsorption system itself.

- a) Long chain amines are adsorbed on stainless steel powder to form, most probably, a vertically oriented monolayer.
- b) This monolayer is not fully condensed at room temperature and increases in temperature reduce both the adsorption at any given concentration and the limiting adsorption level.
- c) Different chain length amines reach the same adsorption plateau at high concentrations and the same temperature. Longer chain length amines are more strongly adsorbed than shorter ones.
- d) About one-third of the total adsorbed amine is irreversibly adsorbed. The remainder is reversible and obeys some of the requirements of the Langmuir adsorption system, especially at high temperatures.
- e) There is some evidence of lateral interaction forces between amine molecules as the packing density increases.

CHAPTER THREE

BOUNDARY LUBRICATION USING LONG-CHAIN AMINE SOLUTIONS

3.10. Introduction

In this chapter the type of boundary lubrication referred to as "oiliness" in the main introduction is investigated. This was shown by Sir William Hardy in a series of experiments in the 1920's (64) to result from the adsorption of large organic molecules on the lubricated metal surfaces. The surfaces can then slide between these adsorbed layers rather than in the metal itself. Hardy's lubricating model is shown in figure (3.1a). The exact thickness of such lubricating oily layers is still in doubt but it has been shown that just one or two monolayers of strongly adsorbed material (less than 10 nm. thick) can provide good boundary lubrication between quite rough steel surfaces, (65) (66).

There is little evidence that this type of lubricating film causes changes within the surface of the metal itself. In this respect it differs from the extreme pressure films considered in chapter 5. Lubrication seems to be provided entirely by polar material being adsorbed either physically or chemically on the metal surfaces. Several attempts have been made at relating the quality and strength of the adsorbed films to their lubricating characteristics. In general, however, these have tended to concentrate on the lubricating properties and relate these to only hypothetical adsorption systems.

The work in this chapter consists of a systematic attempt to investigate the lubrication of stainless steel with a long chain amine in hexadecane. The variables observed are friction, temperature and amine concentration in solution. These lubrication results are then compared with the adsorption results of the previous chapter. Having actual adsorption values available

for the same system means that no assumptions need to be made about the surface phase. Under any conditions the amount of amine adsorbed on the surface is known exactly.

The friction results are considered with particular reference to conditions of lubricant breakdown or "scuffing", so that the state of adsorption at this point can be established.

3.20. Review

3.21. The role of adsorption in boundary lubrication

Hardy (64) carried out much of the early experimental work on boundary lubrication. He studied a number of hydrocarbon-type surfactants both pure and in solution in petroleum ether. For a given homologous series he found that μ_s , the coefficient of static friction, decreased linearly with increasing molecular weight. For fatty acids, however, μ_s levelled off at about 0.05 with molecular weights greater than 200. He pictured lubrication as resulting from an adsorbed film of surfactant which reduced the field of force between sliding surfaces (figure (3.1a)). The larger the adsorbed molecules the more the force field would be diminished. Hardy's work has been extended by Levine and Zisman (67) who found that alcohols also caused μ_s to level off at 0.05, but only at molecular weights higher than 280.

The question then arises; how thick are these adsorbed films in boundary lubrication? Hardy himself was not always clear about this. At times he assumed lubrication as resulting from only two, primary adsorbed layers (68). In other papers, under conditions of lighter loading, he envisaged orientation effects extending hundreds of nanometers into the liquid (13). Thick films of this sort of depth have also been postulated by Fuks (69), Deryagin (33) and other scientists (70). On the other hand, a number of authors have shown conclusively that monolayer adsorption is

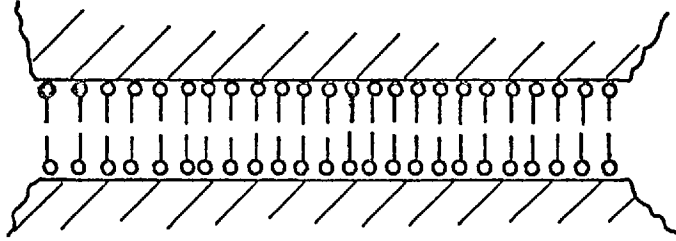


Figure 3.1.a Hardy's model

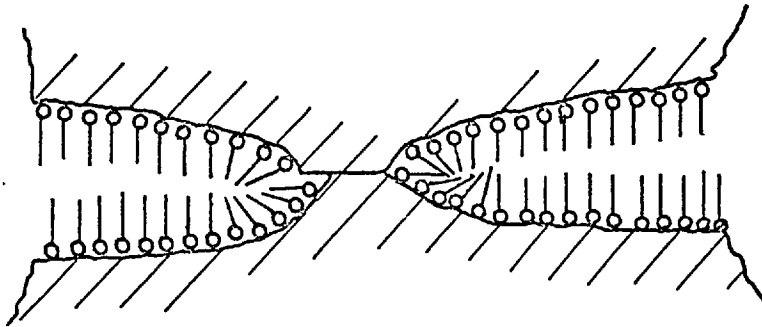


Figure 3.1.b Bowden and Tabor's model

Boundary lubricating models

perfectly adequate in giving good boundary lubrication with a coefficient of friction of less than 0.1.

It has already been demonstrated, in chapter 2, that the amine-alkane system on stainless steel gives only monomolecular films. In this brief survey attention will therefore be concentrated on monolayer lubrication. Good, modern reviews of thick boundary lubricating films, which are now thought to result from corrosion reaction products rather than physical adsorption are to be found in references (35) and (37).

Many workers have demonstrated that very thin, even monomolecular, films give good boundary lubrication. Desvaux (71), Frewing (72) and Gregory (73) are some of those who have worked in this field. Frewing found that the coefficient of friction for various alcohols and acids was the same whether an excess of lubricant was used or whether individual monolayers were built up by the Langmuir-Blodgett method (74). Gregory calculated the minimum fatty acid coverage required to provide effective lubrication. He placed small quantities of 0.1% lauric acid solution in paraffin oil on to a cadmium surface. This gave good lubrication. By gradually extending the area covered by the oil Gregory was able to show that newly covered surface would not lubricate when there ceased to be enough acid to provide a monolayer.

The most elegant demonstration that only individual monolayers are required for boundary lubrication has been provided by Bailey and Courtenay-Pratt (75). They spread calcium stearate monolayers on two sheets of mica which they then rubbed together. The film thickness between the mica layers was monitored during sliding using multiple beam interferometry. Bailey and her colleague proved, in this way, that good lubrication was provided by a layer only 4.5 nm. thick.

Bowden and Leben (76) investigated the durability of thin films in

providing lubrication. They showed that a stearic acid monolayer gave good lubrication on stainless steel only for one or two runs over the same track. As the number of layers was increased, so the film became progressively more durable, until, after 53 monolayer equivalents had been deposited, repeated running had no effect on the film at all. Presumably when there were only a few monolayers on the surface, no fatty acid was available to plug gaps torn in the film at asperity metal contacts. This problem would not arise if there were many monolayers or an excess of stearic acid solution.

Experiments carried out by Rabinowicz and Bowden (77) demonstrate that even during good boundary lubrication some metal-metal contact occurs through the adsorbed film. They monitored the amount of wear during sliding by making one metal surface radioactive, and showed that approximately two percent of the total contact area during boundary lubrication was metal to metal. Bowden and Tabor modified Hardy's model of lubricated surfaces to take this metal contact into account (see Fig. (3.1b)). They expressed the frictional force as derived from two sources, the work required to shear the lubricating film and the work to shear the metal-metal contact (18).

This can be expressed as:

$$\text{Frictional Force} = A[\alpha S_m + (1-\alpha)S_f] \quad \text{..... 3.1}$$

A = total area of contact

α = fraction of metal-metal contact

S_m = shear strength of metal-metal contact

S_f = shear strength of lubricant

Applied load and sliding velocity can both affect the friction in a boundary lubricating system, simply by heating the film or in a more complicated fashion. A distinction must be made, however, between gradual changes in the coefficient of friction of a lubricating film due to load and speed and the sudden breakdown of the film as a result of some imbalance

in the system. This second effect will be considered in the next section.

At low speeds, coefficient of friction is usually independent of load over a wide intermediate range ($170 - 170,000 \text{ kN/m}^2$). At very low and very high loads μ increases slightly (78),(79). The effect of speed on friction at slow sliding speeds is complex. Friction can either increase or decrease with speed, depending on the efficiency of the lubricating film.

3.22. Relationship between adsorption and lubricant breakdown

The coefficient of friction in a boundary lubricating system often rises sharply at a characteristic temperature. Tabor (80) showed that for pure hydrocarbons this temperature was similar to the melting point. For fatty acids, however, the "critical temperature" was higher than the melting point and increased with increasing molecular weight. Bowden and Tabor (18) ascribed this effect to the formation of a metallic soap by chemical reaction between acid and lubricated metal. They thus supposed that the frictional increase was due to melting of this soap.

Frewing (14),(72) observed similar results but noted that the lubricant failure temperature rose as the surfactant solution concentration was increased. On the basis of this he suggested that a lubricating solution could work in the same way as a deposited monolayer - i.e. by reversibly adsorbing a monolayer of surfactant on the rubbing surfaces. Since the adsorbed layer was in contact with the bulk solution it could be treated using equilibrium thermodynamics.

Frewing carried out experiments rubbing steel on steel at low speeds in surfactant solutions. He increased the temperature gradually whilst monitoring friction, and thus obtained critical temperatures for different concentrations, where friction increased and rubbing became irregular. He was thus measuring:

$$T_B = f(C)W, V \quad \text{..... 3.2}$$

T_B = critical lubricant failure temperature

C = concentration of surfactant in solvent

W, V = constant load and velocity

Frewing assumed that the adsorbed species was in constant equilibrium with the bulk fluid. By combining a form of the Langmuir isotherm (kinetic derivation)

$$K = \frac{x}{C(1-x)} \quad \text{..... 3.3}$$

x = fraction of surface covered at equilibrium

K = equilibrium constant

$$\text{with } \frac{d \ln K}{dT} = - U/RT^2, \text{ (the Van't Hoff Isochore)} \quad \text{..... 3.4}$$

R = gas constant

U = Heat of adsorption of surfactant with respect to bare metal and by assuming that the friction transition occurred when the surface fraction of adsorbed surfactant dropped to a constant, critical value, he obtained;

$$\ln \frac{x}{C(1-x)} = \frac{U}{RT_B} + \text{Integration Constant} \quad \text{..... 3.5}$$

This expression, (3.5) predicts a linear relationship between $\log_{10} C$, and $1/T_B^\circ K$. Frewing (14) plotted these two functions and obtained a series of straight lines with negative gradients, for different lubricants. Because of this agreement between his theory and experiments he felt justified in calculating values of U . He found these to be generally between -35 and -55 KJ/mol, dropping to 18 KJ/mol for very weak surfactants. (U here would be the energy of adsorption of one mole of surfactant at the critical coverage).

This type of extrapolation, from experimental results to a mathematical

model by graphical comparison can be somewhat hazardous. This was noted in chapter 2. Plotting a reciprocal against a logarithm is also quite similar to plotting logarithm vs. logarithm and will yield a straight line for quite a number of relationships. Frewing carried out no actual adsorption experiments and so could not know the true state of the adsorbed system.

The most significant of the friction-adsorption comparisons was carried out by Hutchinson and Rideal (16) who set out to prove directly the connection between reversible adsorption and lubricant breakdown. They carried out friction and adsorption experiments with long chain surfactants on sodium nitrate crystals. Using increasingly concentrated surfactant solutions they found the concentration at which a given solution started to lubricate effectively. This corresponded well with the concentration at which there was a sharp rise in the adsorption isotherm. Hutchinson and Rideal chose sodium nitrate so as to be sure of a well-defined and reversible system. Their experiments proved conclusively that boundary lubrication could be obtained by a physically adsorbed film, and that the amount adsorbed is critically important. This work was limited to room temperature so that the variations of lubricant failure and adsorption with temperature could not be correlated.

In 1965, Askwith, Cameron and Crouch (81) extended Frewing's thermodynamic approach. They showed that the equilibrium constant, K , given in equation (3,3) could be related to the free energy of adsorption of the surfactant by:

$$\Delta G^0 = -RT \ln K \quad \dots\dots\dots 3.6$$

Since

$$\Delta G = \Delta H - T\Delta S,$$

Askwith, Cameron and Crouch, assuming a Langmuir adsorption isotherm, obtained the expression:

$$-\frac{\Delta H^{\circ}}{T_B} + \Delta S^{\circ} = R(\ln \frac{\theta}{1-\theta} - \ln C) \quad \text{..... 3.7}$$

ΔH° = standard enthalpy of adsorption

ΔS° = standard entropy of adsorption

θ = fractional monolayer coverage at lubricant breakdown

They thus found the value of the integration constant in equation (3.5). By assuming that film breakdown occurred at fractional monolayer coverage $\theta = \frac{1}{2}$, Askwith, Cameron and Crouch calculated values of ΔS° , the standard entropy change on adsorption, for different long chain surfactants. This assumption of $\theta \sim \frac{1}{2}$ was not as serious as all that, since $\ln(\theta/1-\theta)$ varies little between the range $0.2 < \theta < 0.8$, so the exact value of θ chosen was not critical.

Askwith, Cameron and Crouch also noted a correlation between lubricant breakdown and the length of surfactant molecules compared to that of the solvent molecules. Thus higher loads and temperatures were required break down hexadecylamine in hexadecane lubrication than were needed for either tetradecylamine or octadecylamine in the same solvent in the same molar proportions. A similar effect was noted with acids and alcohols.

This work was continued by Grew and Cameron (15) who investigated the variation of lubricant failure temperature with concentration of dodecanoic acid in a series of different chain length alkane solvents. Plots of $\log_{10} C$ vs. $1/T_B$ were drawn in the same way as Frewing (14), and enthalpies of adsorption were obtained from equation (3.7). These varied between -45 and -200 kJ/mol depending on the solvent chain length. The steepest gradient (largest enthalpy of adsorption) occurred when chain lengths of solute and solvent matched. In this case the enthalpy of adsorption (-200 kJ/mol) was of the same order as the sublimation energy of the fatty acid.

Cameron and Grew (15) extended their experiments to compare a naturally

occurring surfactant with the fatty acid they had used previously. A surface-active material had been extracted from natural mineral oils by Groszek (82), and Grew and Cameron measured lubricant breakdown temperature using several different concentrations of this in various solvents. Again plots of $\log_{10} C$ against $1/T_B$ gave straight lines suggesting that the mechanism of lubrication was similar for both natural surfactant and fatty acids. The gradient of the lines obtained using the mineral oil extract was largely independent of solvent.

Two authors have experimented with the effect of parameters other than concentration on the lubricant breakdown of simple polar systems. Cowley and co-workers (83) and Sharma (84) have both investigated the dependence of breakdown temperature on applied load. They investigate the relationship:

$$T_B = f(W)_{C,V}$$

W = applied load

C, V = constant concentration and speed

Both experimenters showed that for low speeds, where frictional heating could be neglected, increasing load decreased the breakdown temperature initially, but at high loads the film breakdown temperature reached a limiting value which was load-independent.

Sharma (84) also investigated the effect of surface roughness on lubricant failure temperature of long chain amines on steel. He found an optimum roughness at which a higher temperature was needed to cause film breakdown than was required for both rougher and smoother surfaces. Changes in load and surface roughness generally had a much smaller influence on lubricant failure than did temperature.

It must be stressed that we have been considering low speed sliding conditions. At higher speed, load and velocity both contribute to a frictional film heating effect which dominates lubricant breakdown.

3.23. Other solid-surfactant adsorption systems

It has been noted in the previous section that very often the relationship between lubricant breakdown temperature and surfactant concentration for a simple lubricating oil is:

$$\log_{10} C \propto 1/T_B$$

T_B = breakdown temperature

A similar relationship has also been found for other surface desorption systems.

Bigelow, Glass and Zisman (52) found this sort of relationship for the critical temperature of wetting of metals with surfactant solutions. They showed that when very clean metal surfaces were prepared and dipped into surfactant solutions (long chain acid, amines etc. in alkanes) then the metal surface appeared quite dry on withdrawal from solution. A whole series of experiments were carried out (23),(85),(24), to show that this resulted from an adsorbed monomolecular layer on the metal which presented a low energy surface to the supernatant liquid, and thus would not wet under normal conditions. The surface could be made to wet if either the concentration of surfactant solution was lowered or the solution temperature was increased. The relationship between these two variables for critical wetting was:

$$\log_{10} C \propto 1/T_w$$

T_w = wetting temperature $^{\circ}\text{K}.$

and the gradients of the straight lines so obtained were quite similar to those obtained by Frewing (14).

A valuable outcome of this work has been to provide a useful criterion for cleanliness of metal surfaces. It is normally very difficult to prepare a metal surface free from organic contaminants, but the non-wetting condition was found to be very sensitive indeed to such contamination. Thus in

obtaining a non-wetting surface one has a visual relative measure of its degree of cleanliness.

Sakurai and Baba (86) also obtained a linear $\log_{10} C$ vs. $1/T$ relationship. They measured the rectification effect of a thin film of adsorbed surfactant between a flat plate and hemispherical surfaces. The temperature at which this effect vanished abruptly was related to the concentration of various long chain acids and soaps in hydrocarbon solvents. Similar gradients of $\log_{10} C$ vs. $1/T$ were obtained to those of Frewing (14) and Zisman and co-workers (52).

3.24. Scuffing

Up till now in this chapter, the phrases "lubricant breakdown" or "film failure" have been used to describe the sudden increase in friction from good to bad lubrication which is sometimes observed when the operating conditions of a lubricating system are changed. It is often more convenient to use the word "scuffing" to describe this phenomenon. Some explanation of this is needed, however, since the practical engineer's concept of scuffing is generally rather different from just a sudden rise in friction. The word was originally coined to describe an effect that is sometimes seen in practical boundary lubrication, a sudden rise in friction accompanied by severe deformation of the rubbing surfaces. The Institute of Mechanical Engineers have given the definition (87):

"gross damage characterised by the formation of local welds between sliding surfaces."

The extent of damage and the catastrophic nature of scuffing depend, however, largely on the load and sliding velocity. Thus if friction increases due to preliminary film breakdown, the heat generated at high sliding speeds will greatly exacerbate the failure. At low sliding velocities,

on the other hand, in test rigs especially, initial film breakdown can be identified in its early stages merely as a rise in friction. The subsequent violent tearing and vibration that take place under fast running do not occur in such mild conditions.

Throughout this thesis a sudden rise in friction from $\mu \sim 0.1$ to $\mu \sim 0.2$ will be referred to as "scuffing" since it is recognised that at normal running speeds this would in fact take place.

3.25. Summary

Previous work has shown that solutions of long chain surfactants in hydrocarbons provide a good boundary lubrication up to some critical condition. In most cases this critical condition is very dependent on temperature and lubricant composition and, at low speeds, is less dependent on sliding speed and applied load.

Lubrication can be provided by physically adsorbed monolayers although chemically formed monolayers and multilayers may also occur.

Various authors have suggested a connection between the breakdown of a physically adsorbed monolayer and critical scuffing conditions. By assuming adsorption models they have been able to show that such an approach is reasonable. It remains unproven, however, until a direct comparison of known adsorption with known lubricating capacity is made. Only Hutchinson and Rideal (16) in one experiment at one temperature have attempted such a comparison.

This chapter concerns an investigation into the lubricating properties of long chain amine solutions in hexadecane on stainless steel. This is to relate the critical scuffing conditions as a function of temperature and concentration to the adsorption results of the previous chapter.

3.30. Experimental

3.31. Experimental aims and design

A method was required of testing the variation of friction with lubricant composition and temperature whilst operating under conditions of boundary lubrication. The need for accurate temperature control made it essential to use a very low speed apparatus so as to avoid the complication of frictional heating and also ensure boundary lubrication conditions. Other desirable features were a lubricant holder which did not need too much fluid (hexadecane is rather expensive) and a machine which would use metal test pieces of shapes easily obtainable as stainless steel.

The standard Bowden-Leben apparatus was chosen, which rubs a ball on a flat metal plate (see next section). This had the advantage of operating both at very low sliding speeds and in the correct load range. The load had to be large enough to ensure full boundary lubricating conditions but not so large that the compressive yield stress of the rubbing metal was exceeded. Matveevsky (88) has shown that anomalous lubricant behaviour may occur if such extremely high loads are used.

One major feature of the experimental design was the control of temperature to a constant value before each run. The run was then carried through at this constant temperature. In this respect the lubrication tests described in this chapter are different from those of Frewing (72) or Grew (15), who raised the temperature during each run, but similar to those of Hutchinson (16) and Matveevsky (88).

The constant temperature approach was used specifically to ensure equilibrium adsorption. Equilibrium conditions are fundamental to the thermodynamic analyses of Frewing and Cameron et al. and it was thought that both these authors changed the external conditions rather too fast to be sure of maintaining an equilibrium situation at the surface. This is

particularly important since it was shown in chapter 2 of this thesis that half an hour was needed to reach equilibrium adsorption on steel at 50°C.

3.22. Bowden Leben apparatus

The Bowden Leben machine was devised in 1939 (89) to measure coefficient of friction at low speeds as a function of load, temperature and velocity with different lubricant and rubbing metal combinations. A diagram of the apparatus used in this series of experiments is shown in figure (3.2) with a photograph in figure (3.3).

The frictional system used was a 15.9mm ($\frac{5}{8}$ ") diameter steel ball rubbing against a flat steel plate. The steel plate lay in a shallow trough so that it could be completely flooded in lubricant. This trough was heated externally. Both the lower plate and its containing trough could be moved smoothly and at constant speed with a hydraulic piston arrangement. This provided the frictional couple since the ball, which was held against the plate, remained stationary.

The steel ball was fastened in a chuck and spring loaded against the plate. The vertical force was measured with a spring balance. Between the chuck and a rigid mounting block was a spring-steel plate to which was attached a strain gauge system. This measured the horizontal displacement of the ball and chuck and thus indicated the frictional force on the ball. A signal passed from the strain gauges through an amplifier to a fast response pen recorder.

The temperature of the rubbing surfaces was measured on a potentiometer from thermocouples immersed in the lubricant and held close to the contact region. A special feature of the apparatus was the temperature control device. Normally on the Bowden-Leben, the temperature of the fluid is raised continuously throughout a run. In these experiments the heater was controlled

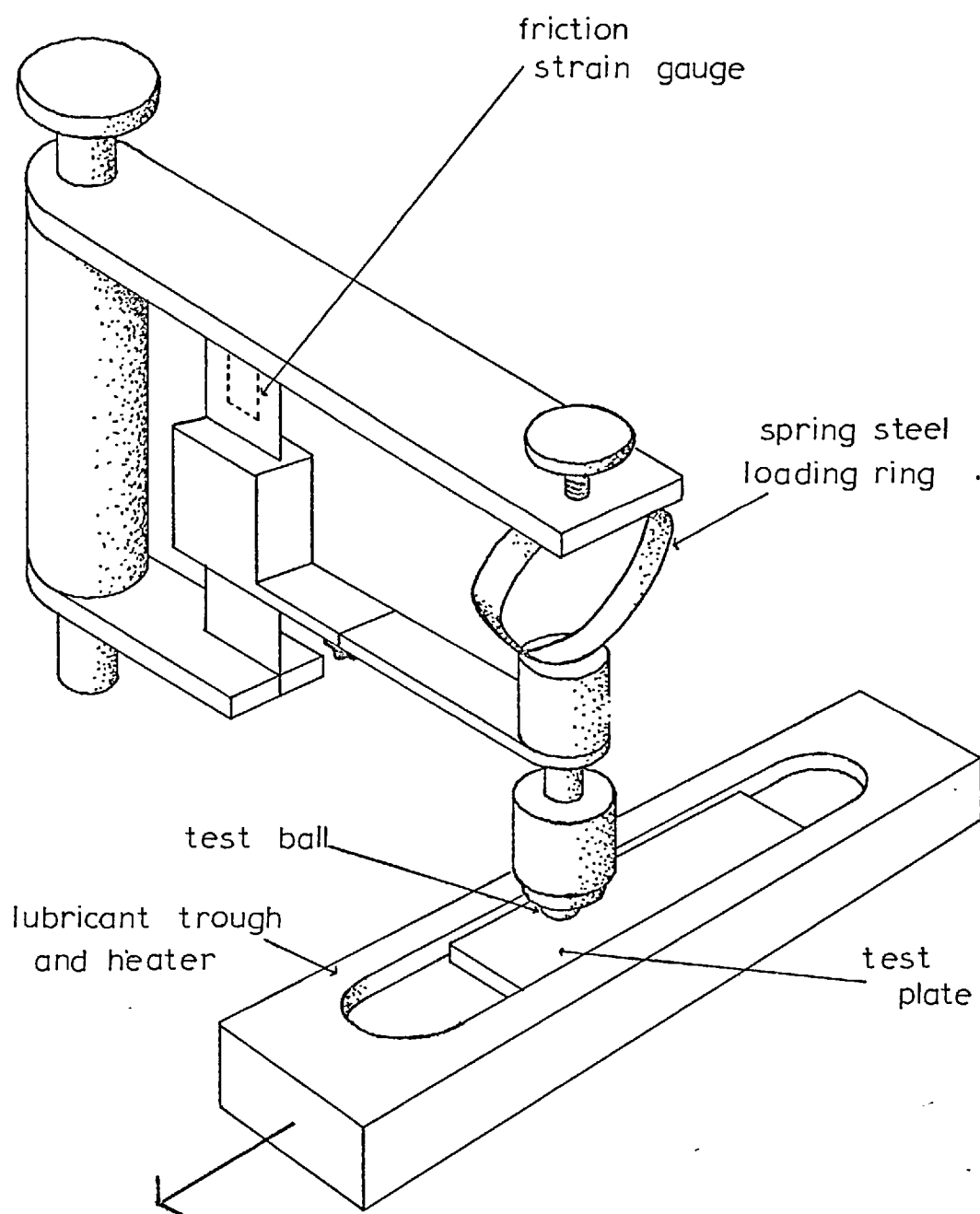


Figure 3.2. Bowden-Leben apparatus (schematic)

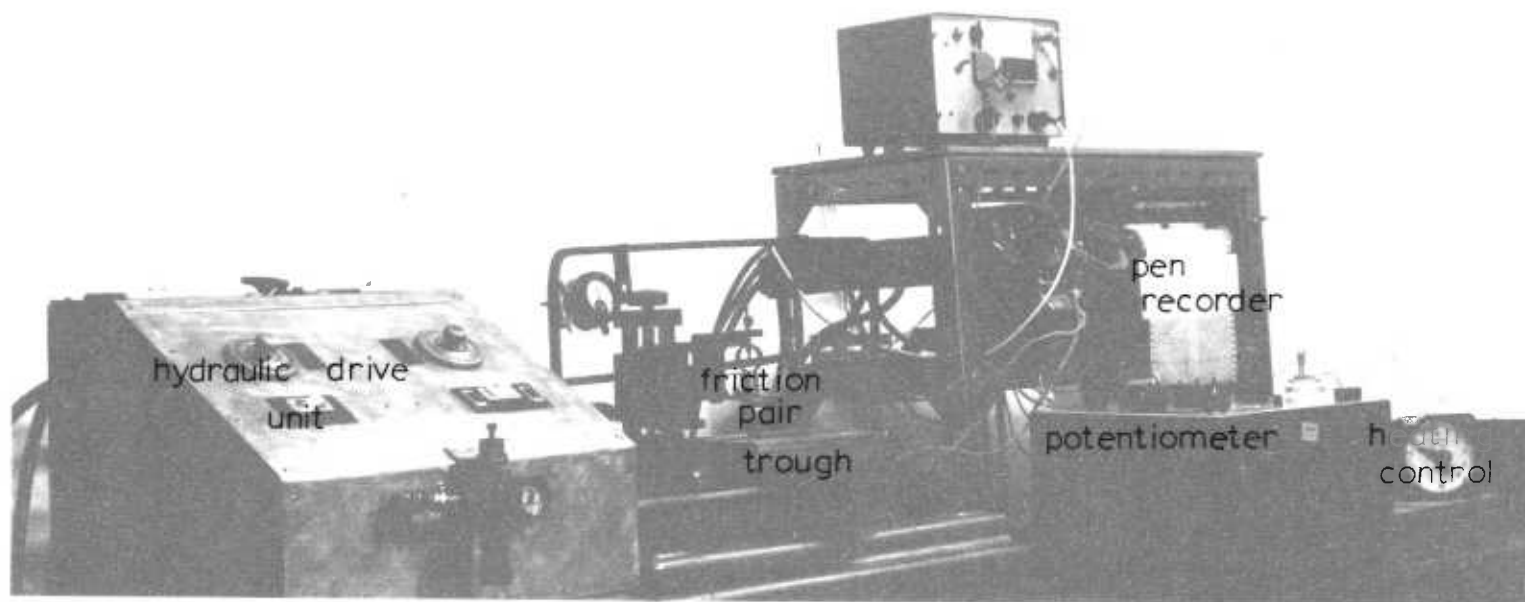


Figure 3.3. Bowden-Leben apparatus

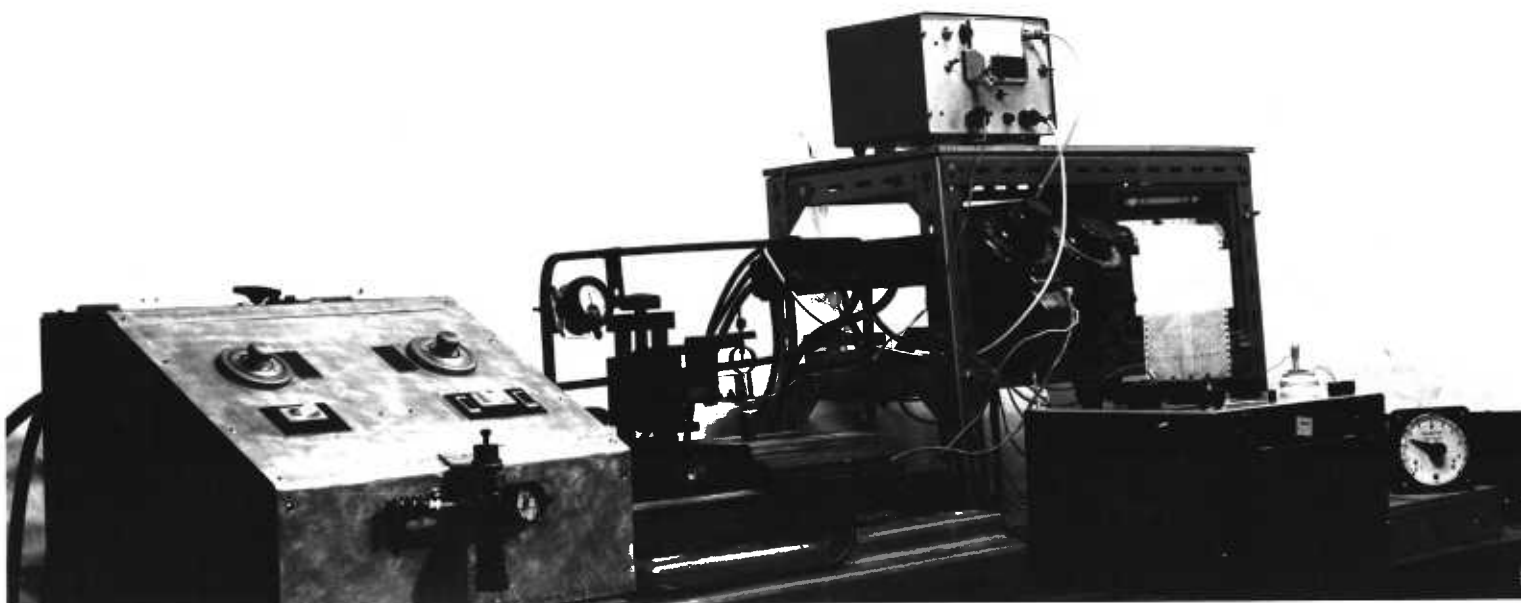


Figure 3.3. Bowden-Leben apparatus

by a thyristor unit which responded to feed-back from a pair of thermocouples immersed in the lubricant. (This was the same control system as was used in chapter 2). So as to ensure constant temperature conditions, a metal cover was placed over the whole trough throughout each run. In this way it was possible to preset and control the temperature quite accurately.

3.33. Materials

The amine used in all these experiments was n-octadecylamine. It was the same sample as that used in chapter 2. The n-hexadecane was also similar in make and purity to that used in the adsorption experiments of chapter 2. Its purity and surface-active properties are described in appendix A.

The 18/8 steel plate was of specification EN58B and the steel balls EN58A (A.I.S.I. 302). These specification compositions are shown in Table (3.1).

Table (3.1)

	C	Si	Mn	S	P	Ni	Cr	Mo	Ti
EN 58A	0.16 max	0.20 min	2.00 max	0.045 max	0.045 max	7.0- 10.0	17.0- 20.0	-	-
EN 58B	0.15 max	0.20 min	2.00 max	0.045 max	0.045 max	7.0 10.0	17.0- 20.0	-	4x C min

Specification of Stainless Steels (wt %).

3.34. Experimental technique

The steel plate was first cleaned and then normally immersed immediately in freshly prepared amine solution of known concentration at room temperature. (Some experiments were done to test the effect of pre-adsorbed water on lubrication. In this case the plate was not immersed straight after cleaning,

but first treated in a way which will be discussed, together with the results, in section (3.44).)

The plate was left in amine for not less than twelve hours, when it was transferred into the Bowden-Leben trough and covered with more amine solution of the same concentration. Then the steel ball, which had been thoroughly cleaned, was fastened in the chuck, rubbed gently with 400 grade carborundum paper and dipped into the amine. The chuck was mounted so that the ball rested gently on the steel plate, half covered with lubricant.

After adjusting the thermocouples in position just touching the contact, the metal cover was placed over the apparatus. The temperature was then raised to its required value and maintained for at least $\frac{1}{2}$ hour (only 15 minutes at 90°C). After this time the ball was loaded against the plate and a run carried out at constant speed and load. The speed used was always 0.1 mm/s. and the load 17.8N (4lbf), which corresponded to the maximum Hertz pressure of 0.87GN/m^2 (125,000 p.s.i.).

This type of experiment was repeated using different concentrations and different temperatures. In each experiment a fresh solution was used and the metal pieces thoroughly cleaned. The cleaning procedures of both plate and ball will be discussed in the next section.

After each experiment, the effect of frictional force was calibrated on the pen recorder by laterally displacing the chuck with a spring balance arrangement. From this calibration plot and the frictional trace, values of coefficient of friction could be worked out for each run (see section 3.36).

3.35 Cleaning procedures

Cleanliness is of prime importance in boundary lubrication since, as has already been mentioned, single monolayers of surfactant on surfaces change their friction characteristics completely. Experimenters in the

past have had difficulty in standardising the cleanliness of their metal surfaces. In this thesis, Zisman's concept of wettability (23) was adopted as the criterion of a sufficiently clean surface. Zisman showed that only the most rigorous of cleaning methods gave a surface that was not wetted by a long chain surfactant-alkane solution.

Simple soxhletting of steel in organic solvents was found to be inadequate. Finger prints left on the steel balls were not removed completely even after twenty-four hours, in boiling toluene. Nor were non-wetting surfaces obtained by such a technique. Grew (90), after much experimentation, adopted an abrasive cleaning procedure which entailed repeated rubbing of each surface with carborundum paper. This, he found, usually gave surfaces which would not wet with long chain acid solution.

In these experiments the much simpler procedure of ionic bombardment was adopted. This method of cleaning surfaces is based on bombardment by medium energy ions and electrons. Using this technique, clean steel surfaces which gave non-wetting monolayers in concentrated amire solution were invariably produced. A diagram of the apparatus is shown in Figure (3.4). The steel plates were always abraded with 320 and 400 grade carbonundum paper before ionic bombardment so as to remove any deeply penetrating surface contamination.

It was not feasible to clean the steel balls by ionic bombardment, so these were soxhletted in boiling toluene for four hours and then plunged into analar acetone. After being mounted in the chuck, each ball was rubbed gently with 400 grade carborundum paper to remove any remaining contamination by abrasion. No ball was used for more than three experimental runs and each was soxhletted between each run.

3.36. Stick-slip and friction

It was found that the Bowden-Leben machine rarely gave a smooth curve

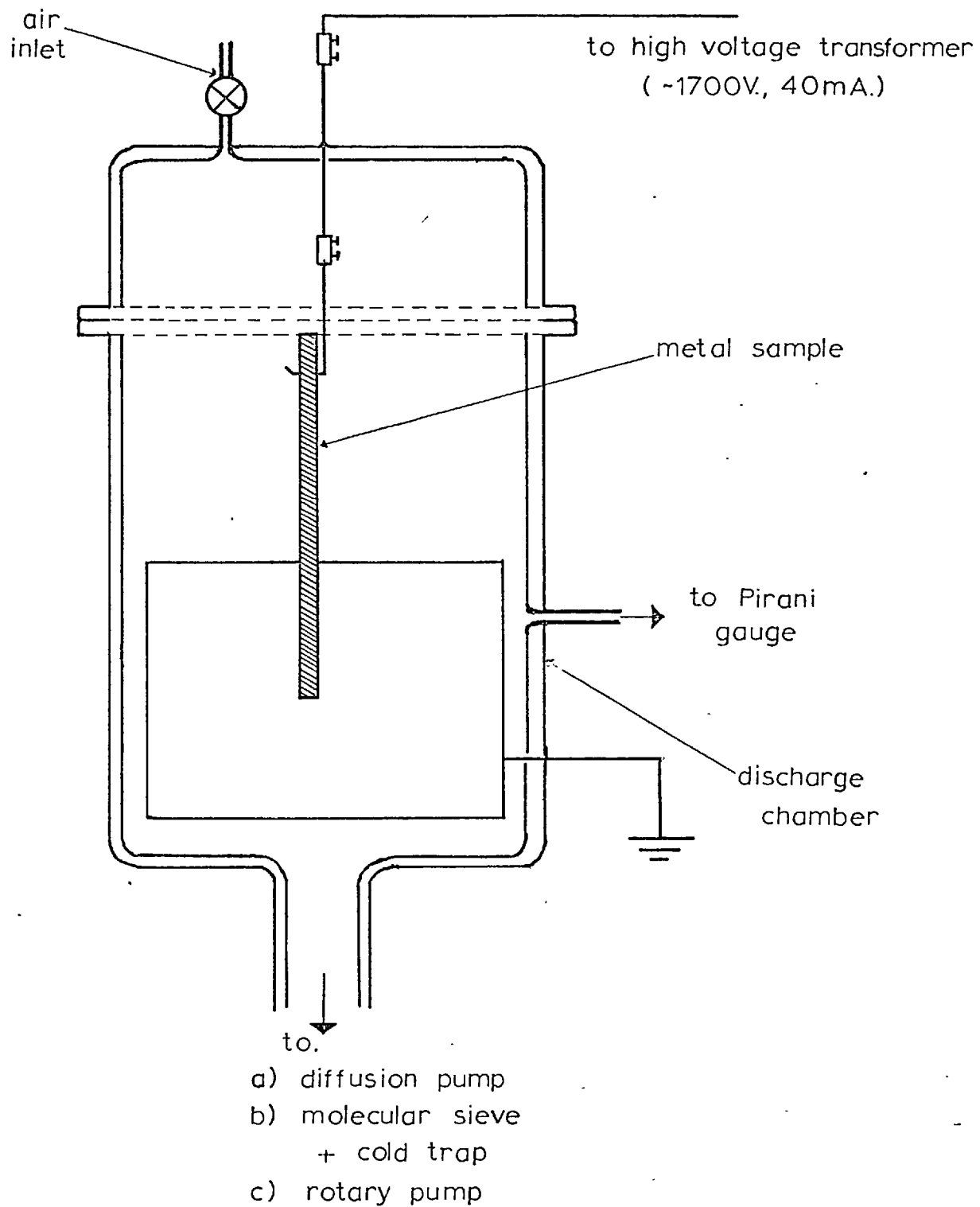


Figure 3.4. Ionic bombardment apparatus (ref. 37)

of frictional displacement against time. Generally some degree of "stick-slip" occurred. This is a form of intermittent motion that can be considered as resulting from the coefficient of static friction being greater than the coefficient of kinetic friction. The ball and plate stick together until there is sufficient spring force to overcome the static friction. The ball then slips quickly, since once moving, kinetic friction between ball and plate is at first insufficient to halt sliding. The whole procedure is then repeated.

From mathematic analysis of stick-slip it can be shown that the shape of the stick-slip curve is characteristic of the machine employed. Particularly important are the stiffness of the stationary rubbing member, its degree of damping and its mass. In the Bowden-Leben apparatus used, the spring holding the ball horizontally in position was quite weak and poorly damped. This meant that the apparatus was particularly prone to stick slip. (On the other hand it also meant that the frictional displacement was large and thus could be accurately measured.)

In these experiments, the peak coefficient of friction just before slip has been used as the measured variable. This can be roughly identified with the static coefficient but it will always be somewhat lower than the real static coefficient value because of inertia forces. Thus it must be stressed that the value, μ , measured in this work is not a true constant of the lubricating system but is also characteristic of the mechanics of the machine used. Fortunately this did not matter in these experiments since it was a relative change in friction which was being studied under independent conditions rather than any absolute value.

The convention of taking the peak coefficient of friction in stick slip as μ , the static coefficient and of taking scuffing to be a sudden increase in μ from 0.1 to > 0.2 is the same as that adopted by Grew (90).

It differs from Frewing (72), who took scuffing to occur when smooth sliding suddenly deteriorated to stick-slip. Bristow (91) has criticised the use of the stick-slip transition in this way as being more dependent on the friction-velocity relationship than the friction-temperature variation.

3.37. Accuracy

The overall accuracy of these experiments was less than the adsorption measurements of the previous chapter. This represents the difference between the two types of system. Adsorption is relatively straightforward and reproducible. The variables are easily controlled. Scuffing, on the other hand, depends on many variables that are much more difficult to reproduce, the most notable being the rubbing surfaces themselves. There is thus a much wider statistical scatter since any one of the several small factors can trigger lubricant breakdown before it would normally be expected.

In this section the accuracy of each of the measured variables will be considered in turn. Concentration accuracy is most easily dealt with. The solutions used could be prepared to within 0.1% down to quite low concentrations. This error was thus negligible compared to others.

Temperature control varied depending on the range involved. Up to 50°C it could be determined to $\pm 2.5^{\circ}\text{C}$. (0.5°C at room temperature). At 75°C the variation was $\pm 4^{\circ}\text{C}$ and at 90°C, $\pm 7^{\circ}\text{C}$. The problem did not lie in maintaining a non-fluctuating temperature. The control device was such that the actual variation with time was only $\pm 1.5^{\circ}\text{C}$ even at 90°C. The main difficulty was in determining the exact temperature of the contact. Cooling of the chuck in air produced a temperature gradient between the liquid and the steel ball. This was mitigated but not completely prevented by placing a metal shield over the rubbing area. The temperature variations quoted therefore represent the maximum estimated error in the actual contact

temperature value. Since the temperature control was preset, the variation between points on a single temperature curve was only $\pm 1.5^{\circ}\text{C}$.

Coefficient of friction was the least accurate of the three parameters studied. For good lubrication ($\mu \sim 0.10$) the variation was less than $\pm 15\%$. At conditions of lubricant breakdown, however, the accuracy of μ was only $\pm 40\%$. Fortunately such an accuracy level was acceptable since the range of μ being studied between scuffing and non-scuffing values greatly exceeded the combined error.

3.40. Results

In this chapter the experimental results are separated from the discussion, which will follow in section (3.50).

3.41. Effect on immersion time on friction and scuffing

No specific experiments were carried out to test the effect that time of immersion in the lubricant had on friction. It was noted, however, that for concentrations below 5×10^{-6} moles/mole of amine, an oleophobic monolayer was not found for several minutes at room temperature. At higher concentrations non-wetting occurred almost instantly. Because of this time lag, at high temperatures the temperature was always held for at least $\frac{1}{2}$ hour (15 minutes at 90°C).

3.42. Reversibility of lubricant breakdown

Before applying thermodynamics to the lubricant breakdown process it was important to ascertain whether this was reversible. A sequence of experiments was therefore carried out to test reversibility with temperature. Friction was measured at a series of different temperatures, each being maintained for 15-30 minutes. After each run the steel plate was left in

the original amine solution and the temperature changed to a new value. The results of this set of experiments are shown in Table (3.2) and Figure (3.5), where the friction-time plots are reproduced to indicate the sort of traces actually obtained. It can be seen that lubricant breakdown was reversible for the system studied.

Table 3.2.

Stainless steel lubricated with octadecylamine in hexadecane

Runs in Order	Temp. $^{\circ}\text{C}$	Time at $^{\circ}\text{C}$	load lbf	speed mm/s	Amine Conc. moles/mole	μ
1	21 $^{\circ}$	24 hrs.	4(17.8N)	0.1	9×10^{-5}	0.10
2	35 $^{\circ}$	30 min	4(17.8N)	0.1	9×10^{-5}	0.10
3	55 $^{\circ}$	30 min	4(17.8N)	0.1	9×10^{-5}	0.12
4	68 $^{\circ}$	20 min	4(17.8N)	0.1	9×10^{-5}	0.135
5	90 $^{\circ}$	15 min	4(17.8N)	0.1	9×10^{-5}	0.24
6	68 $^{\circ}$	20 min	4(17.8N)	0.1	9×10^{-5}	0.12
7	55 $^{\circ}$	30 min	4(17.8N)	0.1	9×10^{-5}	0.12
8	35 $^{\circ}$	30 min	4(17.8N)	0.1	9×10^{-5}	0.11

3.43. The effect of temperature and concentration changes on friction for water-free systems

Friction results are presented in graphical form in Figs. (3.6) and (3.7)., where coefficient of friction in individual runs is plotted against $\log_{10} C$ at a series of ambient temperatures.

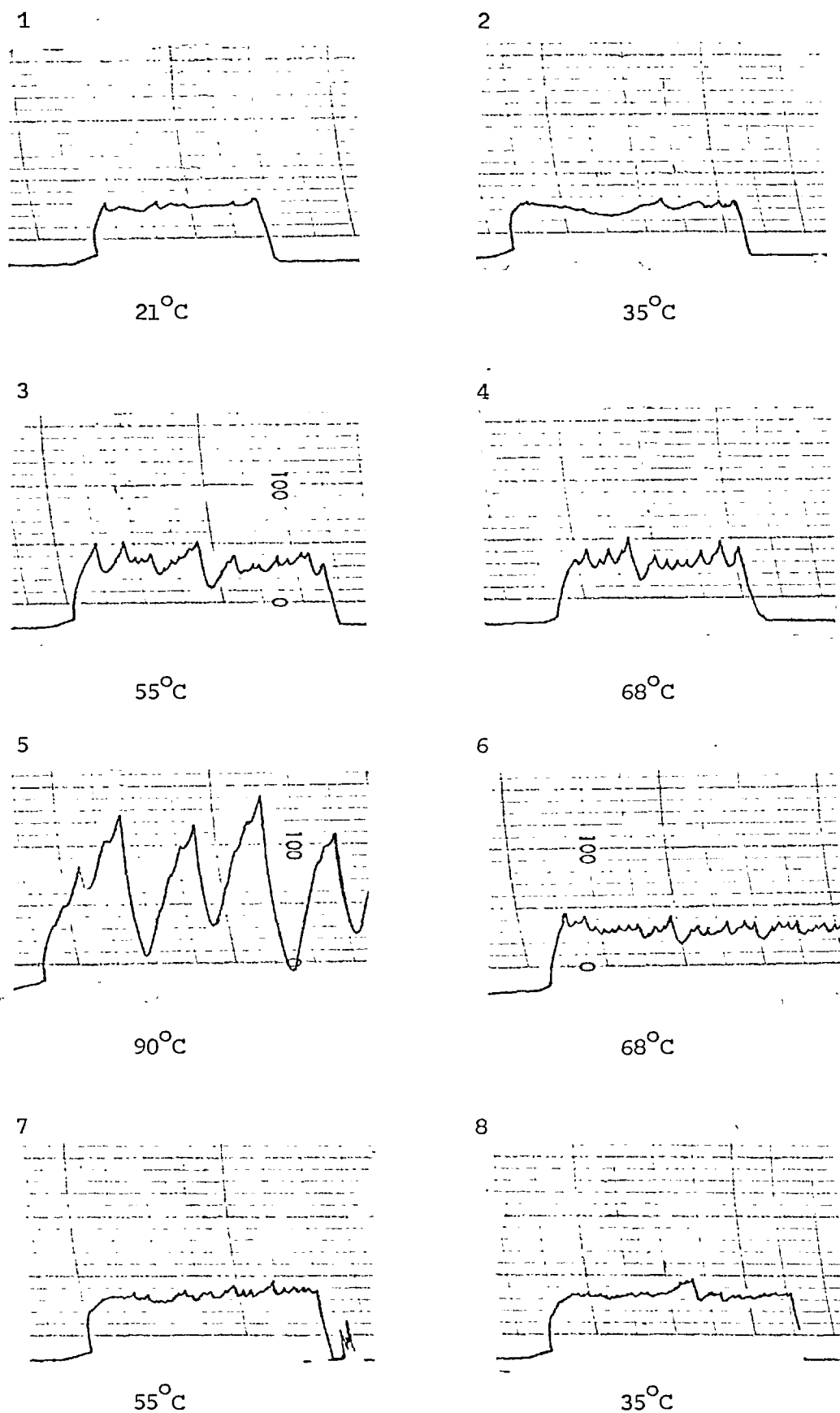


Figure 3.5. A series of friction traces showing the reversibility of lubricant breakdown. Octadecylamine on stainless steel. Concentration = 6×10^{-5} mol/mol.

Figure 3.6. Change in friction with concentration for octadecylamine on stainless steel

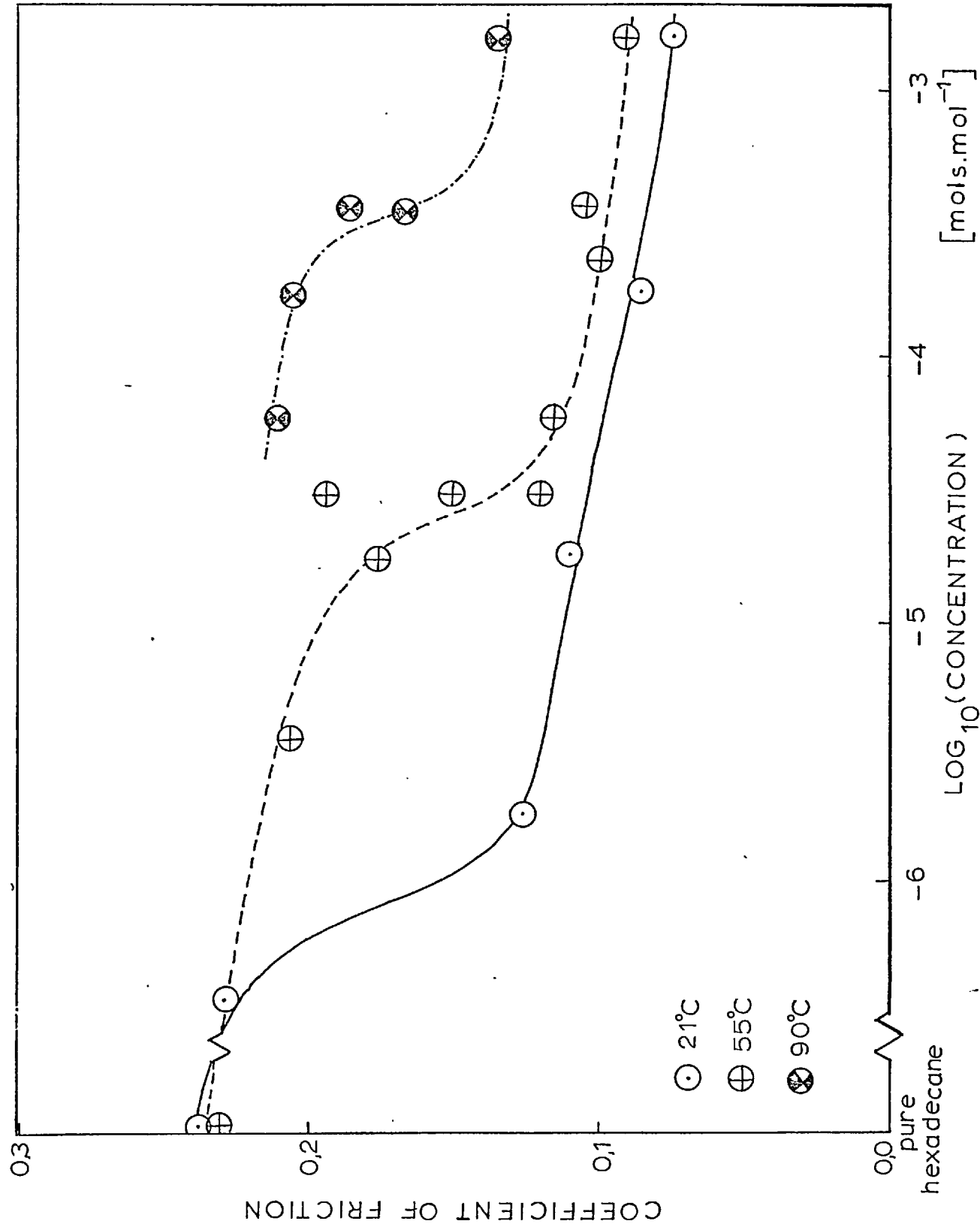
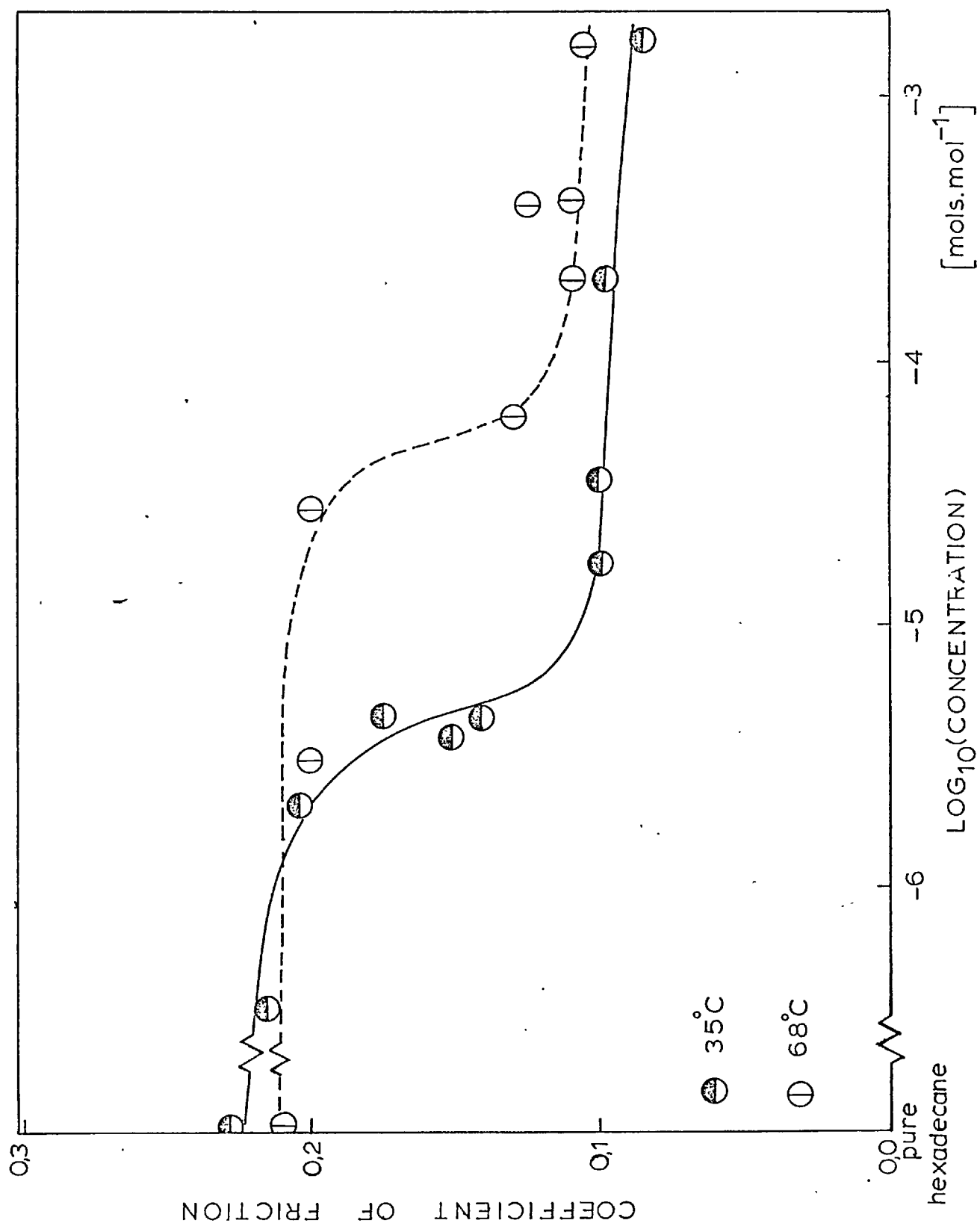


Figure 3.7, Change in friction with concentration for octadecylamine on stainless steel



In these experiments the steel plate was taken from the ionic bombardment cleaner and plunged immediately into amine solution, so that water had little opportunity to adsorb from the atmosphere.

It can be seen from figures (3.6) and (3.7) that there were three main friction ranges at a given temperature. At zero and low amine concentrations only poor lubrication occurred ($\mu = 0.2 - 0.3$) and there was high amplitude stick-slip. At higher concentrations of amine the coefficient of friction was much lower ($0.08 - 0.12$) and only very mild stick-slip took place. In the intermediate range, which was scattered over about one third of an order of magnitude of concentration, the friction value appeared to be in transition between good and bad lubrication. This transition region can be taken as the scuffing point although, under the mild running conditions of the Bowden-Leben apparatus, the only obvious change was a slight increase in friction, wear scar and stick-slip.

The exact values of C at very low concentrations in figures (3.6) and (3.7) should be treated cautiously since adsorption of amine on the metal plate may, in these instances, have slightly changed the final concentrations of the amine-hexadecane solutions. The amount of octadecylamine solution used in each run was approximately 30 cm^3 .

3.44. Effect of adsorbed moisture on friction and scuffing

The surface of an ionically bombarded metal might be expected to be much cleaner than that of the steel powder used for adsorption in chapter 2. The powder had been exposed to normal atmospheric conditions for several weeks and would thus be likely to have a well-developed adsorbed water film.

To make a useful comparison between polar adsorption and lubrication it was necessary to test for the effect of adsorbed water on friction. This was equivalent to contaminating the metal plates until they corresponded

to the metal powder. Two modifications were made to the normal experimental method to accomplish this. In one set of tests the octadecylamine solutions were wetted to 25% relative humidity at 25°C in the same manner as described in section (2.34). The newly cleaned metal plates were then immersed in this slightly damp solution. The second technique was far more drastic, and probably produced a steel surface more like the metal powder used in chapter 2. The ionically bombarded steel plate was suspended in a closed glass vessel which contained a pool of water in the bottom. The steel was left in this saturated atmosphere for fourteen hours before being immersed in amine solution.

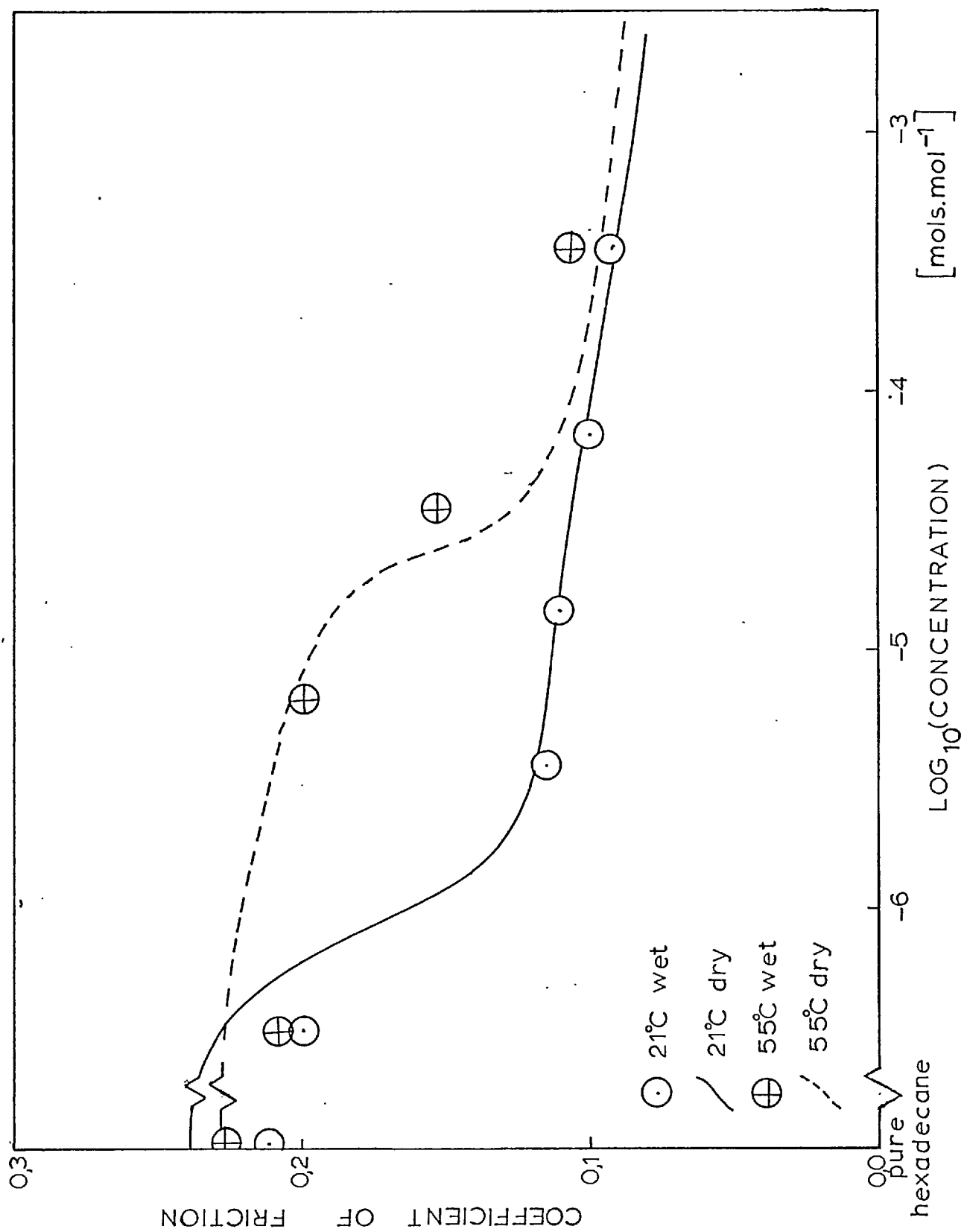
Experimental friction measurements using this second technique are shown in Figure (3.8) together with the curves obtained for the dry solution-metal system. It can be seen that friction results were similar in both wet and dry cases, suggesting that changes in the amount of adsorbed water, at least above a certain minimal level, do not greatly affect the lubricating properties of the system. Oleophobic monolayers were also obtained on the damp metal.

3.45. Oleophobic monolayer effects

The oleophobic character of adsorbed amine films was not investigated specifically. Retracting surfaces were, however, observed when transferring the metal plates from amine solution to the Bowden-Leben trough at room temperatures. There seemed to be rough correlation between this oleophobicity and the ability of the amine to give good boundary lubrication.

The oleophobic effect provided evidence of the high stability of the amine film once it had adsorbed, and its effectiveness in preventing surface contamination by impurities. Two steel plates which had oleophobic surfaces, and some supernatant (10×10^{-5} moles/mole) amine solution retracted in

Figure 3.8. Effect of adsorbed water on friction for octadecylamine solution with stainless steel



globules on top of it, were left in the open on a laboratory bench for one week. There was no indication, after this time, that any of the original oleophobic character had been lost due to penetration of impurities from the London atmosphere.

3.46. Effect of load on friction

A few experiments were carried out changing the load on the ball during a run. In this way the effect of applied load on friction could be assessed.

In the well lubricated region it was found that coefficient of friction gradually increased with load but remained considerably below the values characteristic of lubricant breakdown. This effect was probably due to increasing penetration of the film by metal-metal contact at high loads without actual collapse of the boundary lubricating film.

In the poorly lubricated region, μ was much more dependent on load and increased from 0.25 at 17.8N (41b) to 0.40 at 35.6N (81b).

3.50. Discussion

3.51. The effect of concentration and temperature on scuffing

It can be seen from figures (3.6) and (3.7) that there is quite a narrow range of amine concentration over which friction changes from a typical, good boundary value of $\mu = 0.10$ to a poorly lubricated one of $\mu = 0.20$. These coefficients of friction correlate well with values found elsewhere in the literature for good and bad lubrication in similar systems. Thus Albertson and Wolfram (92) found μ_s to be 0.23 for pure white oil lubricating cast iron, but 0.13 when the white oil contained 1% octadecylamine.

Figures (3.6) and (3.7) also confirm other experimenters in showing that, for a given concentration of octadecylamine, good lubrication breaks down at a specific temperature above which the remaining lubrication is

characteristic only of the solvent. Further comparison with the work of Frewing (14) and Grew and Cameron (15) can be made by plotting, as did these authors, the values $\log_{10} C_B$ against $1/T_B$, where T_B and C_B are the critical temperature and concentration at which coefficient of friction suddenly increases. Such a plot is shown in figure (3.9). The failure conditions at various temperatures were taken as the points of inflexion in the curves in figures (3.6) and (3.7). From figure (3.9) a good straight line is obtained, and using Frewing's scuffing theory (14), the energy of adsorption works out as 65 ± 15 kJ/mol.

3.52. Correlation between adsorption and scuffing

The friction experiment results of the previous section are now compared with the adsorption results for the octadecylamine-hexadecane system, reported in chapter 2.

In Figure (3.10), the adsorption plot of $\log_{10} C$ against $1/T^{\circ}K$ at a constant coverage of 1.4×10^{-7} moles. cm^{-2} amine excess is shown on the same graph as the lubricant failure plot of figure (3.9). The amine adsorption under these conditions corresponds to 40% of the total adsorbed at high concentrations. At high temperatures, (greater than $40^{\circ}C$), there is approximate agreement between the two curves, suggesting that the variation of adsorption and of scuffing with temperature is similar. This conclusion can be extended to suggest that at these high temperatures, scuffing occurs at approximately constant amine film coverage, as Frewing's theory (14) predicts.

There is, however, a marked divergence between the scuffing and constant adsorption curves in the low temperature range. This can best be explained by considering a film failure model. If scuffing is characterised by failure of the adsorbed film, then the values being measured in adsorption

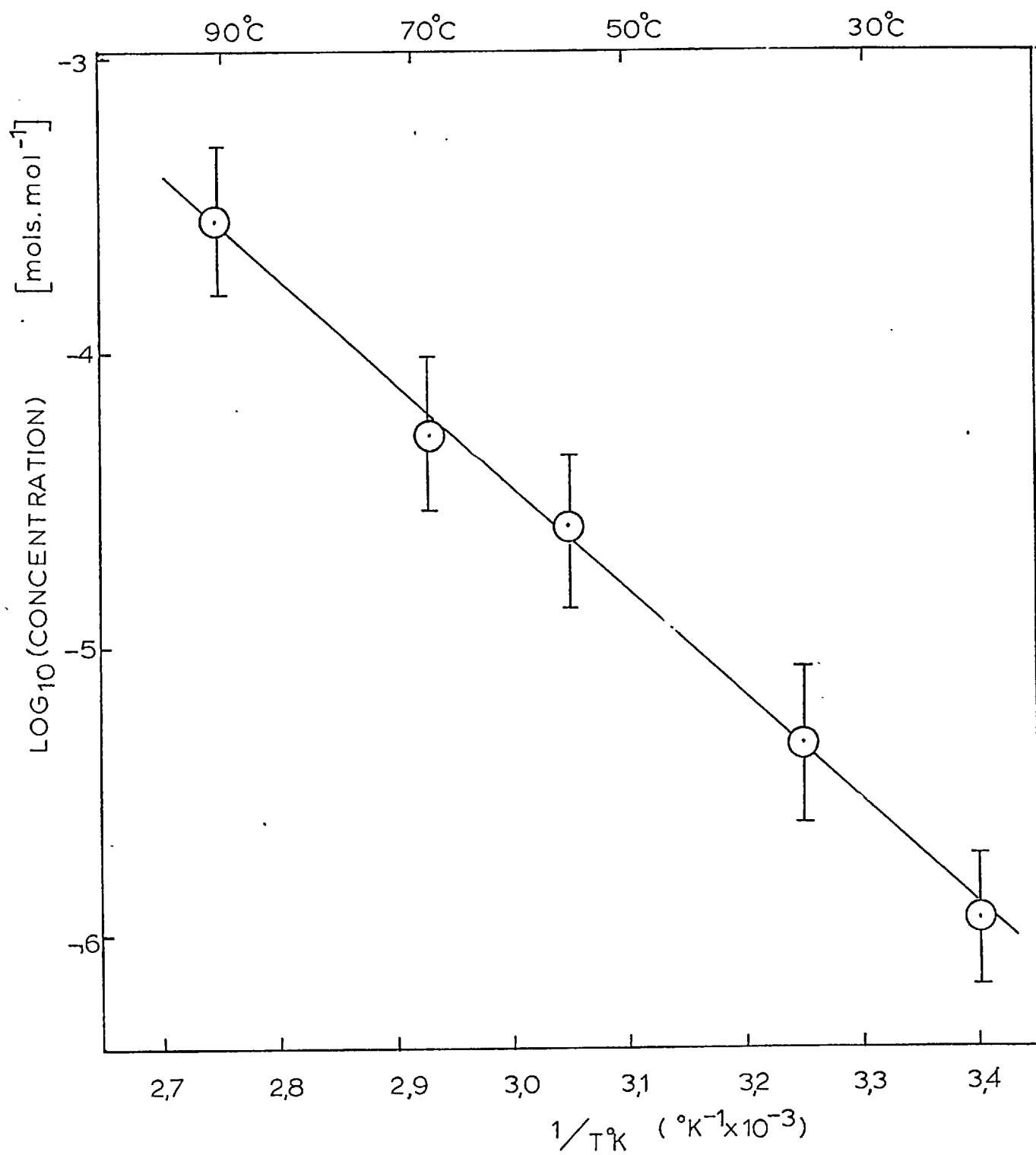


Figure 3.9. $\log_{10} C$ vs $1/T$ plot for lubricant breakdown conditions

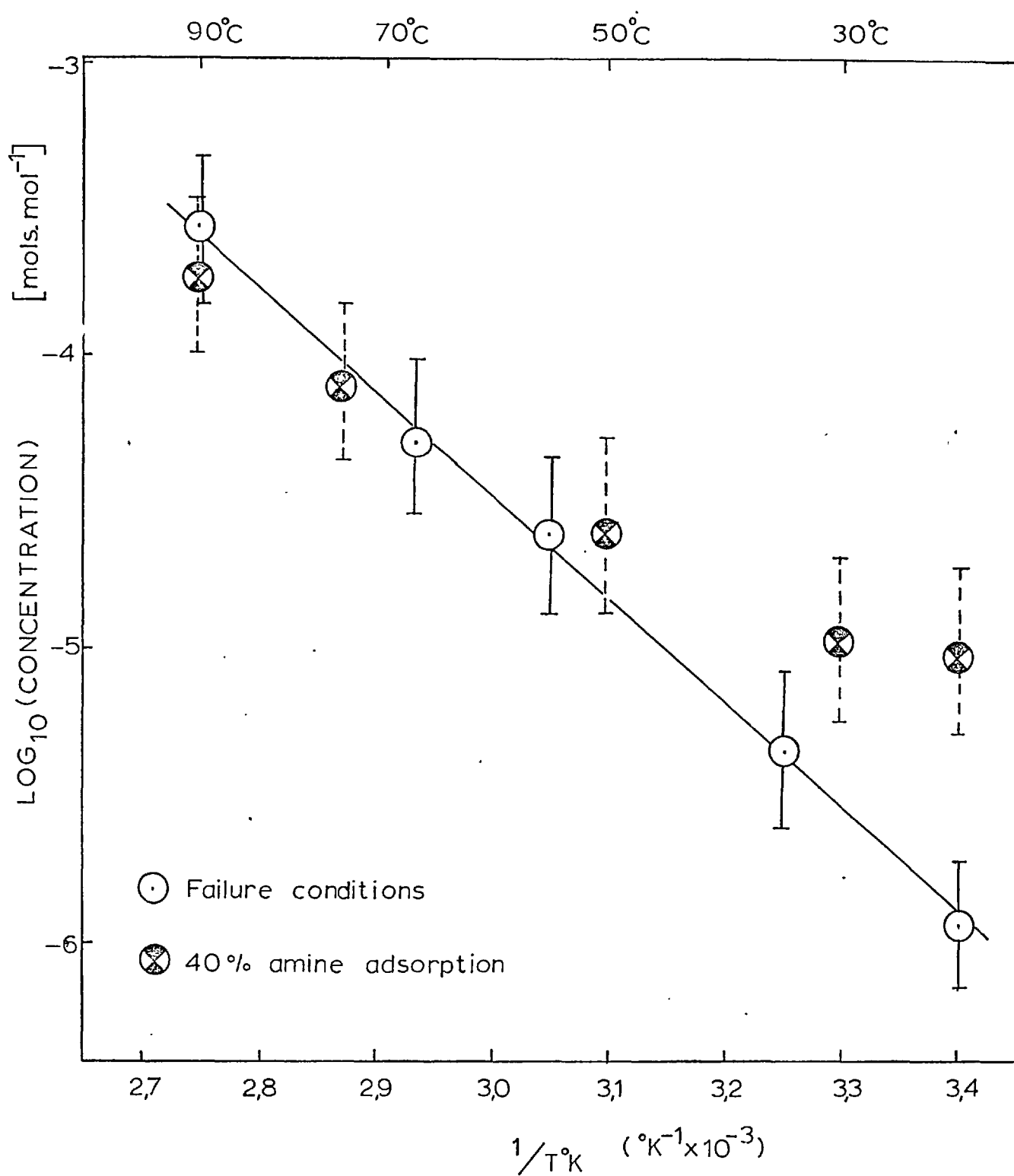


Figure 3.10. Comparison of scuffing and 40% amine adsorption conditions for the same system. (octadecylamine on stainless steel)

and scuffing are rather different.

For amine adsorption, the quantity being evaluated as the gradient of the $\log_{10} C$ vs. $1/T$ plot for constant coverage is the difference between the enthalpy of adsorption of amine and that of the hexadecane, both on the bare metal: the adsorption is essentially competitive.

Thus:

$$\Delta H_{\text{meas.}} = \Delta H_{\text{amine}} - \Delta H_{\text{hexadecane.}}$$

The low gradient at low temperatures for adsorption was ascribed, (chapter 2), to high values of $\Delta H_{\text{hexadecane}}$ under these conditions as a result of a pre-freezing phenomenon.

Film breakdown with increasing metal-metal contact is a desorption process that is not necessarily the true reverse of equilibrium adsorption. There are two ways of regarding it. One can either say that strongly adsorbed hexadecane at low temperatures strengthens the adsorbed film so that less amine coverage is required to withstand scuffing. Alternatively one can picture the surface being transformed on scuffing from amine-covered to either bare metal or metal with just a little adsorbed hexadecane. From this viewpoint the enthalpy measured will be largely the enthalpy of adsorption of amine on bare metal, since the desorption is not competitive.

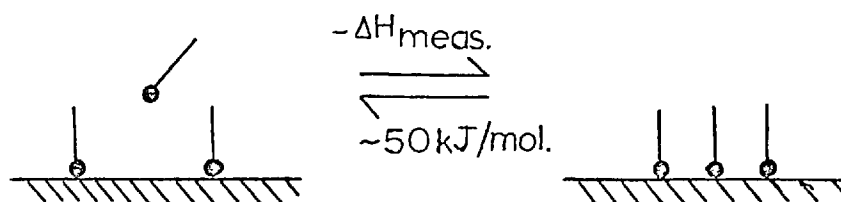
A continuing small heat of adsorption of hexadecane on metal, even at high temperatures, would also explain the slight overall difference between the adsorption and scuffing curves in figure (3.10). Since the difference lies within the experimental error, however, it is not possible to decide whether it is significant.

The fact that scuffing occurs, in the experiments studied, well below coverages of amine at which lateral interaction forces become important means that these interactions played no part in the lubricant breakdown process.

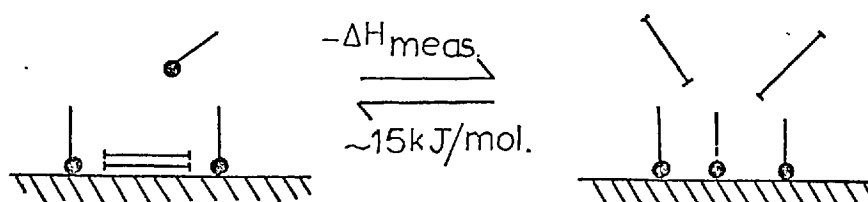
The difference between adsorption and scuffing can be represented schematically:-

Adsorption

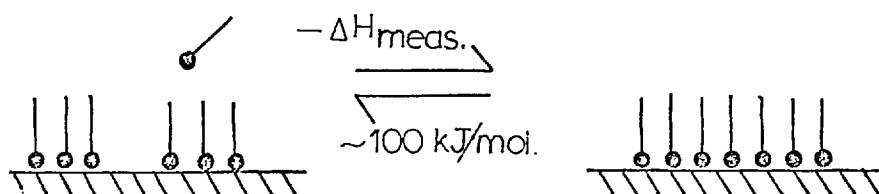
a) At high temperatures



b) At low temperatures. (strongly adsorbed hexadecane)

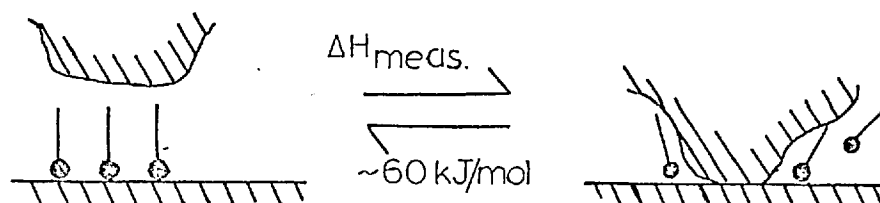


c) At low temperatures, high coverages (lateral interactions)

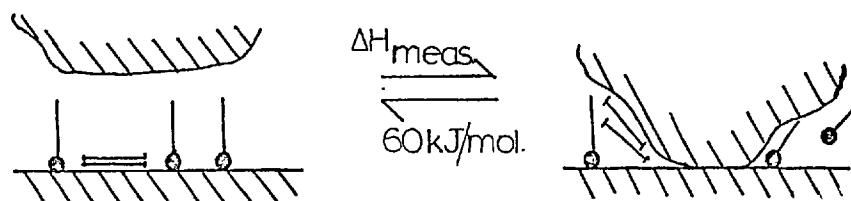


Lubricant Breakdown

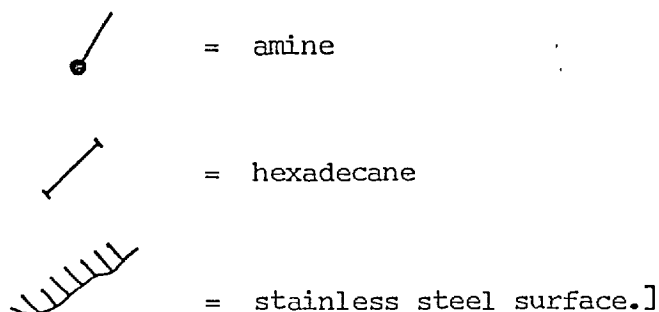
a) At high temperatures



b) At low temperatures



[In these diagrams, molecules are presented as only adsorbing on one of the metal surfaces. This is purely for simplicity since adsorption will, of course, take place on both.]



In comparing adsorption and lubricant breakdown it has been assumed that the same thermodynamics can be applied for normal adsorption and for adsorption at the heavily loaded interface. There are two main problems in this assumption. One is the effect of pressure on the thermodynamic equilibrium and the second involves possible changes that may occur in the thermodynamics as a result of alterations in orientation of the adsorbed layer brought about by applied load.

Fortunately solvent and solute molecules have approximately the same size. This means that applied pressure should not greatly affect the position of the adsorption equilibrium, since increasing load will not favour adsorption of one component with respect to the other.

Any changes in orientation will alter the overall energy of adsorption, but if the main contribution to the strength of adsorption under film failure conditions is the attraction between the metal and the amine

functional group, then the thermodynamics will remain qualitatively similar in stressed and unstressed systems. Only if the main adsorption strength were due to lateral interactions would alterations in film orientation change the thermodynamics of film failure. Since it has already been shown that the scuffing range lies in the region where lateral interactions are unimportant, it is reasonable to compare adsorption at the loaded and unloaded interfaces without further knowledge of how the film deforms. Because of possible changes in film orientation, however, a quantitative comparison of adsorption and failure would be only speculative.

3.53. Chain matching

In figure (3.11) is shown the adsorption $\log_{10}C$ vs. $1/T$ plot for a series of contact coverages of amine using the hexadecylamine-hexadecane results of chapter 2. Also on the graph are scuffing results for the same system due to Grew and Cameron (15). It is clear that there is a correlation between scuffing and constant adsorption as was observed using octadecylamine, although it seems that for hexadecylamine a higher amine coverage is needed to support an equivalent load. An especially interesting feature of figure (3.11) is, however, the absence of any unusual effect due to chain matching.

Chain matching is an anomalous film strength that has been found to occur when long chain solute and solvent molecules both have the same number of carbon atoms. References to the effect in lubrication, corrosion, adsorption, coacervation and viscosity are to be found in refs. (15), (93), (24), (94) and (95). Most chain matching results come from fatty acid-alkane systems, but Askwith (81) and Bewig (24) mention the effect in connection with long chain amines.

The most thoroughly investigated occurrence of chain matching in boundary lubrication has been reported by Grew and Cameron (15), who plotted

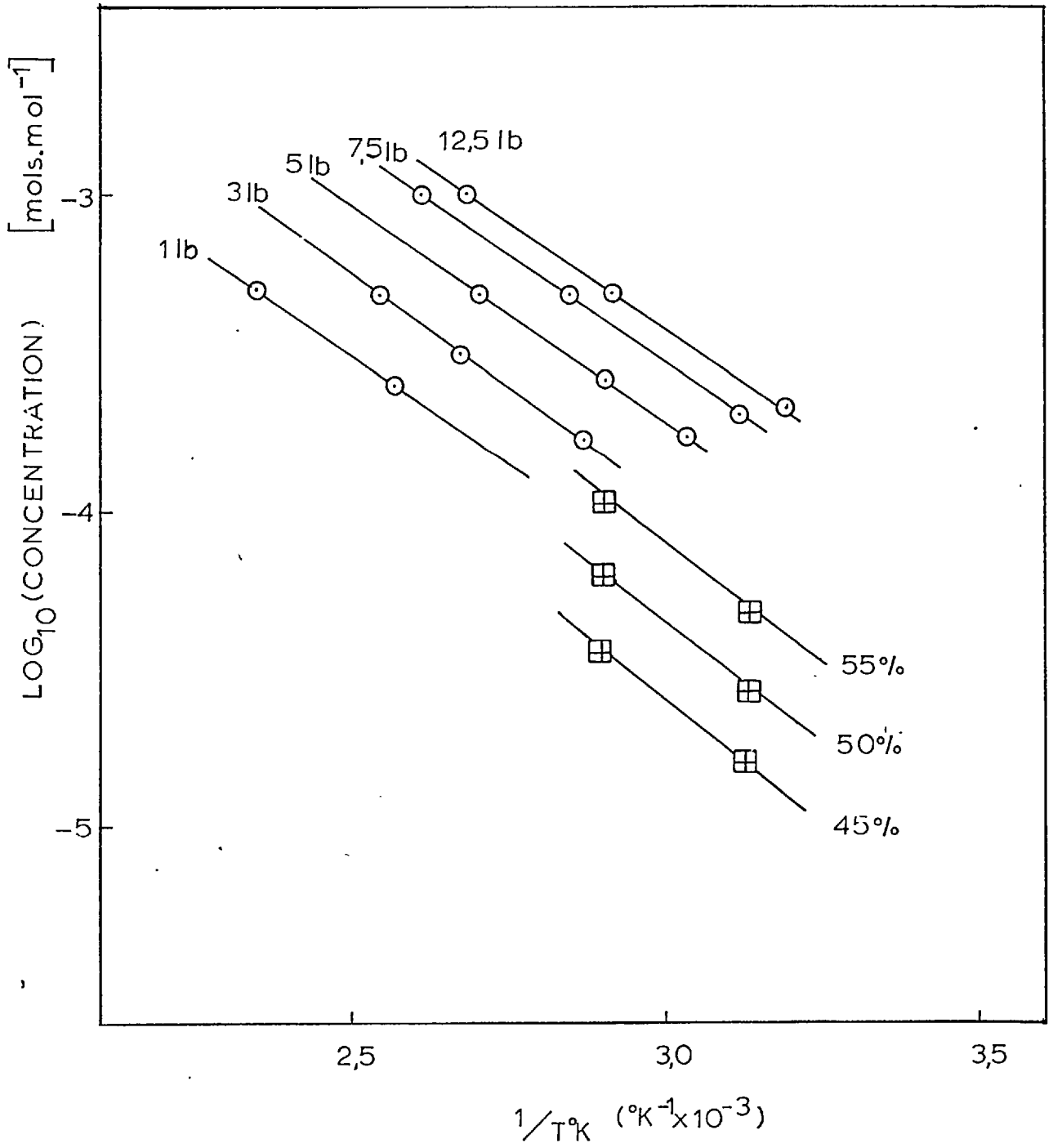


Figure 3.11. Comparison of scuffing and percentage monolayer adsorption for hexadecylamine on stainless steel. Scuffing data from ref (15)

$\log_{10} C_B$ vs. $1/T_B$ for lubricant breakdown using a series of long chain hydrocarbons with dodecanoic acid. For extreme non-matching combinations the energy of adsorption, as worked out from the gradient of the line obtained, was 40-50 kJ/mol. This rose to 180 kJ/mol for dodecanoic acid in dodecane. Such a high value of adsorption energy is characteristic of a system with full lateral interaction energy as well as acid-metal polar attractive forces. It is similar to the energy of sublimation of the fatty acid. Presumably the lower energy of adsorption of ~ 50 kJ/mol represents the case for which lateral interactions are minimal.

Work by Grew (15), and in this thesis suggests that there is no such enhanced energy of adsorption, at the scuffing range studied, for matching amine systems, although Bewig and Zisman (24) have found that matching amine and hydrocarbon does have a specially high stability in adsorption at low temperatures. From the adsorption results in chapter 2, the observation that lateral interactions begin at high coverages suggest that they do not occur at lower amine coverages for the non-matching octadecylamine-hexadecane system.

It would thus seem likely that the scuffing systems where matching chain effects occur, involve the failure of a laterally interacting film, which has a much higher temperature sensitivity than polar adsorption. Fatty acid may promote the formation of such a laterally interacting film, perhaps containing adlineated alkane molecules of the same chain length. Certainly this would be more likely with chemically bound acid than with amine, because of its low mobility.

Bewig and Zisman's (24) matching results with amine adsorption only occur at high coverages where lateral interaction would exist anyway. Finally Askwith, Cameron and Crouch's matching chain results for amines may have occurred because they were working under high loads in a 4-ball

rig. Figure (3.11) shows that higher amine coverages are necessary to support higher loads. Conceivably the coverage required to withstand scuffing in these tests, at such high loads, was so great that lateral interactions existed between the adsorbed amine molecules.

This is only a tentative explanation for the differences observed between matching and non-matching systems, although it seems very likely that lateral interaction forces are the key to the whole question.

3.60. Conclusions

At high temperatures, satisfactory correlation is obtained between $\log_{10} C$ vs. $1/T$ plots derived both from direct adsorption and friction experiments. This indicates that in this range scuffing occurs at a constant adsorbed amine coverage, dependent on the load. Below 40°C an extra term must be introduced to account for solvent effects, which suggests that the coherence of the adsorbed film rather than simply the amount of amine adsorbed is the critical factor.

CHAPTER FOUR

ADSORPTION THEORY APPLIED TO HIGH SPEED SCUFFING SYSTEMS

4.10. Introduction

The preceding chapter has described an investigation into thin film lubrication at very low sliding speeds. It was shown that the variation in scuffing was consistent with an adsorption model. Low speeds were used so as to make the system as simple as possible, by avoiding frictional heating, and also to ensure that equilibrium conditions were attained. In this chapter it is demonstrated that a similar adsorption model can be applied at higher speeds. Two series of scuffing results are taken from the literature and each is analysed. Both sets of data are shown to be compatible with the model which was applied at low speeds.

4.20. Adsorption theory applied to medium speed scuffing

Data is taken from a paper by Askwith, Cameron and Crouch, published in the Proceedings of the Royal Society (81). They measured scuffing of one - inch, (25.4 mm), diameter EN31 steel balls in a 4-ball test rig, using hexadecanoic acid in n-hexadecane as the lubricant. The scuffing load was determined as a function of concentration of acid in alkane at a constant speed of 200 rpm (154 mm/sec). Their results are shown in figure (4.1a). In figure (4.1b) is a graph from the same paper indicating the typical coefficients of friction obtained for different loads.

Askwith, Cameron and Crouch measure the relationship

$$C_B = f(W_B) \cdot V \cdot T_{amb}$$

C_B = concentration of acid in alkane at scuffing

T_{amb} = ambient temperature (constant)

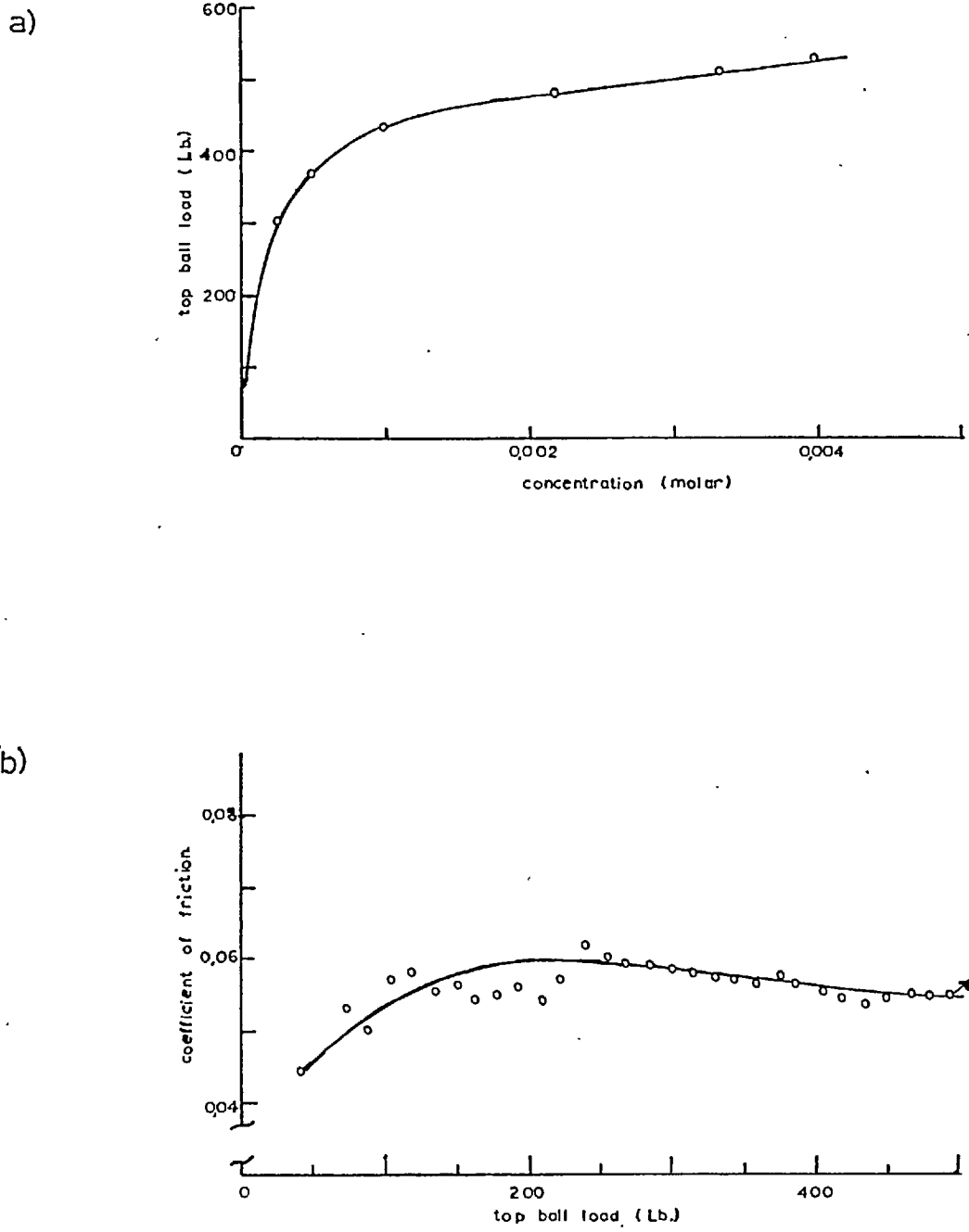


Figure 4.1. Scuffing and friction results taken from ref (81).

V = Velocity (constant)

W_B = load at scuffing.

It is important to note, however, that scuffing is also dependent on the temperature of the lubricating film which, since frictional heating occurs, is not equal to the ambient temperature but is a function of applied load. Thus;

$$T_{\text{film}} = T_{\text{amb}} + \Delta T_f \quad \text{..... 4.1.}$$

T_{film} = total film temperature

ΔT_f = friction rise in temperature (flash temperature)

and since frictional heating depends on load and velocity;

$$T_{\text{film}} = T_{\text{amb}} + f(W, V)$$

The aim of this analysis is to show that the high speed scuffing system varies with concentration in exactly the same way as the low speed one, except for this frictional heating effect.

The temperature increase due to high speed sliding has been the subject of a series of papers of increasing complexity ever since the pioneer work of Blok (96). In this analysis Blok's original formula is used. Its validity and the effect of applying different temperature equations will be considered in the assumptions, listed at the end of this section.

Blok gives the expression for the maximum flash temperature between sliding surfaces, which is the temperature at which the film is most likely to break down as;

$$\Delta T_{f.m} = \frac{2\mu P[1 + \frac{1}{\sqrt{2}}]V.r}{4\alpha\rho C[1 + (\pi Vr/8\alpha)^{\frac{1}{2}}]} \quad \text{..... 4.2.}$$

μ = coefficient of friction

P = mean Hertz pressure

V = sliding velocity

r = Hertz contact radius

α = thermal diffusivity of steel

ρ = density of steel

c = heat capacity of steel

For the 4-ball machine used, this simplifies to:

$$\Delta T_{f.m.} = \frac{0.949 \text{ nW}^{2/3} \mu}{k[1+0.627(\frac{Vr}{\alpha})^{1/2}]} \quad \dots\dots\dots 4.3.$$

k = thermal conductivity

W = top ball load (lbs). (lbs are used in this analysis since they are the units employed by Askwith et al.)

n = no. of revolutions per second of the top ball.

Values for k and α , taken from ref.(97) are:

$$\alpha = 6.045 \text{ mm}^2/\text{sec.}$$

$$k = 2.604 \text{ kg/sec.}^\circ\text{C.}$$

The values V and r can be represented as

$$r = 4.07 W^{1/2} \times 10^{-2} \text{ mms}$$

$$V = \frac{25.4n\pi}{60/3} \text{ mms/sec.}$$

This formula (4.3) gives the flash temperature as a function of load.

Values have been computed for each measured point in fig. (4.1a). The coefficient of friction in each case was taken from the results shown in figure (4.1b). These flash temperatures are shown in table (4.1) with Askwith, Cameron and Crouch's experimental data.

Table (4.1)

μ	Wlb	$\Delta T_{\text{flash}}^{\circ\text{C}}$	$T_{\text{film}}^{\circ\text{K}}$	$1/T_{\text{film}} \times 10^3$	Conc. moles %	$\log_{10} C$
0.058	300	73.0	368.0	2.717	0.025	- 1.60
0.055	375	78.0	373.0	2.681	0.050	- 1.30
0.054	425	82.5	377.5	2.649	0.100	- 1.00
0.054	480	88.5	383.5	2.608	0.220	- 0.65
0.054	510	91.8	386.8	2.586	0.33	- 0.48
0.054	525	92.8	387.8	2.579	0.40	- 0.40

$$T_{\text{ambient}} = 295^{\circ}\text{K}$$

From this table, a graph of $\log_{10} C$ against $1/T_{\text{film}}$ is plotted in figure (4.2.) T_{film} represents the total film temperature in equation (4.1), where the ambient temperature is 295°K .

As can be seen, a very good straight line is obtained for this plot, similar to those found at low speeds. Using the formula (chapter 3).

$$\Delta H = 2.3 R \times \text{Gradient}$$

one obtains the value,

$$\Delta H = -170 \text{ kJ/mol.}$$

This is different from most values found for ΔH (14) (52), which are normally about -50 kJ/mol . It is, however, very similar to the only other matching chain solute-solvent scuffing system which has been measured. Thus Grew and Cameron (15) found the anomalously high value of $\Delta H = -190 \text{ kJ/mol}$ for dodecanoic acid in dodecane.

It has thus been shown that the graph obtained for high speed scuffing at different concentrations, whilst at first sight very different in form to the low speed case, gives on analysis a similar relationship between

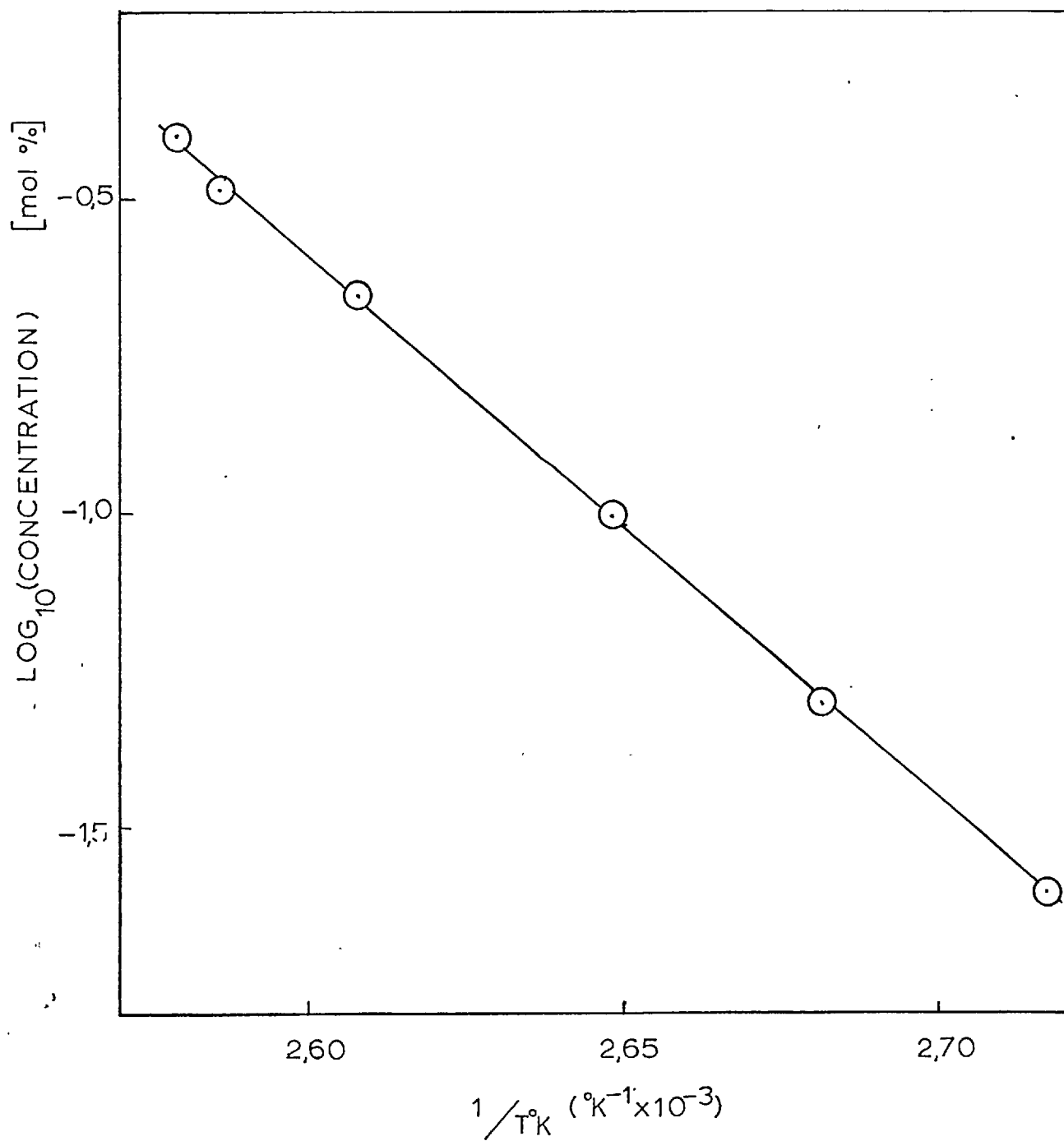


Figure 4.2. $\text{Log}_{10}C$ plotted against $1/T^{\circ}\text{K}$ for medium speed scuffing

concentration and scuffing temperature. This suggests that the same sort of model holds in both cases.

4.21. Assumptions

a) The adsorption system is in equilibrium during running. There is no direct way of verifying this, although the step method of applying load used by Askwith, Cameron and Crouch does ensure that frictional heating takes place quite slowly.

b) The ambient temperature of the solution was constant at 295°K (22°C). This assumes that the frictional heating did not raise the bulk temperature greatly. Since the speed was quite low, and the flash temperatures small, this is a reasonable supposition. The actual ambient temperature quoted by Askwith was $10\text{--}15^{\circ}\text{C}$. This is probably slightly in error since hexadecane freezes at such temperatures. A typical indoor temperature is $18\text{--}22^{\circ}\text{C}$. The actual value chosen was not critical, since the ambient temperature does not change the form of the $\log_{10} C$ vs $1/T$ plot markedly, but only shifts it laterally.

c) It was assumed that Blok's flash temperature formula was valid. Blok's formula was employed since it was both the simplest and the most thoroughly tested of the various friction heating equations. More sophisticated mathematical treatments have been carried out by Jaeger (98) and later by Francis (99). Recent work by Bailey (100) and Blok (101) has suggested that Blok's original estimate may have been approximately 15% too low. It was found, however, that the addition of a consistent 15% to the flash temperature values calculated in table (4.1) did not change the gradient of the curve in figure (4.2) by a significant amount, but only shifted it laterally. The choice of flash temperature equation was therefore not critical.

d) A major assumption in this analysis was that loading served only to increase temperature and had no direct effect on scuffing. This is supported by the work of Cowley (83) and Matveevsky (88), who have shown that at high loads and low speeds, the scuffing temperature response to changes in load is very small.

4.30. Lubrication at very High Sliding Speeds

In this second analysis, the idea that scuffing occurs when the adsorbed film desorbs is extended to account for a phenomenon which is observed at very high sliding speeds. This is the apparently enhanced strength of the lubricant film between gear teeth under these conditions. Thus, whereas at low sliding velocities, the scuffing load of gears decreases with increasing speed, at very high sliding velocities the effect is suddenly reversed and much higher loads are required for scuffing. This effect has been observed by Borsoff (102), Niemann (103) and Ku (104). The results analysed in this section are the gear tests of Borsoff (102) (105) using S.A.E. 30 mineral oil. These have been chosen because they are especially well documented and the data is presented in great detail.

Three of Borsoff's experimental curves are shown in fig. (4.3). Fig. (4.3a) portrays the basic scuffing curve of load against rotating speed. Fig. (4.3b) shows a plot, derived from this, of scuffing load against the actual sliding time of two rubbing gear surfaces. Fig. (4.3c) illustrates the effect of increasing ambient temperature. The scuffing load is plotted against different oil inlet temperatures for a series of runs at the same speed.

It can be seen from fig. (4.3b) that there are two distinct scuffing regimes, with the changeover region lying at between ten and twenty microseconds sliding time. Each regime will be considered in turn.

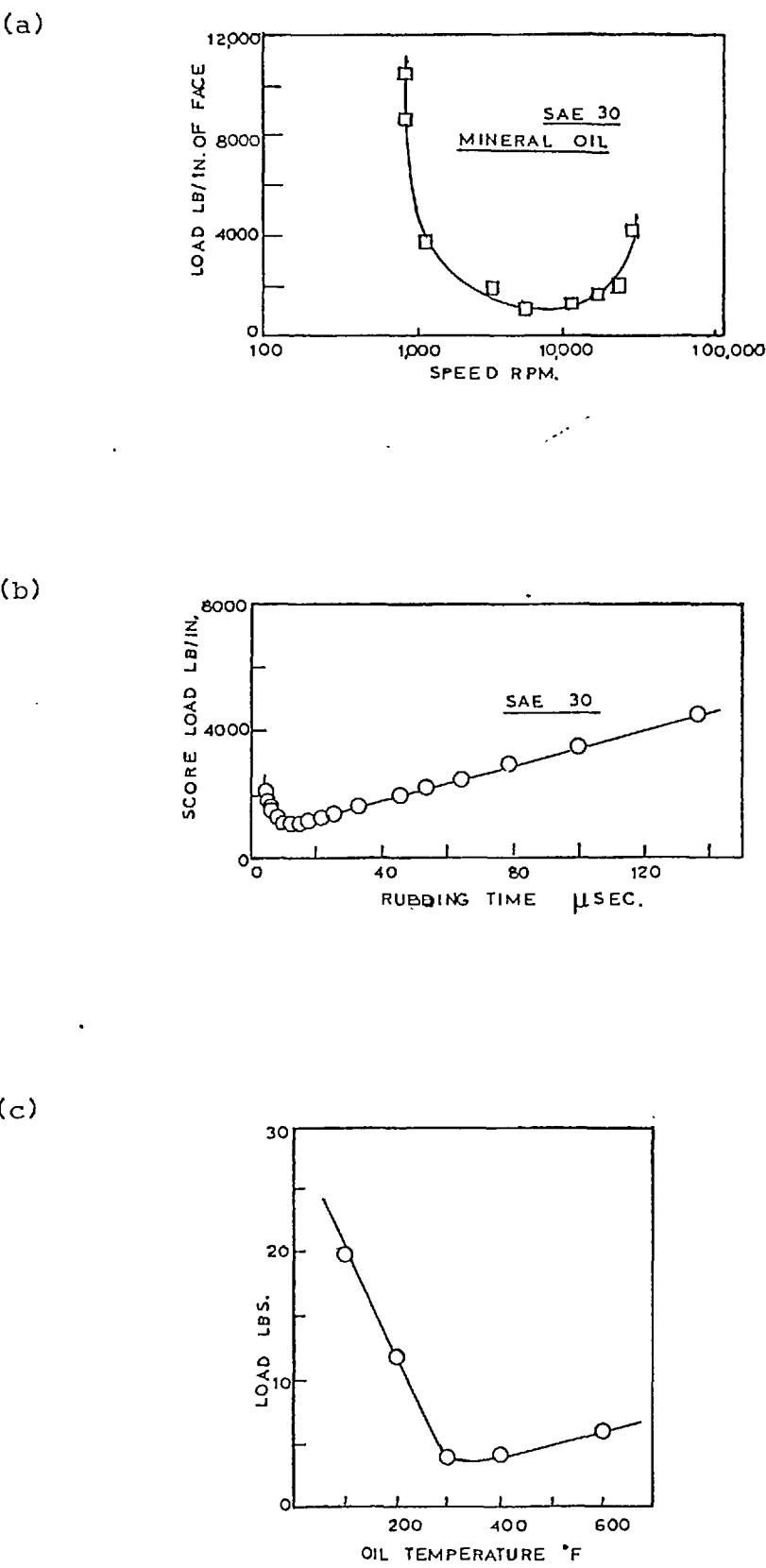


Figure 4.3. Gear test results from refs (102), (105)

The first part of the curve, where the sliding contact time is large, corresponds to the lower speed region in fig. (4.3a) and its shape can be easily explained in terms of Blok's critical scuffing criterion (96). This has been discussed in the preceding section where it has been shown that scuffing can occur when

$$T_{\text{film}} = \text{constant} = T_{\text{amb}} + f(W, V) \quad \dots\dots\dots 4.1.$$

For gears, Blok predicted that the maximum flash temperature would be given by (106):

$$\Delta T_{\text{f.m.}} = f(W, V) = a\mu^{\frac{3}{4}}V^{\frac{1}{2}}$$

$$a = \text{constant}$$

$$\mu = \text{coefficient of friction}$$

This formula has been tested many times (107), (108). In practice the indices of W and V have been found to vary from system between 0.5 and 1.0, probably partly because coefficient of friction is also a variable.

Plotting $\log_{10} W$ against $\log_{10} V$ for Borsoff's data gives a good straight line in the lower speed region, indicating that Blok's critical temperature criterion may be obeyed. From fig. (4.3c) the actual flash temperature value can be calculated. Fig. (4.3c) shows that the scuffing load decreased with ambient temperature. From equation (4.1) it can be seen that when $W = 0$,

$$T_{\text{film}} = T_{\text{amb}} = 180^{\circ}\text{C}.$$

(The flattening-out of the scuffing curve in Fig. (4.3c) at high ambient temperature is probably due to extreme pressure action of the sulphur in the mineral oil. This would be able to react continuously with the out-of-contact gear surfaces at high ambient temperatures).

Thus we have a straightforward model for scuffing in the lower speed range. The scuffing load has that value which will just raise the flash

temperature above 180°C. At this temperature, the film desorbs during sliding and the rubbing gear teeth scuff.

The main purpose of this analysis is to show that the second regime in fig. (4.3b), where the constant temperature scuffing model breaks down, can also be explained in terms of an adsorption model.

The explanation involves a non-equilibrium desorption model. The anomalous scuffing behaviour is observed when the actual gear contact time is only of the same order as the residence time of the molecules at 180°C. Thus one explanation for the Borsoff high speed effect is that the lubricating molecules simply do not have time to desorb whilst the the surfaces rub. In this case, no film breakdown could occur in practice even though it should on thermodynamic grounds.

Some calculations show this to be quantitatively reasonable. If desorption is first order, as suggested by de Boer (109), then:

$$-\frac{d\theta}{dt} = k_1(\theta - \theta_1)$$

θ = fractional monolayer coverage

t = time

k_1 = desorption rate constant

θ_1 = coverage at time $t = 0$

also from de Boer,

$$k_1 = \frac{e^{-\Delta H/RT}}{\tau_0}$$

ΔH = enthalpy change in desorption

τ_0 = fundamental time of oscillation on the surface

T = temperature in °K.

Hence

$$-\frac{d\theta}{\theta - \theta_1} = \frac{e^{-\Delta H/RT}}{\tau_0} dt \quad \dots\dots\dots 4.4.$$

A very approximate way of evaluating this is to assume constant temperature during contact. Then, integrating equation (4.4) over a given rubbing time t_h gives:

$$\left[\log_e (\theta - \theta_1) \right]_{\theta_{t_h}}^{\theta_1} = \frac{t_h}{k_1}$$

Scuffing can occur when the mean residence time of the molecules ($1/k_1$) is roughly less than or equal to the total contact time t_h .

$$\left[\log_e (\theta - \theta_1) \right]_{\theta_{t_h}}^{\theta_1} \approx 1$$

This is not a very useful approximation, however, since the temperature T increases continuously during sliding contact so that the residence time decreases concomitantly. The temperature at time t during a sliding contact is:

$$T_t = T_{amb} + \Delta T_{f.t.}$$

$$\Delta T_{f.t.} = \text{flash temperature at time } t.$$

, During sliding,

$$\Delta T_{f.t.} = \Delta T_{fm} (t/t_h)^{\frac{1}{2}}$$

$$\Delta T_{fm} = \text{maximum flash temperature rise} \\ \text{(as calculated from Blok's equation)}$$

thus:

$$T_t = T_{amb} + \Delta T_{fm} (t/t_h)^{\frac{1}{2}} \quad \dots\dots\dots 4.5.$$

Combining (4.4) and (4.5) gives:

$$-\frac{d\theta}{(\theta-\theta_1)} = \frac{e}{\tau_0} dt \quad -\Delta H/R(T_{amb} + \Delta T_{fm} (t/t_h)^{1/2})$$

This equation takes into account the change in mean residence time ($1/k_1$) of the adsorbed molecules during sliding.

For the whole sliding period,

$$\left[\log_e (\theta - \theta_1) \right]_{\theta_{t_h}}^{\theta_1} = \frac{1}{\tau_0} \int_0^{t_h} e^{-\Delta H/R(T_{amb} + \Delta T_{fm} (t/t_h)^{1/2})} dt$$

$$\left[\log_e (\theta - \theta_1) \right]_{\theta_{t_h}}^{\theta_1} = \frac{t_h}{\tau_0} \int_0^1 e^{+A/(1+Bx^{1/2})} dx \quad \dots\dots\dots 4.6.$$

$$A = -\Delta H/RT_{amb}$$

$$B = \Delta T_{fm}/T_{amb}$$

As in the approximate analysis, film breakdown can be assumed to occur when:

$$\left[\log_e (\theta - \theta_1) \right]_{\theta_{t_h}}^{\theta_1} = 1$$

This gives a criterion for film breakdown of

$$t_h > \frac{\tau_0}{I_c}$$

where I_c is the R.H.S. integral in equation (4.6). τ_0 and I_c can both be evaluated.

τ_0 can be estimated from an equation by de Boer (109)

$$\tau_0 = 4.75 \times 10^{-3} \left(\frac{MV}{T_s} \right)^{2/3} \text{ sec.}$$

M = mean molecular weight

V = molar volume

T_s = melting temperature $^{\circ}\text{K}$

This gives an approximate value of

$$\tau_o \approx 2 \times 10^{-12} \text{ sec.}$$

ΔT_{fm} can be taken as 160°C (from fig. (4.4c)) T_{amb} , is approximately the inlet temperature (300°K). In this analysis, a series of values of ΔH was taken, between 70 kJ/mol and 30 kJ/mol. This is the typical adsorption range for polar surfactants on steel (14), (52). I_c , the integral expression in equation (4.6) was computed iteratively. Using the above values of τ_o , $T_{flash\ max}$ and T_{amb} , we obtain scuffing if

$$t_h \geq 20 \text{ } \mu\text{sec.} \quad \Delta H = 45 \text{ kJ/mol}$$

$$t_h \geq 10 \text{ } \mu\text{sec.} \quad \Delta H = 43 \text{ kJ/mol}$$

This is in reasonable agreement with the observed results. It can be seen that, from fig. (4.4b), the anomalous scuffing regime occurs when t_h drops below 10-20 $\mu\text{sec.}$

Thus the explanation postulated is that when the sliding time is less than 20 $\mu\text{secs.}$, the molecules do not have time to desorb in response to the normal flash temperature rise before the period of contact ends. In this situation, for scuffing to occur, the temperature must be increased (by increasing the load) in order to decrease the residence time below the contact time.

4.31. Assumptions

The main assumptions made in this analysis are:

- a) That first order desorption is occurring and that the condition for scuffing is $\left[\log_e (\theta - \theta_1) \right]_{\theta_{th}}^{\theta_1} = 1$ This assumption that the logarithm

equals unity is a conventional one and can never be perfectly true. In practice the logarithm will give a constant value between 0 and 1. The assumption of first order is not critical. Spink (110) has suggested a zero-order desorption. This will give a similar constant L.H.S. value of unity in equation (4.6).

b) Scuffing in the lower speed range follows a constant temperature criterion and the film fails at 180°C .

c) The normal skin temperature of the gears just before sliding is equal to the oil inlet temperature. This probably true at low speeds but is less accurate as the rotational velocity increases. The possible variations are discussed by Kelley (111).

4.40 Conclusions

Both medium and very high speed scuffing have been related to the low speed adsorption model proposed in chapter 3. Medium speed scuffing has been shown to differ from the low speed case only as a result of frictional heating. A tentative explanation for high speed scuffing effects in a discontinuous sliding system has been given in terms of a non-equilibrium model.

CHAPTER FIVE

THE REACTION OF DIBENZYLDISULPHIDE ON

STEEL SURFACES FROM HEXADECANE

SOLUTION

5.10. Introduction

Extreme pressure additives were first widely used in the 1930's, as the loads and frictional temperatures had become too high, in some applications, for the traditional mineral oils to withstand. It was then found that the addition of certain chemically reactive organic compounds enabled higher loads and temperatures to be used. These chemicals were therefore called "extreme pressure" additives.

Effective extreme pressure (or e.p.) additives usually contain one or more atom of an element that can react with metal surfaces under boundary lubrication conditions. These are the non-metals to the right of the periodic table, notably sulphur, chlorine, phosphorus and iodine.

It has been found that, in very general terms, an e.p. additive functions by reacting chemically with a rubbing metal surface to form an adhering film which has a lower shear strength than the metal itself. The film then acts as a solid lubricant and takes over the task of lubrication when metal to metal contact would normally occur.

A successful extreme pressure lubricant is designed to react only when temperatures are reached such that normal, oily boundary lubrication breaks down. This prevents continual corrosion of the metal surface under ordinary running conditions. Generally speaking, phosphorus and chlorine additives are used at lower temperatures than sulphur containing ones. Iodine has been used for the lubrication of titanium.

Although the overall mode of action of e.p. additives has been

understood for a long time, only recently have experiments been done to investigate the exact mechanism of formation of the protecting layer. This is remarkable since appreciation of the mechanism would seem to be essential in the design of a successful lubricant.

In the next two chapters are described a series of experiments into the reaction of a sulphur e.p. additive on steel. There are two sets of tests and they have been put in separate chapters. This chapter investigates the reaction of the additive, dibenzyl disulphide, by purely chemical means. Chapter six looks at the same additives performance in a simple lubricating system. It is hoped to show the value of combining these two approaches in solving the problem of extreme pressure mechanisms. Since the two methods are closely connected, a single review of work done in the field is presented, in this chapter.

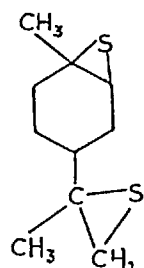
5.20. Literature Review

5.21. The use of sulphur extreme pressure additives

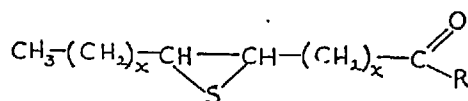
The sulphur containing extreme pressure additives have tended to become progressively more complicated in structure over the years. The simplest, and the first used, was sulphur itself, merely dissolved in the lubricating oil. One of the earliest known references to lubricant additives is a patent of 1859 describing the addition of flowers of sulphur to a mineral oil (112). Since there are naturally occurring fractions of sulphur and sulphur compounds in mineral oils these must have been acting, unrecognised, as e.p. agents long before their value was appreciated.

The most commonly used sulphur additives today are sulphurized fats, olefins and terpenes (113). Their detailed structure is not usually known, since they are manufactured by sulphurizing complex mixtures of naturally occurring terpenes, unsaturated fatty esters and similar compounds. Sulphur is introduced across the double bond.

Typical structures (114) are:

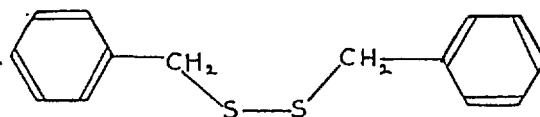


a terpene



a sulphurized fatty ester

Also sometimes used are disulphides. These are especially amenable to experimental analysis, since they are pure chemicals and thus have a well-defined structure. The experimental work in the next two chapters uses dibenzyl disulphide, which has the structure:



dibenzyl disulphide

5.22. Methods of investigating extreme pressure activity

There have been two basic ways of investigating the action of sulphur e.p. agents. The first is the chemical approach. A large number of chemical techniques have been used to study the film produced on metals by sulphur additives, both in rubbing and static conditions. Radiochemical methods have been particularly useful, with S-35 as the radioactive species, (115), (116), (117). Other methods which have been employed include electron probe microanalysis (118), x-ray fluorescence (100), electron diffraction (119), x-ray diffraction (120) and thermogravimetric analysis (121) as well as straightforward chemical analysis (122).

The other approach has been to observe the actual lubricating properties

of various additives as a function of chemical structure (123), e.p. concentration (124) and metal type (100).

Both these types of investigation have led to certain mechanisms being advanced as to the lubricating properties of sulphur additives. These mechanisms will be considered in section (5.26). Before then, some of the specific experiments investigating the effect of temperature, load and speed on e.p. activity will be described.

5.23. Effect of temperature on e.p. films and their lubricating properties

Although it has long been recognised that the function of an e.p. agent is to react with the metal surface under high temperature conditions, remarkably little systematic work has been done (or at least published) concerning the effect of temperature on e.p. reaction. This fundamental importance of temperature was recognised by Bowden (125) who suggested that the name "extreme pressure" agents would be better changed to "extreme temperature".

Prutton et al. (122), in 1946, showed that sulphur organics could form a sulphur-containing film at high temperatures. They mixed iron powder with e.p. solutions at 250°C and by subsequently adding acid were able to measure the extent of reaction from the volume of H_2S evolved.

Some years later, Elliot and co-workers (126) investigated the kinetics of reaction of sulphur and dibenzyl disulphide on steel at three temperatures. They used a radioactive technique and showed that reaction continued indefinitely with time within the limits of their experiments. At 100°C there was very little reaction but this increased at 150°C and 200°C. Dibenzyl disulphide reacted less than sulphur at 150°C but gave a thicker film than sulphur at 200°C. Borsoff and Wagner (127) and Loeser and coworkers (128) carried out the same sort of experiments but under both static and rubbing conditions. Borsoff and Wagner studied the static reaction of dibenzyl disulphide on steel

strip in the range 25 - 190°C. They found reaction rate increased with time and temperature. In similar experiments in a gear system they showed a constant film thickness was produced, which was between five and thirty monolayers deep. Loeser, Wiquist and Twiss (128) carried out static experiments to measure the reaction of zincdialkyl-dithiophosphates on cast iron. They obtained about three monolayers of sulphur at 100°C after twenty hours compared to twenty monolayers at 160°C. In dynamic loaded conditions twenty-five monolayers were formed in twenty hours at 100°C.

An elegant technique for measuring the reaction of sulphur e.p.s at very high temperatures was devised by Barcroft (129). He measured the change in resistance due to corrosion in an e.p. reaction. From the changing resistance he obtained kinetics of reaction up to 700°C. Barcroft showed that the reaction rate obeyed Arrhenius equation in the range 500-700°C for dibenzylidisedisulphide on stainless steel.

Sakurai et al. (120) used Barcroft's technique to investigate further the rate laws governing the reaction of e.p. agents. They found that corrosion of iron and stainless steel usually followed a parabolic law. The exception to this was with dibenzylidisedisulphide on iron, which at high temperatures reacted abnormally quickly. This Sakurai ascribed to the formation of cracks in the surface of the metal and sulphide film which permitted further sulphur penetration. No such effects were observed with stainless steel. Typical thicknesses obtained for dibenzylidisedisulphide on stainless steel were 30 nm. at 410°C, 80 nm. at 560°C and 160 nm. at 650°C, all after ten minutes. On iron the films were generally about ten times thicker.

Manteuffel and co-workers (115), in 1964, investigated the effect of temperature and load on lubricating properties of various sulphur additives. For dibenzylidisedisulphide they observed a sharp increase in reaction in the

120°C region, where sulphur film thickness rose rapidly in both the rubbing and unscarred regions.

Dorinson and Broman (130) investigated the reaction of two aliphatic disulphides on iron powder in the temperature range 165–250°C. They showed that at least five monolayers of ferrous sulphide could be formed without altering the observed zero-order reaction rate.

Recently Matveevsky (121) has measured the reaction of various e.p. additives with iron powder using thermogravimetric analysis. He relates the degree of reactivity of each e.p. additive to its lubricating capacity.

A good deal of work has been done in the study of corrosion to investigate the action of extreme pressure type chemicals on pure metals such as iron and nickel. Thus Llopis, Arizmendi and co-workers (131) (132) (133) have looked into the effect of temperature on the reaction of sulphur, mercaptides and organic sulphides on iron and nickel. Generally speaking reaction rates always increased with increasing temperature although the various rate constants were different in different temperature ranges.

5.24. The effect of sliding load and speed on extreme pressure activity

In general, increasing load and rubbing speed seems to produce a thicker e.p. film. Loeser et al. (128) showed that in the dynamically loaded case twenty-five monolayers of sulphur were produced on cast iron using zincdialkyldithiophosphate. This compared to only three monolayers under static conditions. The same effect was noted by Borsoff and Wagner (127) using dibenzylidisulphide in a gear system. The film depth increased from ten to thirty monolayers of sulphur in the range of load studied. Borsoff and Wagner noted that the actual film thickness at a given load reached a constant value with time shortly after the run was started.

Campbell (117) also investigated the reaction of radioactive dibenzyl disulphide on hypoid gears during running. He showed that a steady film thickness of 100 nm. was reached on the driving faces of the gear teeth. On the coast side, the thickness was about half this value.

Manteuffel and co-workers (115) measured the quantity of sulphur in both the loaded wear track and the unscarred metal surface at different loads in a 4-ball test rig. They found the sulphur content of the wear track to be about 100 times as great as that of the unscarred region.

Barcroft and Daniel (134) calculated the thickness of sulphur e.p. films in hypoid gears. They used S-35 and found average film thicknesses of about 50 nm. for an unscuffed gear surface, assuming 25% of sulphur in the film. This corresponds well with Eorsoff's values (127). Barcroft and Daniel also measured the depth of penetration of reacted sulphur by progressively polishing away known thicknesses of the gear surface and measuring the radioactivity remaining. The limit of penetration under normal conditions proved to be about 700 nm. For shock-loaded crown-wheel teeth the penetration was much deeper, however, and radioactive sulphur was detected at 5,000 nm. depth.

Recently Allum and Forbes (118) have measured the film thickness of e.p. sulphur films in the wear track of a 4-ball rig using electron probe microanalysis. They estimated maximum film thickness under these, loaded, conditions as 300-500 nm.

5.25. Anti-wear and anti-seizure effects of extreme pressure lubricants

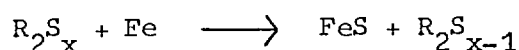
Davey and Edwards (135), in 1957, differentiated between two lubricating properties a sulphur additive could have. These were the production of a chemical film to prevent scuffing - an "anti-seizure" film, and the formation of a film on the bare metal or on the previously formed chemical

film which reduced friction and wear, - an "anti-friction" or "anti-wear" film. The first of these could be measured in terms of the maximum load to seizure. The second was represented by the wear scar diameter before scuffing. Davey and Edwards found that different disulphides and monosulphides could have better or worse anti-wear and anti-seizure properties depending on their chemical structure.

Allum et al. (123) (136) have extended this work and suggested a mechanism for the different effects, which will be discussed in the next section.

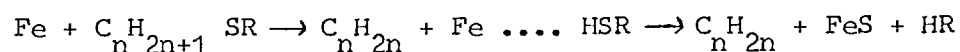
5.26. Mechanisms of extreme pressure action

Prutton et al. (122) were the first to suggest a specific mechanism for the formation of sulphur extreme pressure films. They observed that dibenzylidisedisulphide was more reactive than phenyldisulphide and monosulphides and suggested the mechanism:

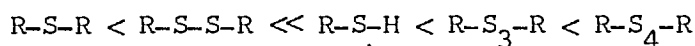


for disulphides although they could not ascertain whether the additive split up on the iron surface to give sulphur prior to the main reaction.

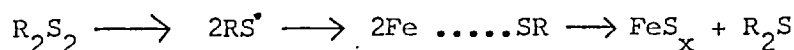
A good deal of work on metal-organic sulphide reaction mechanisms has been done in corrosion studies. The reaction of monosulphides on iron has been investigated by Titz (137) and Baladin (138). Titz and his colleagues suggested that mercaptan was formed in solution by thermal decomposition and this then reacted with iron. Baladin, however, could find no evidence of mercaptan and suggested that decomposition took place on the surface according to the sequence.



Llopis et al. (131) investigated the surface reaction of a series of organic sulphides on iron. They showed then the speed of reaction was in the order

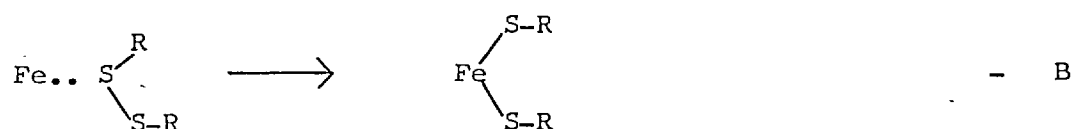


in nitrogen but that air enhanced the reactivity of mono- and disulphides whilst suppressing the mercaptan and higher sulphide reactions. Llopis proposed a reaction of disulphide via the radical sequence



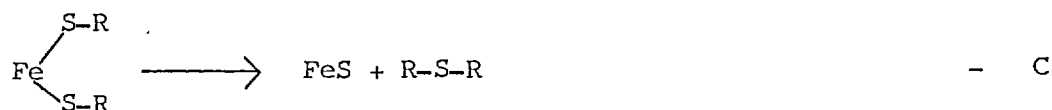
and he suggested that oxygen increased radical formation.

Davey and Edwards (135), using evidence obtained in lubrication tests, put forward a three stage process for the reaction of disulphides on steel. The first two involved the formation of an adsorbed layer, and a mercaptide layer.



Both these products, they suggested, protected the surface, like a fatty acid film, to reduce wear.

Finally under conditions of heavy loading and temperature these gave ferrous sulphide with good anti-seizure properties but only poor anti-wear properties.

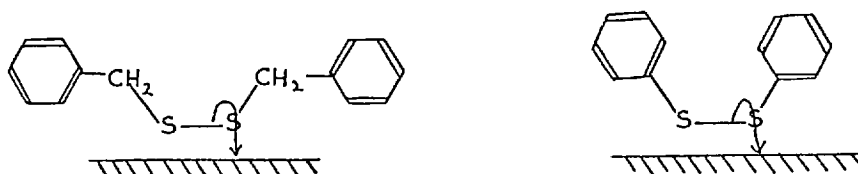


This mechanism, which is very similar to Baladin's (138) has been greatly developed by Allum et al. (123) (136), who suggested that the efficiency of a

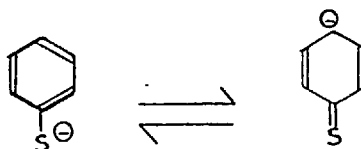
given disulphide as an anti-wear or anti-seizure lubricant depended on its structure.

Allum and Ford (123) showed that the anti-seizure activity of different disulphides was related to the strength of the C-S bond. The weaker this bond, the more effective the additive in forming a sulphide film and thus preventing scuffing.

Later Allum and Forbes (136) demonstrated that anti-wear efficiency was related to the strength of the S-S bond, so that the weaker this bond the more effective the compound as an anti-wear additive. Thus for example, diphenyldisulphide is a poor anti-seizure but a good anti-wear additive relative to dibenzylidisulphide. This, as Allum and co-workers points out, fits in very well with the Davey and Edwards type model. If anti-wear requirements are the formation of mercaptide layers, this can be represented pictorially as:

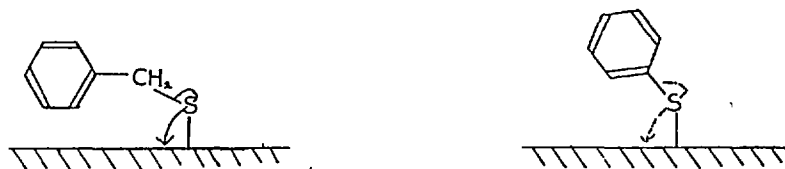


for dibenzylidisulphide and diphenyldisulphide respectively. (In these diagrams, the arrows represent the movement of electrons). Obviously the mercaptan ion or radical intermediate is stabler in the phenyl case than the benzyl, being α - to the benzene ring, since it is stabilized thus: (ref. (139))



[The ionic case has been drawn, but the reaction may go through a radical intermediate. Stabilization would occur in a similar fashion].

The reverse holds true for the formation of FeS. In this case the C-S bond will be cleaved e.g.



In this case the benzyl cation or radical would be stabilized by delocalisation, with the charge α - to the benzene ring, whereas the phenyl would not. Thus dibenzyl C-S bonds would break more easily. This explanation for the different lubricating effects of various disulphides is reasonable although it has been inferred primarily from the effect of chemical structure on lubrication with little other, supporting evidence.

So far only the mechanisms of sulphur film formation have been considered. It is also necessary to show how such films, once formed, serve to lubricate. There has been quite a lot of controversy in recent years over the exact composition of the anti-seizure film. Since Prutton (122) showed that sulphur was present in the layer, it had generally been assumed that the film consisted mainly of iron sulphides. The majority of film thicknesses mentioned earlier in this review were worked out from the actual sulphur content assuming such a structure. Some detailed analysis by Godfrey (119) in 1962, however, using x-ray and electron diffraction, showed that for some sulphur e.p. additives the main film constituents were oxides of iron. Godfrey thus suggested that sulphur catalysed the formation of iron oxides and it was a combination of these with just a small quantity of sulphide which gave good anti-seizure properties.

Sakurai et al. (120) carried out similar experiments using x-ray diffraction and showed that whereas diphenyldisulphide gave mostly oxides at 490°C , dibenzyliddisulphide produced mainly a sulphide film. The whole

situation is thus very confused.

It is obvious that a sulphide layer by itself is insufficient to give good lubrication, as is often observed in the extreme pressure range. Greenhill (4) describes some experiments on the lubricating properties of artificially built up sulphide layers. He found that even when the optimum film thickness of 200 nm. was reached, the coefficient of friction was still 0.4. For thinner sulphide films it was much higher. Greenhill also found that if fatty acid in paraffin oil were added to the sulphide film, the coefficient dropped to 0.1, even at temperatures where fatty acid and paraffin oil on the clean metal would not lubricate. Thus the combination palmitic acid and sulphide layer was better than the individual components, lubricating up to 200°C on copper and steel.

Sakurai et al. (140) demonstrated a similar effect. They showed that fatty acid and dibenzyl disulphide molecules were both more strongly adsorbed on sulphide layers than on normal metal oxide surfaces. Thus it seems likely that an extreme pressure film is not a simple sulphide layer. Not only may it contain a complex mixture of oxides, but there is perhaps also an associated physically or chemisorbed monolayer on top of it.

One further analysis of the mechanism of e.p. lubrication needs mentioning. This is a series of papers by Sakurai and co-workers who have developed a rate mechanism for the action of e.p. films in terms of the opposing effects of sulphide film formation and the film being abraded away (141) (116).

5.27. Summary

The action of sulphur e.p. additives is, as the literature survey shows, extremely complex. Even for pure disulphides neither the mechanism of film formation nor the way this film then lubricates is fully established.

Increasing temperature always increases the film thickness of the sulphur affected layer. There is a large variation, however, in the actual

depth found by different authors.

Both loading and sliding increase the sulphur film depth. It is not clear whether this is due to enhanced reaction at higher frictional temperatures, to the generation of nascent metal, to the formation of cracks down which a chemical reaction can take place or merely to sulphur containing material being physically ground into the surface. A number of studies have shown that a constant film thickness is attained under sliding conditions, as opposed to static conditions where film thickness seems to build up indefinitely with time.

There are no detailed studies of low temperature reaction of e.p. additives on steel. Borsoff and Wagner (127) have published the main work in this range but they do not fully describe the starting conditions of the reaction.

The next two chapters present experiments into the effect of temperature on the reaction of the sulphur-containing e.p. agent dibenzylidisedisulphide. This chapter includes chemical investigations. The next correlates these results with tests on lubricating systems.

5.30. Experimental

5.31. Experimental aims and design

The aim of these experiments was to investigate the chemical reaction of an e.p. sulphur compound on various steel surfaces. For the main part of the work a radioactive technique was employed using the weak β -particle emitter, S-35. By this method a large range of film thickness could be measured, down to less than one monolayer coverage, simply by varying the activity of the solution. The radioactive technique also overcame the difficulties posed by sulphur inclusions in the steel itself which complicated

other sulphur analytical measurements.

The original intention was to measure the extreme pressure reaction on the steel powder used in chapter 2, by monitoring the changing concentration of sulphur additive in solution using a liquid scintillation counting method. This was found to be impractical because there were very low reaction rates below 130°C , so that no significant change in the concentration could be detected. Also, above 130°C , the hexadecane solvent tended to char, producing a yellow colour in solution. This colour then acted as a quencher to lower the efficiency of the liquid scintillation measurements. To overcome these difficulties a solid scintillation counting method was employed.

It was not practical to extend the radioactive tagged solution technique above 170°C . At temperatures higher than this, radioactive fumes were being evolved as quickly as they could be safely dispersed by the fume cupboard extractor. To see how the reaction proceeded beyond this temperature a few experiments were therefore carried out using electron probe microanalysis.

3.32 Materials

n-Hexadecane was the solvent used in all the experiments in this chapter. It was obtained from the same source and purified in a similar manner to that used in chapter 2, (see Appendix A).

The non-radioactive dibenzyl disulphide was purchased from Hopkins and Williams Ltd. and was a microanalytical standard. Radioactive dibenzyl disulphide was obtained, ready prepared, from Radiochemicals Ltd., Amersham. It had a specific activity on arrival of 23 mCi/m.mole and was tagged with S-35.

A wide variety of steels were tested in these experiments, generally in the form of small 19.0 mm (0.75 in) diameter metal discs. EN 58B stainless steel and mild steel were the most commonly used, and discs of these two metals were punched from 76 μm (0.003 in) thick plate and then ground with carborundum paper down to 600 grade.

Several other steels were also used and the effect of heat treatment on reaction was investigated. For these steels, each disc was parted off a 19.0 mm (0.75 in) diameter bar and then surface-ground on both sides to the required thickness. Before use, each disc was rubbed with 600 grade carborundum paper. Those metal discs to be heat-treated were heated after parting-off but before being ground down. A list of the steels used, along with their heat treatment and hardness just before use is shown in table (5.1). The thickness of each disc was 50 to 75 μm . (0.002 - 0.003 ins.)

Table (5.1)

Steel specification	Heat Treatment	Hardness Vickers
EN 58B	NONE	170
Mild steel	NONE	100
EN 40B	NONE	290
EN 40B	880°C for 30 minutes. Oil quenched. 240°C 30 minutes	510
EN 39B	NONE	267
EN 31	NONE	210
EN 31	840°C 30 minutes Oil quenched. Not tempered	1010

5.33. Apparatus

Two types of apparatus were used. The first was designed to stir the

metal samples in the solution, but this was simplified after it had been shown that stirring was not an important factor in the reaction.

The initial apparatus consisted of a stirrer with several glass holders attached down its length. These were designed to hold 19.0 mm (0.75 in) diameter metal discs whilst covering up only a very small fraction of their surface area. The stirrer was rotated slowly in a large quickfit test-tube, which it entered through a mercury trap. Solution was placed in the test-tube and heated by a surrounding mantle. The temperature was measured using thermocouples placed in a thin walled indentation in the bottom of the test-tube and thermocouples also served to control the overall temperature by feedback to the mantle through a thyristor control unit. The disadvantages of this technique were:

- a) A lot of radioactive solution was required to immerse the metal discs.
- b) It was difficult and time consuming to extract a metal disc for counting.

To overcome these disadvantages later experiments simply used an open, tall glass beaker surrounded by a controlled heating mantle. The discs were laid in the bottom of the beaker for a specified time and then withdrawn with tweezers.

The solid scintillation counter was type 663 from Isotopes Development Ltd., Aldermaston and a Panax P7502A counter was used.

5.34. Experimental technique

Each disc was cleaned before use by rubbing with 600 grade carborundum paper, soxhletting in benzene and finally being immersed in analar acetone.

Initial experiments used the stirring apparatus. Several cleaned metal discs were mounted on the stirrer so that they rotated in a radioactive

dibenzyl disulphide solution at the requisite temperature. Periodically the stirrer was halted and metal discs removed and washed. Washing was a standardised procedure normally consisting of two minutes in each of ten small beakers of acetone, followed by a final brief rinse from an acetone wash bottle.

Each disc was then dipped twice into a 6% solution of collodion-acetone (B.P.C. 1949) in acetone. This was a precautionary measure developed from reference (142) to deposit a thin protective coating over the reacted surface so as to prevent possible volatilization of radioactive material in the scintillation counter. There was no positive evidence of any such volatilization but the precaution was continued since the scintillation counter was being used by several other experimenters. The weight deposited at each collodion dip was < 0.0005 gms., and was thus negligible in terms of blocking the radioactive emission.

After each disc had been dipped in collodion, it was left to dry and then placed in the pan of the solid scintillation counter. The count rate of each disc was measured for a period of time dependent on its activity. This will be discussed in section (5.36).

Using the second experimental technique, the discs were laid face down in the bottom of a beaker of radioactive solution. After withdrawal they were washed and counted as outlined above.

The radioactivity of the test solution was adjusted to suit the conditions of the experiment. Thus a quite high activity of $10\mu\text{ Ci/cm}^3$ had to be used at room temperature but the normal solution activities at higher temperatures were much lower.

No disc was used for more than one experiment and no radioactive solution for more than one short series of runs at high temperature, since there was a possibility that oxidation of the solvent might interfere with

the reaction.

5.35. Calibration

It was necessary to calibrate the solid scintillation counter readings in order to estimate the exact amount of sulphur per unit apparent surface area.

This was done by making liquid scintillation readings using the test solution. Then:

$$\text{Atoms S/mm}^2 = \frac{(\text{cpm})_S}{(\text{cpm})_L} \cdot \frac{(\text{Eff})_L}{(\text{Eff})_S} \cdot \frac{C}{A_d}$$

$(\text{cpm})_S$ = count rate on test disc

$(\text{cpm})_L$ = count rate using 1 cm³ radioactive solution

$(\text{Eff})_L$ = efficiency of liquid scintillation counter

$(\text{Eff})_S$ = efficiency of solid scintillation counter

C = concentration of solution (S atoms per cm³)

A_d = surface area of disc (mm²)

By using different units for C (e.g. molecules of dibenzylidisulphide per cm³), the amount reacted could be obtained in different units.

The two efficiencies were calculated using reference samples of known activity. This involves the assumption that the efficiency of both solid and liquid counter were the same for the reference samples and test samples. This is reasonable since the reference standards were C-14, with a β -particle energy very similar to S-35.

The ratio of $(\text{Eff})_L / (\text{Eff})_S$ found was 1.04.

5.36 Accuracy

The main source of experimental error was the scatter of the amount

reacting. This varied depending on the conditions but was $\pm 10\%$ up to 130°C and $\pm 25\%$ at higher temperatures.

A series of experiments on the same system were carried out to estimate the standard deviation from the mean. The results are shown in Table (5.2)

Table 5.2

Sample no.	Upper Face cpm	Lower Face cpm
1	2760	3120
2	2180	1890
3	2280	2610
4	1960	1220
5	2280	1600
6	1400	1320
7	1610	2540
8	1800	2690
	mean =	2140 cpm
	standard dev. =	500 cpm

0.8 wt % dibenzyl disulphide in hexadecane reacting
on EN 58B at 140°C .

The wide scatter in the results meant that counting inaccuracies could be neglected by comparison. The exception was at low temperatures when there was only a little sulphur reaction. In this region the count rate was not much greater than background and counting had to be prolonged

in order to obtain satisfactory accuracy. The theoretical counting deviation was always $< 5\%$.

It is interesting to note from table (5.2) that there was no difference between reaction on the upper steel disc face and that which lay against the bottom of the glass beaker.

5.40. Results and Discussion

5.4.1. Effect of stirring on the reaction of dibenzyl-disulphide on stainless steel

The difference in reaction of the same system in stirred and non-stirred experiments was tested using EN 58B stainless steel discs. These were immersed for ten minutes at 145°C in 0.8 wt% dibenzyl-disulphide solution. No significant difference was observed between stirring and static results and the simpler static apparatus was used in all subsequent work.

5.42. Effect of temperature on the reaction of dibenzyl-disulphide on steel

A series of runs were carried out at different temperatures, holding the other variables constant. Two types of steel were used, EN 58B stainless steel and mild steel. The concentration of dibenzyl-disulphide in hexadecane was 0.8 wt% and each disc was immersed in solution for 10 minutes. The results are shown in figs (5.1) and (5.2). Each point is the mean of four counts, two discs measured on either side. The two graphs for different steels are similar both in overall shape and quantitatively. There are three different regions on the reaction curves. At very low temperatures, below 60°C , the amount of sulphur reacting on the surfaces was very small and corresponded to much less than a complete monolayer of

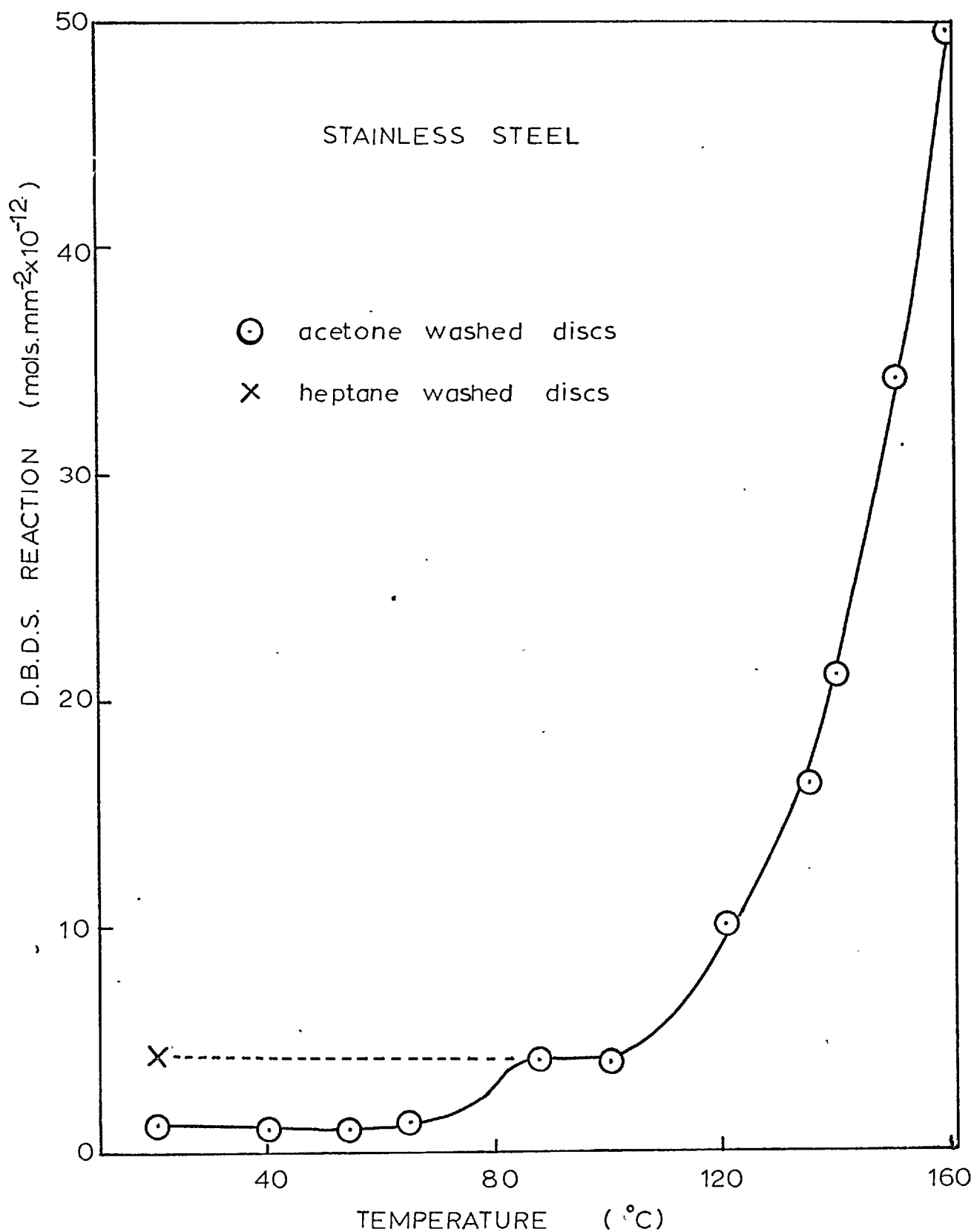


Figure 5.1. Reaction of dibenzyl disulphide with stainless steel.

(Ten minutes immersion, 0.8wt% solution)

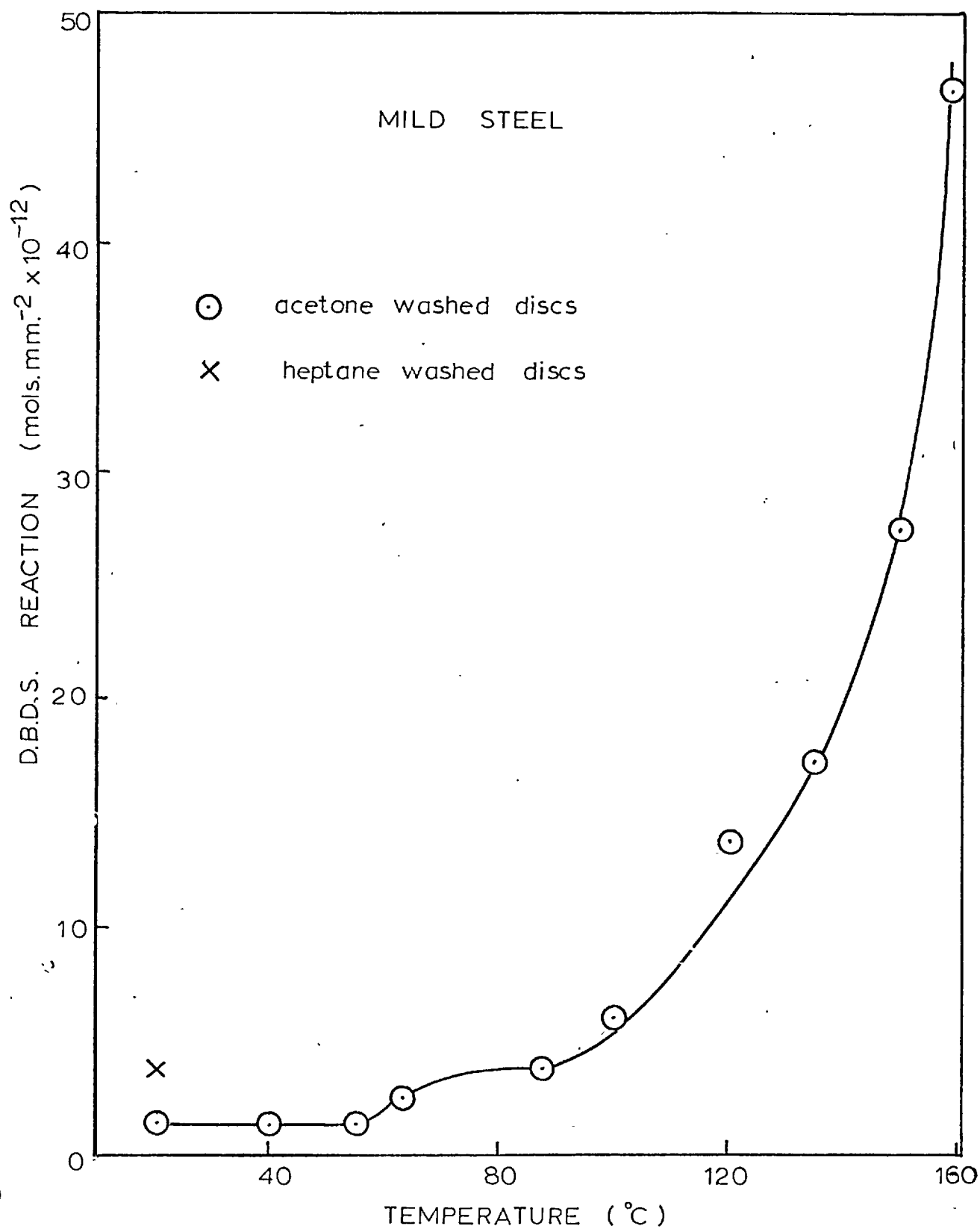


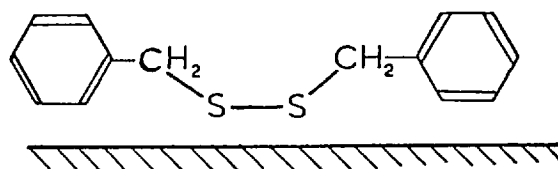
Figure 5.2. Reaction of dibenzyl disulphide with mild steel (ten minutes immersion, 0.8wt% solution)

dibenzylidysulphide. From 60°C to 110°C, the amount reacting was independent of temperature, at 3.5×10^{-12} mols. dibenzylidysulphide per mm^2 . Finally above 110°C, the reaction was exponential with temperature, obeying the Arrhenius equation.

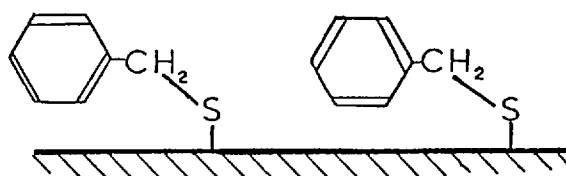
These three different temperature regions can be explained by a single adsorption-reaction sequence. The low temperature region corresponds to very limited chemical reaction. There may, however, be reversibly adsorbed dibenzylidysulphide which would be washed off with acetone. The second region is in the right order to correspond to a monolayer of dibenzylidysulphide molecules. The apparent area per molecule observed is $\sim 0.50 \text{ nm}^2$, whereas the area of dibenzylidysulphide varies between 0.8 and 1.2 nm^2 dependent on its molecular orientation. The real to apparent surface area of the steel is probably a ratio of between one and two (143) which would make the density of reacted disulphide correspond quite well to a chemically adsorbed monolayer of dibenzylidysulphide or mercaptide. Above 110°C this molecular layer presumably starts to break down to give a sulphide film. Since the thickness in Fig. (5.1) corresponds to a layer of $\alpha\text{-FeS}$ 0.5-0.8 nm thick at 160°C, the dibenzylidysulphide must have decomposed to give a more compact layer.

The suggested reaction sequence is shown schematically in Fig (5.3). It corresponds well with the sequence inferred by Davey (135) and Allum and co-workers (123), (136) from the effect of molecular structure on lubricant efficiency.

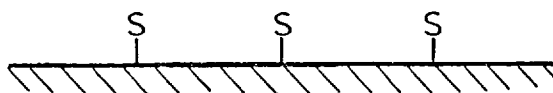
To test whether physical adsorption of dibenzylidysulphide occurred at low temperatures, experiments were carried out at 20°C where the steel discs were washed only three times on withdrawal from solution, and with heptane rather than acetone. This solvent might not be so effective in



a) Below 80°C . No irreversible chemical reaction



b) Between 80°C and 110°C . Formation of chemically adsorbed monolayer, probably mercaptide



c) Above 110°C . Scission of C-S bond begins to form sulphide film. Only a slow reaction until 150°C .

Figure 5.3. Suggested dibenzyl disulphide reaction sequence

physically desorbing adsorbed disulphide. It can be seen from figs (5.1) and (5.2) that in both cases the amount of adsorption left after this treatment corresponded to the monolayer of dibenzylidysulphide. This may have been due merely to inefficient washing-off of the supernatant liquid but it quite possibly represents a physically adsorbed monolayer at low temperatures.

Two features of the reaction mechanism remain unresolved. These are whether the main reaction goes through a radical intermediate and also whether disulphide breakdown of the sulphur-sulphur bond occurs in solution or on the metal surface. Unfortunately the structures that favour a radical intermediate will usually favour carbanion stability, so structural indications are not very helpful. The effect of oxygen in enhancing the reaction of dibutylidysulphide with iron (131) is interesting in this respect and may indicate an ionic intermediate.

5.43. Reaction rate of dibenzylidysulphide on steel

The kinetics of reaction were not specifically investigated although a few runs were done to test the effect of immersion time on reaction. These are shown in Fig (5.4). The steel used was EN 58B stainless steel, and the solution was 0.8 wt% dibenzylidysulphide in hexadecane.

At 80°C the amount reached a constant value after a few minutes. At higher temperatures there was no evidence of any such limiting thickness, which is in accord with the results of Llopis (131) and Borsoff and Wagner (127).

5.44. Effect of steel composition and hardness on reaction

The effect on reaction of both steel composition and hardness were tested. A standardised experiment of 10 minutes immersion at 140°C

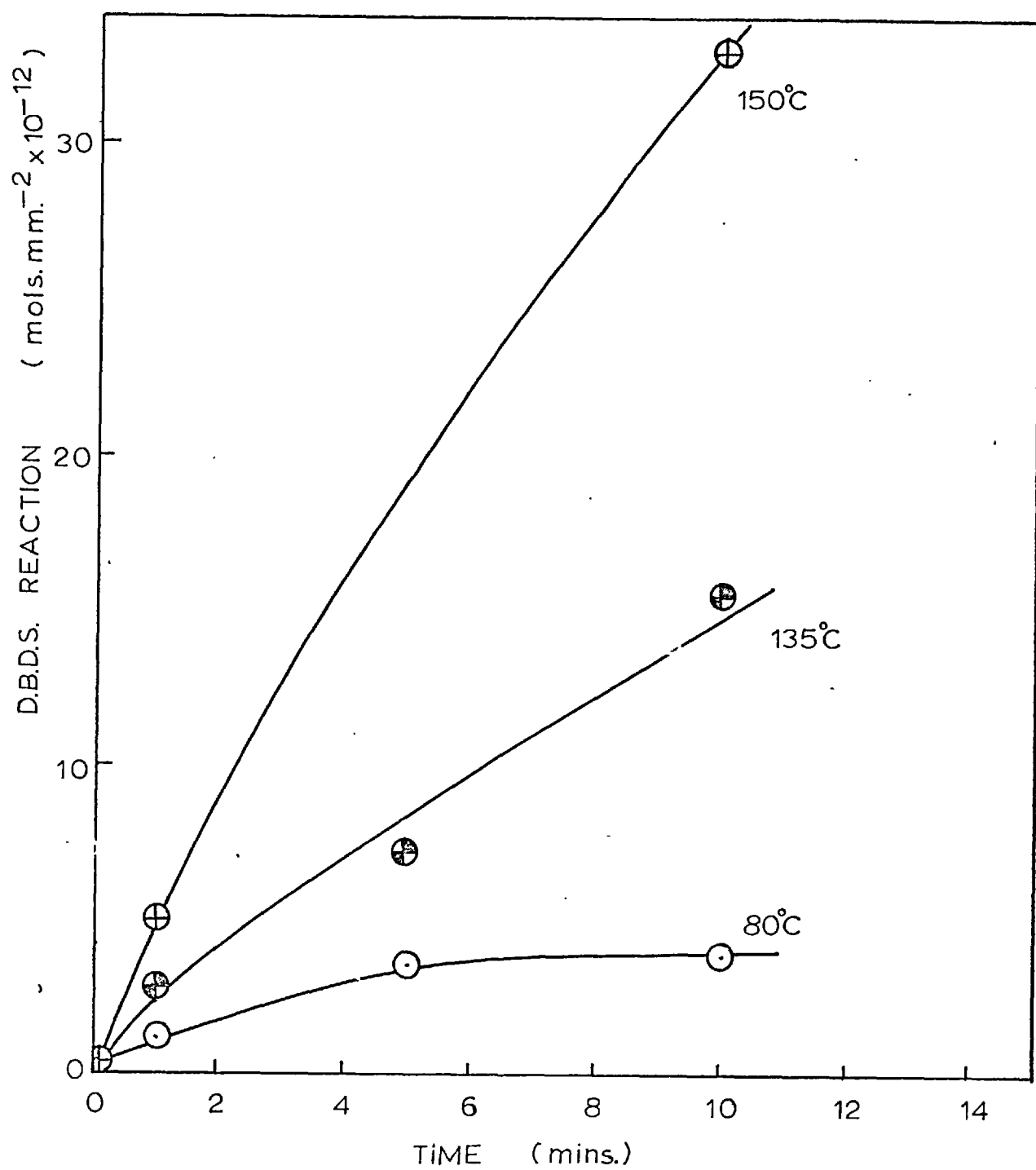


Figure 5.4. Reaction kinetics of dibenzyl disulphide on stainless steel. 0.8wt% solution

in 0.8 wt.% dibenzylidysulphide solution was carried out on a series of different metal discs. The results are shown in fig. (5.5), where each reaction level was taken as the mean of four disc-face measurements. In this figure the various steels are:

A	EN 58B	18/8 stainless steel.
B	EN 56J	13% Cr. Rust-Resisting steel.
C	EN 31	1% Carbon-Chromium steel
D	EN 31	1% Carbon-Chromium steel. Heat treated.
E	EN 40B	3% Chromium-Molybdenum steel
F	EN 40B	3% Chromium-Molybdenum steel. Heat treated.
G	EN 39B	4½% Ni, Cr, Mo steel.

(for heat treatment and hardness details see section (5.32)).

Taking into account the scatter of the results, as observed in section (5.36), only metals E and G can be considered as significantly more reactive than the rest.

This similarity between the reaction of different metal types is indicated even more effectively by the correspondence between figs (5.1) and (5.2). Although the two steels were very different in composition, the overall reaction was the same in both cases, except, possibly, in that mild steel seemed to react at slightly lower temperatures.

5.45. Effect of oxide film

During most of these experiments the presence of an oxide layer was assumed, since immersion occurred several hours after the steel discs had been rubbed with carboundum paper. A few runs, however, were carried out

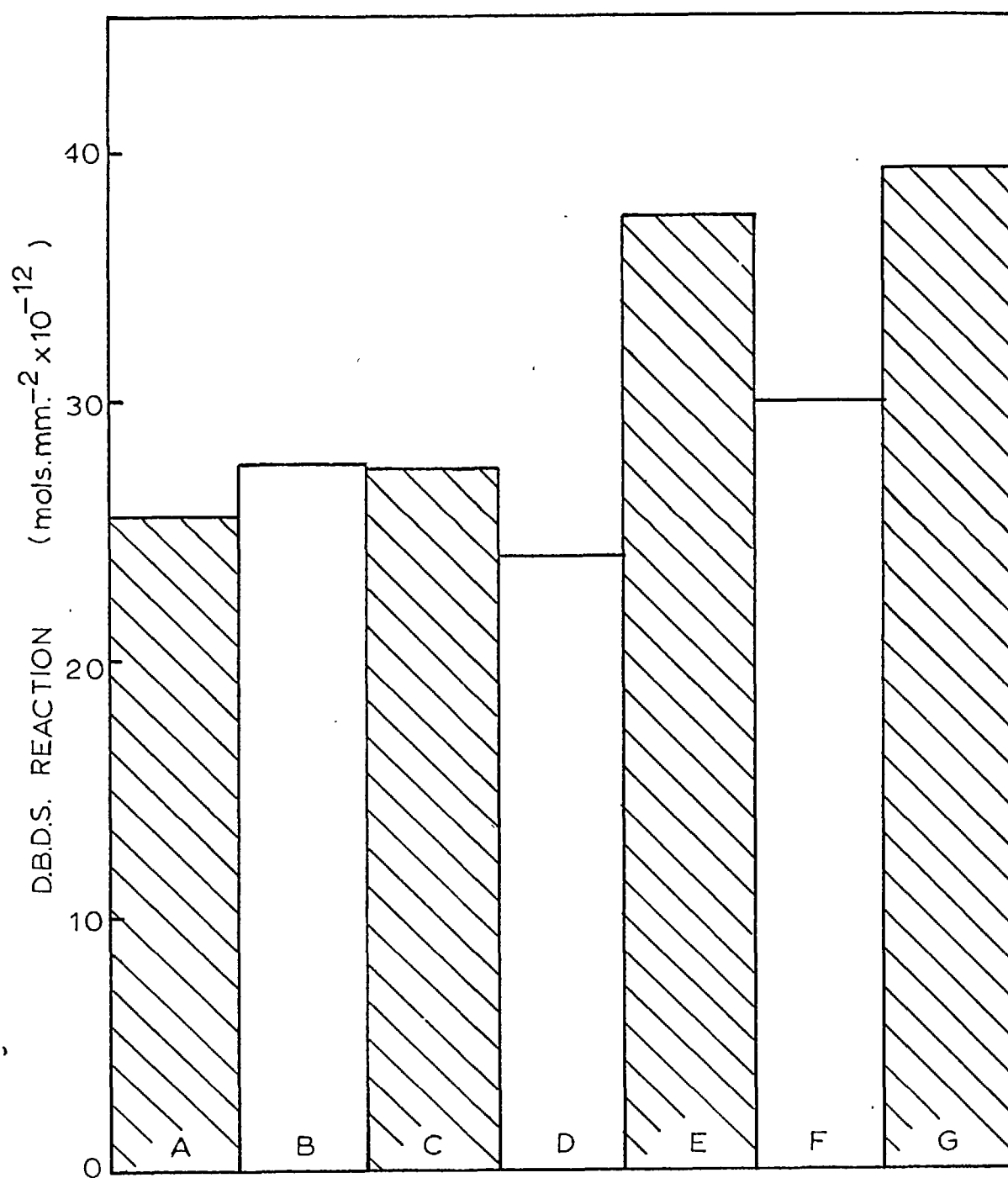


Figure 5.5. Effect of steel composition and hardness on reaction with 0.8wt% dibenzylidisedisulphide at 140°C. (ten minutes immersion)
For steel types see text.

with discs rubbed with 600 grade carborundum paper immediately before immersion. No significant differences were observed, but this is not very conclusive since no effort was made to prepare an oxygen-free dibenzylidisedisulphide solution.

5.46. Reaction of dibenzylidisedisulphide at high temperatures and in a low speed wear track. Electron probe.

The radioactive monitoring technique was not extended above 170°C. A few tests were, however, done at higher temperatures and the results analysed by electron probe microanalysis.

In these experiments 25x20x5 mm blocks of EN 58B steel were laid in a Bowden Leben trough (see Chapter 3) so that they were fully immersed in 0.8 wt % solutions of dibenzylidisedisulphide in hexadecane. The temperature was maintained for ten minutes before the blocks were withdrawn and washed in acetone. After about eight minutes immersion in dibenzylidisedisulphide solution a slow speed wear track was made on each block using a 15.9 mm ($\frac{5}{8}$ in) diameter stainless steel ball under 17.8N (4 lb) load.

The amount of sulphur on both the unscarred surface and in the wear track was measured using pulse height analysis. Unfortunately the presence of purple-grey inclusions in the steel, which contained high concentrations of sulphur and titanium, made it impractical to try and obtain quantitative results since the measurements of one of these inclusions would have completely upset an area count. Qualitative estimates of the reaction were possible from the line traces, however, by comparison with traces from a fresh piece of metal.

Samples below 130°C showed very little extra sulphur over untreated metal, either inside or outside the wear track. From 145°C to 255°C the amount on the unscarred metal increased successively and showed no sign of

reaching a limiting value at high temperatures. The tracks in the metal samples heated above 130°C showed more sulphur content than the outside metal, with the difference becoming more pronounced at higher temperatures. An interesting feature of the high temperature results was a grouping of trace spikes, typical of small sulphur-containing inclusions, along the edge of the wear tracks.

These microprobe results show that the reaction continued to increase with temperature well above 170°C . The fact that the enhanced sulphur content in the wear track was only observed at high temperatures suggests that it is unlikely to result from local extremely high temperature flashes due to asperity contact. More likely reasons are grinding-in of sulphur-containing material by sliding action, or the formation of cracks in the surface down which sulphur could penetrate.

5.50. Conclusions

The reaction of dibenzyl disulphide solution with steel has been investigated. Three different effects have been identified, at different temperatures, which have been combined to provide a reaction sequence.

It was found that the initial reaction of dibenzyl disulphide was little affected by the exact nature of the steel under the conditions studied.

CHAPTER SIX

LUBRICATION OF STEEL WITH DIBENZYLDISULPHIDE

6.10. Introduction

This chapter describes tests carried out to investigate the friction - temperature characteristics of dibenzylidithiolane. The results of these tests are then compared with experimental work from the previous chapter to decide the state of a surface during extreme pressure lubrication.

6.20. Experimental

6.21. Experimental aims and design

Since the effect of temperature on the extreme pressure reaction was of prime interest, slow speed lubrication tests were probably best. These avoid any of the complications resulting from frictional heating. A ball on triplane machine was used since it had good temperature control and was enclosed, so that high temperatures could be maintained without undue evaporation of the lubricant. Another advantage of this apparatus, which made it more satisfactory for this work than the Bowden-Leben machine was that the friction-measuring device was rigid. No stick-slip could occur, which would have greatly confused the results, since these were generally in the high coefficient of friction range, 0.2 to 0.3.

To aid comparison between the surface chemical experiments of chapter 5 and these lubrication results, both systems were made as similar as possible. A 0.8 wt % solution of dibenzylidithiolane in hexadecane was thus used in most of the tests.

6.22. Ball on triplane apparatus

This machine, shown in Fig. (6.1), was a development of the standard 4-ball test rig. It consisted of an upper ball which rotated against the

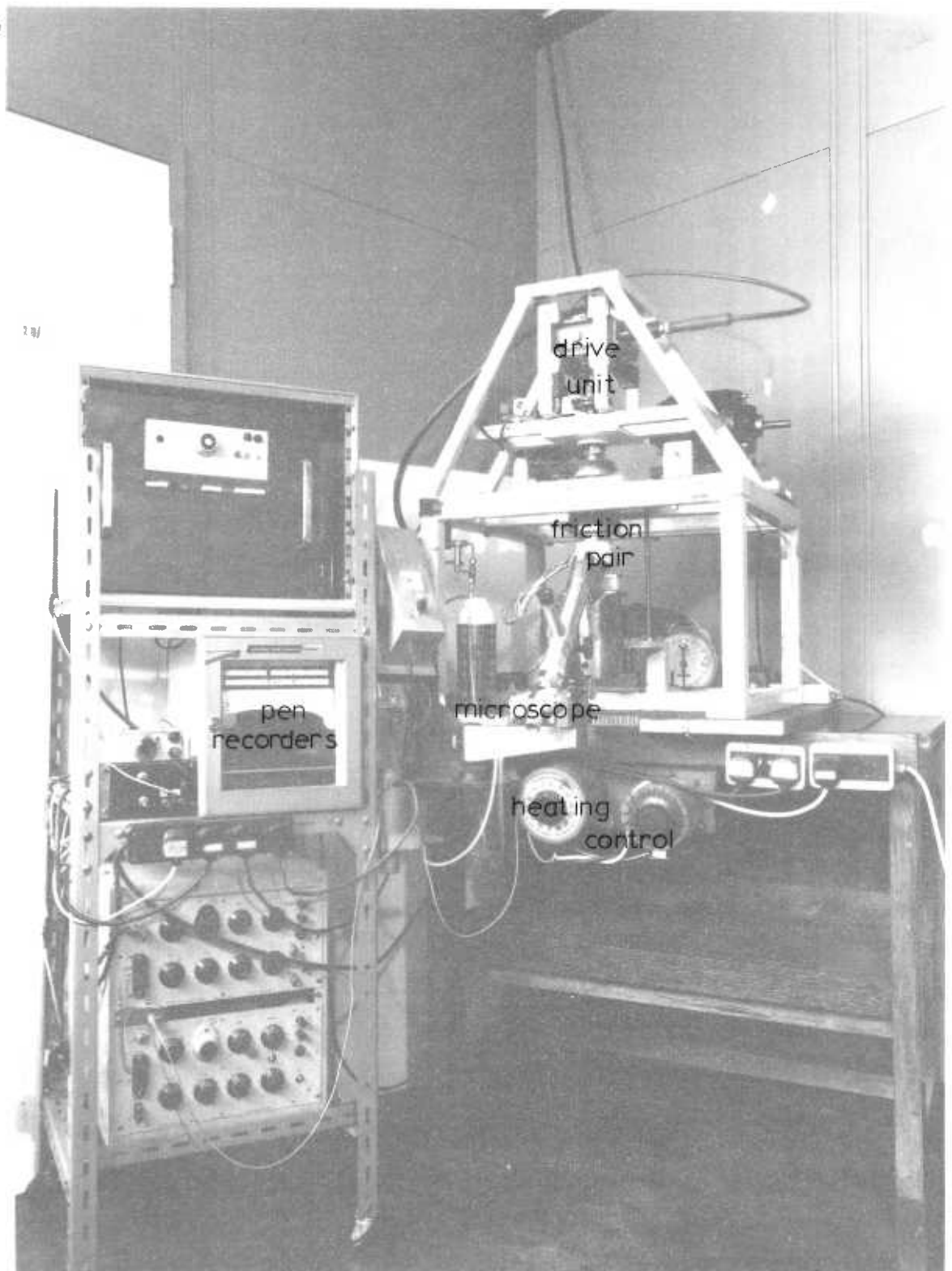


Figure 6.1. Ball on triplane apparatus.

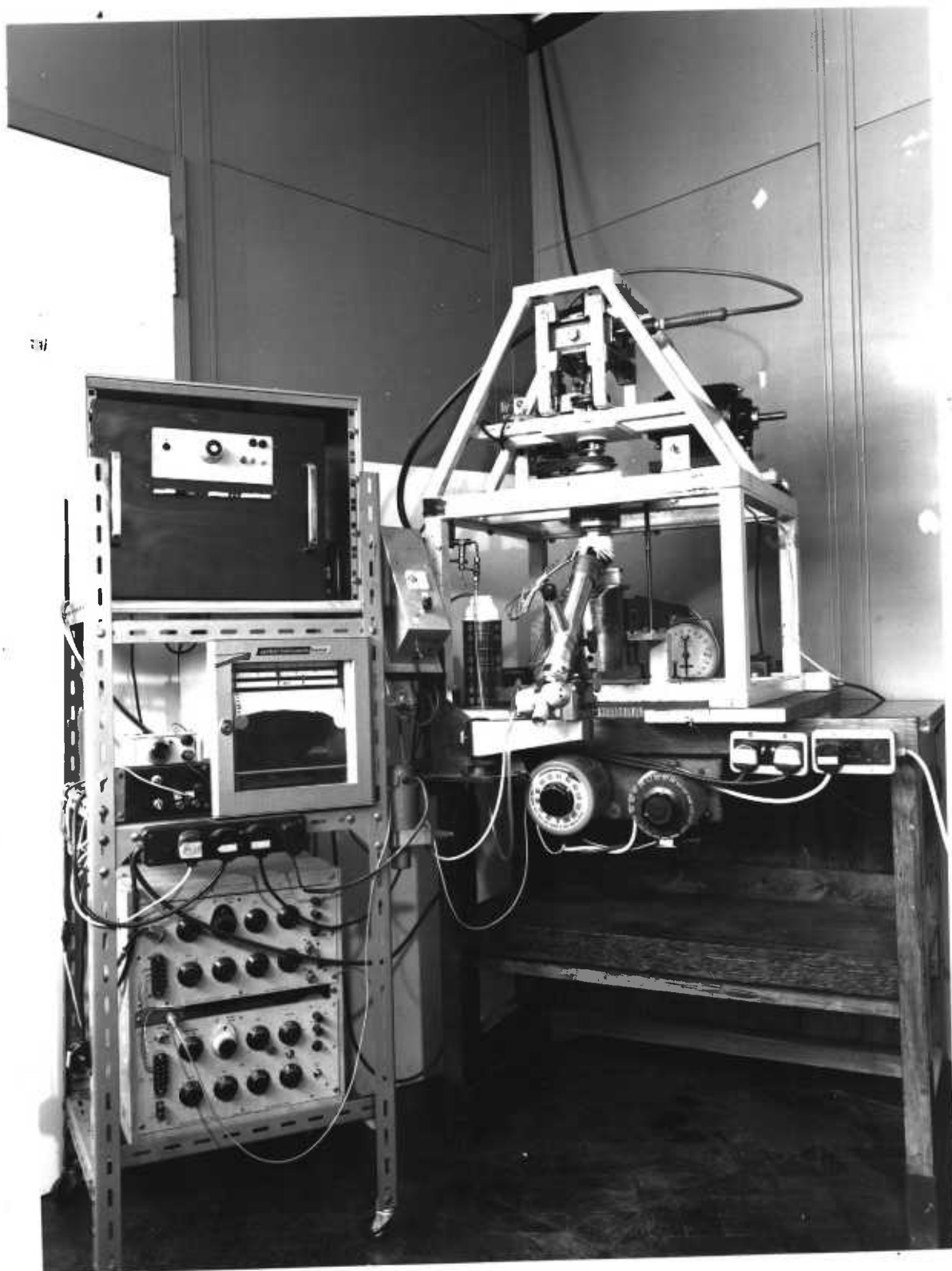


Figure 6.1. Ball on triplane apparatus.

flat ends of three pegs whose axes coincided at the centre of the ball. The geometrical arrangement of the pegs with respect to the ball is shown in table (6.1) and was chosen so that each peg gave a separate wear track on the ball. Presland and Francis (144) have shown that, in the 4-ball rig,

Table (6.1)

Peg	Angle to Vertical	Circumferential Angle
A	45°	0
B	$55^{\circ} 45'$	$+137^{\circ} 42'$
C	$34^{\circ} 15'$	$- 99^{\circ} 36'$

inconsistent behaviour can result from all the lower balls rubbing in the same track. The pegs, held in a steel cup, were arranged so that each carried the same load.

The lubricant was contained with a detachable shield which screwed on the cup, and around the shield was wrapped an electric heating wire controlled by a Variac transformer.

The whole assembly was mounted on a cyndanio platform which was loaded from beneath by a pivoted loaded arm. The load acted through a thin-walled torque tube fitted with strain gauges to measure friction. Temperature was monitored continuously by two thermocouples, one resting lightly on the rotating ball surface and the other against one of the pegs. Signals from both torque tube and thermocouples were recorded.

Using a low power microscope, the wear track could be observed continuously during running, through a window in the peg cup. Advantages of this apparatus over the standard 4-ball rig were:

a) Three wear tracks were produced instead of one. This improved the repeatability of results since it diminished the effect of individual inconsistencies in the steel surface. Thus a small scratch present before running, instead of having a large effect on the single wear track and possibly causing scuffing, would affect only one the wear tracks and thus play a less important part in the overall friction trace.

b) A wider variety of materials could be made in the form of pegs than was obtainable as one inch balls, and such pegs were cheaper to produce. Also the pegs, being smaller, were easier to clean in large numbers than the corresponding balls.

6.23. Materials

The dibenzylidisedisulphide used was a micro-analytical standard produced by Hopkins and Williams Ltd. The same make of hexadecane was used as was employed in earlier chapters. Its purification is described in appendix A.

Tests were done using two ball and peg metal combinations. Stainless steel ball and pegs were used in most experiments, the ball being EN 58J and the pegs, specification EN 58B. Also tested was a combination of EN31 ball and pegs. The specified composition of these steels is given in table (6.2).

Table (6.2)

	C	Si	Mn	S	P	Ni	Cr	Mo
EN 31	0.90- 1.20	0.10- 0.35	0.30- 0.75	0.050 max	0.050 max		1.00- 1.60	
EN 58B	0.15 max	0.20 min	2.00 max	0.045 max	0.045 max	7.0- 10.0	17.0- 20.0-	
EN 58J	0.12 max	0.20 min	2.00 max	0.045 max	0.045 max	8.0- 12.0	17.0- 20.0	1.5- 2.5

The balls were 25.4 mm. (one inch) diameter and the pegs 4.7 mm.

(³/16 inch) diameter.

6.24. Experimental technique

Ball and pegs were soxhletted in toluene for not less than four hours and then, whilst still hot, immersed in analar acetone. They were then taken out, allowed to dry, and assembled in the cup holder, which was immediately filled with lubricant. No load was applied for twenty minutes, so that equilibrium had time to be established. The upper ball was then rotated at one r.p.m. and a load of 8.9N (2lb) was applied to the pivot arm. This load and speed, which corresponded to ~ 1 mm/s and a maximum Hertz pressure of 1.17 GN/m^2 (170,000 p.s.i.) was used throughout the experiments in this chapter.

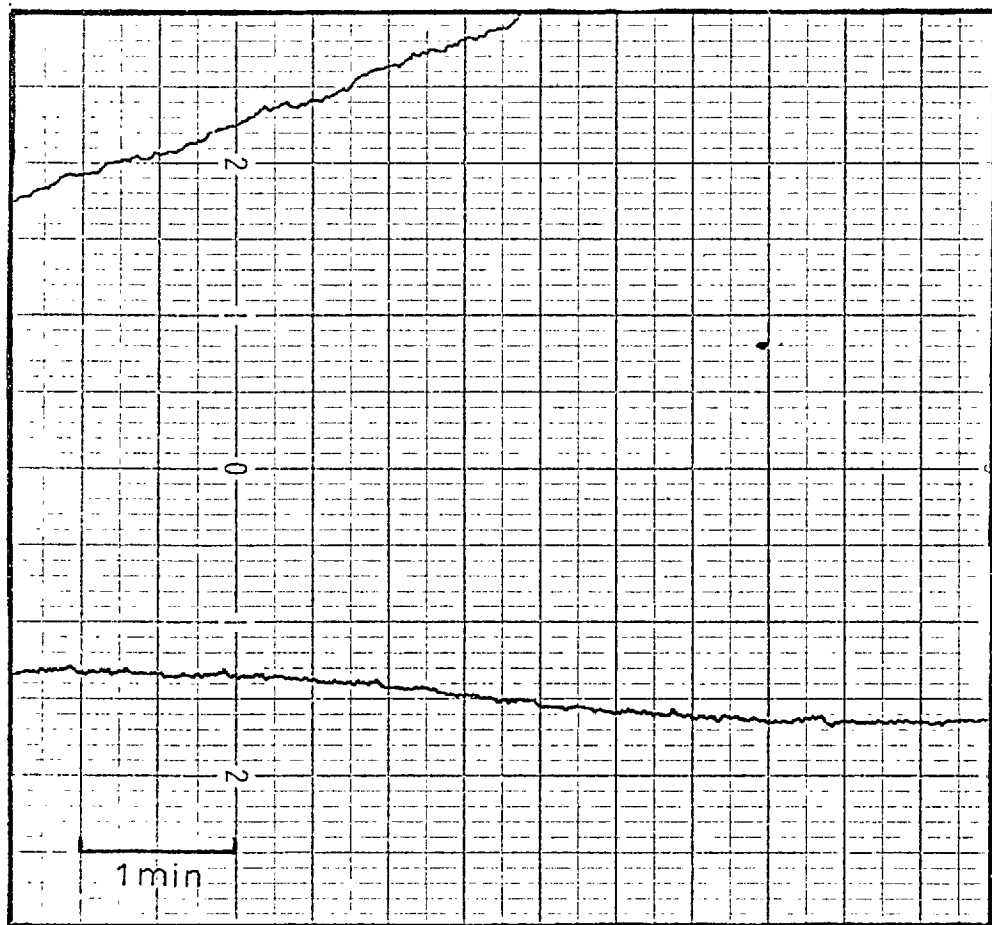
When the friction had stabilized at room temperature, the heating unit was switched on so that the lubricant temperature rose steadily. In this way continuous traces of friction and temperature were obtained throughout a run.

No lubricant sample, peg or ball was used more than once, and between each experiment the cup and metal shield were cleaned in an ultrasonic bath, both with toluene and acetone.

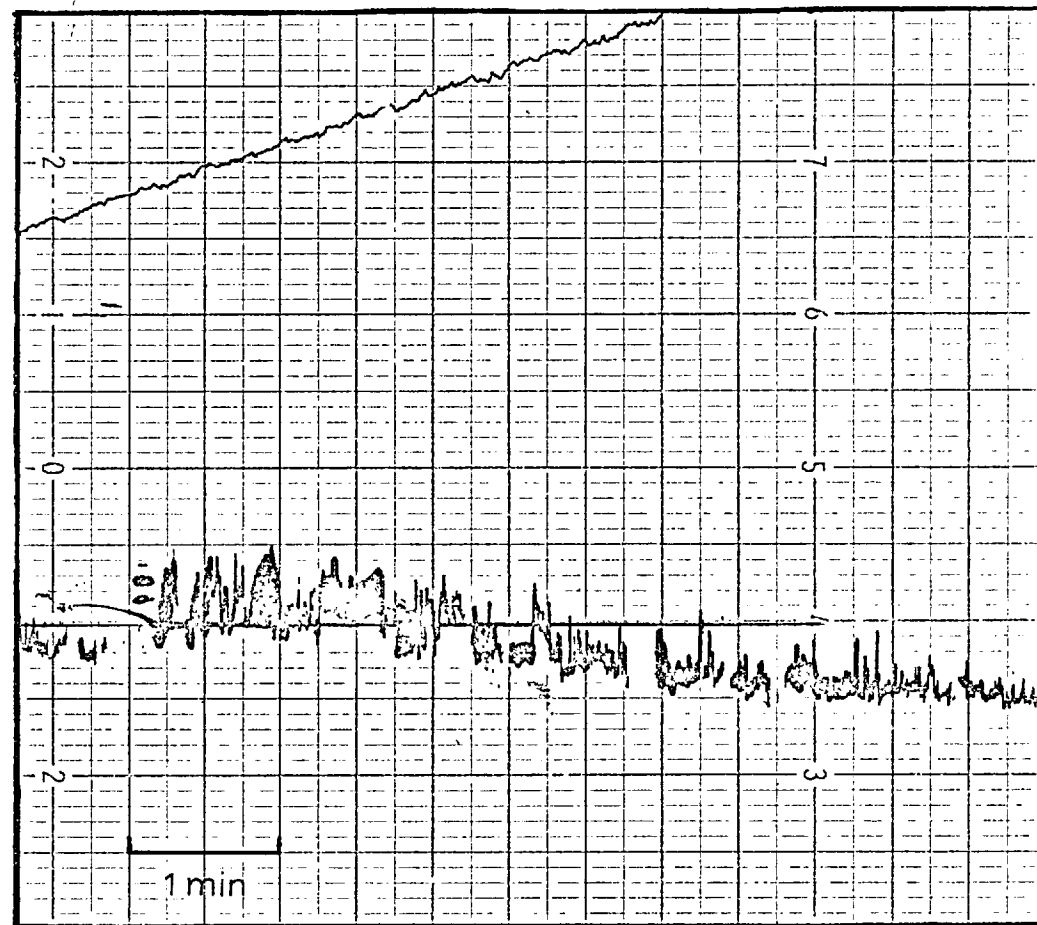
6.25 Accuracy

Part of a typical trace is shown in fig. (6.2). It can be seen that the friction response fluctuated rapidly about a well-defined mean. This mean kinetic coefficient of friction could be determined to $\pm 8\%$.

There was considerable scatter between different runs using the same system, and actual friction values could differ by up to 20%. This was probably due to surface scratches and slight variations in the peg heights. Generally, the mean coefficient of friction of several runs was taken. For all runs with the same system, relative changes with temperatures were always identical even if the absolute friction values might differ slightly between runs.



Trace for EN 31 steel



Trace for Stainless steel

Figure 6.2. Ball on triplane traces for 0.8wt% dibenzylidisedisulphide in hexadecane.

Upper trace = temperature; lower trace = friction

6.30 Results

6.31. Lubrication of stainless steel using 0.8 wt % dibenzylidisulphide in hexadecane.

Several runs were carried out using this system, raising the temperature up to 250°C. In each case the friction dropped at 160-170°C from poorly lubricated conditions, not much better than pure hexadecane, to a much lower value. The mean of the friction traces is shown in fig. (6.3), together with a friction curve for pure hexadecane. The average rate of heating was 6°C per minute.

To test whether rate of temperature rise had any effect on the drop in friction, an experiment was done at a much lower heating rate of 1.5°C per minute. No significant difference was noted, the drop in friction beginning at ~160°C.

6.32. Reversibility of the lubricating effect

A trial friction run was carried out using 0.8 wt % solution of dibenzylidisulphide on stainless steel but switching off the heater control at 190°C so that the temperature started to fall. The traces of temperature and friction with time are shown in fig. (6.4) where it can be seen that the friction began to increase again as soon as the temperature dropped below 160°C.

6.33. Effect of dibenzylidisulphide concentration on the lubrication of stainless steel

A test was done using 6.4 wt % dibenzylidisulphide in hexadecane. The results are shown in fig. (6.5), together with the characteristic friction trace at lower concentrations. The disulphide was not fully soluble at room temperature at such a high concentration and the solution did not clear until the temperature reached approximately 65°C. The friction results were

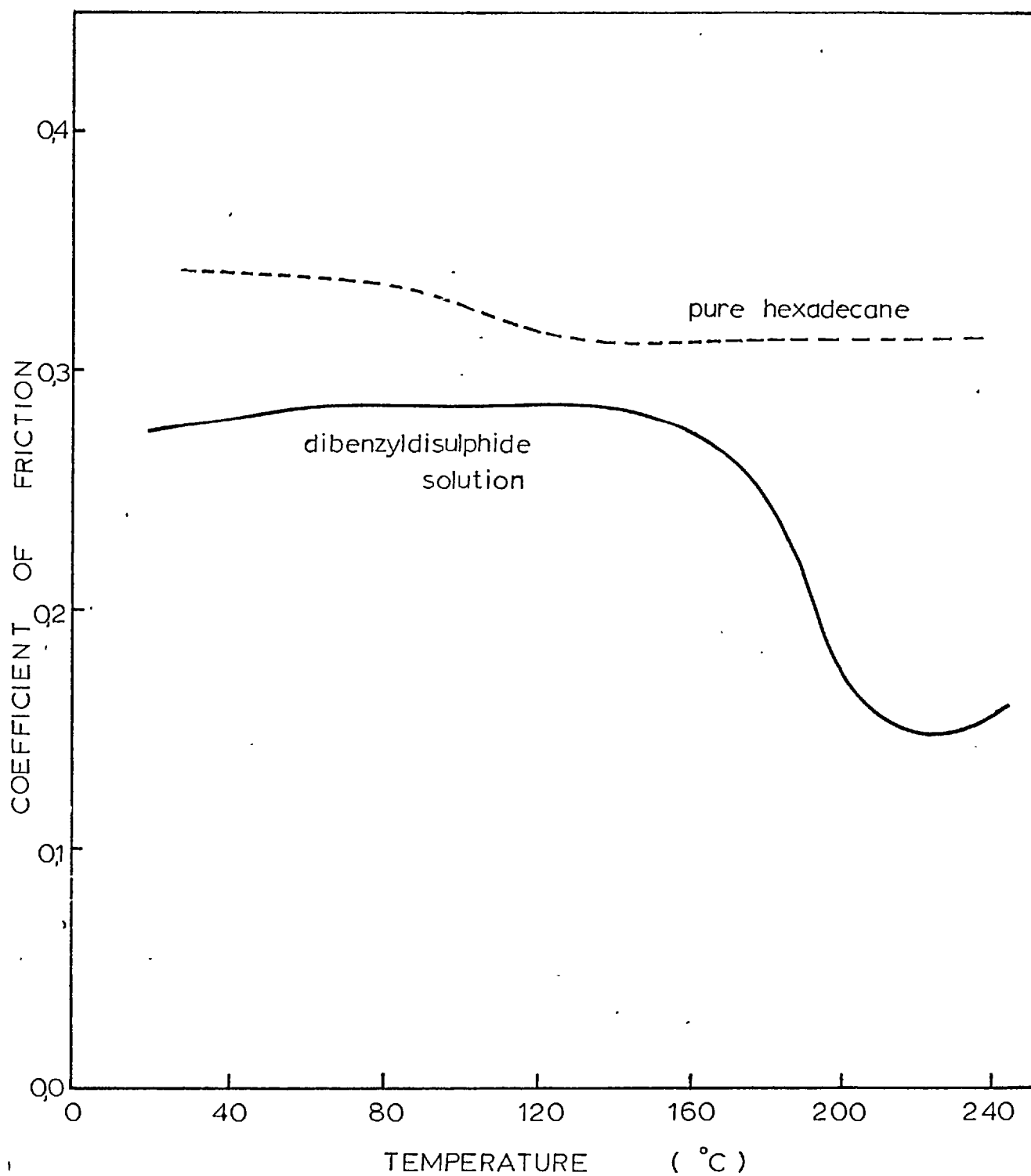


Figure 6.3. Variation of friction with temperature for 0.8wt% dibenzyl-disulphide on stainless steel.

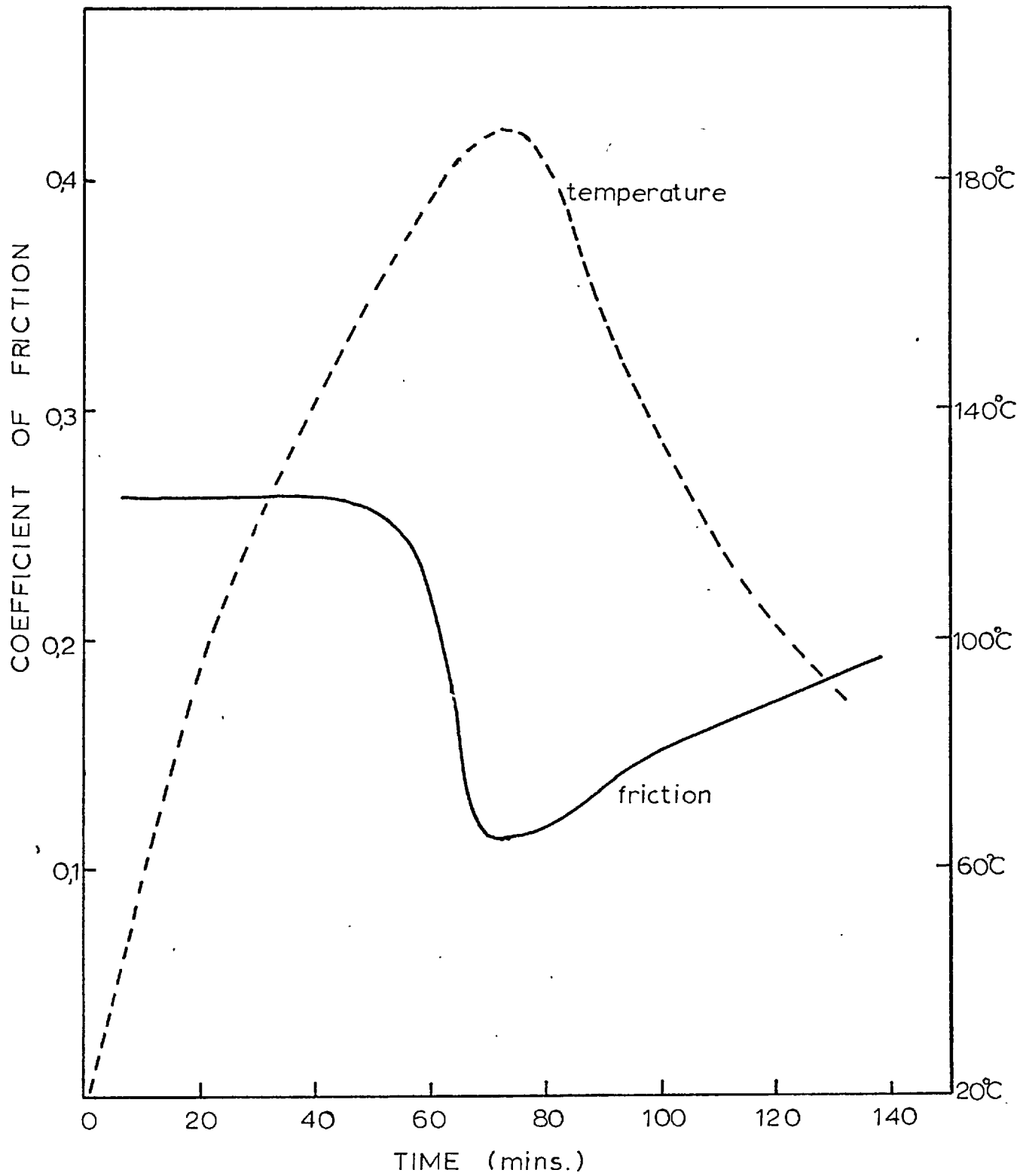


Figure 6.4. Reversibility effect of extreme pressure activity with temperature for stainless steel

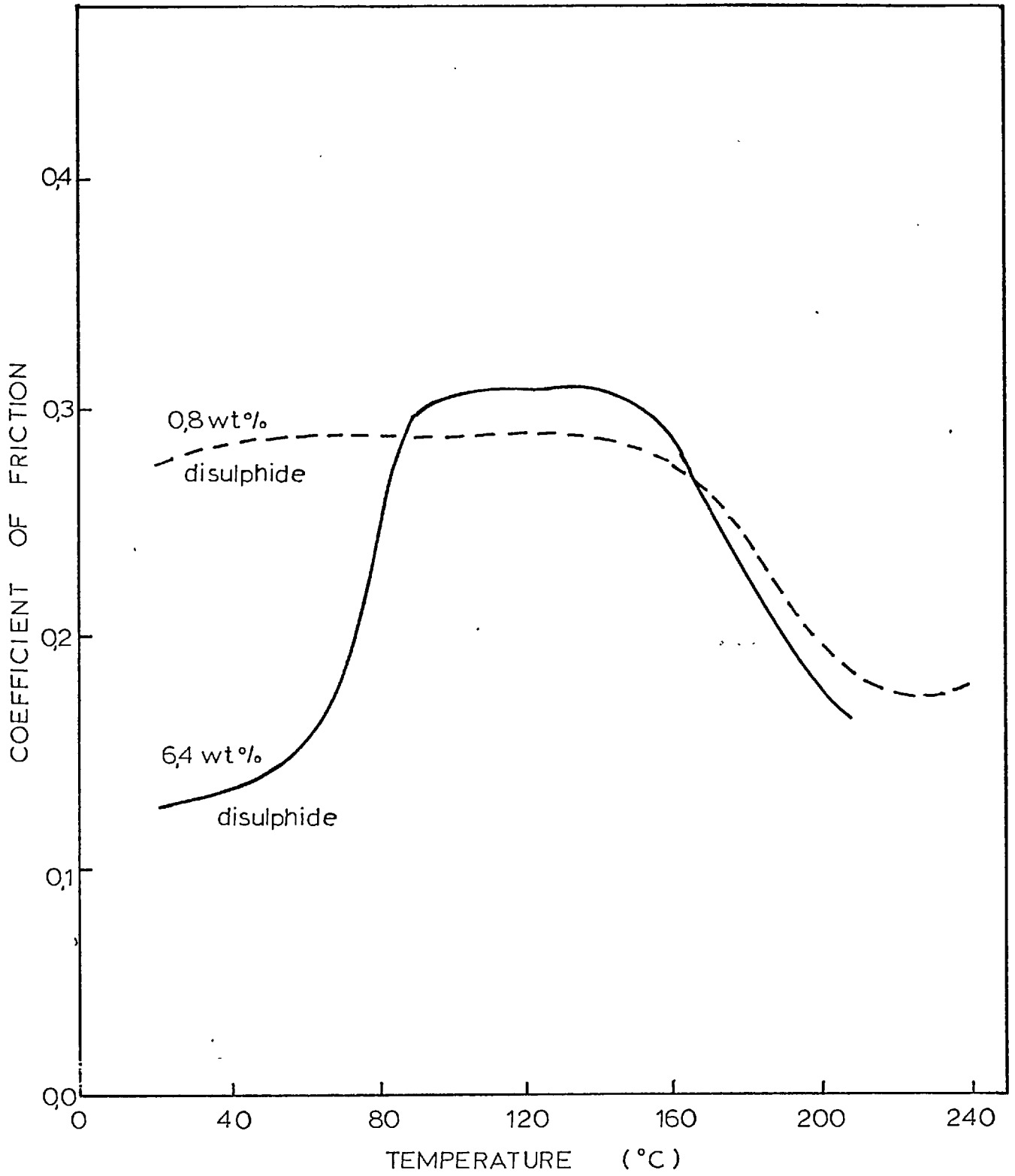


Figure 6.5. Effect of dibenzyl disulphide concentration on lubrication of stainless steel

quite similar to those at 0.8 wt % concentration and coefficient of friction fell from 0.3 to 0.15 at 160–170°C. The only difference between the two concentrations was at very low temperatures. Below 70°C the coefficient of friction of the very concentrated solution was unusually small, probably because undissolved dibenzylidisedisulphide was acting as a solid lubricant.

6.34. Effect of metal on lubrication using dibenzylidisedisulphide solution

To test the effect of steel composition on the lubricating system, an experiment was carried out using 0.8 wt % dibenzylidisedisulphide solution in hexadecane but with EN 31 ball and pegs. The friction-temperature curve in this system was rather different from stainless steel and is shown in fig. (6.6). There were two lubricating transitions in the range studied, one occurring at 160–170°C, as for stainless steel, but the other being a smaller drop in friction at 65–70°C.

6.40. Discussion

A notable feature of the dibenzylidisedisulphide solution lubricating results was the repeatability of the drop in friction at 160–170°C. This occurred in the same temperature range independent of concentration, metal type and rate of heating.

It is suggested that this drop in friction results from the formation of an anti-seizure extreme pressure film. It was noted in chapter 5 that sulphide layer build-up starts at 110°C and increases rapidly with temperature. The lag between this initial reaction at 110°C and the extreme pressure effect at 150°C probably represents the time required for a sufficiently thick film to form.

There are two possible modes of extreme pressure film formation during a test. The sulphur-containing film may be building up continuously from 110°C until there is a thick enough layer to operate. Alternatively the

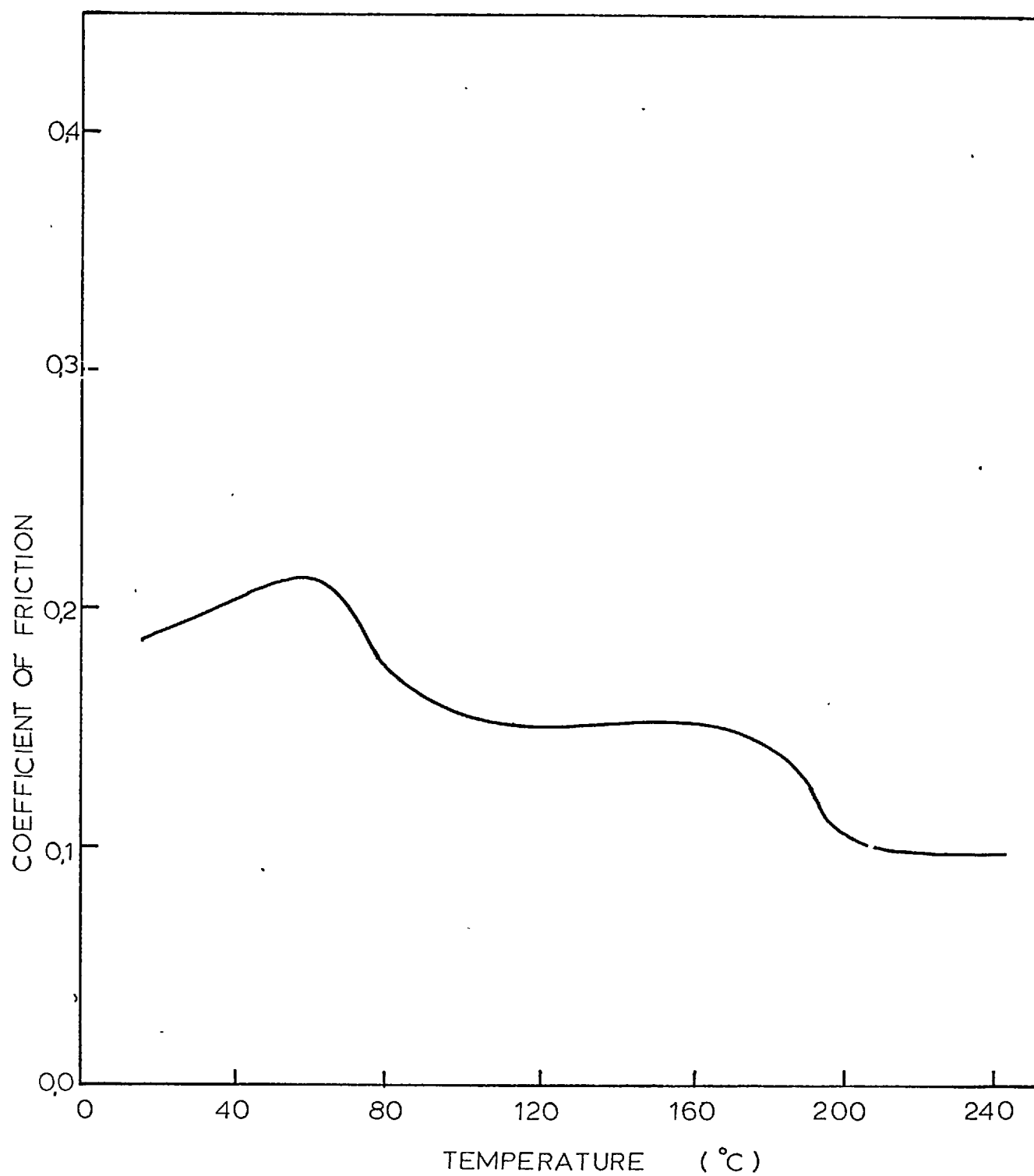


Figure 6.6. Lubrication of EN31 steel ball and pegs with 0.8wt% dibenzyl disulphide

newly formed film may be almost entirely scraped away during each rotation in which case extreme pressure lubrication would only occur when a suitable film was built up during one revolution.

Three pieces of evidence support this second possibility.

a) The fact that heating rate changes had little effect on the temperature at which the extreme pressure film became effective suggests that continual build up throughout the test is not relevant.

b) The fast rise in friction as the temperature fell below 160°C suggests that the film was continually being abraded away, so that below this temperature it could not be replenished quickly enough.

c) Work by Bailey (100) on the lubricating properties of different metal combinations has shown that the out of contact time is a vital feature in controlling scuffing.

The critical lubricating film must therefore be the film building up at 165°C in a time of one minute (one revolution). This corresponds, from chapter five, to just one or two monolayers of sulphide. Such an analysis assumes that all the film is scraped off during rubbing. However much is abraded, it is evident from the results that, unless dibenzylidisedisulphide is much more reactive to scratched than unscratched steel, the extreme pressure film need be only a few monolayers thick to give anti-seizure lubrication.

There is no reason to suppose that a sulphide layer alone is providing the lubrication above 160°C . Sakurai(140) has shown that fatty acid and dibenzylidisedisulphide are irreversibly adsorbed on iron sulphides. It is thus likely that oxidation products of hexadecane and also dibenzylidisedisulphide itself will form a chemisorbed lubricating film on sulphide as soon as this is produced.

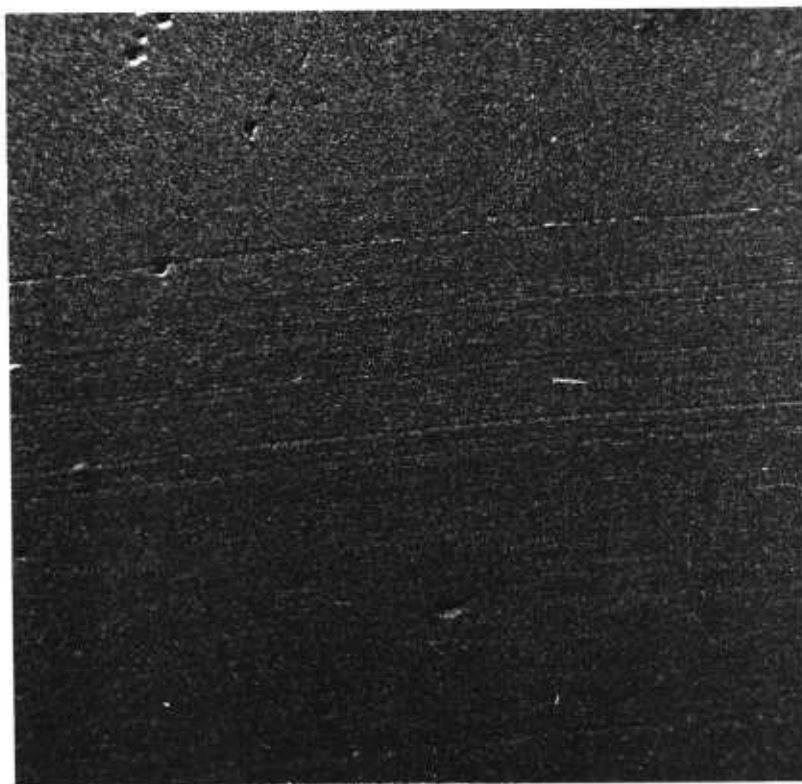
The drop in friction at $65-70^{\circ}\text{C}$ for EN 31 steel may be due to the formation of a mercaptide film with some degree of lubricating activity.

At low temperatures for both steels no lubricating action was observed and dibenzylidisedisulphide molecules were presumably only weakly adsorbed on the metal and easily squeezed off. The transition at $65-70^{\circ}\text{C}$ for EN 31 corresponds well with the formation of a chemisorbed monolayer of dibenzylidisedisulphide or mercaptide shown for mild steel in fig. (5.2), and may indicate the presence of a film not so easily displaced from the surface. This may possibly correspond to the "anti-wear" region referred to by Davey (135) and Allum et al. (123) (136).

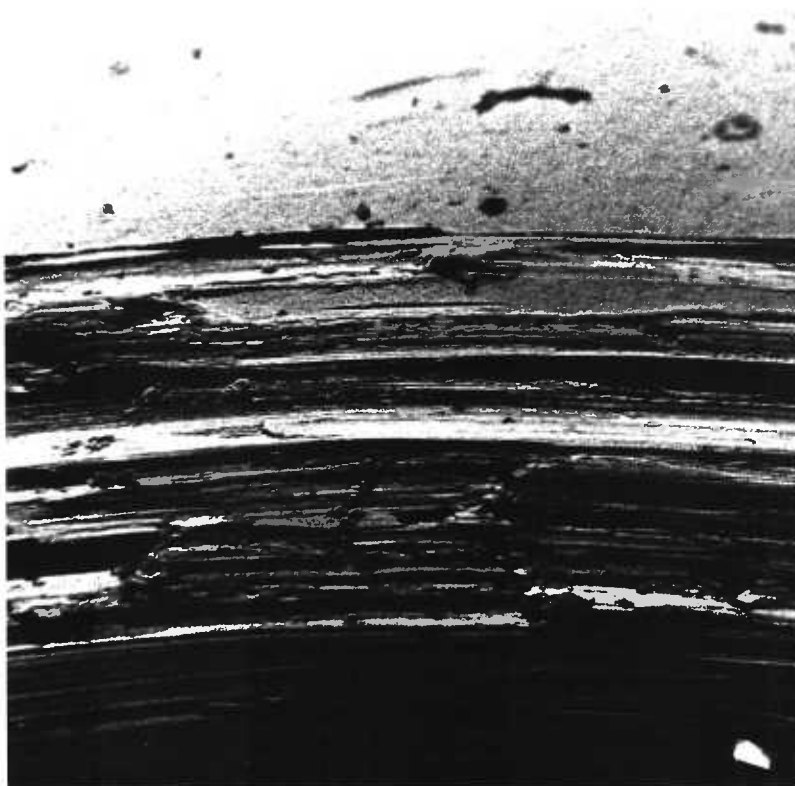
There are two possible reasons why stainless steel should not show this lower temperature friction drop. It may be that the less reactive EN 58 steel does not bond so strongly with dibenzylidisedisulphide or mercaptide in this region, and so will not lubricate. It was, however, shown in fig. (5.1) that a chemical monolayer of disulphide forms on stainless steel above 80°C . A more likely explanation is that stainless steel is too soft and easily deformed to give boundary lubrication with only a monolayer of disulphide. The wear tracks on EN 58 and EN 31 steel balls are shown in fig. (6.7). Both photographs were taken after standard runs with 0.8 wt % dibenzylidisedisulphide solution up to 240°C . It can be seen that EN 31 was lightly scratched whereas the softer EN 58 stainless steel was heavily torn with a wide wear-scar being produced. A thin monolayer of chemically adsorbed dibenzylidisedisulphide would clearly be much more effective on the smoother EN 31 track. It was, indeed, remarkable that the transition at $160-170^{\circ}\text{C}$ was so similar for the different steels and that just a thin sulphide layer could lubricate the heavily scratched EN 58 wear track.

6.50. Conclusions

Investigations have been carried out into both the reaction and lubrication of dibenzylidisedisulphide on steel. Two types of lubricating



Wear track on EN31 steel ball X 350



Wear track on stainless steel ball X 74

Figure 6.7. Wear tracks using 19.8N load and 0.8wt% dibenzylidisedisulphide up to 250°C

activity have been identified which can be tentatively compared to "anti-wear" and "anti-seizure" activity, as described by Davey (135) and Forbes (113). Anti-seizure activity corresponded to the formation of a very thin sulphide layer, which occurred at 170°C under the conditions studied. The possible anti-wear lubricant activity corresponded to the a chemisorbed monolayer of disulphide or mercaptide, and was found in the temperature range $70\text{--}170^{\circ}\text{C}$.

Anti-seizure lubrication was observed with both stainless and EN 31 steel. The proposed anti-wear lubrication, on the other hand, was not effective with stainless steel. This may be one reason why stainless steel is so difficult to lubricate.

These tests provide chemical evidence to support the anti-wear and anti-seizure breakdown mechanisms of Allum et al. (123) (136). They imply, as Allum suggests, that anti-wear activity is controlled by S-S bond cleavage, to give a mercaptide, whereas anti-seizure activity depends on the breaking of the C-S link to form a sulphide layer.

CHAPTER SEVEN

INTERFERENCE EFFECTS IN BOUNDARY LUBRICATION

7.10. Introduction

This chapter describes tests to investigate the interference effects that surfactant oil additives have on the action of the extreme pressure agent, dibenzylidisedisulphide. The experimental techniques are the same as those used in previous chapters and comparison is drawn between e.p. activity without added polar compounds and the same systems with polar material. Such work is obviously of practical importance in the field of boundary lubrication since antagonistic interference must be minimised in order to produce an efficient additive package.

7.20. Literature Review

Almost all references to additive interference found in the literature concerned competitive effects at the metal surface. These are less easy to predict than straightforward chemical interactions in solution and more difficult to circumvent.

The commonest type was the inhibition of extreme pressure activity due to the presence of polar surfactants. Smalheer and Mastin (145), in 1956, described some practical axle tests in which two types of boundary lubrication were observed, one operating at high speeds and the other at high torque. They found that those additives required to mitigate high torque conditions, carboxylic acids and esters, tended to reduce or negate the effectiveness of the sulphur e.p. lubricants added for high speed lubrication, and vice versa.

Okrent (146) in 1961 pointed out that oil-soluble soaps and surfactants having detergent properties lowered the efficiency of anti-wear

additives in V-8 engine tests. Similarly Studt (147) showed that long chain acids and alcohols reduced the effectiveness of chlorine containing e.p. agents. Thus pure 1.1.1.3 dodecyltetrachloride in hexadecane solution had a higher failure load than when mixed with either lauryl alcohol or lauryl acid in the same solvent. Studt also noted that the fatty acid had a greater antagonistic effect than the alcohol and suggested that the polar additives reacted with the metal surface to form a protective layer against e.p. attack.

This approach was greatly extended by Grew and Cameron (15) who carried out a series of experiments to show that hexadecylamine interfered with the activity of diphenyldisulphide on steel by adsorbing on the metal surface. Grew demonstrated that, using variable load, high speed 4-ball tests, mixtures of 0.3% wt amine and 1.0% wt amine with 1.1% wt disulphide behaved in scuffing as though there were no disulphide present at all, in failing at quite low loads.

When the ambient temperature of the test was raised from 22°C to 100°C, the 1.0% wt amine + disulphide solution continued to show no e.p. activity. The 0.3% wt amine + disulphide solution, on the other hand, did not scuff within the load range of the test rig, so it was clear that disulphide was acting as an anti-seizure agent.

Grew concluded that normally the applied load raised the surface temperature until the adsorbed, amine film failed. Since this amine layer had prevented disulphide reaction, seizure took place as soon as the amine failure occurred. With 0.3% wt amine solution at 100°C the amine adsorbed film was not close-packed enough to prevent diphenyldisulphide attack. This meant that a sulphide layer could build up unhindered, with increasing temperature, to prevent seizure.

Grew (15) applied the same experimental technique to show that natural base-oil impurities could also lower the effectiveness of anti-wear agents.

He compared the extreme pressure activities of diphenyldisulphide in light stock base oil and pure paraffin oil. Using variable load 4-ball tests he showed that the disulphide prevented scuffing more effectively in paraffin oil solution than in light stock, although the light stock on its own was a more efficient lubricant than pure paraffin oil. Grew also used the hot wire technique of Barcroft (129) to demonstrate that acetic acid corroded steel more rapidly in white oil than in light stock, presumably because of natural surfactant inhibitors in the impure mineral oil.

Rounds (148) has compared the friction of steel using different base oils containing a variety of additives. He showed that the effectiveness of the additives generally increases as the base oil is progressively refined. Rounds also studied the interaction of the friction-modifying additive, chlorinated wax, with a series of oxidation inhibitors. From this work he suggested that base-oil oxidation of a limited nature may be an essential factor in additive response, although too much would be detrimental.

Interference effects at surfaces are not confined to those between an extreme pressure agent and a polar additive. Interference is also possible between a pair of different polar additives or between two e.p. agents.

Clayfield (149) has studied different mineral oils and additive solutions in terms of their spreading properties which, he shows, relate closely to their lubricating characteristics. He demonstrated interference effects between different base-oil mixtures and also showed that interaction between base stock and certain metallic detergent additives could occur, to produce a mixture with a low spreading pressure.

Sprague and Cunningham (150) have shown that such interference can be quite selective. They noted that calcium phenate inhibitor cancelled the anti-friction behaviour of a 0.6% sperm oil solution but had only a small effect on a 0.6% saturated carboxylic acid solution.

Interference between different extreme pressure additives has been demonstrated by Sakurai and co-workers, (116), who showed that sulphur e.p. agents were suppressed by the addition of chlorine containing additives, dependent on the surface activity of the sulphur compound used.

These examples taken from the literature have mostly been surface antagonistic effects. Many other possible types of interference are possible, such as chemical reaction in solution or suppression of a required reaction by the quenching of an intermediate species. An interesting recent example of a possible type of interference that an additive formulator would have to consider is given in a recent paper by Ratnasamy and Fripiat (151), who show that thiophene and ethanethiol react chemically to decompose on the surface of MoS_2 . This raises the question of whether solid MoS_2 , a widely used chemical in lubricants, would adsorb other sulphur-containing additives. Such interference is not put forward as a particularly likely possibility, but merely as an illustration of the numerous difficulties that may arise in trying to prepare a non-interfering additive package.

7.30 Experimental

All the experiments described in this chapter used experimental techniques discussed earlier in the thesis. No specific discussion of experimental technique or accuracy is therefore necessary.

7.31 Materials and lubricants

The steels, octadecylamine, dibenzyl disulphide and hexadecane were all the same samples as those used in previous chapters. In some tests a calcium sulphonate solution was employed. This was a commercial additive, Aloa 246B, containing neutral calcium sulphonate with 2.46% Ca and 2.85% S.

The T.B.N. value was 20.8. This additive is used in concentrations up to 5% as a high temperature detergent.

A series of experimental lubricating solutions were prepared, which had the following composition:

I	Hexadecane solvent. 0.040 wt% (3.6×10^{-4} m/m) octadecylamine.
II	Hexadecane solvent. 0.040 wt% (3.6×10^{-4} m/m) octadecylamine 0.80 wt% dibenzylidissulphide
III	Hexadecane solvent. 4.5 wt% calcium sulphonate solution (corresponding to 0.12 wt%S)
IV	Hexadecane solvent. 4.5 wt% calcium sulphonate solution (corresponding to 0.12 wt%S) 0.80wt% dibenzylidissulphide

No experimental solution was used more than eight days after preparation.

7.40 Results

7.41. Interference in radioactive reaction tests

Experiments were carried out to test the effect of two surfactant species on the chemical reaction of dibenzylidissulphide on steel. Exactly

similar radioactive techniques were used to those described in chapter 5, the only difference being that a small quantity of polar material was placed in the disulphide solution before reaction.

Curves obtained for dibenzyl disulphide reacting on stainless steel with added octadecylamine (II) and calcium sulphonate (IV) are shown in figs (7.1) and (7.2). On each graph is superimposed the reaction curve of pure 0.8 wt% dibenzyl disulphide solution. As in chapter 5, each reading was taken after ten minutes immersion, and the discs washed in acetone.

It can be seen that octadecylamine was especially effective in suppressing radioactive film formation at very low temperatures, so that below 50°C almost no radioactivity could be detected on the surface. At higher temperatures sulphur-containing film build-up was reduced 20-40% by the added amine.

Sulphonate did not shield the surface from radioactive sulphur attack as effectively as amine at very low temperatures. There was, however, a very striking suppression of S-35 film formation above 60°C, which persisted up to at least 170°C. This effect was quite dramatic and reduced the radioactive reaction fifty-fold in some instances.

Similar experiments were carried out using mild steel discs, and, almost identical results obtained.

7.42. Interference effects in ball on triplane lubricating tests

A series of tests were done to measure the change in friction with temperature using the ball on triplane technique described in chapter six. Four lubricant mixtures were used, octadecylamine in hexadecane (I), octadecylamine + dibenzyl disulphide in hexadecane (II), calcium sulphonate in hexadecane (III) and calcium sulphonate + dibenzyl disulphide in hexadecane (IV). Friction traces for pure surfactant solutions on stainless steel are

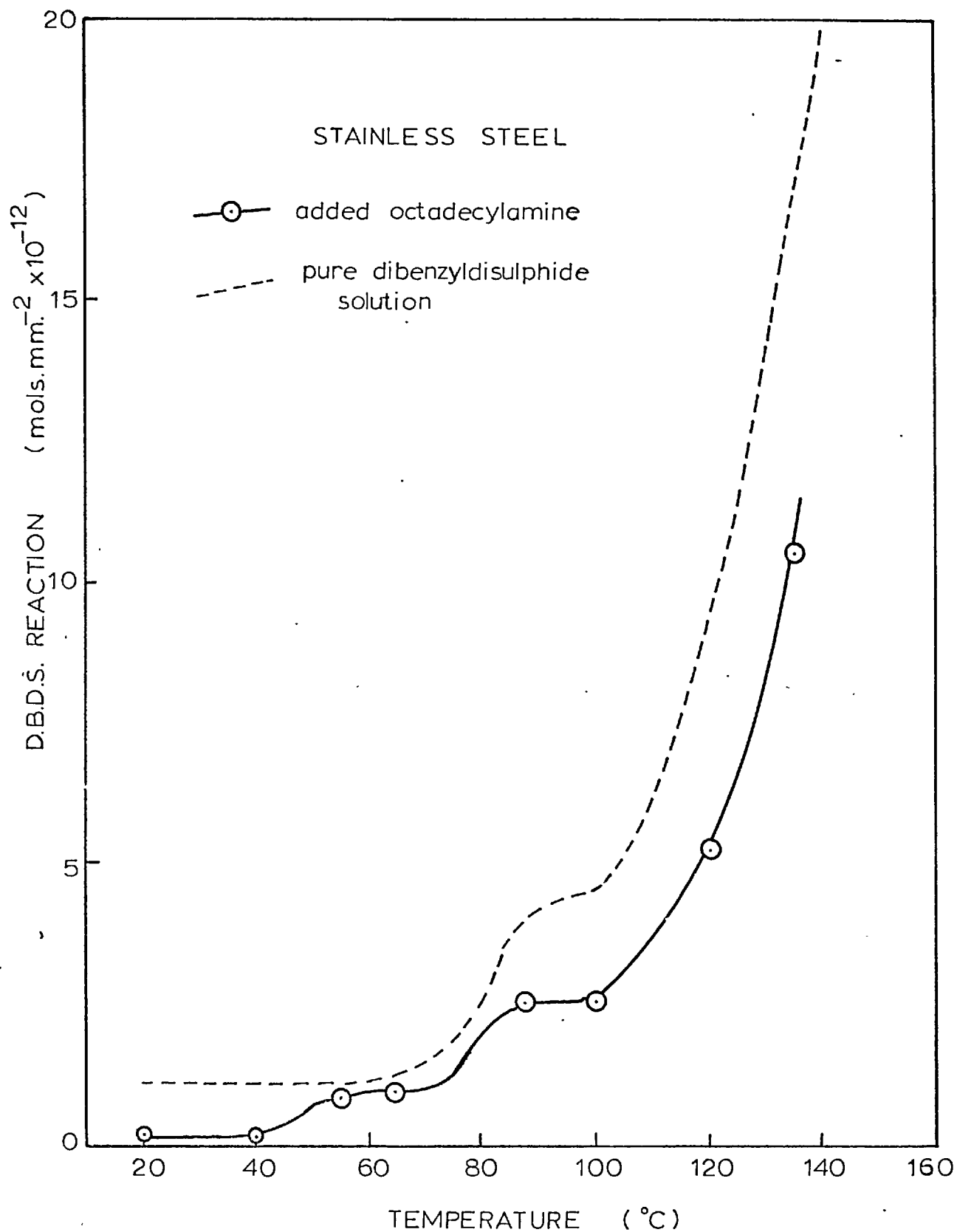


Figure 7.1. Effect of added octadecylamine on the reaction of dibenzyl disulphide on stainless steel

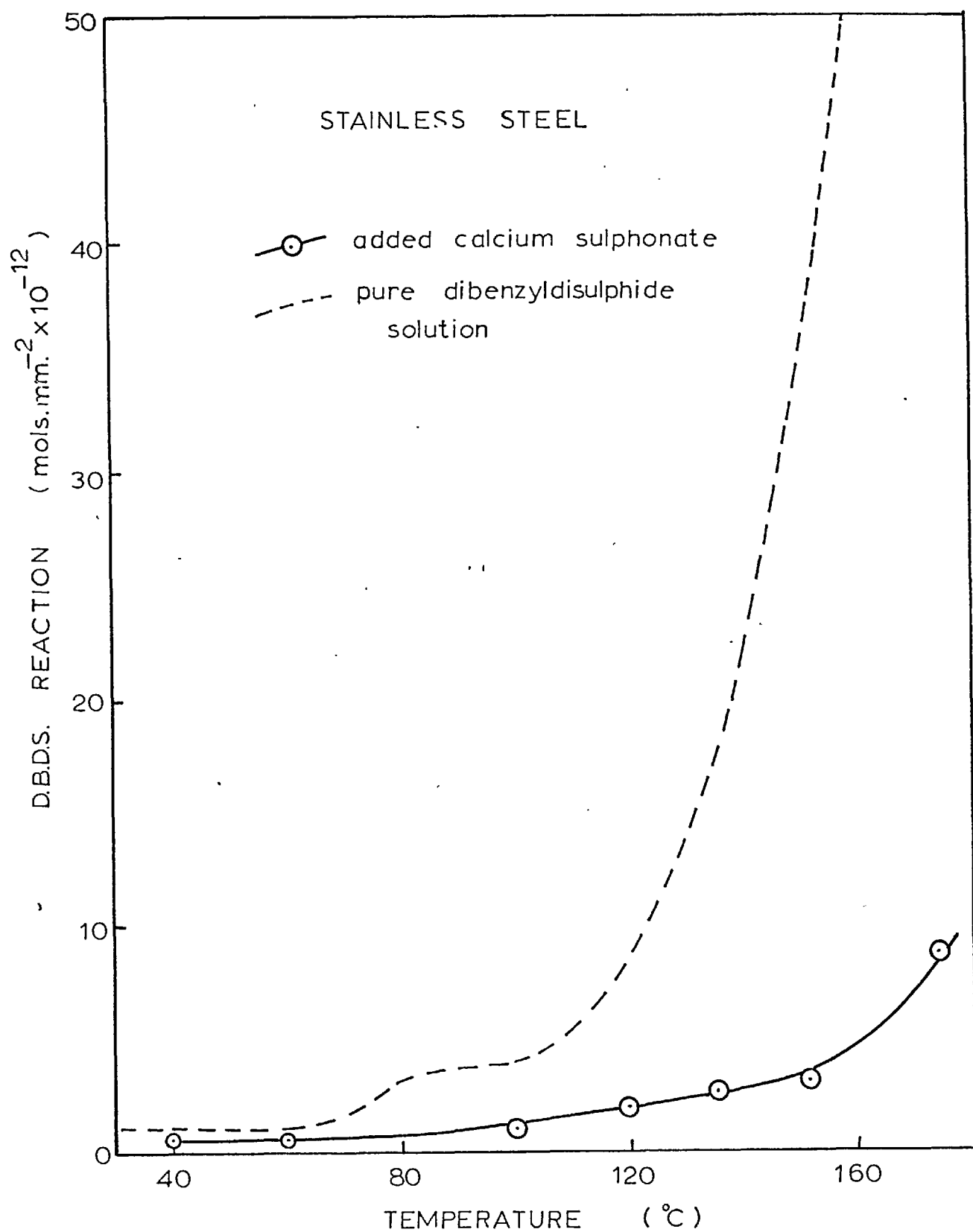


Figure 7.2. Effect of added neutral calcium sulphonate solution on the reaction of dibenzyl disulphide on stainless steel

shown in figs (7.3) and (7.4), together with superimposed traces for pure hexadecane. In figs (7.5) and (7.6) are the friction curves for the surfactant-disulphide mixtures (II) and (IV) and also the trace for pure dibenzyl disulphide. In all cases an 8.9N (2lbf) load and one r.p.m. speed were employed.

At the concentrations used it can be seen that the pure surfactant solutions, amine and sulphonate, behaved similarly. Both gave good boundary lubrication up to a temperature in the range 60–80°C. At this point friction rose abruptly and thereafter lubrication was characteristic of the hexadecane solvent.

Both surfactant-disulphide solutions gave similar friction results to pure surfactant at low temperatures. With added disulphide, friction was slightly lower in the 20–40°C temperature range but the difference was not very significant. At intermediate temperatures, 80–150°C both traces gave high friction values, similar to pure hexadecane and pure surfactant solutions. Above 160°C the surfactant-disulphide mixtures both showed the characteristic e.p. friction drop noted in chapter 6, but there was a marked difference in magnitude for the two surfactants. Octadecylamine had very little effect on the e.p. friction drop, so that the curves for disulphide, and disulphide + amine were similar. Sulphonate, however, suppressed the e.p. reaction so that the friction decrease at 160°C was quite small.

7.50 Discussion

7.51. Interference in the radioactive reaction experiments

It is immediately clear that both octadecylamine and neutral calcium sulphonate suppress the reaction of dibenzyl disulphide on steel.

In the concentration used the amine interfered most effectively whilst it was still quite close-packed with lateral interaction, up to 50°C. At

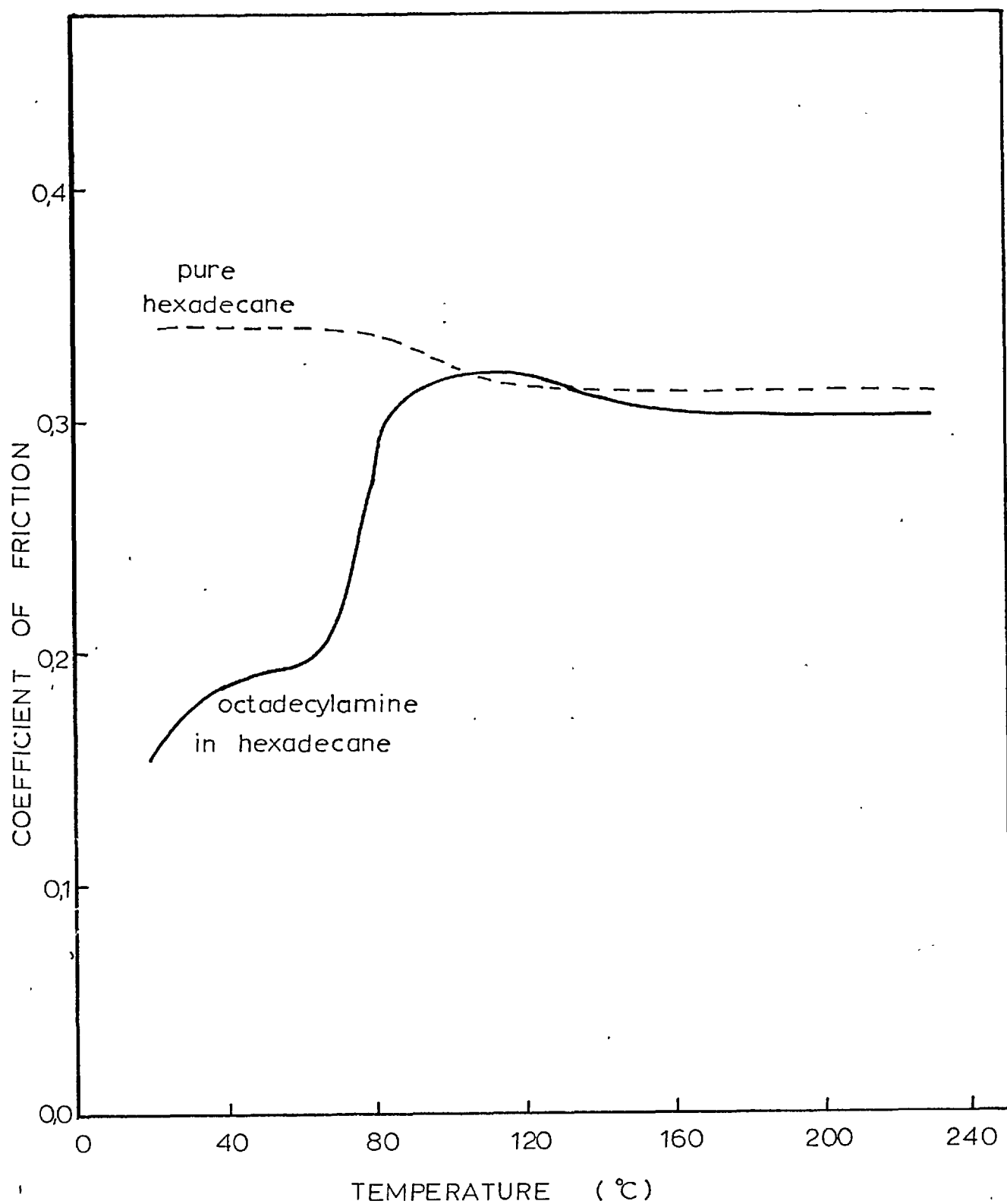


Figure 7.3. Friction variation with temperature for octadecylamine solution on stainless steel (3.6×10^{-4} mol/mol)

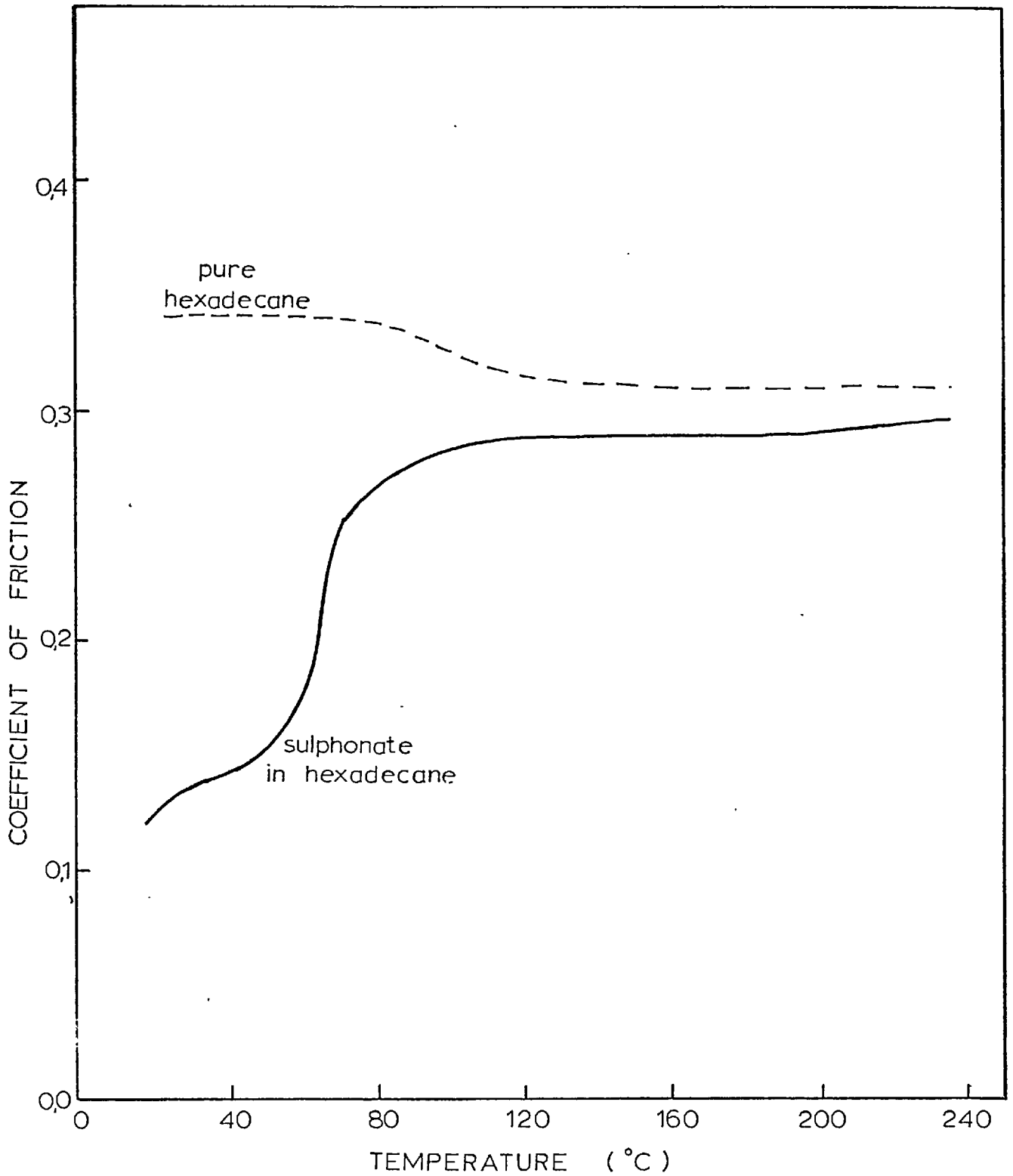


Figure 7.4. Friction variation with temperature for calcium sulphionate solution on stainless steel

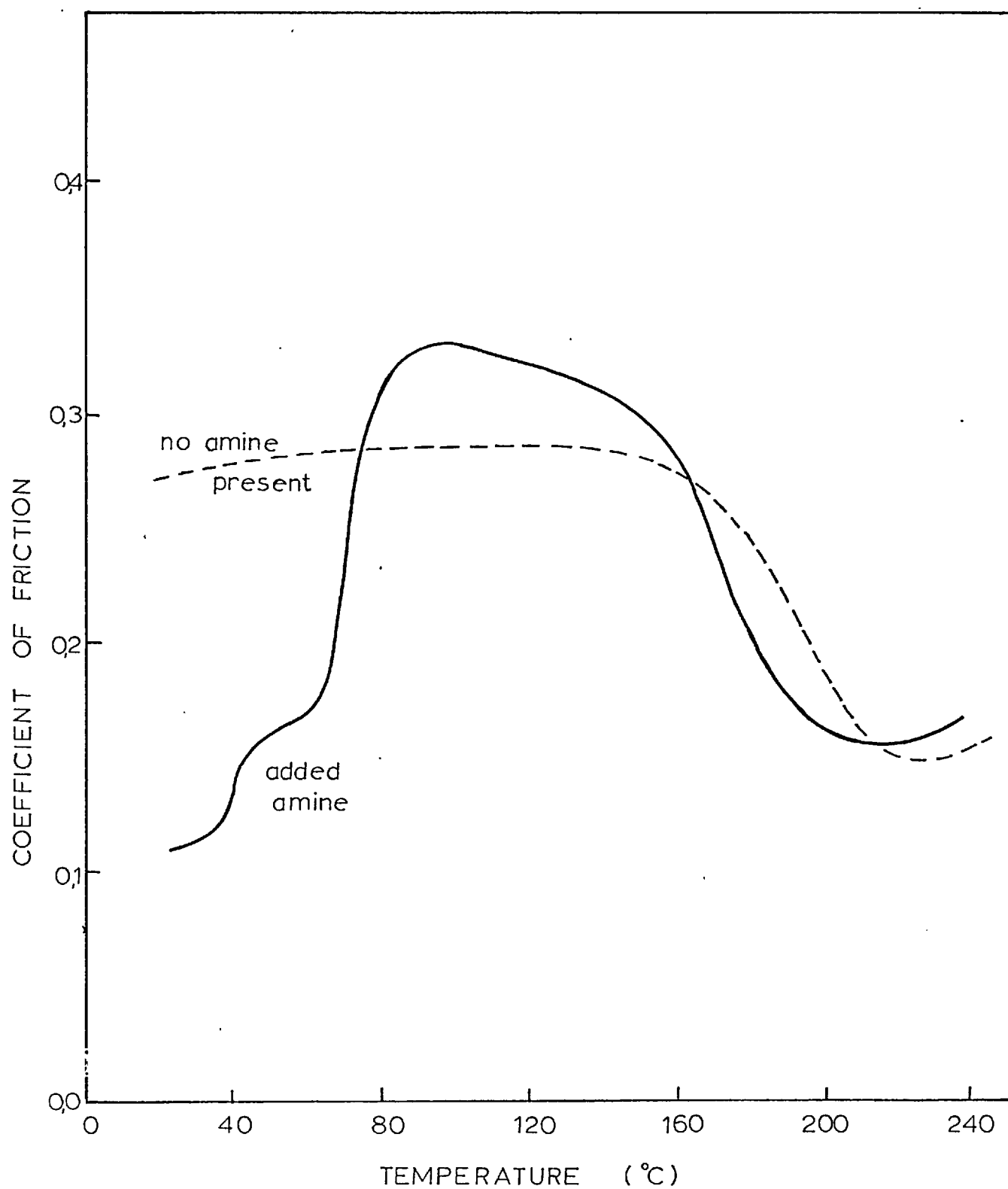


Figure 7.5. Friction variation with temperature for an octadecylamine-dibenzyl disulphide solution mixture

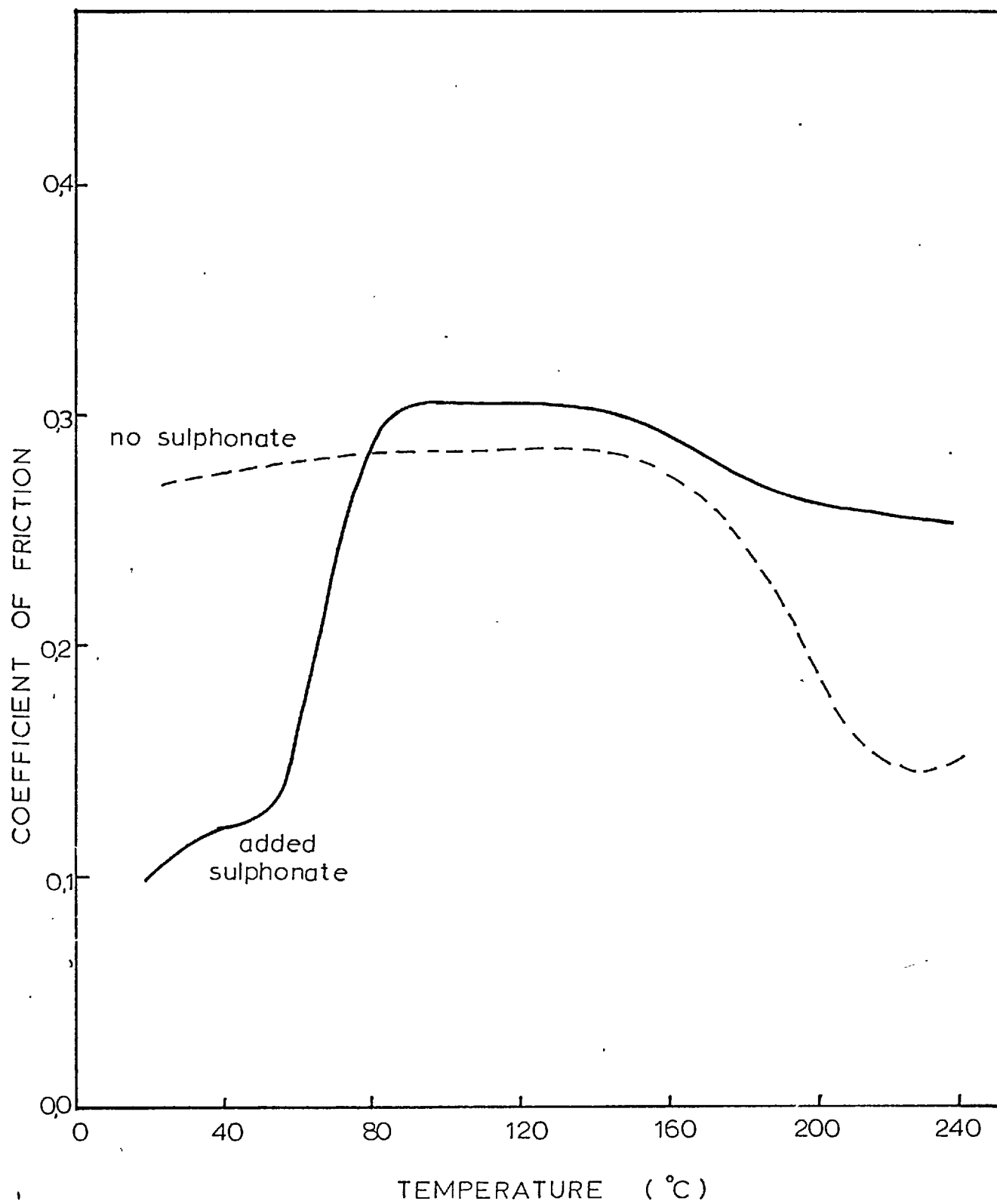


Figure 7.6. Friction variation with temperature for a calcium sulphate-dibenzyl disulphide solution mixture

these temperatures the adsorption results (chapter 2) show that the amine would form a laterally interacting, coherent monolayer through which dibenzylidisedisulphide could not penetrate. A temperature of 50°C corresponds to an amine coverage of approximately 60% of the total.

The amine film need not be immobile to prevent dibenzylidisedisulphide reaction, and there may be a rapid exchange of octadecylamine molecules between solution and the surface. Dibenzylidisedisulphide would not, however, be able to avail itself of such continually created adsorption sites - so long as there were a high overall mean amine coverage. This is because dibenzylidisedisulphide, to adsorb flat would need simultaneous desorption of a group of about eight adjacent amine molecules.

At higher temperatures, amine suppressed the reaction by approximately 25%. This may represent the 30% irreversibly adsorbed fraction noted in earlier adsorption work (chapter 2). Alternatively it may just be the average effect of a continuing reversible adsorption interference at high temperatures.

The behaviour of neutral calcium sulphonate is significantly different from amine. It is not such an efficient inhibitor of disulphide reaction at low temperatures, perhaps because it does not form such a coherent, laterally interacting, adsorbed film. At higher temperatures, however, the sulphonate is extremely effective at suppressing e.p. chemical reaction. The importance of this in terms of lubrication will be shown in the next section.

Various suppressive mechanisms are possible, on the surface or in solution. Suppression on the metal surface could be purely steric, with the surfactant acting as a screen to prevent disulphide attack. In this case, sulphonate would probably form a disoriented chemical film at high temperatures, not coherent enough to lubricate but able to limit preliminary

adsorption of the bulky disulphide molecules. Alternatively interference on the surface may result from the quenching of one of the disulphide decomposition steps.

Chemical reaction in solution is unlikely to cause the degree of interference observed, in view of the high concentration of disulphide compared to amine or sulphonate. Also, the very efficient low temperature amine interference suggests a surface adsorption process, since any chemical interference would be expected to become more effective at high temperatures. A few simple tests were done mixing amine and disulphide and warming the two together. No difference occurred in spectrophotometric adsorption at 416 nm (see chapter 2) as compared to a similar solution of pure amine, which shows that there is no simple chemical reaction under these conditions.

On balance a surface interference mechanism is most likely, and this is probably a steric effect, at least for amine interference and for sulphonate interference at low temperatures. For sulphonate at high temperatures, interference may be either steric or chemical at the surface. Further tests on the adsorption of sulphonate on metals at high temperatures would be necessary to elucidate this.

7.52. Interference in lubrication tests.

The lubricating effect of adsorbed layers of sulphonate and amine at low temperatures is clearly seen in figs (7.3)-(7.6). Octadecylamine ceased to lubricate at between 60 and 80°C. This is slightly lower than the corresponding scuffing temperature on the Bowden Leben apparatus (chapter 3), probably because the Hertz pressure at the surface was 35%

higher in the ball on triplane experiments. The amine was a reversibly adsorbed film in this low temperature range (chapter 2) and the sudden friction rise resulted from desorption. It is not clear whether sulphonate was physically or chemically adsorbed at low temperatures.

At intermediate temperatures neither oily lubrication or e.p. activity occurred in any of the systems tested. This is shown clearly in figures (7.5), and (7.6). Lubrication is provided only by the solvent.

The especially interesting feature of the friction tests is the effect of added surfactant on e.p. lubrication at high temperatures. Thus, although octadecylamine does not lubricate above 80°C , it does not interfere markedly with the action of the e.p. dibenzyl disulphide at 160°C . Calcium sulphonate ceases to lubricate above 80°C , in the same way, but suppresses the e.p. activity strongly above 160°C . This corresponds well with the radioactive tests, which also showed that sulphonate inhibited e.p. reaction much more than amine.

This is quite an important result. Two surfactants have been tested, both giving similar lubricating properties at low temperatures. One of them, however, continues to interfere strongly with e.p. reaction above its oily failure temperature, whereas the other does not affect e.p. lubrication.

Fig. (7.5) demonstrates very clearly the phenomenon known as the "temperature gap". This was described by Whyte (15 2), and is the non-lubricating region between normal mineral oil lubrication and e.p. additive protection as temperature rises. It can clearly be eliminated in two ways, either by extending low temperature protection up to $\sim 160^{\circ}\text{C}$ or by lowering the temperature of e.p. attack to the low temperature failure region. A successful way to achieve the first of these has so far eluded manufacturers. The second alternative risks continual corrosion

of the lubricated surface leading to heavy wear.

7.60 Conclusions

The effect of added polar compounds on e.p. activity has been tested, both chemically and in lubricated tests. It has been demonstrated that octadecylamine suppresses the reaction of dibenzyl disulphide only slightly, and does not significantly affect its lubricating action. Neutral calcium sulphate, however, in the concentrations in which it is normally used as a detergent, suppresses both the chemical reaction and the e.p. lubricating properties of the disulphide.

Both surfactants behave as normal oily boundary lubricants at low temperatures.

CHAPTER EIGHT

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

This thesis has described investigations into several aspects of boundary lubrication. The general approach has been to compare surface reaction with friction properties for a series of simple metal-lubricant combinations. This technique has helped elucidate the way lubrication works in such systems.

The thesis can be divided into three parts, each covering a particular facet of boundary lubrication. In this, concluding chapter, these different aspects are considered in turn. The main conclusions from the experimental work carried out, and possible resulting lines of research in the future, are then summarized.

8.10. Oily Boundary Lubrication. - Experiments with Long Chain Amines (Chapters 2, 3 and 4).

Conclusions

1) The adsorption of long chain amines on stainless steel gives a predominantly reversible, vertically oriented monolayer.

2) At temperatures above 40°C, such reversible amine adsorption obeys the Langmuir adsorption isotherm, at least over the concentration range studied. For low temperatures, lateral interactions between adsorbed molecules, and solvent adsorption effects, cause deviations from this simple model.

3) A comparison of friction and adsorption has shown that, for the long chain amine - stainless steel system, good boundary lubrication can be provided by a physically adsorbed, reversible monolayer.

4) Detailed friction and adsorption tests at a series of temperatures have demonstrated that lubricant failure can result from desorption of the physically adsorbed amine. When adsorption obeys the Langmuir model, lubricant failure occurs at constant amine coverages. Outside the Langmuir range the mode of failure suggests that the important parameter may be the total adsorbed film energy with respect to bare metal.

5) Analysis of high speed scuffing results has shown that a low speed adsorption model may be quite simply extended to cover faster running conditions, taking into account the relation between the contact time and the time for desorption.

Suggestions for future work

There are two directions in which the polar adsorption work of chapters 2 and 3 could be extended.

Firstly it would be of interest to investigate the extent of reversible adsorption on other, more reactive, steels, to see whether such adsorption is as important on these as it is on stainless steel. More detailed work on naturally occurring surfactant fractions, after the manner of Grew and Cameron (15), would also be useful, to discover the extent of physical adsorption for these polar compounds.

Secondly, quantitative adsorption and friction experiments on a much more controlled system than stainless steel would be interesting. If adsorption and lubrication were measured for a crystal surface, as was done by Hutchinson and Rideal (16), a completely reversible system would probably result. Tests at different temperatures would then permit direct calculation of the film energy of the adsorbed phase, and it would be possible to examine a quantitative comparison between total adsorbed film energy and the work done by the applied failure load. Such an approach

has been attempted, in a rudimentary way, by Van Olphen (153) and Rabinowicz (154), but has yet to be applied satisfactorily. This type of analysis was, unfortunately, not feasible using the results in this thesis since full reversibility is needed to calculate adsorbed film energy, and flat surfaces are required to estimate the potential energy expended by the applied load.

8.20. Extreme Pressure Lubrication. - Experiments with Dibenzylidissulphide (chapters 5 and 6).

Conclusions.

1) It has been shown that irreversible chemical adsorption of dibenzylidissulphide on steel begins in the range 60-80°C, with the formation of a monomolecular film of disulphide or mercaptide.

2) Above 110°C, for both mild and stainless steel, a rapid build-up of sulphur-containing film occurs, equivalent to a thickness, in the time of the experiment, of several ferrous sulphide monolayers. This film formation was exponential with temperature.

3) When both stainless and EN31 steel are lubricated with dibenzylidissulphide at high temperatures there is a characteristic friction drop which corresponds to the formation of a very thin (one or two monolayers deep) sulphide film on the metal. Since much of this layer is scraped away during contact, the critical feature of this type of film is the amount forming between metal-metal contact periods. This type of lubrication may be "anti-seizure" (see section (5.25)).

4) It is evident from these results that the sulphide film alone is not providing the observed lubrication. A likely possibility is that further chemical adsorption takes place on the reacted film to give "oily" lubrication.

5) EN31 steel exhibits a friction drop under conditions which correspond to the formation of a monomolecular, chemically adsorbed mercaptide or disulphide layer. This occurs in the range 70°C to 160°C for the system studied and has been tentatively compared to "anti-wear" extreme pressure activity (see section (5.25)).

Suggestions for future work

The extreme pressure work in chapters 5 and 6 demonstrates the value of using both surface chemical and simple lubricating test techniques to study oil additive action. Successful correlation of both provides the initial predictive link in a sequence that must be completed to understand fully a lubricant's activity. The whole chain is: a) surface chemical experiments: b) low speed laboratory rig tests: c) high speed laboratory rig tests: d) high speed test-machine runs: e) engine tests. Recent work by Bailey (100) has also provided a link between b) and c) for extreme pressure activity.

Future work should evidently aim at further correlation between chemical reaction and extreme pressure lubricating ability for more additives. Fortunately there is a suitable phosphorous isotope, P-32 , so that radiotracer reaction experiments can be studied for both sulphur and phosphorus.

An interesting experiment using the radioactive technique of chapter 5 would be abrade the reacting metal surface in solution. This would determine the importance, if any, of nascent metal on the e.p. reaction.

With the ball on triplane apparatus, work at variable low speeds would be useful, to determine the importance of the reaction kinetics on e.p. activity.

8.30 Additive Interference. - Effect of Surfactants on Extreme Pressure Activity. (Chapter 7).

Conclusions

1) The radioactive monitoring technique has proved a useful way of studying additive interference on metal surfaces. Antagonistic effects are more easily and accurately detectable by this method than by using laboratory test rigs.

2) It has been shown that n-octadecylamine shields steel surfaces very successfully from e.p. attack at low temperatures, when the amine has an ordered film. At high temperatures there is a continuing 25% shielding effect but this did not make a significant difference to extreme pressure efficiency in the laboratory test rig used.

3) Neutral calcium sulphonate, in concentrations used commercially prevents the build-up of a sulphur-containing extreme pressure film on steel. This is so marked that the extreme pressure lubricating efficiency is greatly reduced.

4) A comparison of adsorption and interference experiments for octadecylamine suggests that direct screening of the surface is the most likely interference mechanism for this system. With calcium sulphonate the interference may be screening or alternatively a chemical effect at the surface.

Suggestions for future work

Once the metal samples have been prepared, the radioactive test technique described in chapter 5 is extremely quick and straightforward. The approach could easily be extended to assess the interaction of a whole group of additives with a view to eliminating particularly antagonistic

types. The same method could also perhaps be employed to try to develop a detergent with lower antagonism to e.p. agents at high temperatures. The amine results show that such surfactants do exist.

It would be of interest to investigate the adsorption of calcium sulphonate at high temperatures, as has been done for amine (chapter 2). This would indicate whether this additive's interference was steric in nature.

These experiments have all looked at very simple and pure chemical systems. As such they have been easily controllable and provided some conclusive information on lubricating mechanisms. Working on this basis tests can be done on progressively more complex lubricants - white oil then mineral oil solvents, commercial sulphurized organic e.p. additives and finally complicated additive mixtures. It is hoped that the work in this thesis provides a useful foundation for such a development.

APPENDIX A

Solvent Purification

Hexadecane solvent was purchased from Koch Light Laboratories Ltd., and was "puriss". It arrived in brown, sealed bottles but was invariably found to have a pronounced odour when opened. Since hexadecane itself is odourless, this indicated the presence of impurities, most probably oxidation products or unsaturated hydrocarbons. Very pure solvent was essential for the work in this thesis since obviously any surfactant contaminant would have interfered directly with the lubrication and adsorption results being measured. It was thus necessary to purify the hexadecane before use.

Purification technique

The hexadecane was purified by shaking with activated alumina and activated silica gel in a brown glass bottle. The ratio of solid to liquid was approximately 1:2 by volume. It was noticed that after two days of continual shaking, the odour of the contaminated hexadecane had entirely disappeared. The mixture was then left, without shaking, for at least a fortnight before use. When it was required, hexadecane was passed through an activated silica gel column and then pumped through a sintered glass filter to remove solid alumina and silica gel. The glassware used in this filtration procedure had been previously cleaned with concentrated nitric acid and ethyl alcohol to give a hydrophilic surface, then washed with distilled water and dried.

Measurement of hexadecane purity

Experiments were carried out to estimate the purity of both the untreated and purified hexadecane by measuring their surface tensions with

respect to water. The drop volume technique was used, which considers the maximum limiting volume of a drop of liquid which can be suspended on the edge of a capillary (155).

The apparatus, which is shown in fig. (A.1), was similar to that used by Adam (156). It consisted of a U-tube attached at one end to a water manometer, the other end housing a glass capillary which was fed by a micrometer syringe pipette. The U-tube was partially dipped in a water bath at 22°C.

The free end of the capillary had been polished in a small, cylindrical metal jig with successively finer carborundum paper until no edge imperfections were visible under a magnification of x20. Its external diameter was measured, using a travelling microscope, as 5.52 ± 0.01 mm. All the glassware was cleared before use with concentrated nitric acid followed by ethanol, until a hydrophilic surface was obtained.

The purity of the distilled water used in these experiments was of extreme importance since the surface tension between water and hexadecane will reflect the presence of surfactant in the water just as strongly as in hexadecane. To obtain acceptably pure water, singly distilled water was passed through a resin bed and activated charcoal and then distilled from a quartz heating unit. The conductivity of the resulting water was 1.5 μ mho.

In each experiment distilled water and hexadecane were shaken together in 3:1 proportions for 15 minutes and then allowed to separate. Aqueous phase was placed in the bottom of the U-tube (see fig. (A.1)) with 20 to 40 mm depth of hexadecane on top in the open end. The micrometer syringe was also filled with aqueous phase, and the capillary tip dipped ~ 4 mm under the surface of the hexadecane.

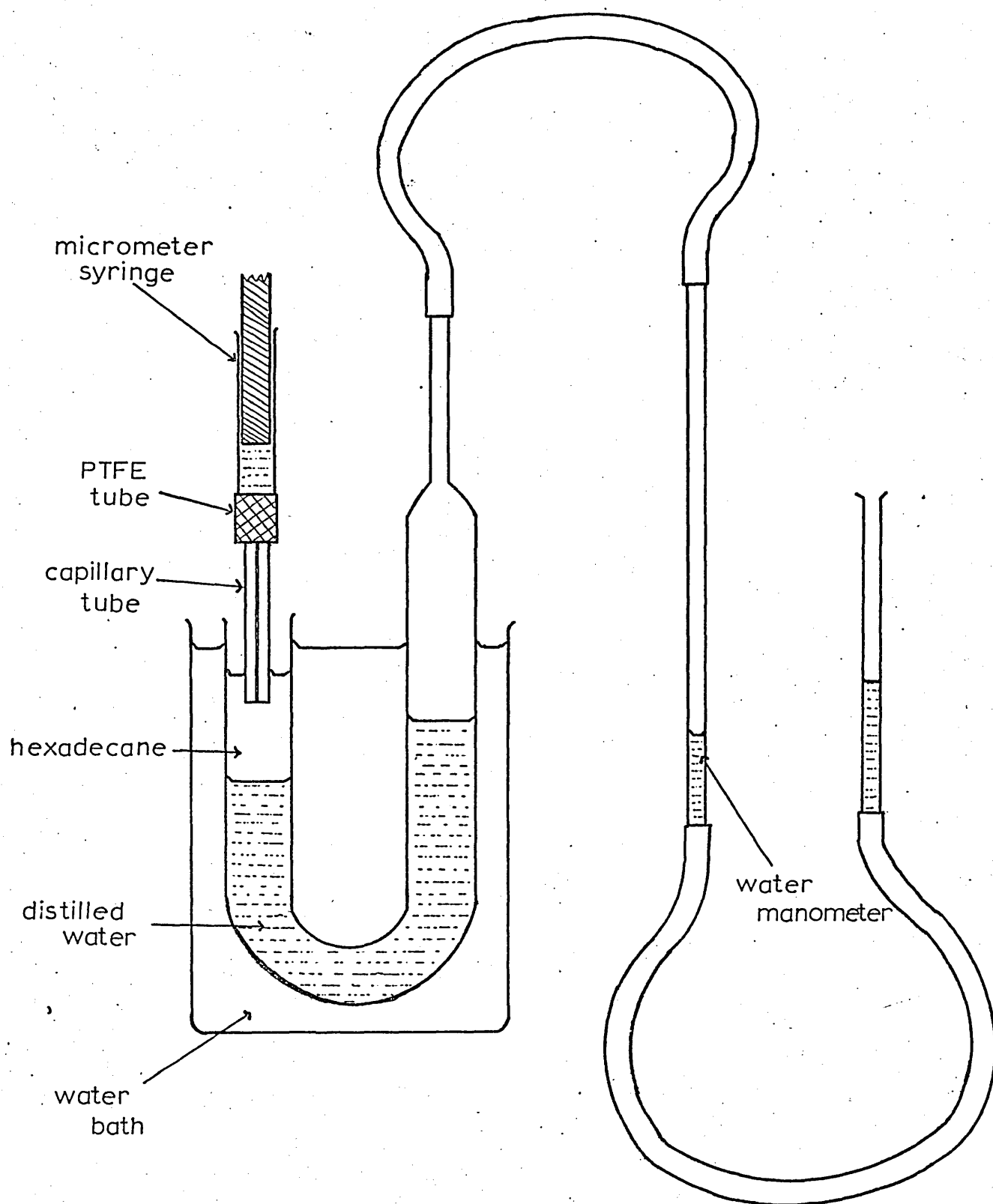


Figure A.1. Drop-volume apparatus for measuring surface tension

After 10 minutes equilibration, a drop of water was formed in the hexadecane and enlarged until it just began to "neck". The drop was then left for 5 minutes and finally its volume was increased until it detached. At this point the scale on the micrometer was measured and the whole drop-forming process repeated. From the difference between the volumes at detachment of each drop, the individual drop-volume could be calculated.

The drop-volumes found were generally so large that only one measurement could be made for each syringe full of water. To refill the syringe and thus obtain more readings, without dismantling the apparatus, the right hand arm of the water manometer was raised. This raised the distilled-water level in the left hand side of the U-tube so that the syringe could be refilled directly.

Surface tension between two phases can be calculated from the equation:

$$\gamma = \frac{F \cdot V \cdot (\rho_1 - \rho_2) \cdot g}{R} \quad \dots\dots\dots A1.$$

γ = surface tension between phases 1 and 2 in mJ/m^2

g = acceleration due to gravity (9804 mm./sec^2)

ρ_1 = density of water (0.998 gm/cm^3 at 22°C)

ρ_2 = density of hexadecane (0.770 gm/cm^3 at 22°C)

R = radius of capillary (2.76 mm.)

V = volume of drop (cm^3)

F = factor dependent on V/R^3

The factor F is an empirical constant given in tables by Harkins and Brown (157).

The experimental results and the calculated surface tension for both purified and non-purified hexadecane are shown in table (A.1). Each volume reading was measured six times to obtain a mean and standard

deviations. The factor F used were taken from ref.(A1).

Table A.1.

Temp = 22°C	Purified Hexadecane	Non-purified Hexadecane
drop-volume $V, \text{ cm}^3$	0.2837	0.2166
standard deviation of V	± 0.0007	± 0.0010
F	0.2348	0.2390
surface Tension, $\gamma, \text{ mJ/m}^2$	53.5 ± 0.1	42.0 ± 0.2

These experimental values can be compared with values obtained in a precise series of experiments by Aveyard and Haydon (158) using extremely pure hexadecane.

20°C	53.77	mJ/m^2
25°C	53.30	mJ/m^2
30°C	52.90	mJ/m^2

It can be seen that the experimental value obtained for purified hexadecane in this thesis was very close (within experimental error) to the literature value. This indicated that the purification procedure to remove surfactant was satisfactory.

A noteworthy feature of these results is the extremely high surface activity of the commercial "puriss" hexadecane. A trial experiment showed that even a 10^{-5} mol/mol solution of octadecylamine in pure hexadecane did not have such a low surface tension with water as the non-purified hexadecane.

This work illustrates the danger in using unpurified hydrocarbon solvent in experiments concerned with surfaces. Throughout this thesis the hexadecane was purified as described in this appendix. Doyle and Ellison (42) have shown that long chain hydrocarbons oxidise quite quickly at room temperature. They noted the reappearance of some surface active properties only 19 hours after an alkane had been purified. For this reason, no solution was used, in the work in this thesis, more than one week after its date of preparation, and care was also taken to store all solutions in a dark cupboard.

APPENDIX B

AMINE-STAINLESS STEEL ADSORPTION RESULTS1. n-Octadecylamine in n-hexadecane on stainless steel at 30°C

Concentration (mol/mol x 10 ⁻⁵)	Adsorption (mol/g x 10 ⁻⁷)	Concentration (mol/mol x 10 ⁻⁵)	Adsorption (mol/g x 10 ⁻⁷)
33.7	2.80	2.69	1.90
28.4	2.60	1.58	1.55
21.2	2.55	0.94	1.35
12.0	2.45	0.88	1.41
10.3	2.45	0.45	1.18
9.05	2.30	0.28	1.07
6.60	2.10	0.19	0.87
2.90	1.65		

2. n-Octadecylamine in n-hexadecane on stainless steel at 50°C

Concentration (mol/mol x 10 ⁻⁵)	Adsorption (mol/g x 10 ⁻⁷)	Concentration (mol/mol x 10 ⁻⁵)	Adsorption (mol/g x 10 ⁻⁷)
45.0	2.15	8.2	1.75
33.0	2.05	6.5	1.65
20.2	2.05	2.02	1.40
19.3	1.90	1.33	1.35
15.3	2.00	0.45	1.15

3. n-Octadecylamine in n-hexadecane on stainless steel at 75°C

Concentration (mol/mol $\times 10^{-5}$)	Adsorption (mol/g $\times 10^{-7}$)	Concentration (mol/mol $\times 10^{-5}$)	Adsorption (mol/g $\times 10^{-7}$)
8.45	1.35	2.12	1.20
4.50	1.28	0.87	1.11
2.49	1.32		

4. n-Octadecylamine in n-hexadecane on stainless steel at 90°C

Concentration (mol/mol $\times 10^{-5}$)	Adsorption (mol/g $\times 10^{-7}$)	Concentration (mol/mol $\times 10^{-5}$)	Adsorption (mol/g $\times 10^{-7}$)
49.0	1.80	9.9	1.30
37.5	1.60	4.50	1.25
29.5	1.52	3.50	1.15
15.3	1.55	2.69	1.05
10.2	1.35	1.96	0.95

5. n-Hexadecylamine in n-hexadecane on stainless steel at 50°C

Concentration (mol/mol $\times 10^{-5}$)	Adsorption (mol/g $\times 10^{-7}$)	Concentration (mol/mol $\times 10^{-5}$)	Adsorption (mol/g $\times 10^{-7}$)
19.5	2.20	4.0	1.80
15.7	2.15	2.2	1.60
11.1	2.10	1.21	1.38
9.4	1.90	0.55	1.21
6.6	1.85		

6. n-Hexadecylamine in n-hexadecane on stainless steel at 75°C

Concentration (mol/mol $\times 10^{-5}$)	Adsorption (mol/mol $\times 10^{-7}$)	Concentration (mol/mol $\times 10^{-5}$)	Adsorption (mol/g $\times 10^{-7}$)
25.0	1.85	5.9	1.60
18.9	1.80	2.7	1.40
16.2	1.75	2.3	1.35
12.6	1.75	1.25	1.10
10.4	1.65	0.82	1.10
9.9	1.65		

APPENDIX C

THE THERMODYNAMICS OF ADSORPTION FROM
SOLUTION ON TO SOLID SURFACES

a) Derivation of Isosteric Heat of Adsorption

For the liquid phase, the chemical potential, μ_1^L , of each component varies with temperature and solution composition (pressure assumed constant). If the solution is dilute and ideal (which it probably is for the amine used in this thesis) then:

$$\begin{aligned} d\mu_1^L &= \left(\frac{\partial \mu_1^L}{\partial T} \right)_{x_1^L} dT + \left(\frac{\partial \mu_1^L}{\partial x_1^L} \right)_T dx_1^L \\ &= -\bar{S}_1^L + \left(\frac{\partial \mu_1^L}{\partial x_1^L} \right)_T dx_1^L \end{aligned} \quad \text{..... A.2.}$$

$-\bar{S}_1^L$ is the partial molar entropy of component 1 in the liquid phase.
 x_1^L is the mol fraction of component 1 in liquid phase.

For the adsorbed phase there is a similar expression but it is slightly more difficult to define the surface concentration. One satisfactory definition is the surface excess, Γ_1 , where:

$$\Gamma_1 = \frac{n_O \Delta x_1^L}{m} = n_1^S x_2^L - n_2^S x_1^L \quad \text{..... A.3.}$$

(the terms of this equation are defined for equation (2.1))
 i.e. the number of moles of one component in a surface sample greater than the number in the bulk sample when both contain the same total number of moles.

Then, assuming that the area of the surface and the pressure are constant, and that the adsorbate is inert,

$$\begin{aligned} d\mu_1^S &= \left(\frac{\partial \mu_1^S}{\partial T} \right)_{\Gamma_1} dT + \left(\frac{\partial \mu_1^S}{\partial \Gamma_1} \right)_T d\Gamma_1 \\ &= -\bar{S}_1^S + \left(\frac{\partial \mu_1^S}{\partial \Gamma_1} \right)_T d\Gamma_1 \end{aligned} \quad \text{..... A.4.}$$

$-\bar{S}_1^S$ is the partial molar entropy of component 1 in the adsorbed phase.

At equilibrium,

$$d\mu_1^S = d\mu_1^L$$

so that, from equations A2 and A4,

$$-\bar{S}_1^L + \left(\frac{\partial \mu_1^L}{\partial x_1^L} \right)_T dx_1^L = -\bar{S}_1^S + \left(\frac{\partial \mu_1^S}{\partial \Gamma_1} \right)_T d\Gamma_1$$

For isosteric conditions, i.e. at constant Γ_1 ,

$$\left(\frac{\partial \mu_1^L}{\partial x_1^L} \right)_{T, \Gamma_1} = -(\bar{S}_1^S - \bar{S}_1^L) \quad \text{..... A.5.}$$

In solution at constant temperature:

$$d\mu_1 = RT \ln a_1$$

(a_1 = activity of component 1 in solution.)

Then, assuming an ideal solution and unit mole fraction as the standard state,

$$\begin{aligned} d\mu_1 &= RT \ln x_1 \\ &= RT \frac{dx_1}{x_1} \end{aligned} \quad \text{..... A.6.}$$

Substituting equation A5 in equation A6 gives:

$$\left(\frac{RT}{x_1} \right) dx_1 = -(\bar{S}_1^S - \bar{S}_1^L) dT$$

or

$$\left(\frac{\partial \ln x_1}{\partial T} \right) \bigg|_1 = - \frac{(\bar{S}_1^S - \bar{S}_1^L)}{RT}$$

The enthalpy of adsorption at equilibrium for one component can be given by:

$$-\Delta \bar{H}_{\text{ads.}} = -(\bar{H}_1^S - \bar{H}_2^L) = -T(\bar{S}_1^S - \bar{S}_1^L)$$

thus

$$\frac{-\Delta \bar{H}_{1 \text{ ads.}}}{RT^2} = \left(\frac{\partial \ln x_1}{\partial T} \right) \bigg|_1$$

or

$$\frac{-\Delta \bar{H}_{1 \text{ ads.}}}{R} = \left(\frac{\partial \ln x_1}{\partial (1/T)} \right) \bigg|_1$$

$\Delta \bar{H}_{1 \text{ ads.}}$ is the equilibrium or differential enthalpy of adsorption of one mole of component 1 from unit mole fraction solution of component 1 under "ideal dilute" conditions, at constant pressure. As measured it represents the difference between enthalpy of adsorption of component 1 and component 2.

The isosteric heat of adsorption " q_{st} " is often used. Since the system is at constant pressure,

$$q_{\text{st}} = -\Delta \bar{H}_{1 \text{ ads.}}$$

b) Application of Model Isotherms to Adsorption Data.

The normal way of calculating the standard free energy of adsorption in a two component system is via the equilibrium constant K . From this we have the relationship:

$$\Delta G^{\circ} = -RT \ln K$$

K can be found by equating the chemical potentials of each component in the two phases,

$$\mu_i^L = \mu_i^S$$

and suitably defining standard states of both the liquid and adsorbed phases.

This gives an equation of the type (ref. 53):

$$\ln K = - \bar{A}_2^* \int_{a_2^L=1}^{a_2^L=0} \left(\frac{n_o \Delta x_1^L}{mx_1^L} \right) d \ln a_2^L$$

a_2^L = activity of component 2 in liquid phase

$\bar{A}_2^*$ = partial molar area of component 2 in adsorbed phase

so that K can be determined by integration over the adsorption isotherm.

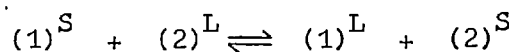
This sort of formula is difficult to apply, however, unless data are available over the whole range of concentration.

A simpler technique is to assume a model of adsorption which gives a functional relationship between concentration, adsorption and equilibrium constant, and which can be expected to apply reasonably well to the system being studied. Everett has described two such models, one applying to perfect adsorption systems with two components both having nearly the same sized molecules, and the second taking into account regular solutions, differences between solute and solvent molecular size, and, briefly, surface heterogeneity (57) (159).

In analysing the adsorption results of chapter 2, it was decided to use Everett's simple model, which would suffice to give a rough approximation of the free energy of adsorption.

For a perfect, two-component adsorption system with both components having the same size we have the equilibrium between surface and solution

as:



The equilibrium constant for this can be written as:

$$K = \frac{x_1^S \cdot x_2^L}{x_1^L \cdot x_2^S} \quad \dots\dots\dots \text{A.7.}$$

where $x_i^\alpha = \frac{n_i^\alpha}{n^\alpha}$ = mol fraction of component i

in phase α .

Since $x_1^\alpha = (1-x_2^\alpha)$, equation (A7) can be represented as:

$$\frac{x_1^S}{x_1^L} = \frac{K}{1+(K-1)x_1^L} \quad \dots\dots\dots \text{A.8.}$$

From equation (A3), the surface excess Γ_1 can be expressed:

$$\Gamma_1 = \frac{n_o \Delta x_1^L}{m} = n_1^S x_2^L - n_2^S x_1^L$$

or alternatively,

$$\frac{n_o \Delta x_1^L}{m} = n^S (x_1^S - x_1^L) \quad \dots\dots\dots \text{A.9.}$$

Equations (A8) and (A9) give:

$$\frac{x_1^L x_2^L}{(n_o \Delta x_1^L / m)} = \frac{1}{n^S} (x_1^L + 1/(K-1)) \quad \dots\dots\dots \text{A.10}$$

which simplifies for very dilute solutions to:

$$\frac{x_1^L}{(n_o \Delta x_1^L / m)} = \frac{x_1^L}{n^S} + \frac{1}{n^S (K-1)}$$

This is the expression used in chapter 2 to calculate K and n^S .

A similar formula can be obtained directly from the Langmuir isotherm. This is hardly surprising since both Everett's perfect model and Langmuir's model make similar starting assumptions. The Langmuir model presupposes a two-component system. (originally gas and adsorbing solid, but also solute and adsorbing solid with an inert solvent, or solute and solvent with an inert adsorbate). With the assumptions;

- a) The energy of adsorption of each molecule is the same irrespective of coverage.
- b) The number of adsorption sites is fixed and all are occupied by one of the two components. (If one of the two components is the solid this means, in effect, an empty site).

then a formula of the type;

$$\frac{\theta_1}{a_1(1 - \theta_1)} = K \quad \text{..... A.11.}$$

θ_1 = fraction of sites covered by component 1

a_1 = activity of component 1 in solution

K = equilibrium constant

can be obtained either by statistical mechanics or by kinetic models. (The form of equation (A.11) is dictated by the two assumptions. Thus a constant energy of adsorption implies a constant value of K and a fixed number of sites divided between two components provides the $\theta/(1-\theta)$ expression).

For the case of an ideal dilute solution adsorbing on an inert solid this can be modified to;

$$\frac{N_1/N_S}{C_1(1-N_1/N_S)} = K$$

N_1 = no. of sites occupied by component 1.

N_S = total no. of sites available (N_1+N_2)

C_1 = concentration of component 1 in solution.

Which can be rearranged to give an expression of the same form as

Everett's equation,

$$\frac{C_1}{N_1} = \frac{1}{N_S K} + \frac{C_1}{N_S}$$

A recent and thorough treatment of the various methods of calculating K for more sophisticated systems is to be found in reference (53).

REFERENCES

REFERENCES

1. Herschel, J.F.W.
 "Light"
 Enc. Metropolitana Vol IV (1845) sect. 557
2. Reynolds, O.
 "On the Theory of lubrication and its Application to Mr. Beauchamp
 Tower's Experiments including an Experimental Determination of the
 Viscosity of Olive Oil."
 Phil. Trans. 177 (1886) p157.
3. Grubin, A.N.
 "Contact Stresses in Toothed Gears and Worm Gears" (in Russian)
 Cent. Sci. Res. Inst. for Tech. and Mech. Eng. (Moscow 1949)
 Book no.30 D.S.I.R. Trans. no.337.
4. Greenhill, E.P.
 "The Lubrication of Metals by Compounds containing Sulphur".
 J. Inst. Pet. 34 (1948) p659
5. Rowe, C.N., Fein, R.S. and Kreuz, K.L.
 Relationship Between Lubricant Oxidation and Wear.
 Part I. Friction and Wear Reduction by Fatty Acid Lubricants".
 A.C.S. Petrol Div. Chem. of Friction and Wear symposium Sept. (1958).
6. Lockhart, L.
 "Iranian Petroleum in Ancient and Modern Times".
 J. Inst. Pet. 25 (1939) p1.
7. Little Brit. Patent 12,571 (1849)
 Information taken from ref.(8).
8. Smalheer, C.V. and Kennedy Smith, R.
 "Lubricant Additives"
 Lezius-Hiles Co. Cleveland Ohio (1967).

9. Fowkes, F.M., Schick, M.J. and Bondi, A.
 "Oil-Soluble Surface-Active Copolymers of Alkenes and Polar Monomers."
 J. Coll. Sci. 15 (1960) p531.
10. Lorensen, L.E. and Hewett, W.A.
 "Pour Point Depression II Structure vs. Activity".
 ACS Petrol. Div. Preprints 7 No.4 (1962) p71.
11. Rowe, G.W.
 "The Chemistry of Tribology".
 R.I.C. Reviews 1 (1968) p135
12. Rudston, S.G. and Whitby, R.D.
 "The Effect of Model Lubricating Oil Constituents on the Wear of Steel."
 J. Inst. Pet. 57 (1971) p189
13. Hardy, Sir William
 "Problems of the Boundary State".
 Phil. Trans. Roy. Soc. A230 (1931) p1.
14. Frewing, J.J.
 "The Heat of Adsorption of Long Chain Compounds and their Effect
 on Boundary Lubrication."
 Proc. Roy. Soc. L. A 282 (1944) p270.
15. Grew, W.J.S. and Cameron, A.
 "The Thermodynamics of Boundary Lubrication and Scuffing"
 Proc. Roy. Soc. L. (To be Published).
16. Hutchinson E. and Rideal, E.K.
 "Adsorption and Lubrication at Crystal Surfaces"
 Trans. Farad. Soc. 43 (1947) p435.
17. Freundlich, H.
 "Colloid and capillary chemistry".
 Methuen. London (1926).

18. Bowden, F.P. and Tabor, D.
"The Friction and Lubrication of Solids".
Clarendon Press. Oxford (1950).
19. Smith, H.A. and McGill, R.M.
"The Adsorption of n-Nonadecanoic Acid on Mechanically Activated
Metal Surfaces".
J. Phys. Chem. 61 (1957) p1025.
20. Smith, H.A. and Allen, K.A.
"The Adsorption of n-Nonadecanoic Acid on Metal Surfaces".
J. Phys. Chem. 58 (1954) p449.
21. Groszek, A.J.
"Heats of Preferential Adsorption of Boundary Additives at Iron
Oxide/Liquid Hydrocarbon Interfaces".
A.S.L.E. trans. 13. (1970) p278.
22. Greenhill, E.B.
"The Adsorption of Long Chain Polar Compounds from Solutions on
Metal Surfaces."
Trans. Farad. Soc. 45 (1949) p625.
23. Bigelow, W.C., Pickett, D.L. and Zisman, W.A.
"Oleophobic Monolayers. I. Films adsorbed from Solution in Non-Polar
Liquids".
J. Coll. Sci. 1 (1946) p513.
24. Bewig, K.W. and Zisman, W.A.
"Investigation of Solution Adsorption on Platinum of Pure and Mixed
Films of Fatty Amines by Contact Potentials".
J. Phys. Chem. 68 (1964) p1804.
25. Smith, H.A. and Fusak, J.F.
"The Adsorption of Fatty Acids on Nickel and Platinum Catalysts"
J. Am. Chem. Soc. 68 (1946) p229.

26. Roberts, R.W., McElligott, P.E. and St. Pierre, L.E.
 "Effect of Adsorbed Olefines on the Oxidation of Aluminium Film".
 Nature 206 (1965) p710.
27. Dawihl, A. and Doerne, E.
 "Adsorption Reaction on the Surface of Powders, Sintered Metals
 and Oxides".
 Powder Met. Int. 1 (1969) p11.
28. Bernett, M.K. and Zisman, W.A.
 "Effect of Adsorbed Water on the Critical Surface Tension of
 Wetting on Metal Surfaces.
 J. Coll. and Inter. Sci. 28 (1968) p243.
29. Bascom, W.D.
 "The Wettability of n-Octadecylamine, n-Octadecyl Alcohol and
 and n-Octadecanoic Acid Films Adsorbed on Thermally Treated Metal
 Oxide Surfaces".
 J. Coll. and Inter Sci. 26 (1968) p89.
30. Davidson, E. and Kipling, J.J.
 from reference (48) p119.
31. Harding, R.D.
 "Studies in the Surface Chemistry of Boundary Lubrication".
 Ph.D. Thesis. University of London (1968).
32. Daniel, S.G.
 "The Adsorption on Metal Surfaces of Long Chain Polar Compounds
 from Hydrocarbon Solutions".
 Trans. Farad. Soc. 47 (1951) p1345.
33. Deryagin, B.V., Karasev, V.V., Zalchavaeva, N.N. and Lazarev V.P.
 "Short and Long Range Action in the Theory of Boundary Lubrication".
 Wear 1 (1957) p277.

34. Gaines, G.L. Jr.
Some Observations on Monolayers of Carbon-14 Labelled Stearic Acid".
J. Coll. Sci. 15 (1960) p321.
35. Allen, C.M. and Draughlis, E.
"Boundary Layer Lubrication : Monolayer or Multilayer?".
Wear 14 (1969) p363.
36. Sherwood, A.F. and Rybicka, S.M.
"Surface Properties of Titanium Dioxide Pigments".
J. Oil Col. Chem. Assoc. 49 (1966) p648.
37. Smith, A.J.
"The Thinning of Liquid Films on Metal Surfaces".
Ph.D. Thesis. University of London (1971).
38. Bowden, F.P. and Moore, A.C.
"Physical and Chemical Adsorption of Long Chain Compounds on
Radioactive Metals".
Trans. Farad. Soc., 47 (1951) p900.
39. Hirst, W. and Lancaster, J.K.
"Effect of Water on the Interaction between Stearic Acid and Fine
Powders".
Trans. Farad. Soc. 47 (1951) p315.
40. Cook, E.L. and Hackermann, N.
"Adsorption of Polar Organic Molecules on Steel".
J. Phys. Chem. 55 (1951) p549.
41. Walker, D.C. and Ries, H.E.
"Direct Measurement of Adsorption of Radiostearic Acid onto
Vapour Deposited Metal Films."
Adv. Chem. Ser. 43 (1964) p295.

42. Doyle, W.P. and Ellison, A.H.
 "Co-adsorption of n-Octadecane and Stearic Acid on Metal Surfaces".
 Adv. Chem. Ser. 43 (1964) p268.
43. Block, A. and Simms, B.B.
 "Desorption and Exchange of Adsorbed Octadecylamine and Stearic Acid
 on Steel and Glass".
 J. Coll. and Inter. Sci. 25 (1967) p514.
44. Haydon, D.A.
 "Boundary Potentials and Adsorption at the Metal-Oil Interface".
 Koll. Zeit. 188 (1963) p141.
45. Timmons, C.O., Patterson, R.L. and Lockhard, L.B.
 "The Adsorption of C-14 Labelled Stearic Acid on Iron".
 J. Coll. and Inter. Sci. 26 (1968) p120.
46. Cook, H.D. and Ries, H.E. Jr.
 "Adsorption of Radiostearic Acid and Radiostearyl Alcohol from
 n-Hexadecane on to Solid Surfaces". J. Phys. Chem. 63 (1959) p226.
47. Sakurai, T. and Baba, T.
 "Surface Chemical Behaviour of Polar Compounds in Non-Aqueous Liquids.
 Dispersing Effect of Soap Solutions".
 Wear 3 (1960) p286.
48. Kipling, J.J.
 "Adsorption from Solution of Non-Electrolytes".
 Academic Press. N.Y. (1965).
49. Pearce, A.S. and Streatfield, E.L.
 "Determination of Amines in Water".
 Analyt. Abs. 12 (1965) No. 6766.
50. Baumann, R.P.
 "Adsorption Spectroscopy".
 Wiley (1967).

51. Everett, D.H.
 "Thermodynamics of Adsorption. Part II. Thermodynamics of Monolayers on Solids".
 Trans. Farad. Soc. 66 (1950) p942.
52. Bigelow, W.C., Glass, E., and Zisman, W.A.
 "Oleophobic Monolayers. II. Temperature Effects and Energy of Adsorption."
 J. Coll. Sci. 2 (1947) p563.
53. Tideswell, M.W.
 "Calorimetric Studies of the Graphon/Alkane Interface".
 Ph.D. Thesis University of Nottingham (1971).
54. Isirikyen, A.A. and Kiselev, A.V.
 "Adsorption Isotherms of Nitrogen, Benzene and n-Hexane and the Heats of Adsorption of Benzene and n-Hexane on Graphitized Carbon Blacks".
 J. Phys. Chem. 65 (1961) p601.
55. Madden, P.J. and Marsh, J.D.F.
 "The Determination of Surface Area from Krypton Adsorption Isotherms".
 J. Phys. Chem. 63 (1959) p1309.
56. Salem, L.
 "Attractive Forces between Long Saturated Chains at Short Distances."
 J. Chem. Phys. 37 (1962) p2100.
57. Everett, D.H.
 "Thermodynamics of Adsorption from Solution Part I. - Perfect Systems".
 Trans. Farad. Soc. 60 (1964) p1803.
58. Kitchener, J.A.
 "Mechanism of Adsorption from Aqueous Solutions. Some Basic Problems".
 J. of Photo. Sci. 13 (1965) p152.

59. Fox, H.W.
"Force-Area and Potential-Area Relations of Monolayers of Terminally Fluorinated Octadecylamine and Octadecanoic Acid".
J. Phys. Chem. 61 (1957) p1058.
60. Bornong, B.J. and Martin, P. Jr.
"Adsorption of Polar Organic Molecules on Chromium".
J. Phys. Chem. 71 (1967) p2731.
61. Brockway, L.O. and Karle, J.
"Electron Diffraction Study of Oleophobic Films on Copper, Iron and Aluminium."
J. Coll. Sci. 2 (1947) p227.
62. Bigelow, W.C. and Brockway, L.O.
"Variation of Contact Angle and Structure with Molecular Length and Surface Density of Adsorbed Films of Fatty Acids".
J. Coll. Sci. 11 (1956) p60.
63. Epstein, H.J.
"On the Structure of Monolayers and Multilayers of Polar Hydrocarbon Molecules on Solid Substrates."
J. Phys. and Coll. Chem. 54 (1950) p1053.
64. Hardy, Sir William
"Collected Scientific Papers".
Cambridge Univ. Press (1936).
65. Gregory, J.N. and Spink, J.A.
"Lubricating Properties of Molecular Layers of Stearic Acid and Calcium Stearate on Metal Surfaces".
Nature 159 (1947) p403.
66. Greenhill, E.B.
"The Lubrication of Metal Surfaces by Mono- and Multi-Molecular Layers".
Trans. Farad. Soc. 45 (1949) p631.

67. Levine, O. and Zisman, W.A.
 "Physical Properties of Monolayers Adsorbed at the Solid Interface.
 I Wettability of Aliphatic Polar Compounds and Effect of Halogenation."
 J. Phys. Chem. 61 (1957) p1068.
68. Hardy, Sir William and Nottage, M.
 "Adsorption. A Study in Availability and Accessibility."
 Proc. Roy. Soc. L. A 138 (1932) p259.
69. Fuks, G.I.
 "The Polymolecular Component of the Lubricating Boundary Layer".
 Research in Surfaces Forces Vol.2.
 ed. B.V. Deryagin. Consult. Bur. N.Y. (1966).
70. Akhmatov, A.S.
 "Molecular Physics of Boundary Friction".
 Israel. Prog. for Sci. Trans. Jerusalem (1966).
71. Desvaux, H.
 "Le Frottement des Solides: Epaisseur Minimum d'un Enduit
 Lubrifiant." (in French).
 J. de Phys. et la Radium. 5 (1924) p845.
72. Frewing, J.J.
 "The Influence of Temperature on Boundary Lubrication".
 Proc. Roy. Soc. L. A 281 (1942) p23.
73. Gregory, J.N.
 C.S.I.R. (Australia) Tribophysics Div. Report. (1943) A74.
 Information taken from reference (18) p183.
74. Blodgett, K.R.
 "Films Built by Depositing Successive Molecular Layers on a Solid
 Surface".
 J. A. C.S. 57 (1935) p1007.

75. Bailey, A. and Courtenay Pratt, J.S.
 "The Area of Real Contact and the Shear Strength of Monomolecular Layers of a Boundary Lubricant".
 Proc. Roy. Soc. L. A 227 (1955) p500.
 76. Bowden, F.P. and Leben, L.
 "The Friction of Lubricated Metals".
 Trans. Roy. Soc. (London) A 239 (1940) p1.
 77. Rabinowicz, E. and Tabor, D.
 "Metallic Transfer between Sliding Metals. An Autoradiographic Study".
 Proc. Roy. Soc. L. A 208 (1951) p435.
 78. Wilson, R.W.
 "The Contact Resistance and Mechanical Properties of Surface Films on Metals".
 Proc. Phys. Soc. B 68 (1955) p625.
 79. Boyd, J. and Robertson, B.P.
 "The Friction Properties of Various Lubricants at High Pressures".
 ASME trans. 67 (1945) p51.
 80. Tabor, D.
 "Effect of Temperature on Lubricant Films". (letter).
 Nature 145 (1940) p308.
 81. Askwith, T.C., Cameron, A. and Crouch, R.F.
 "Chain Length of Additives in Relation to Lubricants in Thin Film and Boundary Lubrication".
 Proc. Roy. Soc. L. A 291 (1966) p500.
- also (with details necessary for chapter 4)
 "Gear Lubrication".
 Elsevier. Inst. Pet. (1966) II 16.

82. Groszek, A.J. and Palmer, D.J.
"Surface-Active Compounds in Lubricating Oils".
J. Inst. Pet. 47 (1961) p295.
83. Cowley, C.W., Utle, C.J. and West, C.W.
"Influence of Temperature on Boundary Lubrication".
ASLE trans. 1 (1958) p381.
84. Sharma, J.P.
Private communication.
85. Shafrin, E.G. and Zisman, W.A.
"Constitutive Relations in the Wetting of Low Energy Surfaces and
the Theory of the Retractive Method of Preparing Monolayers".
J. Phys. Chem. 64 (1960) p519.
86. Sakurai, T. and Baba, T.
"Surface Chemical Behaviour of Polar-Compounds in Non-aqueous
Solution. 1st Report. Temperature Effect on Adsorption and Adsorption
Energy". (In Japanese).
J. Jap. Petr. Inst. 1 (1958) p33.
87. Institute of Mechanical Engineers.
Memorandum on Definitions, Symbols and Units.
I.Mech.E. London.
88. Matveevsky, R.M.
"The Effect of Load on the Critical Temperature of Oil in the
Lubrication of Different Metals".
Wear 4 (1961) p292.
89. Bowden, F.P. and Leben, L.
"The Nature of Sliding and the Analysis of Friction".
Proc. Roy. Soc. L. A 169 (1939) p371.

90. Grew, W.J.S.
 "Transition Temperatures of Lubricants".
 Ph.D. Thesis. University of London (1969).
91. Bristow, J.R.
 "Kinetic Boundary Friction".
 Proc. Roy. Soc. L. A 189 (1947) p88.
92. Albertson, C. and Wolfram, G.
 "Effect of Boundary Lubricants on the Friction of Cast Iron".
 Lubrication Eng. 25 (1969) p469.
93. Ries, H.E. and Gabor, J.
 "Chain Length Compatibility in Rust Prevention".
 Chem. and Ind. 66 (1967) p1561.
94. Booij, B. and Bungenberg de Jong, N.G.
 "Researches in Plant Growth Regulators - XV the Influence of Fatty
 Acids on Soap Coacervates".
 Bioch. et. Bioph. Acta. 3 (1949) p242.
95. Blakey, B.C. and Lawrence, A.S.C.
 "The Surface and Interfacial Viscosity of Soap Solutions".
 Disc. of the Farad. Soc. 18 (1954) p268.
96. Blok, H.
 "Theoretical Study of Temperature Rise at Surfaces of Actual Contact
 under Oiliness Lubricating Conditions".
 I.Mech.E. Gen. Disc. on Lubrication vol 2 (1937) p222.
97. Woolman, J. and Mottram, R.A.
 "Mechanical and Physical Properties of the British Standard E.N.
 Steels. Vols II."
 Pergamon (1966) p288.

98. Jaeger, J.C.
 "Moving Sources of Heat and the Temperature at Sliding Contacts".
 J. Proc. Roy. Soc. N.S.W. 76 (1942) p203.
99. Francis, H.A.
 "Interfacial Temperature Distribution Within a Sliding Hertzian Contact".
 A.S.L.E. trans. 14 (1971) p41.
100. Bailey, M.W.
 "Critical Conditions in the Lubricated Sliding of Metals".
 Ph.D. Thesis. University of London (1971).
101. Blok, H.
 Private communication.
102. Borsoff, V.N. and Godet, M.R.
 "A Scoring Factor for Gears".
 A.S.L.E. trans 6 (1963) p147.
103. Niemann, G. and Lechner, G.
 "Die Fress-Grenzlast bei Stirnrädern aus Stahl". (in German).
 Erdöl u. Kohle, Erdgas, Petr. 20 (1967) p96.
104. Ku, M.
 (discussion section of reference (105) p91).
105. Borsoff, V.N.
 "On the Mechanism of Gear Lubrication".
 J. Basic Eng. 80D (1959) p79.
106. Blok, H.
 "Measurement of Temperature Flashes in Gear Teeth under Extreme Pressure conditions".
 I.Mech.E. Gen. Disc. on Lubrication vol2 (1937) p14.
107. Lane, T.B. and Hughes, J.R.
 "A Practical Application of the Flash Temperature Hypothesis to Gear Lubrication".

- Proc. 3rd World Petr. Cong. Sect. 7 (1951) p320.
108. Hughes, J.R. and Waight, F.H.
 "The Lubrication of Spur Gears".
 I.Mech.E. Intern. Conf. on Gearing (1958) p135.
 109. de Boer, J.H.
 "The Dynamical Character of Adsorption".
 Clarendon Press. Oxford (1953).
 110. Spink, J.A.
 "Thermal Desorption of Stearic Acid Monolayers from Mica and Silver".
 J. Coll. Inter. Sci. 24 (1967) p61.
 110. Kelley, B.W.
 "A New Look at the Scoring Phenomena of Gears".
 S.A.E. trans. 61 (1953) p175.
 112. Brown, R.R. U.S. Patent 22,621 (1859).
 Information taken from: Musgrave, F.F. J. Inst. Pet. 32 (1946) p32.
 113. Forbes, E.S.
 "Anti-wear and Extreme Pressure Additives for Lubricants".
 Tribology 3 (1970) p145.
 114. Ford, J.F.
 "Lubricating Oil Additives - A Chemist's Eye View".
 J. Inst. Pet. 54 (1958) p198.
 115. Manteuffel, A.A., Yates, K.P., Bickford, H.J. and Wolfram, G.
 "Radiotracers Reveal Activity of Extreme-Pressure Additives in
 Lubrication".
 A.S.L.E. trans. 7 (1964) p249.
 116. Sakurai, T., Okabe, H., and Takahashi, Y.
 "A Kinetic Study of the Reaction of Labelled Sulphur Compounds
 in Binary Additive Systems During Boundary Lubrication".
 A.S.L.E. trans. 10 (1967) p91.

117. Campbell, R.B.
"Study of Hypoid-Gear Lubrication using Radioactive Tracers".
I.Mech.E. Lubrication and Wear Conv. (1963) p286.
118. Allum, K.G. and Forbes, E.S.
"The Load-Carrying Mechanism of Organic Sulphur Compounds. -
Application of Electron Probe Microanalysis".
A.S.L.E. trans. 11 (1968) p162.
119. Godfrey, D
"Chemical Changes in Steel Surfaces during Extreme Pressure
Lubrication".
A.S.L.E. trans. 5 (1962). p57.
120. Sakurai, T., Sato, K., and Ishida, K.
"Reaction between Sulphur Compounds and Metal Surfaces at High
Temperatures".
Bull. Jap. Petr. Inst. 6 (1964) p40.
121. Matveevsky, R.M.
"The Temperature of Tribochemical Reaction between E.P. Additives
and Metals".
Tribology 4 (1971) p97.
122. Prutton, C.F., Turnbull, D. and Dlouhy, G.
"Mechanism of Action of Organic Chlorine and Sulphur Compounds in
Extreme Pressure Lubrication".
J. Inst. Pet. 32 (1946) p90.
123. Allum, K.G and Ford, J.F.
"The Influence of Chemical Structure on the Load-carrying Properties
of Certain Organo-Sulphur Compounds".
J. Inst. Pet. 51 (1965) p145.

124. Forbes, E.S., Allum, K.G., Neustadter, E.L. and Reid, A.J.D.
"The Load Carrying Properties of Diester Disulphides".
Wear 15 (1970) p341.
125. Bowden, F.P. and Tabor, D.
"Area of Contact between Stationary and Moving Surfaces".
Proc. Roy. Soc. L. A 169 (1939) p391.
126. Elliot, J.S., Hitchcock, N.E.F., and Edwards, E.D.
"Hypoid Gear Lubricants and Additives".
J. Inst. Pet. 45 (1959) p219.
127. Borsoff, V.N. and Wagner, C.D.
"Studies of Formation and Behaviour of an Extreme Pressure Film".
Lub. Eng. 13 (1957) p91.
128. Loeser, E.H., Wiquist, R.C. and Twiss, S.B.
"Cam and Tappet Lubrication IV - Radioactive Study of Sulphur in the E.P. Film".
A.S.L.E. trans. 2 (1959) p199.
129. Barcroft, F.T.
"A Technique for Investigating Reaction between E.P. Additives and Metal Surfaces at High Temperatures".
Wear 3 (1960) p440.
130. Dorinson, A. and Broman, V.A.
"Extreme Pressure Lubrication and Wear - The Chemical Reactivity and Extreme Pressure Action of Two Aliphatic Disulphides".
A.S.L.E. trans. 5 (1962) p75.
131. Llopis, J., Gamboa, J.M., Arizmendi, L. and Gomez Minana, J.A.
"Surface Reaction of Iron with Hydrocarbon Solutions of Organic Sulphides".
Corrosion Sci. 4 (1964) p27.

132. Arizmendi, L. and Martinez-Vilche, V.
"Surface Reaction of Nickel with Sulphur Solutions".
Corrosion Sci. 7 (1967) p621.
133. Arizmendi, L. and Martinez-Vilche, V.
"Surface Reactions of Ni with Organic S-Compounds".
Corrosion Sci. 10 (1970) p595.
134. Barcroft, F.T. and Daniel, S.G.
"Extreme Pressure Film Formation on Hypoid Gears - Studied with Sulphur - 35."
I.Mech.E. Lub. and Wear Conv. (1965) p265.
135. Davey, W. and Edwards, E.D.
"The Extreme Pressure Properties of some Sulphides and Disulphides in Mineral Oils, as assessed by the 4-Ball Machine".
Wear 1 (1957) p291.
136. Allum, K.G. and Forbes, E.S.
"The Load Carrying Properties of Organic Sulphur Compounds. Part II. The Influence of Chemical Structure on the Anti-wear Properties of Organic Disulphides".
J. Inst. Pet. 53 (1967) p173.
- , 137. Titz, I.N., Levina, S.Ya., Leonova, A.I. and Karaseva, E.A.
"Synthesis and Catalytic Conversion of Sulphur - Containing Fatty Compounds in Contact with Alumino-Silicate Catalysts". (In Russian).
Zhur. Obshch. Khim. 21 (1951) p242.
138. Baladin, A.A., Kukina, A.I. and Malakhova, E.A.
"Catalytic Decomposition of Dibutylsulphide on α -Iron".
Zhur. Fiz. Khim. 34 (1960) p2030.
139. Sykes, P.
"A Guidebook to Mechanisms in Organic Chemistry".
Longmans (1961).

140. Sakurai, T., Ikeda, S., and Okabe, H.
 "The Mechanism of Reaction of Sulphur Compounds with Steel Surfaces during Boundary Lubrication using S-35 as a Tracer."
 A.S.L.E. trans. 5 (1962) p67.
141. Sakurai, T., Ikeda, S., and Okabe, H.
 "A Kinetic Study on the Reaction of Labelled Sulphur Compounds with Steel Surfaces during Boundary Lubrication".
 A.S.L.E. trans 8 (1965) p39.
142. Gomberg, H.J.
 "A New High Resolution System of Autoradiography".
 Nucleonics 9 (1951) Oct. p28.
143. O'Connor, T.L. and Uhlig, H.H.
 "Absolute Areas of some Metallic Surfaces".
 J. Phys. Chem. 61 (1957) p402.
144. Francis, H.A. and Presland, A.E.B.
 "A Four-ball Machine with Three Wear Tracks."
 J. Physics E (1968) ser. 2. 1 p1234.
145. Smalheer, C.V. and Mastin, T.V.
 "Lubricant Additives and their Action".
 J. Inst. Pet. 42 (1956) p337.
146. Okrent, E.H.
 "The Effect of Lubricant Viscosity and Composition on Engine Friction and Bearing Wear. II".
 ASLE trans. 4 (1961) p257.
147. Studt, P.
 "Zusammenhang zwischen Adsorbierbarkeit und Wirksamkeit von Hochdruckzätzen in Schmierölen" (in German).
 Erdöl u Kohle, Erdgas, Petr. 21 (1968) p784.

148. Rounds, F.G.
 "Effects of Additives on the Friction of Steel on Steel. II.
 Additive-Base Oil Interactions".
 ASLE trans. 8 (1965) p21.
149. Clayfield, E.J., Matthews, J.B. and Whittam, T.V.
 "The Importance of Oil-Metal Adhesion in Lubrication".
 I.Mech.E. Proc. Conf. Lub. and Wear (1957) p326.
150. Sprague, S.R. and Cunningham, R.G.
 "Chemical Additives Control; Frictional Characteristics of Lubrication".
 Ind. Eng. Chem. 51 (1959) p1047.
151. Ratnasamy, P. and Fripiat, J.J.
 "I.R. Study of GeS_2 and MoS_2 and Reaction of H_2 , H_2O , Thiophene and
 Ethanethiol".
 Trans. Farad. Soc. 66 (1970) p2897.
152. Whyte, R.B.
 "Laboratory and Field Evaluations of SAE 75 Grade Gear Oils".
 Inst. Petr. Conf. on Gears, Brighton (1964) pIII. 38.
153. Van Olphen, H.
 "Clay - organic Complexes and the Retention of Hydrocarbons by
 Source Rocks".
 Int. Clay Conf. Stockholm (1963). Pergamon.
154. Rabinowicz, E.
 "Theoretical Criteria for the Effectiveness of a Lubricant Film".
 ASLE trans 1 (1958) p96.
155. Harkins, W.D.
 "Determination of Surface and Interfacial Tension".
 from: "Physical Methods in Organic Chemistry" Vol I ch.IX.
 Ed. Weissberger A. Interscience (1949.)

156. Adam, N.K.
"The Physics and Chemistry of Surfaces" 2nd Edition Oxford, U.P. (1938).
157. Harkins, W.D. and Brown, F.E.
"The Determination of Surface Tension (Free Surface Energy) and the Weight of Falling Drops. The Surface Tension of Water and Benzene by the Capillary Height Method".
J.Am.C.S. 41 (1919) p499.
158. Aveyard, R. and Haydon, D.A.
"Thermodynamic Properties of Aliphatic Hydrocarbon/Water Interfaces".
Trans. Farad. Soc. 61 (1965) p2255.
159. Everett, D.H.
"Thermodynamics of Adsorption from Solution.
Part 2 - Imperfect Systems".
Trans. Farad. Soc. 61 (1965) p2478.