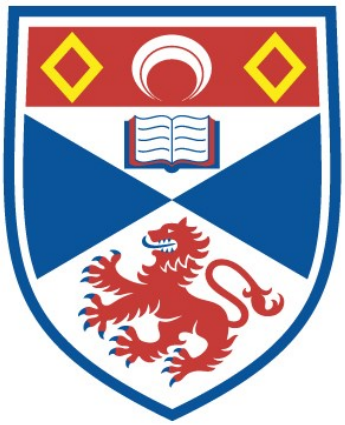
EXCITED STATE PROPERTIES OF 1-NAPHTHOL AND ITS SULPHONATES

Robert M C Henson

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1973

EXCITED STATE PROPERTIES OF

1-NAPHTHOL AND ITS SULPHONATES

A Thesis

presented for the degree of

DOCTOR OF PHILOSOPHY

in the Faculty of Science of the

University of St. Andrews

by

Robert M.C. Henson

May 1973.

United College of
St. Salvator and St. Leonard,
St. Andrews.

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by me, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out at the Department of Chemistry, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Professor P.A.H. Wyatt from the 1st of October 1969, to 1st October 1972.

R.M.C. Henson

CERTIFICATE

I hereby certify that Robert M.C. Henson has spent twelve terms of research work under my supervision, has fulfilled the conditions of ordinance No. 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

P.A.H. Wyatt

Director of Research

ACKNOWLEDGEMENTS

I would like to thank Professor P.A.H. Wyatt for his help and encouragement during the course of this work. My thanks are also due to Dr. T.M. Shepherd for his help with the automatic digitilisation of the microdensitometer, to Mr. J.G. Ward for his help with the flash photolysis apparatus, and my friends and colleagues in the Department of Chemistry.

I am indebted to the University of St. Andrews Purdie Fund for a grant to finance this work and to Professor Lord Tedder and Professor P.A.H. Wyatt for providing research facilities.

Finally I would like to thank the technical staff of the Department of Chemistry who have dealt so ably with a demanding customer and Mrs. Pat Cooper for typing this thesis.

CONTENTS

SUMMARY

The transient absorption spectrum of 1-naphthol was first sought by flash photolysis at higher acidities than had been previously investigated. While no transient absorption was observed for 1-naphthol itself, strong transient absorptions were observed for 1-naphthol-2- and -4-sulphonates even in aqueous solution. This enabled $pK(T_1)$ for the protonation of the naphtholate ions to be measured directly from the strength of triplet-triplet absorptions and this value was compared with the $pK(T_1)$ obtained from Förster Cycle calculations on phosphorescence maxima. Values of $pK(S_1)$ and $pK(S_o)$ were also obtained and the order of the pK values was found to be $pK(S_o) > pK(T_1) >> pK(S_1)$. It is likely that this order is the same for 1-naphthol and therefore disagrees with the results of some recent quantum mechanical calculations.

A strong fluorescence was also observed for 1-naphthol-2-sulphonate in aqueous acidic solutions, in contrast with the weak fluorescence observed for 1-naphthol and 1-naphthol-4-sulphonate. This is explained in terms of intramolecular hydrogen bonding in 1-naphthol-2-sulphonate which prevents quenching of the first excited singlet state by hydrogen bonding with solvent water molecules. The fluorescence intensity of 1-naphthol, 1-naphthol-2-sulphonate, and 1-naphthol-4-sulphonate in aqueous acidic solutions is also found to increase as the water concentration is effectively reduced by the addition of certain solutes in large quantities. A corresponding increase in the triplet yield is also found for 1-naphthol-2-sulphonate in acidic solutions. These increases are also explained in terms of reducing the hydrogen bonding to solvent water molecules and hence reducing the deactivation of the S_1 state.

1-Naphthol sulphonates and protonates in concentrated sulphuric

acid and it is deduced that protonation occurs at a carbon atom in the naphthalene ring. A value of $pK(S_o)$ was determined for this protonation.

CHAPTER 1

INTRODUCTION

1. GENERAL PHOTOCHEMISTRY

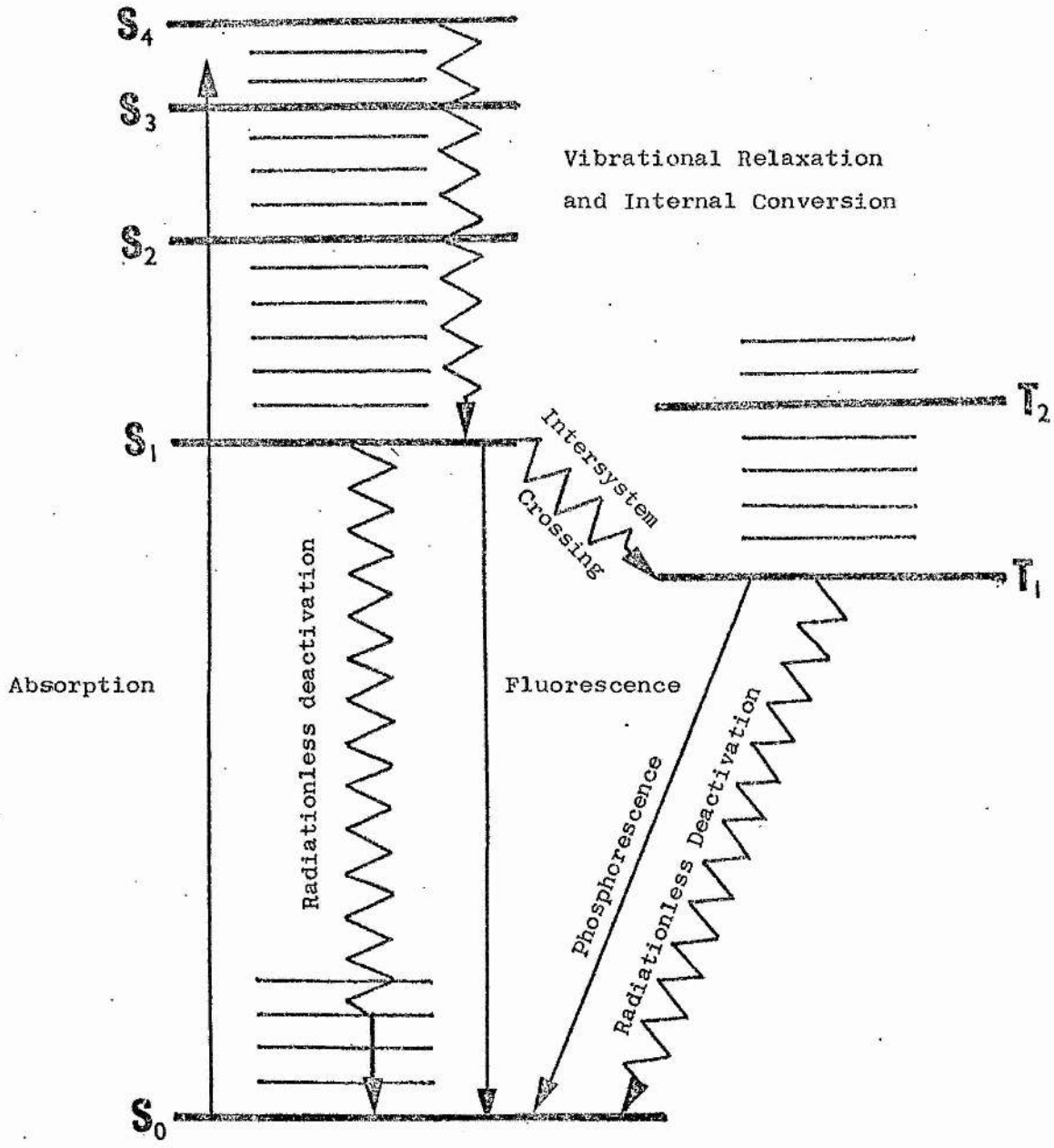
(a) Activation and Deactivation of Excited States

In order to understand fully the reactions of a molecule in an excited state, one must have a knowledge of all the primary photochemical processes, i.e. the mechanisms of electronic activation and deactivation of the molecule under consideration. These processes are usually discussed in terms of a modified Jablonski[1] diagram (see Fig 1.1).

In the absence of external electromagnetic influences, most organic molecules at room temperature or below can be described in the following manner. With few exceptions all filled molecular orbitals contain two spin-paired electrons. This means that for each filled orbital there exist two electrons with spin orientations in opposite directions; therefore each molecular orbital then contributes no net spin to the entire molecular system. When the above condition is fulfilled, the molecule is said to exist in its electronic ground state. Since the resultant spin, S, equals zero the multiplicity, $M = 2S+1$, of this state will be one. States with multiplicities of one are traditionally referred to as singlet states, and it follows that for most organic molecules the ground state is a singlet state which is commonly known as the singlet ground state (S_o).

An electron in the ground state may acquire sufficient energy to be promoted to an unoccupied molecular orbital. If the promoted electron has maintained its spin orientation, the multiplicity of this excited

FIG 1.1 Jablonski Diagram



state will be one also, and is referred to as an excited singlet state (S_1, S_2, S_3 etc.). It is easily seen that there will be a state in which the spin of the promoted electron is reversed. These states with S = 1 and M = 3 are referred to as triplet states (T_1, T_2, and T_3). The energy of the triplet state is always lower than the energy of its corresponding singlet state. The source of this energy difference can be seen from a simple consideration of electron spins and repulsive forces.

Electronic states for molecules in solution are not adequately described by discrete energy levels and a schematic representation of these states is complicated by the presence of vibrational and rotational levels superimposed upon each electronic level. For each electronic state there will be several fundamental vibrational modes, with which one may associate a discrete energy. For each vibrational mode there will, in general, be a number of discrete rotational energy levels. Thus the total representation of a molecular electronic diagram becomes quite complicated. The energy necessary for promotion of an electron from the ground S_o state to an excited singlet state, S_1 or S_2, is easily seen to lie within a range of energies rather than being a discrete energy. In solution the rotational energy levels become "smeared-out" and are no longer discrete, due to rapid intermolecular interaction. Therefore the range of energies necessary for transition between two electronic states becomes essentially a continuum, so that any energy supplied to the molecule between two limits will be capable of promoting an electron. In spectroscopic terms this means that photons with energy $h\nu$, where h is Planck's constant and ν is the frequency, between two limits will be capable of causing promotion of a molecular electron. Thus, the absorption spectra of organic compounds

in solution will in general be broad continua occurring between two limits of wavelength.

When a photon with the appropriate energy is absorbed by a molecule, an electron is raised from the zero vibrational level of the singlet ground state to one of the several vibrational levels of an excited singlet state. According to the Franck-Condon principle[2] this process occurs in 10^{-15} seconds, i.e. within the period of the vibration of the light wave. After a delay of about 10^{-11} to 10^{-13} seconds following the absorption of a photon the molecule reaches by a radiationless process the S_1 state[3]. During this short time numerous internal conversions may have occurred and the excess of electronic, vibrational and rotational energy has been transferred by collision to the solvent molecules. For a large number of molecules the net result of this process, known as internal conversion, is the production of a large population of molecules in the lowest vibrational level of the first excited singlet state, S_1. All of these excited molecules are chemically identical and their existence in this state is independent of their individual previous histories. Some substances may undergo photochemical reaction when raised to upper excited states but the processes leading to such reaction (e.g. dissociation) must take place rapidly to compete with the internal conversion and loss of vibrational energy by collisions, the rate of which is such that a thermodynamic acid-base equailibrium is rarely established in states of higher energy than S_1.

If the molecule can remain in its lowest excited singlet state, S_1, for 10^{-9} s or longer then the situation is favourable for this molecule to emit fluorescence radiation and thus return to the S_o state. This radiational deactivation from S_1 to S_o also results in a band spectrum since any number of vibrational levels in S_1 may be

populated by the S_1 to S_o transition. Thus the low energy band of an absorption spectrum depicts the vibrational spacings of the first excited state, whereas the fluorescence spectrum displays the vibrational spacing of the ground state, and in many cases both bands show similar structured intensity patterns.

Other modes of deactivation from S_1 are available. If the excited molecule interacts with its environment, then there may be a radiationless deactivation of S_1 resulting in production of S_o; the nature of this environment interaction (quenching) will be examined in more detail later. It is possible that high-lying vibrational levels of S_o will overlap the S_1 state; internal conversion can then occur from the S_1 to the S_o state, and vibrational relaxation will give the unexcited ground state molecules. The relative importance of the internal conversion from S_1 to S_o compared with other processes of deactivating the S_1 state is still actively debated however [4].

In addition to the above methods of deactivating the S_1 state; a molecule in the S_1 state can cross from the singlet manifold to the triplet manifold, by a process known as intersystem crossing. In many cases this process can compete effectively with the fluorescence emission process to deactivate the S_1 state. The lowest vibrational level of the lowest triplet state (T_1) is generally situated some way below that of the lowest excited singlet state, but its upper vibrational levels extend upwards to the bottom of the singlet level and intersystem crossing occurs by the molecule crossing over to one of these upper vibrational levels of the lowest triplet state.

There are several deactivation routes open to T_1 molecules; the radiational deactivation of T_1 to S_o in the phenomenon known as phosphorescence. Radiative transitions between states of difference multiplicity e.g. singlets and triplets are theoretically forbidden. In practise, because of spin-orbit coupling, these transitions do take

place, although with extremely low probability compared with singlet-singlet, or triplet-triplet transitions. Low transition probability means that the absorption band will be weak and the radiative lifetime for the reverse transition will be long. Thus the radiative lifetime of the transition from the lowest triplet level to the ground state is usually less than 10^{-4} s and for many molecules it is considerably greater than one second[2]. Because of their exceptionally long radiative lifetimes, molecules in the lowest triplet state can easily lose their energy by a variety of radiationless processes. For example they are very susceptible to collisions with solvent molecules in fluid solution, or to encounters with certain solute molecules. Solute molecules having unpaired electrons e.g. molecular oxygen, are particularly effective in removing triplet excitation energy and can act at exceedingly low concentrations[5-8]. For these reasons phosphorescence from fluid solutions at room temperature had until recently been observed only rarely. By dispersing the substance in a rigid medium or by cooling to low temperature, the rate of radiationless processes is greatly reduced and under these conditions phosphorescence can be observed for many compounds at high intensity. Population of the triplet level by direct absorption of light in the triplet-singlet absorption band is clearly a difficult process experimentally because this absorption band is so weak.

Just as conventional absorption spectra are obtained by exciting molecules in the ground state (S_o) to higher levels of the singlet manifold so singlet (S_o) — singlet (S_n) and triplet (T_1) — triplet (T_n) absorption spectra can be obtained. Triplet-triplet absorptions were first observed in 1954[9] using flash methods, but because of the very short lifetime of the molecule in the S_1 state, absorption spectra originating from this state have only recently been observed using nanosecond flash photolysis techniques with a pulsed laser flash as

source.[10]

(b) Types of Electronic Transition.

It is convenient for photochemical purposes to discuss electronic transitions in terms of initial and final orbitals of the electron involved in the transition. Fluorescence is nearly always associated with the π electron system of an unsaturated molecule. If the unsaturated system does not include an atom such as oxygen, nitrogen or sulphur having a lone pair of electrons, the electronic transition of lowest energy corresponds to the promotion of one of the electrons occupying a π orbital in the ground state to an upper π^* orbital. π^* orbitals are delocalised like the ground state π orbitals but have a nodal plane perpendicular to the bond axis and are therefore antibonding. The $\pi^* \leftarrow \pi$ transitions are generally of relatively low energy and have high intensities (ε_{max} 10^4 to 10^5), unless partially forbidden by symmetry factors. The π^*-π states therefore frequently give rise to fluorescence.

Unsaturated systems containing an atom having a lone pair of electrons often give rise to a transition of lower energy than the $\pi^* \leftarrow \pi$ transition. For example the carbonyl group is made up of one pair of electrons occupying a σ orbital, one pair of electrons in a π orbital, and two lone pairs of electrons on the oxygen, one pair of which occupy a non-bonding or n-orbital. The n-orbital has little overlap with the π orbital. The electrons in the n-orbital have the highest energy and can undergo a transition to an upper π^* orbital, i.e. a $\pi^* \leftarrow$ n transition, which is generally the sinlget-singlet transition of lowest energy. Such transitions have a low probability ($\varepsilon_{max} < 2000$) and the π^*-n excited states have comparatively long radiative lifetimes. They are thus more subject to radiationless deactivation processes than π^*-π states and the fluorescence from

them is very weak. Classifications of transitions as $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ was first used by Kasha[3].

When more complex systems are considered, it is necessary to sub-classify the "lone pair orbitals". Kasha[11] classified these "lone pair electrons" as originating from one of two types of orbitals: n-orbitals (non-bonding) which cannot conjugate with a π-electron system; and l orbitals ("lone pair"), which can conjugate with a π-electron system. The reason for this may be illustrated by reference to the lone pair orbital of nitrogen in aniline. The nitrogen is simply bonded to the ring and the hydrogen atoms and the lone pair electrons therefore occupy the remaining p orbital. If the amino group is coplanar with the ring, the l-orbital is fully conjugated and only $\pi^* \leftarrow \pi$ transitions are expected. If the amino group is twisted through 90^o about the C-N bond, no conjugation of the l-orbital would be possible. At intermediate angles of twist a transition from the lone pair orbital to the π electron system of the ring can occur. This results in a state having considerable charge transfer character. Kasha[11] classified such intramolecular charge transfer transitions as $a_\pi \leftarrow l$; such transitions do not in general behave like true $\pi^* \leftarrow n$ transitions. In particular the radiative lifetime of $a_\pi \rightarrow l$ states is closer to that of $\pi^* \rightarrow \pi$ states and they frequently give rise to both fluorescence and phosphorescence. Thus most phenols and aromatic amines are fluorescent in fluid solution. Compounds such as aniline with lone pairs in l-orbitals have comparatively intense long wavelength transitions.

When both an electron donor group (e.g. O^-, NH_2, OH) and an electron acceptor group (e.g. CO, NO_2) are connected with an electron system it is not possible to consider the transition to the excited state as the movement of one electron between two orbitals. Several

kinds of one-electron transition have to be regarded as contributing to the transition that actually occurs and Porter and Suppan[12] have classified the excited states of lowest energy that result from such transitions as charge transfer (C.T.) states. The transitions are of high intensity, and if the charge transfer state is the excited state of lowest energy, it can give rise to fluorescence.

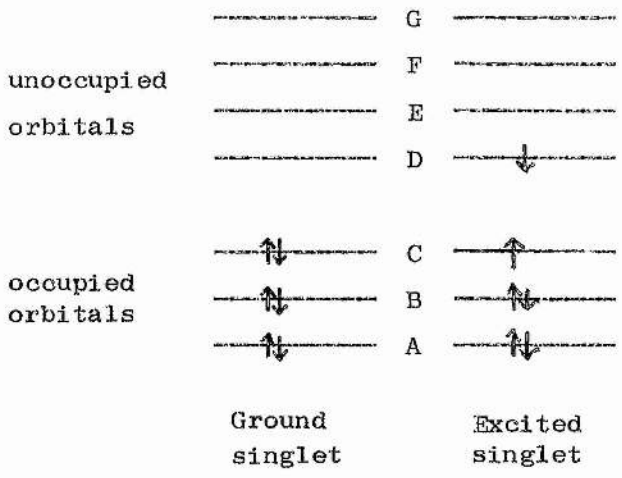
2. REACTIONS OF THE EXCITED STATE

(a) General

Consider an organic molecule whose molecular orbitals are pictorially represented in Fig 1.2.

FIG 1.2

Energy level diagrams for a representative typical organic molecule in the ground and first excited singlet electronic states



The ground state is shown with three filled molecular orbitals (A, B and C) and four unoccupied (unfilled) orbitals (D, E, F and G). If a photon of energy equivalent to the difference in energy between levels C and D is supplied to the ground state molecule, then an electron in level C may be promoted to level D resulting in the

production of an excited state molecule. This resultant state differs from the ground state in two important aspects: the excited state molecule possesses more energy than the ground state molecule; and the molecular orbitals of the excited state are filled in a manner quite different from the manner in which the orbitals of the ground state were filled. Therefore the ground state molecule and the excited state molecule (singlet or triplet) are chemically different species; i.e. one might reasonably expect differences in chemical reactivity of the two states.

(b) Acid-Base Properties

The knowledge of the acid-base properties of molecules in excited states is of primary importance for the chemist who wishes to elucidate a mechanism of photoreaction[13,14] and for the theoretician to whom it gives a possibility of testing his calculations[15]. The study of these properties has been limited to aromatic compounds as opposed to aliphatic derivatives, since the former have suitable absorption bands in the visible or near U.V. and often show intense fluorescence and strong triplet-triplet absorption bands which make the measurement of acidity constants possible in singlet and triplet excited states. Since charge densities are often modified by electronic excitation, one may expect to observe variations of acidity between the ground and the various excited states[16,17].

Acidity and basicity may be defined in different ways, but in this work we shall always use the Brönsted definition[18,19]; a molecule or an ion which under certain conditions can give a proton is an acid, a base is a species which can accept a proton. Equilibria will only be discussed in aqueous solution and therefore the general reaction may be considered as

$$AH + H_2O \rightleftharpoons A^- + H_3O^+$$

The equilibrium constant is given by

$$K = \frac{(A^-)(H_3O^+)}{(AH)} = \frac{[A^-][H_3O^+]}{[AH]} \times \frac{\gamma A^- \gamma H_3O^+}{\gamma AH}$$

where the symbols, ( ) represents activities, [ ] represents concentrations and γ represents activity coefficients.

An approximation which is used for dilute solutions neglects the activity coefficients:

$$K \approx \frac{[A^-][H_3O^+]}{[AH]}$$

This approximation and the following notations will be used in this account.

$pK(S_o) \equiv$ pK of the ground state,

$pK(S_1) \equiv$ pK of the lowest excited singlet state,

$pK(T_1) \equiv$ pK of the lowest excited triplet state,

$pK^* \equiv$ pK of an unspecified excited state.

Determination of pK^* values

Both $pK(S_1)$ and $pK(T_1)$ values can often be obtained by direct measurement of the [AH]/[A] ratios involved. A discussion of these methods is followed by a consideration of the simpler and less time-consuming technique known as the Förster Cycle.

$pK(S_1)$: Fluorescence Spectroscopy

Weber[20] is accredited with having first noticed in 1931 that the shift of an acid-base equilibrium occurred at a different pH, depending on whether this shift was observed by absorption or fluorescence spectroscopy. This observation was correctly interpreted by Förster[21-23] who showed that changes of the fluorescence spectra as a function of pH correspond to a proton transfer in the S_1 state. Weller[24-26] made a detailed study and collected a considerable amount of data. For naphthalene derivatives, and hydroxy and aminopyrene sulphonates, it appeared that the pH values at which the absorption

and the fluorescence spectra change are usually 6 or more units apart and thus the acidity constants in the ground and S_1 states differ by a factor of 10^6 or more. This indicated that protonation and deprotonation can take place in a shorter time than the S_1 state lifetime and that the chemical reaction is not accompanied by deactivation of the excited state. Weller[27] classified aromatic acids into two groups: acids belonging to

group 1: Ar.OH; $Ar.\overset{R}{N}H$; $Ar.\underset{R'}{\overset{R}{N}}H^+$; Ar.SH;

have $pK(S_1) < pK(S_o)$

whereas those of

group II: Ar.COOH; $Ar.\overset{R}{C}{=}OH^+$; $Ar.\overset{R}{C}{=}\overset{R'}{N}H^+$; $Ar{=}{=}NH^+$

have $pK(S_1) > pK(S_o)$

If the acid-base equilibrium is completely established within the lifetime of the excited molecule a value of $pK(S_1)$ can be obtained directly from fluorescence measurements. The effects of pH on the fluorescence spectra of 2-naphthol have been examined by many authors[23,28,29] and it appears that the thermodynamic equilibrium is not reached during the S_1 state lifetime.

For the equilibrium

$$ROH + H_2O \rightleftharpoons RO^- + H_3O^+$$

$pK(S_o) = 9.46$[28], and therefore only the undissociated species is responsible for the absorption of light in the pH range between 2 and 7. The fluorescence emissions of both forms, however, are present over a wide range of pH values from above 9 to below 3. This is due to the fact that some excited ROH molecules ionise but, before the change is complete and equilibrium is reached, the remaining ROH^* molecules return to the ground state with the emission of their characteristic fluorescence. The $pK(S_1)$ value of the excited state dissociation has been shown to be 2.81[28] showing that 2-naphthol becomes a stronger acid in the excited state.

Using the steady state method Weller[24,25,28,30] has derived equations which relate the ratios of the fluorescence intensities of the two forms involved in an excited state protolytic reaction at a given pH value and the various rate constants of the several processes open to the two forms. Independent measurement of the natural lifetimes of both species and determination of fluorescence intensity versus pH curves permit the determination of the rate constants of the protolytic reaction. From these values the equilibrium constant can be obtained. This method enables the $pK(S_1)$ to be obtained in the case where equilibrium is not established in the lifetime of the excited molecule. Since the reaction takes place in a time comparable with the period needed to obtain steady state conditions the steady state theory must be modified to take into account the fraction of molecules which, immediately after excitation, are involved in the protolytic reaction[31]. For example, in the case of an excited state protonation, this fraction consists of these molecules that have an H_3O^+ ion within the reaction distance and therefore protonation can be considered to occur as soon as excitation occurs.

In the cases studied experimentally in this work, equilibrium is not completely established in the excited state. Independent measurements of the natural lifetimes of both species were not accessible unfortunately and so only approximate values of $pK(S_1)$ are obtained. The method by which these values were obtained is described in full detail later.

$pK(T_1)$: Flash Spectroscopy

Phosphorescence is mainly observed in rigid media and, since under these conditions the ground state thermodynamic equilibrium cannot quickly be modified after excitation, it is not in general possible to

use emission intensity measurements to obtain $pK(T_1)$ in the way that fluorescence intensity is used to give $pK(S_1)$. The method first used for the $pK(T_1)$ determinations by Jackson and Porter[32] is based on the measurement of T-T absorption spectra as a function of pH.

Consider an acid-base equilibrium in the ground state between the two forms $ROH(S_o)$ and $RO^-(S_o)$. The high intensity photoflash (500 J in our case) excites a large number of the molecules into the various singlet states. Direct excitation into the triplet manifold is neglected. After about 10^{-13} s all the excited molecules reach the S_1 state. Depending on the acidity conditions, a new equilibrium will be partly established between $ROH(S_1)$ and $RO^-(S_1)$. According to the rates of intersystem crossing and the fluorescence quantum yields of the two species, a fraction of $ROH(S_1)$ and $RO^-(S_1)$ will cross over to the triplet state. Protolytic equilibrium will be established in a time smaller than the natural lifetime of the triplet state[33], since in most cases the lifetime of the triplet states is relatively long, even compared with the relatively slow rates for protonation of a carbon atom[39]. Since the flash duration (10^{-5} s) is much longer than the S_1 state lifetime, the molecules deactivated into the ground state will be re-excited, and after a few "pumping cycles" a high acid and base triplet state concentration in equilibrium is obtained[34].

The concentration ratio of the species is recorded by a spectrographic technique using a spectroflash fired a few microseconds after the photoflash. In these conditions, no molecules remain in the S_1 state, and since for most aromatic derivatives there are always T-T absorption bands located at longer wavelengths than the $S_1 \leftarrow S_o$ transitions there is no interference by the absorption spectra of the molecules remaining in the ground state. The interpretation of results is similar to that used in the determination of $pK(S_o)$ by

absorption spectroscopy and is described in more detail later.

The flash photolysis technique applied to the measurement of $pK(T_1)$ values, may be considered as corresponding to the kinetic method developed by Weller for $pK(S_1)$. In both cases, absolute values of acidity constants are obtained directly at room temperature in aqueous solutions without making any fundamental theoretical assumption. Both techniques give pK^* values with a good accuracy but are rather time consuming.

The Förster Cycle

In addition to the methods based on measurement of fluorescence intensity and T-T absorption spectra, $pK(S_1)$ and $pK(T_1)$ values can also be obtained by a much simpler and less time-consuming technique known as the Förster cycle[22,25,27]. This provides a method of determining the difference of pK($\triangle$pK) between the ground and an excited state. Therefore to obtain pK^* values from the $\triangle$pK's obtained, the $pK(S_o)$ value for the reaction under consideration must be known. This method is based on the determination of the energy gap between the ground and the excited states of the acid and basic forms of the chromophore under investigation.

The transitions from the lowest vibrational level of the ground state to the lowest vibrational level of an excited state (i.e. the O-O band) for both the base (RO^-) and the conjugate acid (ROH) are shown in Fig 1.3.

$\triangle E_{ROH}$ and $\triangle E_{RO^-}$ are the O-O energy differences of the two states for the acid and its conjugate base respectively, and $\triangle H$ and $\triangle H^*$ are the enthalpies of reaction in the ground and excited states respectively.

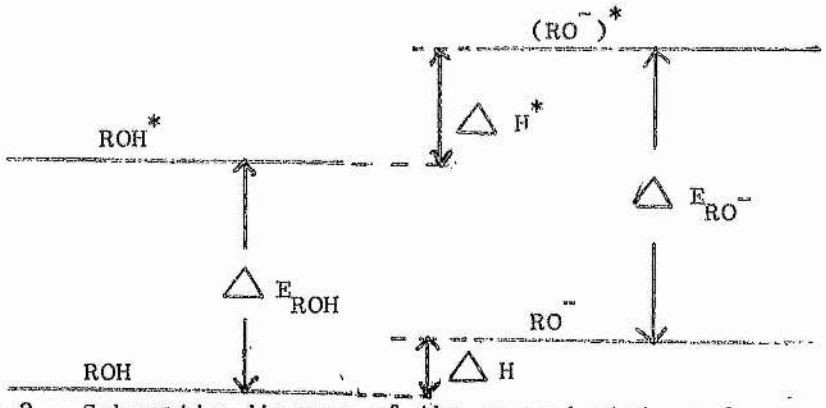


FIG 1.3 Schematic diagram of the ground state and an excited state of an acid and its conjugate base.

It is immediately seen that

$$\triangle H^* + \triangle E_{ROH} = \triangle H + \triangle E_{RO^-}$$

$$\text{or } \triangle H - \triangle H^* = \triangle E_{ROH} - \triangle E_{RO^-} \quad (1.1)$$

The difference in the reaction enthalpies in the experimental conditions will not differ greatly from the difference in the standard enthalpies $\triangle H^{\ominus}$.

$$\text{Now } \triangle H^{\ominus} = \triangle G^{\ominus} - T\triangle S^{\ominus} \text{ and therefore}$$

$$\triangle H^{\ominus} - \triangle H^{*\ominus} = (\triangle G^{\ominus} - T\triangle S^{\ominus}) - (\triangle G^{*\ominus} - T\triangle S^{*\ominus})$$

If the standard entropies of reaction are equivalent in the two states

$$\text{i.e. } \triangle S^{\ominus} = \triangle S^{*\ominus}, \text{ then}$$

$$\triangle H^{\ominus} - \triangle H^{*\ominus} = \triangle G^{\ominus} - \triangle G^{*\ominus}$$

and equation 1.1 becomes

$$\triangle G^{\ominus} - \triangle G^{*\ominus} = \triangle E_{ROH} - \triangle E_{RO^-} \quad (1.2)$$

Since $\triangle G^{\ominus} = -RT \ln K$ equation 1.2 becomes

$$\triangle E_{ROH^-} \quad \triangle E_{RO^-} = -RT (\ln K - \ln K^*)$$

$$\text{or } pK - pK^* = \frac{\triangle E_{ROH} - \triangle E_{RO^-}}{2.303\ RT} \quad (1.3)$$

The $\triangle E$ values are obtained from the spectra of the species involved since $\triangle E = h\nu$, where ν is the O-O frequency of the transition. For the excited singlet the "best value" of the O-O energy is obtained by averaging the absorption and fluorescence maxima[35].

Since the probability of $T_1 \leftarrow S_o$ transition is extremely small in aqueous solutions, absorption measurements are not normally used for application of the Förster cycle to the determination of $pK(T_1)$. The O-O transitions of the base and its conjugate acid are usually estimated directly from the phosphorescence spectra recorded at liquid nitrogen temperature.

If we substitute $\triangle E = h\nu$ into equation (1.3) we obtain the form of the Förster Cycle used later in this work.

$$pK - pK^* = \frac{(\nu_{ROH} - \nu_{RO^-})^h}{2.303\ RT} \qquad (1.4)$$

$$\text{or} \quad pK = \frac{0.625}{T} \quad (\triangle\nu\ /cm^{-1}).$$

The assumptions governing the application of the Förster Cycle were reviewed by Jaffe[36].

(c) Hydrogen Bonding

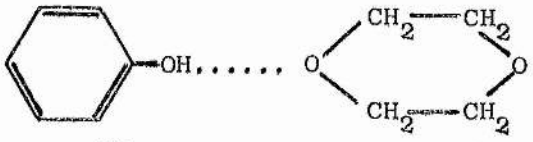
Compounds containing groups such as CO, -OH, $-NH_2$ etc. may in general form hydrogen bonds with appropriate solvents both in the ground state and in the excited state. Hydrogen bonded excited states can thus be produced via two routes as shown by the following scheme in which S represents a solvent molecule.

$$A + S \longrightarrow AS \xrightarrow{h\nu} (AS)^* \qquad (1.5)$$

$$A^* + S \longrightarrow (AS)^* \qquad (1.6)$$

It was shown by Nagakura and Baba[37] that the 1:1 hydrogen bond complexes of phenols, with suitable hydrogen bond acceptors such as dioxane, exhibit absorption spectra which are shifted to longer wavelengths compared to the absorption spectra of the unbonded species. The shifts

were typically about 500 cm^{-1} and indicated a stronger hydrogen bond in the excited state. Comparatively small concentrations of dioxane in heptane were sufficient to produce the effect and since the corresponding O- or N- methylated derivatives did not show it, Nagakura and Baba attributed the abnormal spectral shift to the formation of hydrogen-bonded complexes of the type:



Weller[27] found that the absorption spectrum of 3-hydroxypyrene in methyl cyclohexane was shifted some 0.03 μm^{-1} to longer wavelengths on the addition of hydrogen bond acceptors such as triethylamine or pyridine. He found similar results with 2-naphthol[38], and found that the fluorescence efficiency of both compounds decreased on hydrogen bond formation. He concluded that the excited hydrogen bond complex could be formed by both mechanisms given in equations 1.5 and 1.6.

Hydrogen bond formation in the excited state can be regarded as the preliminary stage of acid dissociation (in which the proton is transferred completely to the base - see Chapter 1. 2b), for which the shifts in absorption bands are considerably greater.

3. INTRODUCTION TO THE EXPERIMENTAL INVESTIGATION

The start of this work coincided with the arrival of a flash photolysis apparatus at St. Andrews. The apparatus was set up and the technique of using it was mastered. Having checked the performance of the apparatus by re-examining the triplet-triplet absorption spectrum of 2-naphthol in sodium hydroxide and sulphuric acid solutions, it was decided to carry out a flash photolysis investigation of 1-naphthol in strong acid solutions. Considerable interest has been centered recently on the excited state acid-base properties of weak bases, because of the

information that can be gained about the validity of acidity functions[39,40]. Difficulties in the investigation of 1-naphthol are encountered because it sulphonates in concentrated sulphuric acid. However considerable information about the excited state reactions (the acid-base properties in particular) has been obtained for the products of the sulphonation of 1-naphthol.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

1. GENERAL TECHNIQUES

Fluorescence and phosphorescence measurements are important analytical tools because of the low concentrations of solutes that can be detected. The degree of purity of glass apparatus and specimens, whose luminescence is to be investigated, must be very high, at least with respect to certain classes of impurity. Parker[2] records the hazards encountered and the precautions that have to be taken.

The acids and inorganic chemicals used in this work were of analytical grade, unless stated otherwise. Any organic solvents used were either Analar or spectroscopic grade, except ethanol, which was purified by Parkers[2] method. Water was purified by distillation from alkaline permanganate using a 4ft. fractionating column. Whenever a fluorescence or phosphorescence determination was performed a "blank" determination was also performed to check the purity of the solvents being used. Details of purification of the particular compounds studied are given later in the text where appropriate.

In the pK determinations, the pH of solutions $> 10^{-2}$ M in acid were calculated from the acid concentration determined by titration with standard alkali. For solution of pH > 2 a Radiometer PHM 26 pH meter was used.

2. GROUND-STATE ABSORPTION SPECTROSCOPY

A Unicam SP 800, with its automatic recording procedure, was used to obtain continuous absorption vs. wavelength curves. This information was useful for initial investigations and qualitative results. For more detailed and accurate work, the Unicam SP 500 machine was employed. Quartz

cells were used in all measurements. The blank solutions to which the sample absorbance was compared were, as far as possible, an exact sample of the solution without the particular solute of interest.

3. TRIPLET-STATE ABSORPTION SPECTROSCOPY

(a) Introduction

If one can excite a significant number of molecules into the T_1 state, one might expect to observe the absorption spectrum associated with the excitations $T_2 \leftarrow T_1$, $T_3 \leftarrow T_1$, ... $T_i \leftarrow T$ etc. These processes were first observed by Lewis, Lipkin, and Magel[41] for fluorescein in boric acid glass. The development of high intensity flash sources has made the detection of triplet-triplet absorptions possible even under conditions where the state T_1 has a very short life-time ($\sim 10^{-4}$ s). Thus Porter and Windsor[9] have detected the $T_i \leftarrow T_1$ absorption of molecules in fluid solutions. The method of observing triplet-triplet absorption is flash-photolysis i.e. the irradiation of a sample by high intensity light flashes and studying the effects at various wavelengths and times. The general principles have been published in great detail[8,42-44]. Basically two methods are used, each of which has limitations, and which are complementary to one another.

(a) The flash photographic technique: this is used for the detection of short-lived species using a spectrograph and photographic plate. This gives information covering a large range of wavelengths at one specific time.

(b) The flash photo-electric technique: this is used for measurement of light absorption changes in the sample by means of a photomultiplier and gives information over a limited range of wavelengths during a specific time interval.

In each case the sample is irradiated by the photolysis or main flash and the observation is subsequently made at right angles to this.

In method (a) a second discharge lamp is used (spectroscopic flash)

to produce a photograph via the spectrograph with the absorption of the sample shown at a time when the second flash was initiated. Hence by varying the delay between the photolysis flash and the spectroscopic flash, one can study the absorption at a series of wavelengths at a specific time after excitation of the sample.

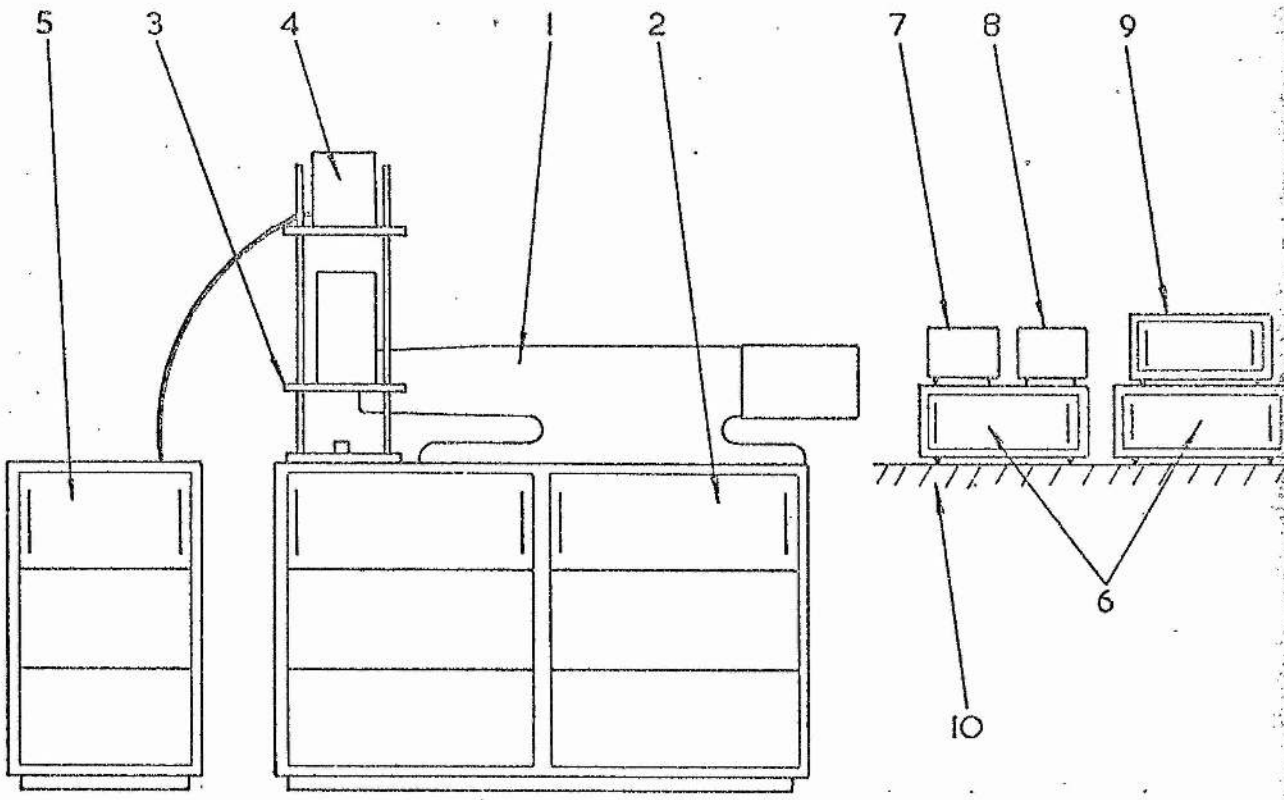
In method (b) a continuous source is used to monitor the changes in transient absorption with time after the photolysis flash. Ideally the only light reaching the photomultiplier should be from the monitoring source, but due to the physical arrangement of the apparatus, some of the light from the photolysis flash is scattered into the photomultiplier, thus producing a pulse of equal duration to the flash. This will obviously mask any transient produced which has a shorter lifetime. Therefore, the shorter the flash duration the wider is the range of transients which may be studied. This will be discussed in greater detail later.

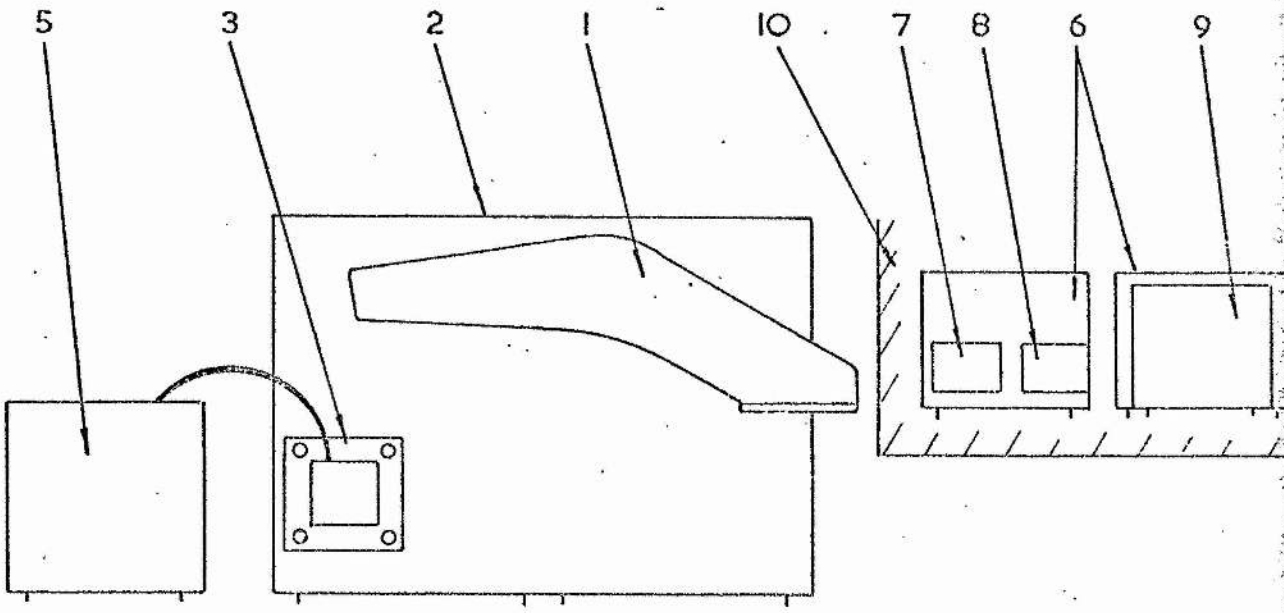
(a) General Description of Instrument

The instrument used for all the flash-photolysis experiments was a Northern Precision FP-1-pH system. The sample cell was held in a vertical position in this system and the instrumental lay-out is shown in FIG. 2.1. The spectrograph (1) is positioned on the main (photolytic) capacitor case (2) which also supports the sample holder assembly (3). The spectroscopic (capillary) flash lamp is housed in (4), and the spectroscopic capacitor case must be placed near by (5). The power supplies (6), control units (7), (8) and delay unit (9) are placed on a table (10) beside the main capacitor banks. With this arrangement several mirrors are used to guide the beam onto the spectrograph slits.

The photolysis (main) capacitor consists of two banks of five microforads which can be operated singly or together. Normally both capacitors were charged to 10 kV before triggering, thus on firing giving a flash energy of 500 J. The type of switch used for the photflash is the simplest type, of just two contacts and a connection bar operated by

FIG 2.1 Instrumental layout of the flash photolysis apparatus.





a solenoid, which operates when the trigger button on the control unit is pressed. This method was used because of its simplicity, absolute action, and lack of electrical interference. A similar method of switches was used to connect the main capacitor banks for the charging procedure. In practice these switches were found to be troublesome, needing continual adjustment and frequent cleaning. When the photolytic flash is fired, large fields are produced and the spectrographic unit must therefore have a high interference immunity. This is achieved by using a device known as an ignitron which gives reliable triggering of the spectrographic flash lamp.

The photolysis lamps are constructed from high purity quartz tubing, two electrode assemblies such that the distance between the electrodes is 20 cm, and filled to a 6 cm pressure with krypton. The spectrographic flash lamp was of a similar design, but smaller. These lamps were found to be reliable and to last well.

The spectrograph was a Hilger Watts Medium Quartz Spectrograph (E498) which took a 4" x 10" (10.2 x 25.4 cms) photographic plate.

For the flash photo-electric technique a Hilger-Watts Scanning Unit E720 was attached to the spectrograph. An E.M.I. IP28 photomultiplier was fitted, the output from which was fed into a Tektronix 545B oscilloscope. The resulting trace was recorded with a Telford Oscilloscope Camera. A quartz-iodine lamp is used as a monitoring source. The supply power is 100 W at 12 V.

(c) Preparation of Samples

The longer life-time of the triplet state compared to the excited singlet state, means that quenching processes tend to affect the triplet molecules to a greater extent than excited singlet species. Oxygen quenching has been used as a diagnostic test for the presence of triplet molecules. Thus in order to observe, triplet-triplet absorptions the solution must be thoroughly degassed prior to use.

The vacuum line used to degas solutions has a mercury diffusion pump backed by a rotary oil pump (Metrovac Type 6S.10) with which pressures much better than 10^{-4} torr were obtained i.e. a sticking-vacuum was obtained in an Edwards 2-G type McLeod gauge and a scale reading $<<$ 0 obtained on an Edwards Pirani gauge model 8/2. The zero needle reading was adjusted to correspond to the best vacuum obtained and all solutions were degassed to this vacuum. A schematic diagram of the vacuum line is shown in Fig 2.2.

X and Y are liquid nitrogen traps. 1, 2, and 3 are connecting points for the degassing vessels. The method of degassing used was the freeze-pump-thaw method and, because of the danger of apparatus cracking during the freezing and thawing procedures, the solution to be degassed was placed in a reservoir. The reservoir was connected directly to a quartz cell. The reservoir supplied originally with the apparatus was cylindrical in shape. Frequent breakages were experienced and a spherical reservoir was then tried, found satisfactory and employed in subsequent work. The flash photolysis quartz sample cell and Pyrex reservoir are shown connected in Fig 2.3. They are connected to the vacuum line by means of a socket (I). The taps A, B, C, are Rotoflow greaseless taps to prevent any contamination of the sample. During the degassing procedure, one has to be sure that all gas bubbles are released from the liquid, and shaking is usually employed. This proved to be tedious since the reservoir and cell had to be disconnected from the vacuum line before each shaking. To combat this a magnetic follower was introduced into the Pyrex reservoir, and so, by placing a magnetic stirrer under the bulb and stirring vigorously, the same effect was achieved. D is a constriction in the glass tubing to facilitate sealing off the cell under vacuum, and E is a quartz-glass seal. F and G are quartz optical flats which were sealed to each end of the cell, the main body being a quartz cylinder

FIG 2.2 Schematic Diagram of Vacuum Line

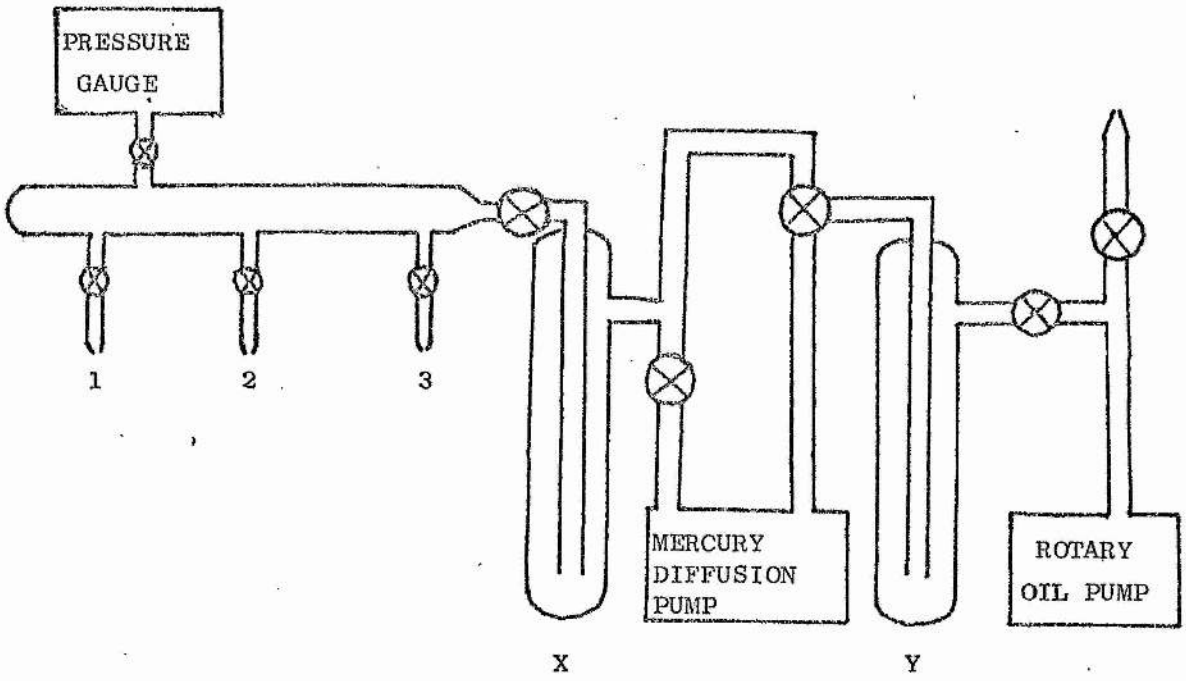
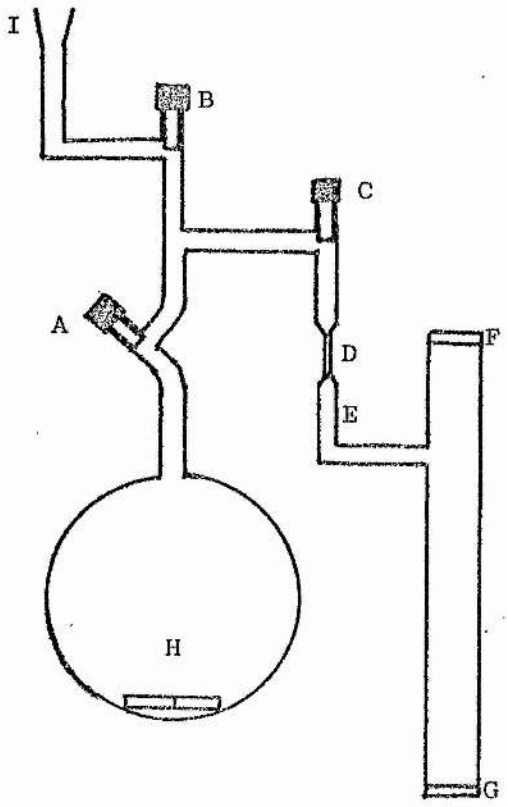


FIG 2.3 Quartz Cell and Reservoir



20.0 cm in length and 20 mm in diameter.

The general degassing procedure was as follows: the sample solution was introduced into the Pyrex bulb through tap A by means of a specially made funnel. The reservoir and cell, which had been joined previously, were then attached to the vacuum line with tap A closed. The solution in the bulb was then frozen to liquid nitrogen temperature and then tap A opened. When the vacuum had reached its lowest pressure again, tap A was closed and the liquid nitrogen removed. As stated previously a great deal of trouble was experienced during the thawing procedure. The best method appeared to be that of surrounding the frozen reservoir with hot water immediately after the liquid nitrogen was removed. This appeared to loosen the frozen sample from the glass and thus make any sudden distortions harmless. It also speeded up the thawing process considerably. The solution was then stirred vigorously, and the freeze-pump-thaw-stir cycle was repeated until the sample was degassed, as indicated by no change in the vacuum line pressure on opening tap A after freezing. After the final cycle tap B was closed and the combined cells were removed from the vacuum line. The solution was then poured over into the quartz cell and the cell sealed by heating the constriction in the glass tubing. This procedure was found to be reliable and effective.

(d) Operation and Analysis of Data

(i) Flash-Photographic Technique

The sealed quartz cell containing the sample under investigation is placed in the flash photolysis apparatus between the photolytic lamps, and the cell holder casing closed. All units are switched on and allowed to warm up whilst in a dark room, a photographic plate (Ilford HP3) is placed in the spectrograph plate holder. The following sequence of experiments is usually performed.

1. Spectroflash only to obtain starting spectrum,

2. Photoflash alone to obtain starting scattered light and any emission from the sample,

3. Photoflash and spectroflash with a set delay between the flashes. This is repeated for the various delay settings required.

4. The spectroflash alone is again recorded to give the final spectrum of the sample, and a measure, if any, of decomposition of the sample.

The ground state absorption spectrum is usually not seen on the photographic plate since, with a concentration of 10^{-4} - 10^{-5} M and a path length of 20 cm virtually no light of wavelength in the region of the ground state absorption spectrum of the solute reaches the plate. U.V. spectra of the sample are recorded before and after flashing and this gives a better measure of any decomposition. A wavelength scale is recorded on the photographic plate and the plate is, of course, moved for each flash.

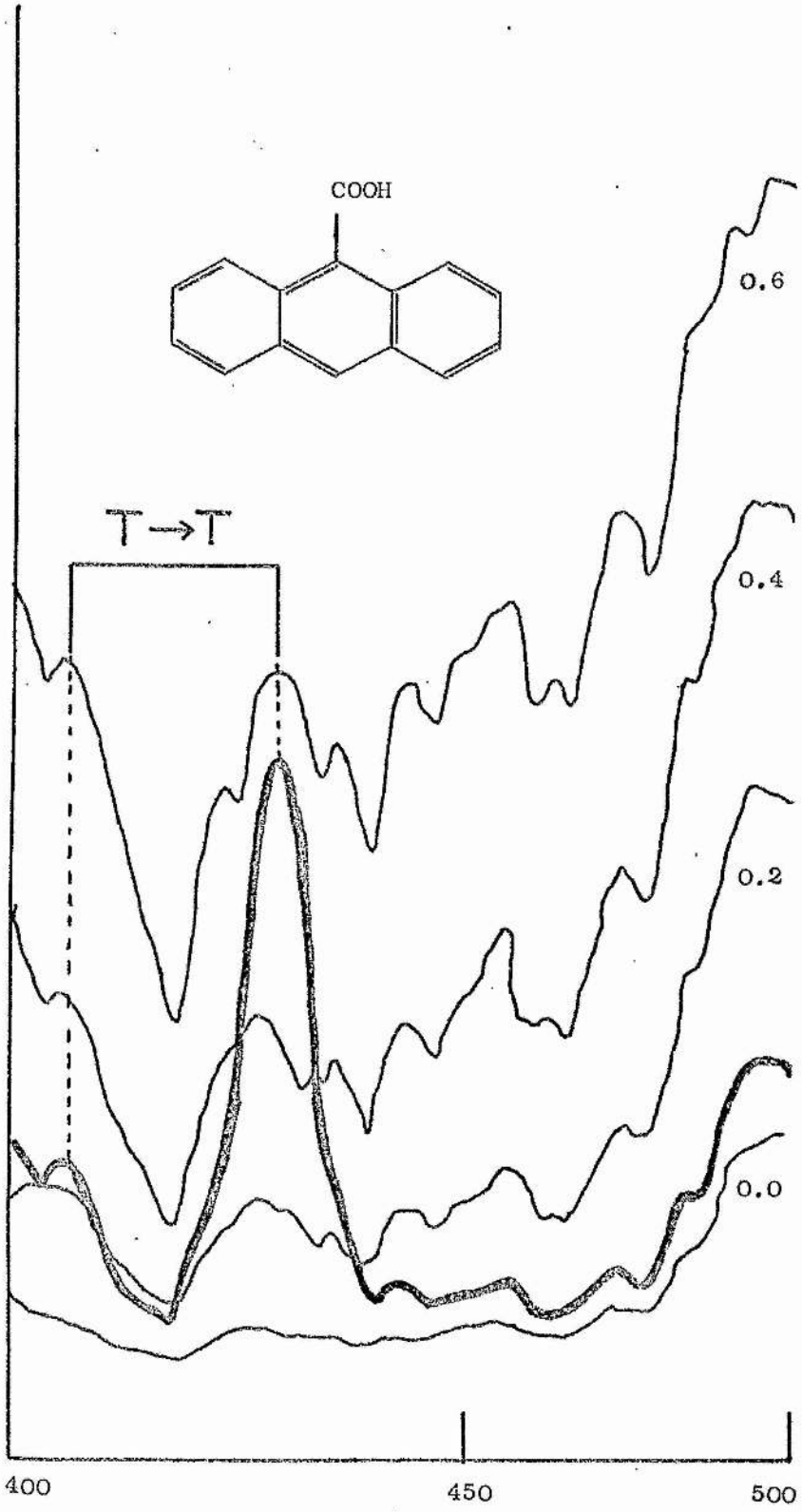
This general procedure is used for preliminary investigations of samples but in cases where measurements are to be made on a particular transient, the spectrographic plate has to be calibrated. This is achieved by keeping the sample in position, introducing a neutral density filter (Barr and Stroud) in front of the spectrograph and firing the spectroflash alone. A step wedge, having about seven narrow steps of varying density in the range required (e.g. 0.2 - 1.4) is often used. This requires only one exposure with the spectroflash. Separate neutral density filters (of O.D, 0.1, 0.2, 0.3, 0.5, 1.0 and 1.5) are used in our case so that any O.D value from 0.1 $\rightarrow$ 2.0 can be made by suitable combinations. This is more time-consuming but thought to be more reliable. Keeping the capacitor charged to the same tension, the spectroflash is fired for each filter required, and the plate moved for each exposure.

The photographic plate is then taken to a dark room, developed in Ilford Contrast FF developer, (4 min was found to give the best results), washed, fixed (Johnson Fix-Sol), washed again and dried in the air. The developing is carried out in complete darkness. The information on the photographic plate is then interpreted using a Vickers M41 Microdensitometer. The microdensitometer measures the extent of blackening of the plate and a record of this against wavelength is traced on a chart output. Microdensitometer traces of all the calibration spectra are first recorded followed by a trace of the sample's "transient" spectrum. All traces are recorded on the same recorder sheet without changing the settings of the microdensitometer. Finally the wavelength scale is obtained on the sheet by running the microdensitometer along the wavelength scale exposed on the photographic plate. Thus, by measuring the optical density of the transient at various wavelengths, the actual absorption spectrum can be constructed.

An example of a microdensitometer trace is shown in figure 2.4.

In certain cases, where the sample being investigated is a very strong fluorescer, the emission obtained from the photoflash will overlap and mask part of the triplet-triplet absorptions. To obtain the true triplet-triplet absorptions this emission must be taken into account. This can be done in two ways. (a) For each calibration exposure the photoflash and spectroflash can be fired, with a sufficiently long delay so that the transient absorption is not seen on the spectrum obtained. Thus the emission is taken into account directly. This method is only applicable if the compound under investigation is photostable.
(b) For each calibration exposure the spectroflash alone is fired as usual. To account for the emission of the sample, the photoflash alone is fired, and providing neutral density filters of sufficiently high

FIG 2.4 An example of a microdensitometer trace showing triplet-triplet absorptions.



values of optical density have been used a measure of this emission can be obtained i.e. the "O.D." of the photoflash is measured at certain wavelengths from the microdensitometer trace. From the relation

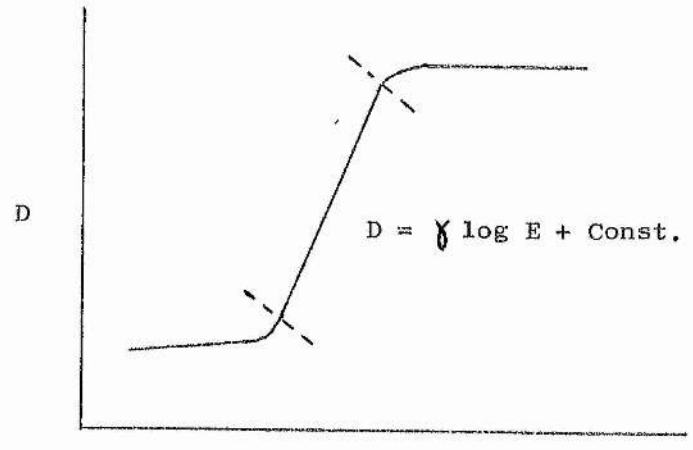
$$O.D. = \log \frac{I_o}{I_t} \qquad \text{where } I_o \text{ is taken as 100\%}$$

I_t the amount of light reaching the photographic plate, when the photoflash is fired alone, can be calculated. By a similar method the amount of light reaching the photographic plate, when the photoflash and spectrographic flashes are fired together can be obtained. Hence, by a straight subtraction and calculating the "true" O.D. of the transient absorption the strong emission can be corrected for. This method is applicable to a solute which is photosensitive, since to measure its transient absorption accurately the photoflash needs firing twice only.

In the methods used above for analysing the data on the photographic plate, it is essential, if we are to get any accuracy at all, that the blackening of the photographic plate varies linearly with the exposure. The density of the photographic image D, over a considerable range, is approximately related to exposure by the expression

$$D = \gamma \log E + \text{const}$$

where γ is a constant. This is shown by the graph below.



For large exposures a point is reached where no matter how much light hits the photographic plate no more blackening occurs. It is essential that we know we are working in the area where D, the blackening of the plate depends linearly upon log E, the logarithm of the exposure.

(ii) The Flash Photo-electric Technique

The sealed quartz cell, containing the sample under investigation, is once again placed between the photolytic lamps and the cell holder casing closed. All units are switched on and allowed to warm up. The wavelength on the scanning unit is selected. The oscilloscope is adjusted for continuous triggering on a fast time base so that a continuous trace is obtained. With the oscilloscope sensitivity on one volt/cm, the best possible light-on, light-off deflection was obtained. 5V for 100% light-on was regarded as a good value and, as far as possible, wide slits on the monochromator rather than high voltage on the photomultiplier were used. In this way the "white noise" was reduced. The oscilloscope triggering was set just below stability so that the trace disappeared, and the oscilloscope was set to single sweep. The photoflash capacitors were then charged up to the required voltage. The oscilloscope camera shutters were opened and the photoflash fired. Finally the camera shutters were closed. In most photographic records the light-on and light-off traces and a trace of the photoflash alone, without the continuous monitoring source, are recorded. At a wavelength where the sample has no measurable absorption initially, it is possible to obtain directly, a plot of the optical density versus time. For this purpose the oscilloscope Y signal which is proportional to light intensity I is converted to optical density.

$$\frac{I}{I_o} = 10^{-O.D.}$$ where I_o is the light-on, light-off signal.

The optical density is proportional to the concentration, c, of the transient species present (if a single species is responsible for the absorption).

$$O.D. = \varepsilon lc$$

Where ε is the molar extinction coefficient of the transient species at the wavelength of observation, and l is the optical path length of the sample cell in the direction of the analysing light. From a plot of O.D. against time (i.e. a plot of c against time for a single species) it is possible to determine if the decay of the transient absorption is first or second order, or shows some mixed kinetics.

(e) Experiments to Determine the Performance of the Apparatus

The wavelength scale of the Hilger Watts Medium Quartz spectrograph was first checked using a copper arc, neon, sodium, potassium and helium lamps. The wavelength scale of the spectrograph was found to be accurate.

(i) The Flash-photographic Technique.

To evaluate the performance of our apparatus, two samples of 2-naphthol were prepared (a) in 0.05 M H_2SO_4 (b) in 0.1 M NaOH. Both of these samples were flashed, and the photographic plates obtained from each sample were analysed. The techniques used were exactly as described in the previous sections. The transient absorption spectra compiled are shown in Figs 2.5 and 2.6. These are in good agreement with the spectra reported by Jackson and Porter[32] and hence the performance of the apparatus was taken as satisfactory.

(ii) The Flash-photoelectric Technique.

A Hilger Watts scanning unit was fitted to the spectrograph for this technique. The calibration of the scanner position was taken

FIG 2.5 The triplet absorption spectrum of 2-naphthol in 0.05 M H_2SO_4: (the spectrum from Jackson and Porter[32] is shown inset).

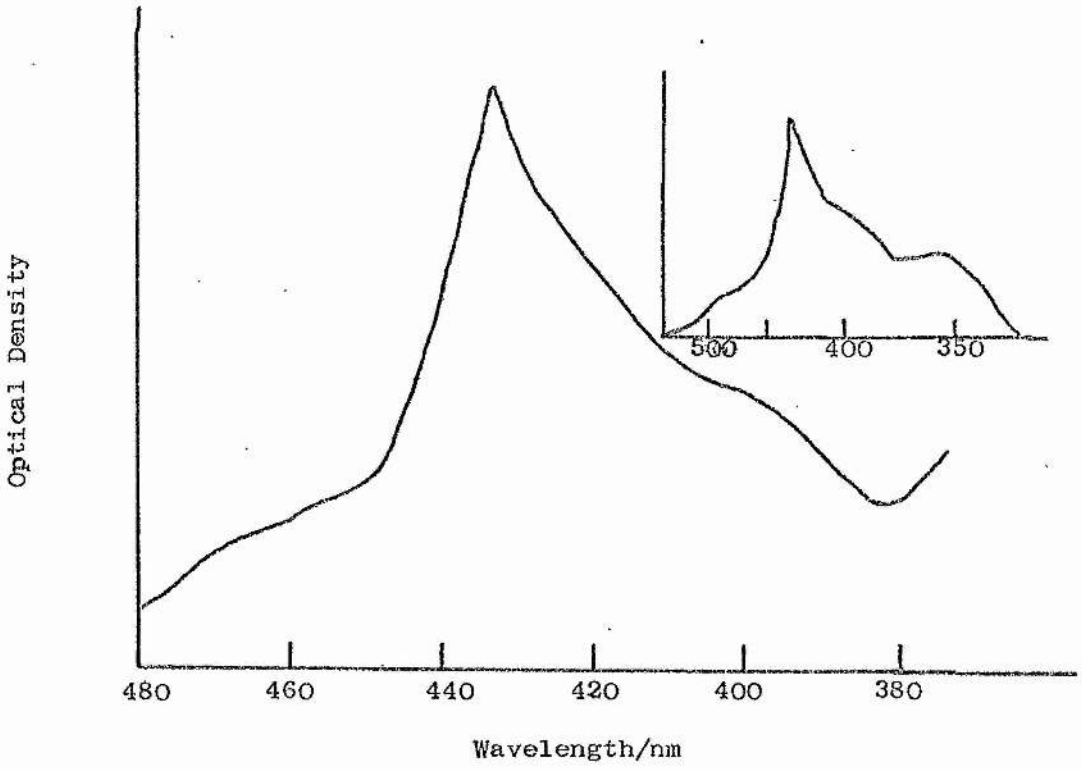
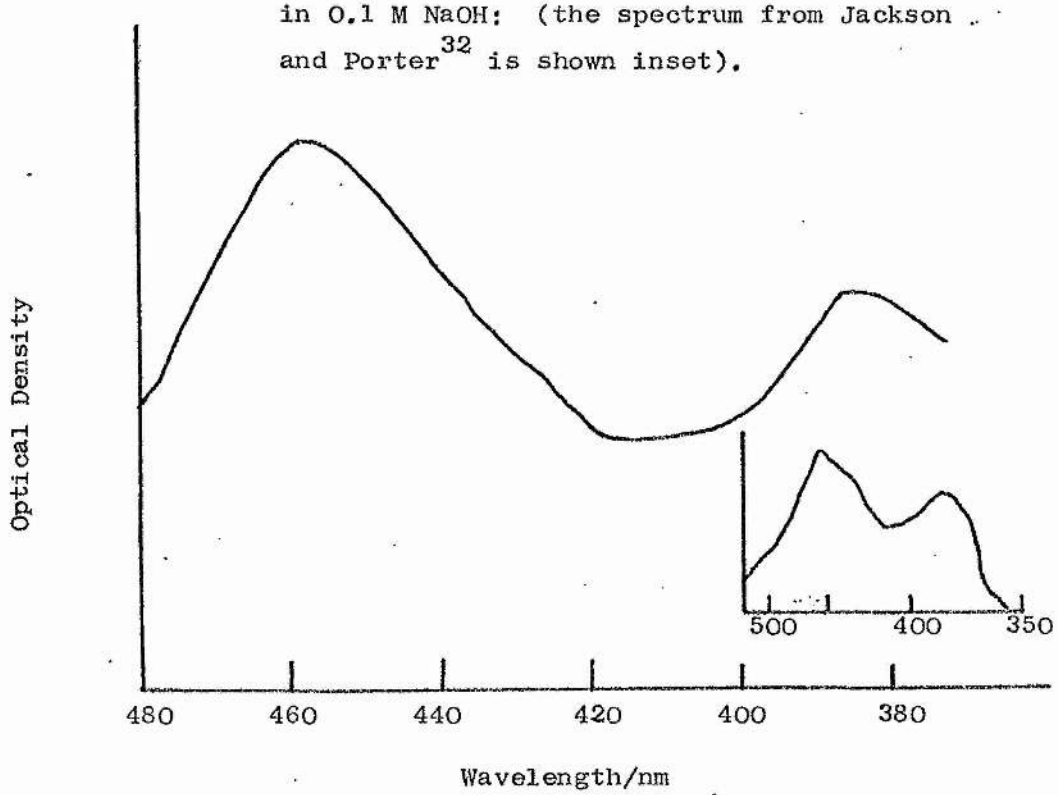


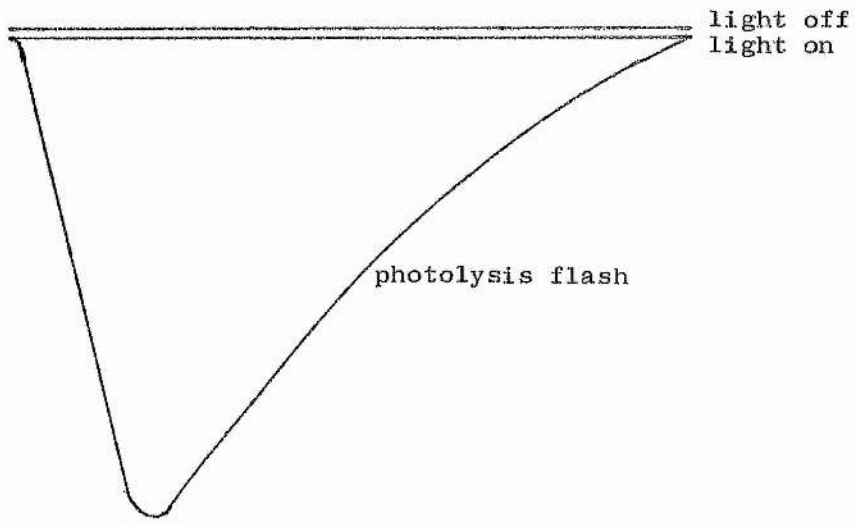
FIG 2.6 The triplet absorption spectrum of 2-naphthol in 0.1 M NaOH: (the spectrum from Jackson and Porter[32] is shown inset).



as in the manual, and no checks were performed, the argument for this being that, since triplet-triplet absorptions are broad and unresolved in fluid solution, the wavelength scale does not need to be highly accurate.

In order to observe the performance of our apparatus when used for the flash-photoelectric technique, a 10^{-4} M of anthracene in hexane was prepared and degassed. The apparatus was set up as described and allowed to warm up. The sample cell was placed between the photolysis lamps.

When the photoflash was fired, the scattered light was found to be more intense than the light-on light-off signal by a factor of approximately 100, as shown in the following diagram.



It is obvious that we would not see any triplet-triplet absorption with so much scattered light. To decrease this scattered light black tubes were fitted between points A and B, and C and D, in Fig 2.6. Baffles were also placed around the sample cell, and any surface capable of reflecting light from the photoflash onto the plane mirror D

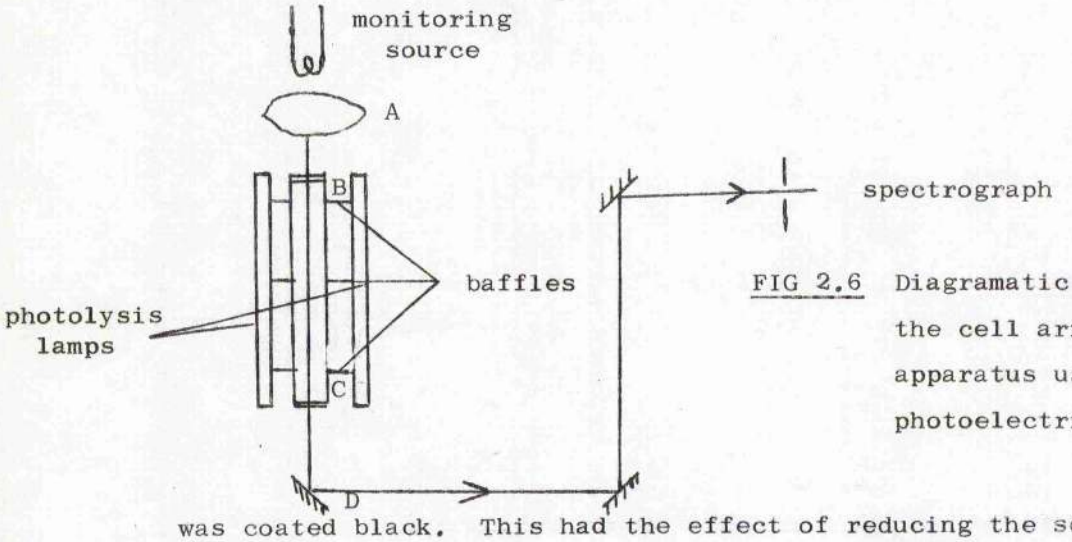
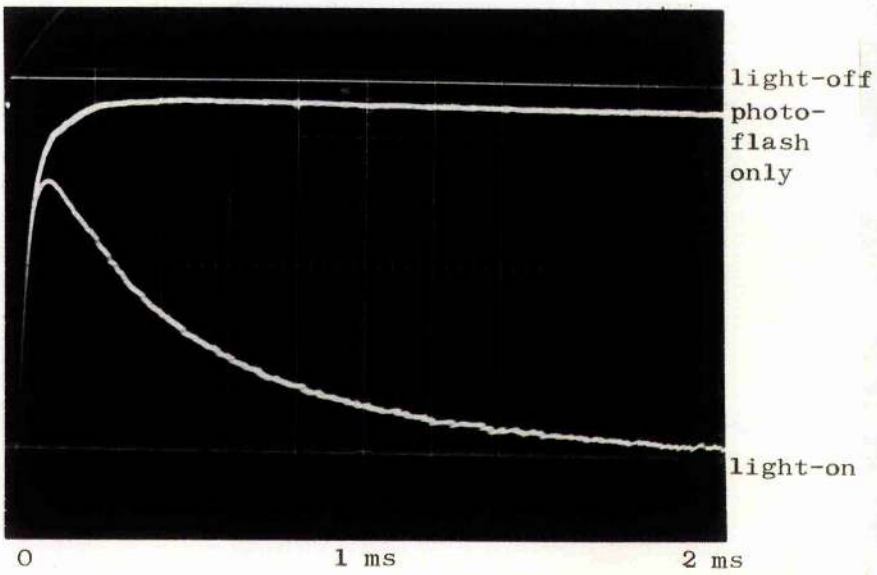


FIG 2.6 Diagramatic representation of the cell arrangement in the apparatus used for the flash-photoelectric technique.

was coated black. This had the effect of reducing the scattered light to slightly less than the light-on light-off signal, and hence a workable system was obtained.

The anthracene in hexane sample was flashed and the resulting photograph is shown in Fig 2.7.

FIG 2.7 The flash-photoelectric trace of anthracene in hexane.



This is in close agreement with the results obtained by Porter and Wright[45]. The performance of the apparatus was therefore regarded as satisfactory. However, if the apparatus is to be used in the flash-photoelectric mode for long-periods it would be advisable to construct a new horizontal cell housing and optical system where the scattered light is reduced to a much smaller intensity.

4. EMISSION SPECTROSCOPY

(a) General Description of Spectrophotometer

The emission spectra were obtained using a Perkin Elmer Hitachi MPF-2A Spectrophotometer[46]. The spectrometer includes two grating monochromators, one for irradiating a sample with monochromatic light in the 200 to 700 nm range (excitation monochromator), and the other for permitting selective measurement of the intensity of the light emitted by the sample in the 220 to 800 nm range (emission monochromator).

Light from the 150 watt xenon lamp source passes into the excitation monochromator where it strikes a beam splitter before dispersion. The portion of the beam which is deflected by the splitter strikes the reference photomultiplier where the reference signal is produced. This signal is used in the ratio recording mode where correction for source intensity fluctuation is made. The portion of the beam which is not deflected by the splitter is dispersed in the excitation monochromator, and light from the excitation monochromator is focussed on the sample. Light emission from the sample is directed into the emission monochromator where it is dispersed. This dispersed light strikes the sample photomultiplier, producing a signal proportional to the intensity of the emitted radiation. This signal is amplified and recorded on a chart. Continuous scanning of either the

excitation or the emission spectrum of a sample is possible. The wavelength passed by either monochromator at a given time is indicated by the wavelength dial and by a wavelength marker that produces marks at 20 nm intervals on the recorder chart paper.

(b) Sampling Techniques

Emission from Fluid Solutions.

The emission was detected at right angles to the incident light. Continuous spectra were recorded using the reference mode except during the preliminary investigations. When a series of measurements were to be taken a reference solution was also employed, viz. a sample of quinone sulphate in 0.5 M H_2SO_4. The intensity of emission from the reference was measured immediately before that of the sample, and all sample measurements could then be corrected to the same light intensity. In all cases, solutions were made dilute enough to avoid inner filter effects. When the removal of dissolved oxygen was required, the freeze-pump-thaw process was employed. 1 cm spectrosil cells were used for all measurements.

Emission from Solid Solutions at Low Temperature.

Phosphorescence and total emission spectra at 77 K were obtained using the phosphorescence accessory of the MPF-2A. Total emission spectra (fluorescence and phosphorescence) were by right-angled optics with the chopper removed from the unit. The sample was contained in a quartz tube which fitted into the Dewar flask containing liquid nitrogen. The most suitable solvents for this type of measurement are those which form perfect, clear glasses at low temperature but, unfortunately, only a few solvents and solvent mixtures do this[47]. The aqueous solutions mainly used in this work form on freezing, cracked glasses, or opaque solids which make quantitative work impossible though useful qualitative

results can be obtained.

The amount of incident light reflected from the sample is dependent on the extent of cracking and thus the emission intensity is very sensitive to the position of the sample tube relative to the incident beam. It is possible to obtain the emission spectrum, although in many cases the resolution is not good, but it is not possible to make quantitative measurements of the intensity. The scattered light from these solid solutions is sometimes very high and can interfere with the measurement of the total luminescence spectrum, although this does not effect the measurement of phosphorescence spectra as the scattered excitation light is cut off by the chopper.

(c) Correction of Excitation Spectra

The excitation spectrum is obtained experimentally by setting the emission monochromator at, or near, the wavelength of maximum emission intensity and then scanning the lower wavelengths with the excitation monochromator. The intensity of fluorescence is plotted against the wavelength of exciting radiation. This uncorrected spectrum depends upon the characteristics of the monochromator and nature of the source and may be a grossly distorted version of the absolute spectrum.

Several methods have been used to determine correction factors for correcting excitation spectra. The correction factors used in this work were obtained by T.M. Shepherd and J.F. Ireland[49] using a method described by Argauer and White[50]. This method utilises the fact that the absorption spectrum and the true excitation spectrum of a compound, which has a constant quantum yield over the wavelengths scanned, are identical. Thus a comparison of the uncorrected excitation spectrum with the absorption spectrum should give a measure of the relative

spectral intensity of the excitation source. Argauer and White suggested the use of the aluminium chelate of 2,2'-dihydroxy-1,1'-azo-naphthalene-4 sulphonic acid sodium salt, and this was used to obtain the correction factors for our spectrophotometer.

(d) Correction of Emission Spectra

Absolute emission spectra relate the quantum intensity (in quanta per unit wavenumber interval) to wavenumber (in cm^{-1}). If Q represents the total number of quanta (of all wavenumbers) emitted by the solution per unit time, then $dQ/d\bar{\nu}$ represents the intensity at a wavenumber $\bar{\nu}$ and the plot of $dQ/d\bar{\nu}$ against $\bar{\nu}$ is the true luminescence emission spectrum. Few spectrofluorimeters measure this directly; most provide an apparent emission curve which is obtained by setting the excitation monochromator at a wavelength at which the sample absorbs, and scanning longer wavelengths with the emission monochromator. The observed photomultiplier output ($A\bar{\nu}$) must therefore be corrected for variation in the photomultiplier sensitivity, the dispersions of the emission monochromator, and light losses. Thus $A\bar{\nu}$ is given by:

$$A\bar{\nu} = (dQ/d\bar{\nu}) (S\bar{\nu}) \qquad 2.1$$

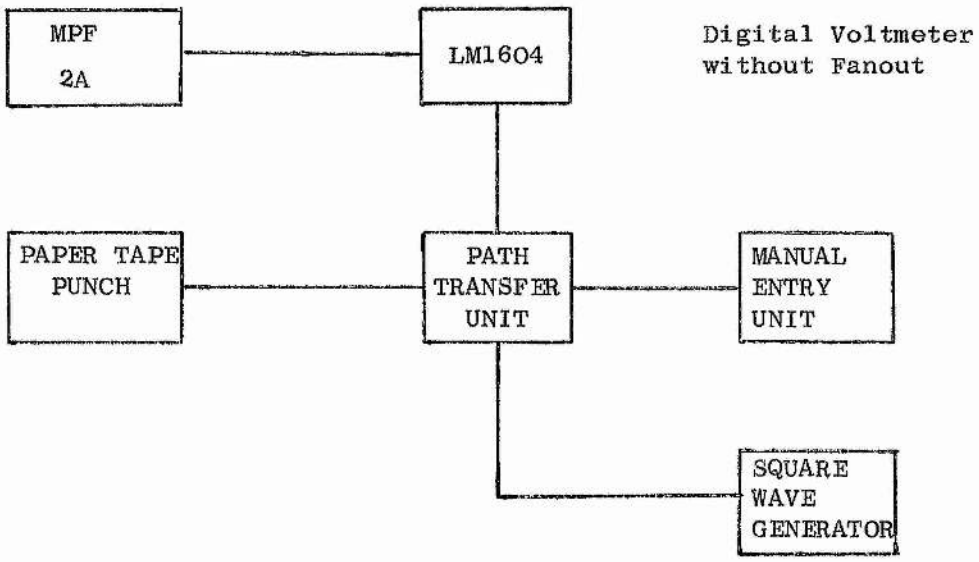
where $S\bar{\nu}$ is the spectral sensitivity factor of the monochromator-photomultiplier combination. This spectral sensitivity curve was obtained for our spectrophotometer by T.M. Shepherd[48] and J.F. Ireland.[49] If the absolute fluorescence emission spectrum has been determined precisely for a series of compounds that emit over the range for which a spectral sensitivity factor is required, then measurement of the uncorrected emission spectrum of these compounds with the instrument to be calibrated permits direct calculation of $S\bar{\nu}$ by application of equation 2.1. Using this method Ireland[49] obtained the spectral sensitivity curve for the range 300 to 800 nm.

(e) Automatic Digitalisation and Correction of Excitation and Emission Spectra.

Correction of spectra can be a tedious process. Several directly correcting spectrofluorimeters have been described where the correction function is stored internally e.g. on a mechanical cam or its electronic analogue[51-54]. Indirect correction of emission spectra using computers has also been used[55,56], but the full potential of these computer-based methods can only be realised if the spectral data can be conveniently and rapidly transferred into a computer-readable form. The apparatus described below achieves this requirement using automatically punched paper tapes. A schematic diagram of the apparatus is shown in Fig 2.8.

FIG. 2.8

Schematic diagram of automatic digitalisation apparatus.



The output signal from the spectrophotometer (MPF-2A) is connected to a Solartron LM1604 digital voltmeter with an EX3054 positive logic fan-out unit. The voltmeter is interlinked, with a Solartron 3230 data transfer unit, with a Facit 4070 paper tape punch acting as an output device. This arrangement allows the uncorrected detector voltage of the MPF-2A to be sampled and recorded at rates up to a maximum of about

four samples per second. This corresponds to a reading approximately every 0.1 nm when the spectrofluorimeter is scanning at its slowest rate of 25 nm per minute. Slower sampling rates are obtained by initiating the sampling cycle from a variable square wave signal generator. The details of operation and computer processing have been given previously by Ireland[49].

5. AUTOMATIC DIGITILISATION OF THE MICRODENSITOMETER

The automatic digitilisation apparatus (Fig. 2.8) was applied to the microdensitometer, in order that the information on the photographic plate records of flash photolysis experiments could be transferred into a computer-readable form.

In flash photolysis experiments, the spectroflash enters the spectrograph after passing through the sample. It is dispersed through a prism in the spectrograph before hitting the photographic plate. Hence the spectral intensities recorded on the photographic plate do not vary linearly with wavelength. The automatic digitalisation apparatus samples at regular intervals and so it is important that the wavelength is related to distance travelled as the microdensitometer scanns the photographic plate. This was done by observing the wavelength scale on a photographic plate under a travelling microscope. The microscope was fixed on the 650 nm marker and the vernier reading noted. The microscope was then racked back and focussed on the 640 nm marker and the vernier reading taken. This was repeated every 10 nm until the 300 nm marker was reached, whence the distance between successive 10 nm markers was known. This operation was repeated for two more plates and reproducible results were obtained. The time taken for the microdensitometer to travel from the 650 nm marker to the 300 nm marker was 139.8 secs. Thus we know the time taken to reach every 10 nm

wavelength marker between 650 nm and 300 nm. This information was fed into the computer on a curve fitting program. The computer output was, therefore, a record of the relationship between wavelength and sampling time. Having obtained this relationship the spectral data in the photographic plates can be transferred to the punch-tape, fed into the computer and the tedious effort of manually compiling transient absorption spectra can therefore be eliminated.

(a) Operation

The detector voltage sampling rate is set to 120 samples per minute by means of the square wave signal generator. Thus for scanning one spectrum from 650 nm to 300 nm, approximately 280 readings are taken. To scan a spectrum on the photographic plate, the microdensitometer is always started at 650 nm. The spectra corresponding to the appropriate neutral density filters are then scanned (in increasing order of magnitude) with the tape punch activated. A symbol indicating the end of each data set (i.e. each spectrum on the photographic plate) is punched on the tape via a Solartron 3209 manual entry unit. Finally the transient absorption spectrum is scanned and a series of symbols is punched onto the tape to indicate the end of the information. To stop each scan at the same position is difficult and so the operator terminates each scan where he so wishes. The program used to analyse the information discovers the number of readings corresponding to the shortest scan and reduces each of the other sets of information to this number of readings. The paper tape is now a digital record of the information recorded on a photographic plate.

This digital record is now entered into an IBM 360/44 computer via a Honeywell 3591 paper tape reader. To analyse this information SPEKC was used. This program incorporates the relation between wavelength

and sampling rate measured as described earlier. The transient absorption spectrum required is produced as a punched card output. This punched card output is used with the plotting program SPEKD. The decision to keep the plotting routine separate was based on the experience that not all spectra need to be plotted. An example of the transient absorption spectrum so obtained, is shown in Fig 2.9.

Listings of SPEKC and SPEKD are given in Appendix I and II. The automatic digitalisation system was set up and the programs SPEKC and SPEKD were written by Dr. T.M. Shepherd with a little assistance from myself.

(b) To Determine the Performance of the Automatic Digitalisation Procedure applied to the Microdensitometer.

The photographic record of the flash photolysis of 1-naphthol 2-sulphonate in 1 M sodium hydroxide was taken. The transient absorption spectrum was compiled (i) from the chart recording output from the microdensitometer as described previously in Chapter 2.3d(i), and (ii) by means of the automatic digitalisation procedure described in Chapter 2.5(a). The two transient absorption spectra obtained are compared in Fig 2.9. The small difference can be explained.

In method (i) the wavelength scale is placed on the microdensitometer chart output by scanning along the wavelength scale of the photographic plate. There is a noticeable time delay between scanning a certain wavelength marker on the plate and the instant when the mark is seen on the chart. In method (ii) each wavelength is known accurately for each sampling time. Thus the transient absorption compiled by method (i) is at a slightly longer wavelength than that obtained by method (ii).

It is concluded that the absorption spectrum obtained from method (ii) is the more reliable. The accuracy of the microdensitometer

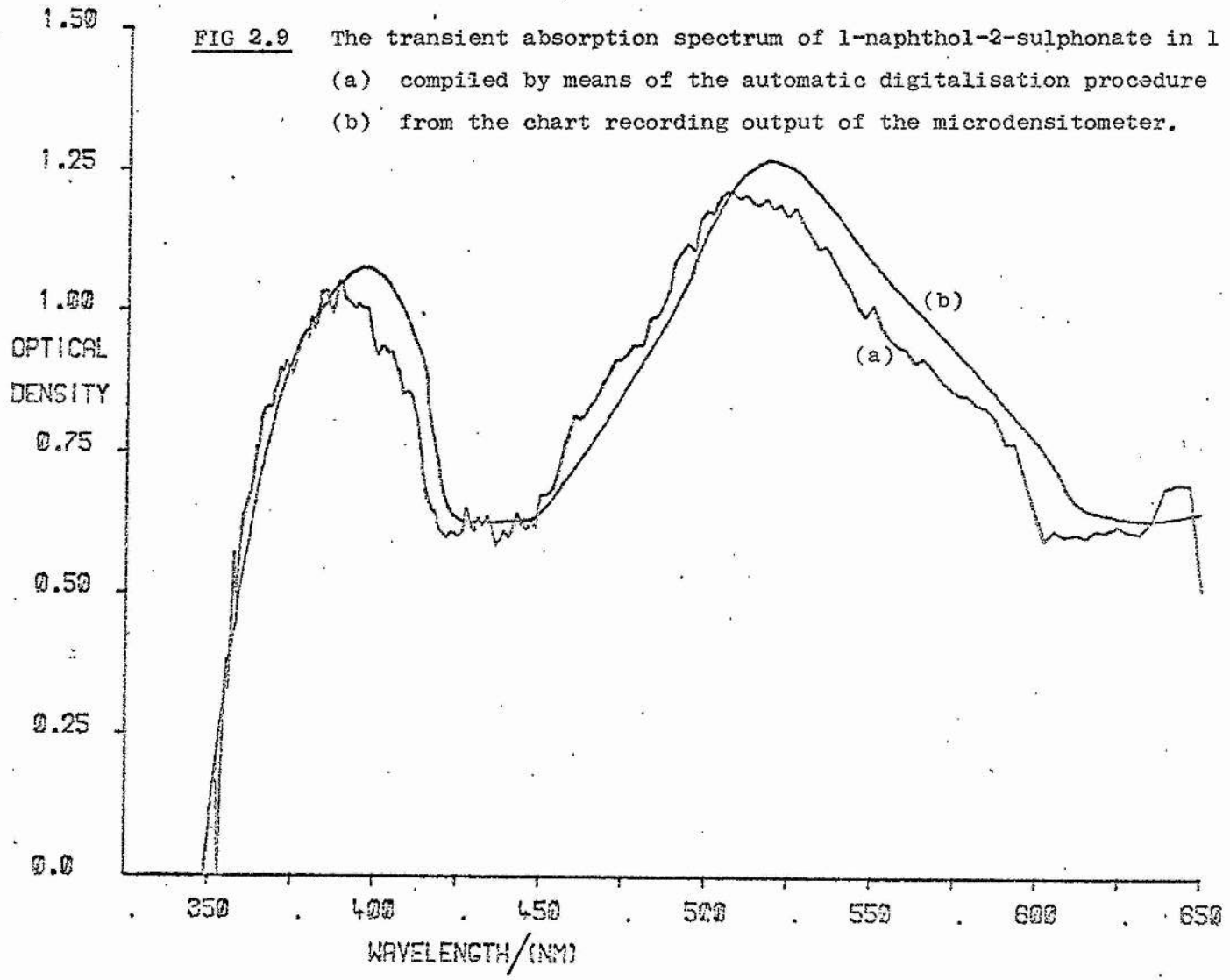


FIG 2.9 The transient absorption spectrum of 1-naphthol-2-sulphonate in 1 M sodium hydroxide.
(a) compiled by means of the automatic digitalisation procedure and
(b) from the chart recording output of the microdensitometer.

is such that one could not quote the wavelength of maxima within $\pm$ 5 nm any way. The triplet-triplet absorption spectra of organic compounds in aqueous solution are usually broad and unresolved. Since the transient absorption spectra in this work are only compiled to determine a wavelength of absorption for following changes in this absorption with pH or H_o, the method (ii) of compiling spectra was quite adequate.

CHAPTER 3

1-NAPHTHOL IN CONCENTRATED ACID SOLUTIONS

(a) Introduction

Förster[21-23] and Weller[57-59] have established that the acidic or basic strength of many organic molecules is quite different, according to whether they are in the ground state or the first excited singlet state. Jackson and Porter[32] have shown that for some compounds the pK of the first excited triplet state is very different from that of the first excited singlet, but close to that of the ground state.

Daudel et al[15], with the aid of quantum mechanical methods, attempted to understand the origin of these differences of pK. They were able to show theoretically that, for electron donating substituents, the variation of pK during the first transition, $S_1 \leftarrow S_o$, is always negative for α and β derivatives of naphthalene: i.e. the molecules become more acidic. They also concluded that the difference between $pK(S_o)$ and $pK(T_1)$ should be less than between $pK(S_o)$ and $pK(S_1)$ for donor substituents in the β position, acceptor substituents in the α and β positions, and a hetero acceptor in the α position. These are the only types of molecules for which Jackson and Porter made measurements and they found in these cases a $pK(T_1)$ near $pK(S_o)$ and very different from $pK(S_1)$.

The calculations of Daudel et al showed that the situation should not be the same for α donating substituents and hetero acceptors in the β position. For these compounds, one might find a $pK(T_1)$ very much further from $pK(S_o)$.

Thus one might expect that the $pK(T_1)$ of 1-naphthol would be quite different from its $pK(S_o)$. Consider Table 3.1.

TABLE 3.1

The acidity constants of 1- and 2-naphthol

	$pK(S_o)$	$pK(S_1)$	$pK(T_1)$
1-naphthol	9.34[61]	2.0[28]	
	9.23[28]		
2-naphthol	9.51[61]	2.81[28]	8.1[32]
	9.49[28]	3.0[32]	7.7[32]

Jackson and Porter did not measure $pK(T_1)$ for 1-naphthol, and were in fact unable to detect any triplet absorption spectra. Since it seemed possible that $pK(T_1)$ might be much more negative than $pK(S_1)$ it was decided to conduct a flash photolysis investigation of 1-naphthol at high acidities.

(b) Purity of 1-Naphthol

Eastman Kodak material was purified by recrystallizing three times from 25% ethyl alcohol after boiling with decolourizing carbon. The melting point was recorded as 95-96°C (lit. 94-96°C).[60] The solid material was dried and stored under vacuum, as a precaution against air oxidation. Before using the material, a sample was vacuum sublimed just prior to use. The apparatus used is shown in Fig 3.1. The 1-naphthol was heated by means of a water bath.

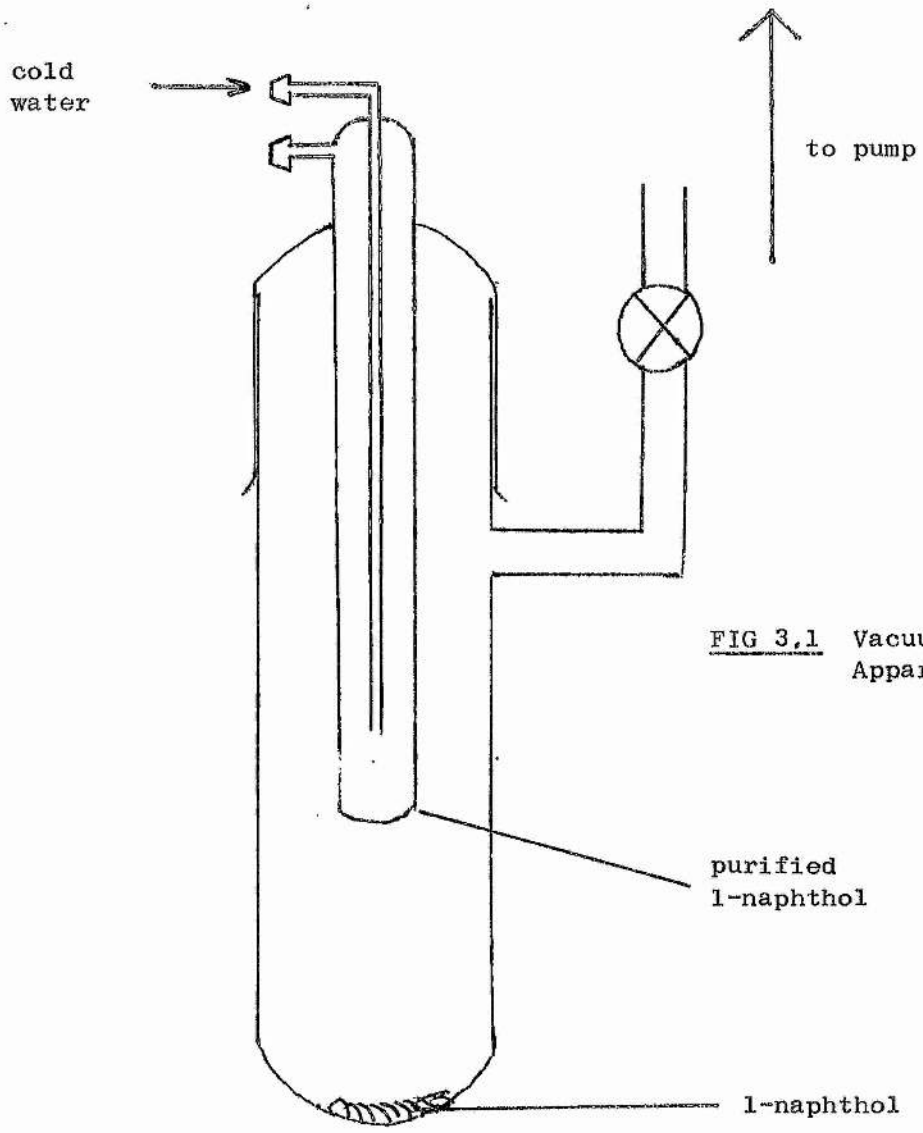


FIG 3.1 Vacuum Sublimation Apparatus

(c) Absorption Spectra

The absorption spectra of 1-naphthol in solutions of pH 7.0 and 14.0 are shown in Fig 3.2. These are in agreement with the spectra previously reported.[61-63] If a sample of 1-naphthol in 98% sulphuric acid is allowed to stand overnight before its u.v. absorption spectrum is recorded, the spectrum seems to have undergone little change, but for a slight solvent shift, from the spectrum of 1-naphthol in water. See Fig 3.3.

However, when the u.v. absorption spectrum of 1-naphthol in 98% sulphuric acid was recorded immediately after preparation, it was found to be considerably different from the spectrum of 1-naphthol in

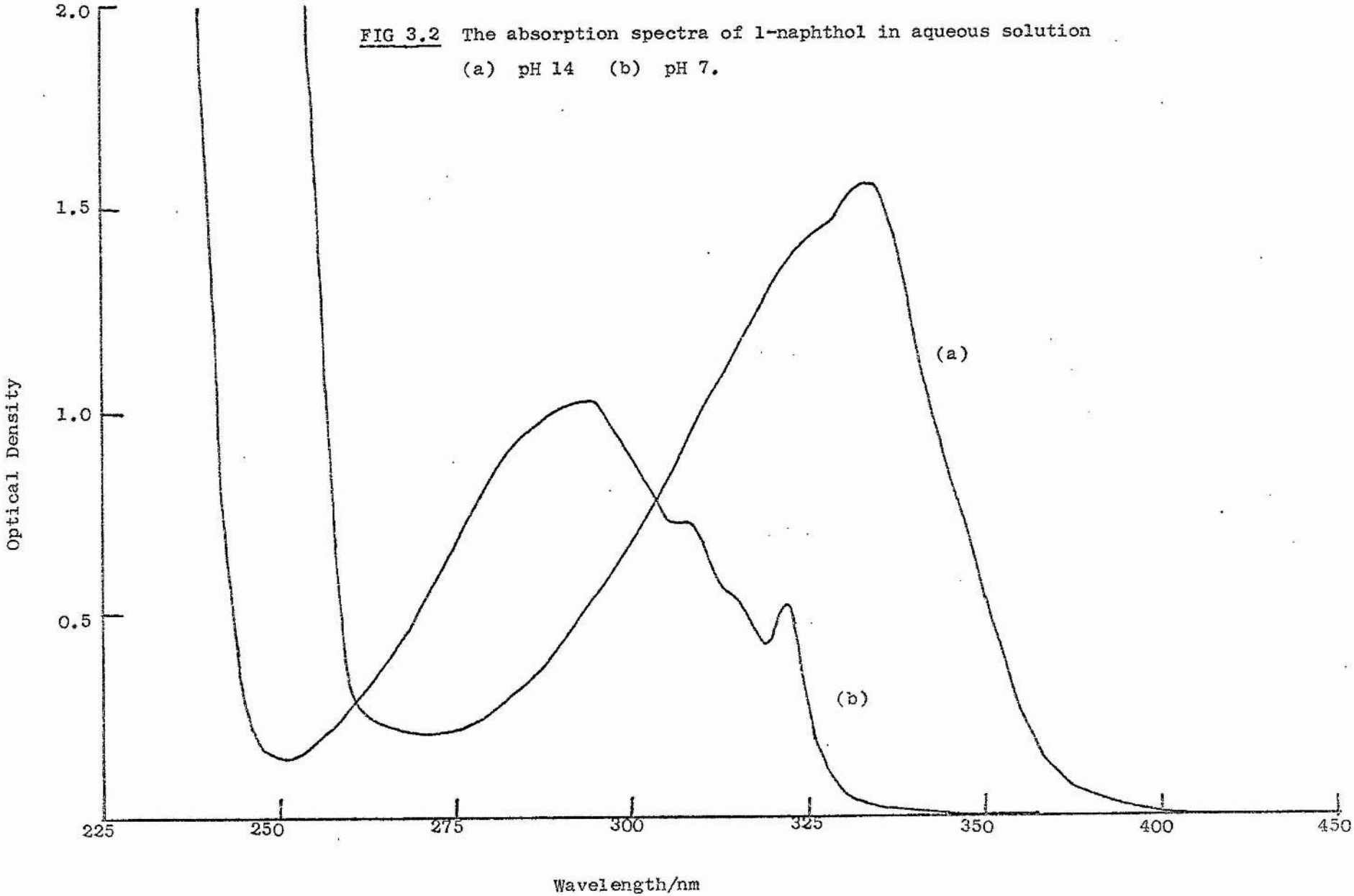


FIG 3.2 The absorption spectra of 1-naphthol in aqueous solution
(a) pH 14 (b) pH 7.

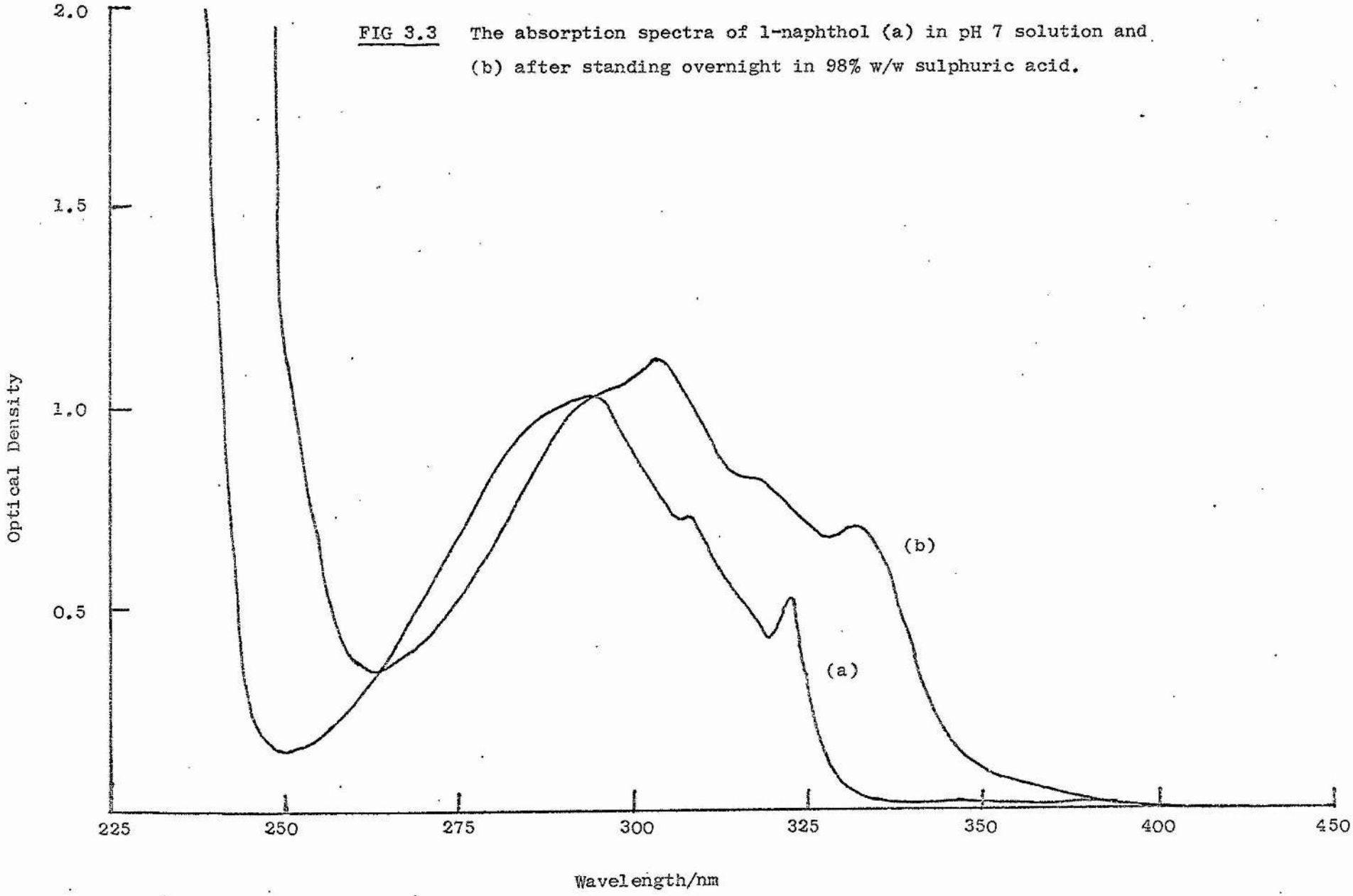
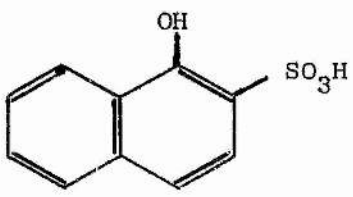


FIG 3.3 The absorption spectra of 1-naphthol (a) in pH 7 solution and (b) after standing overnight in 98% w/w sulphuric acid.

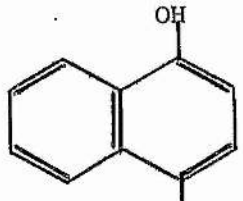
water. See Fig 3.4. A similar spectrum of 1-naphthol was observed in 70% perchloric acid also. This spectrum was also recorded immediately after preparation of the solution. See Fig 3.5.

The change in absorption spectrum with time for 1-naphthol in sulphuric acid is shown in Figs 3.6 and 3.7. The spectrum of 1-naphthol in sulphuric acid solutions below 70% w/w approx. was quite stable with time. The presence of isobestic points in Figs 3.6 and 3.7 implies that a simple reaction is occuring. The situation with 1-naphthol in 70% w/w perchloric acid is not as simple. When the absorption spectrum is followed with time no isobestic points are observed and it would appear that the 1-naphthol was oxidised and completely transformed.

It is known that monosulphonation of 1-naphthol occurs with weak oleum or 100% sulphuric acid[64,65]. Monosulphonation occurs in the 2- and 4-positions to form Schaeffer's (I) and Nevile-Winther's acids (II)



I

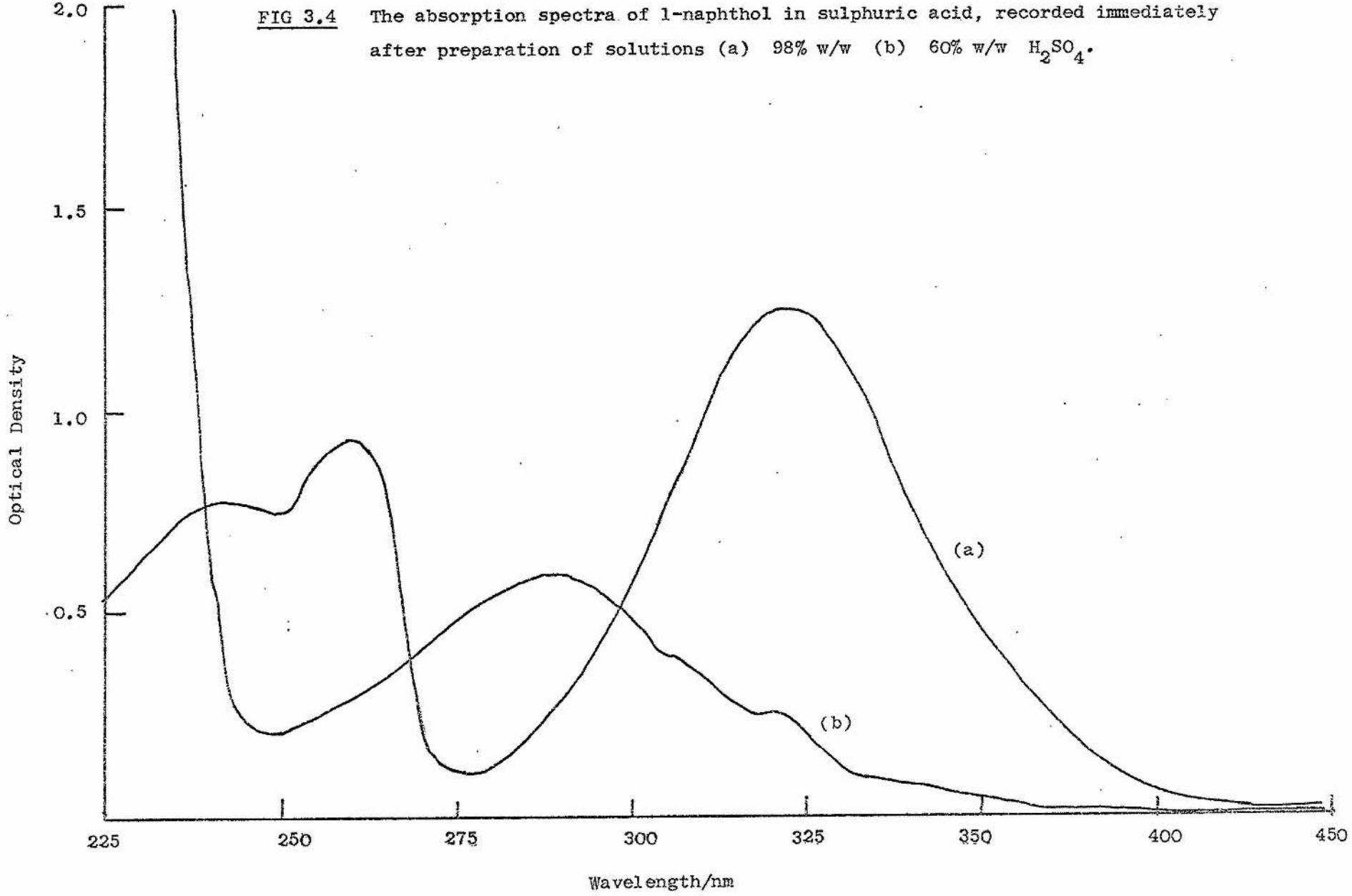


II

Thus 1-naphthol in sulphuric acid of above 70% w/w is undergoing slow sulphonation to form a mixture of 1-naphthol-2- and -4-sulphonic acids. The absorption spectrum of 1-naphthol which had been allowed to stand overnight in 98% w/w sulphuric acid (Fig 3.3) is clearly the spectrum of a mixture of 1-naphthol-2- and -4-sulphonic acids.

This was shown by mixing, in approximately equal amounts, 1-naphthol-2-sulphonic acid and 1-naphthol-4-sulphonic acid in water. The u.v. absorption spectrum was recorded, and was found to be identical with that

FIG 3.4 The absorption spectra of 1-naphthol in sulphuric acid, recorded immediately after preparation of solutions (a) 98% w/w (b) 60% w/w H_2SO_4.



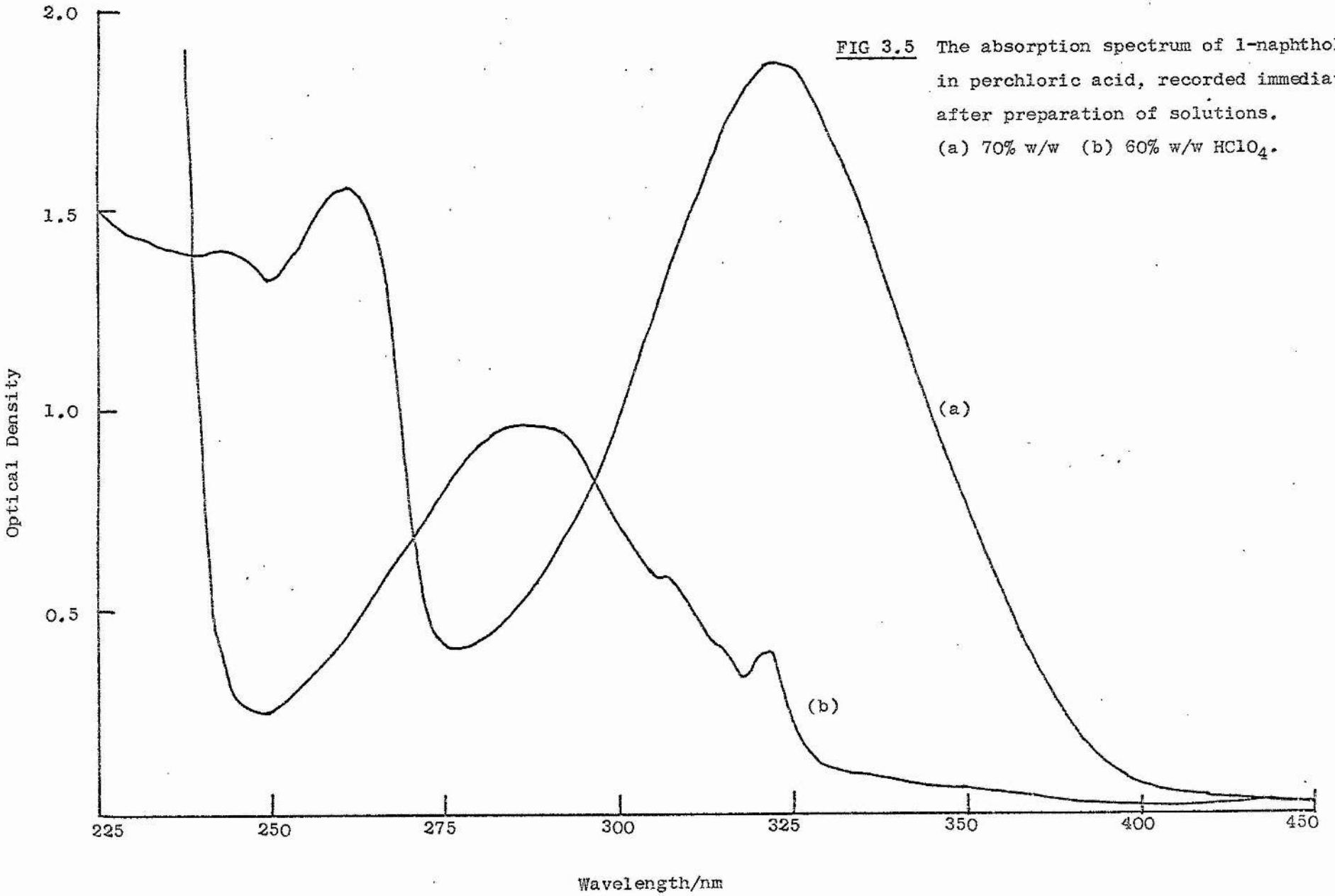


FIG 3.5 The absorption spectrum of 1-naphthol in perchloric acid, recorded immediately after preparation of solutions.
(a) 70% w/w (b) 60% w/w $HClO_4$.

FIG 3.6 The absorption spectrum of 1-naphthol in 84% w/w sulphuric acid recorded after (a) 15 (b) 29 (c) 62 (d) 110 (e) 175 (f) 230 minutes.

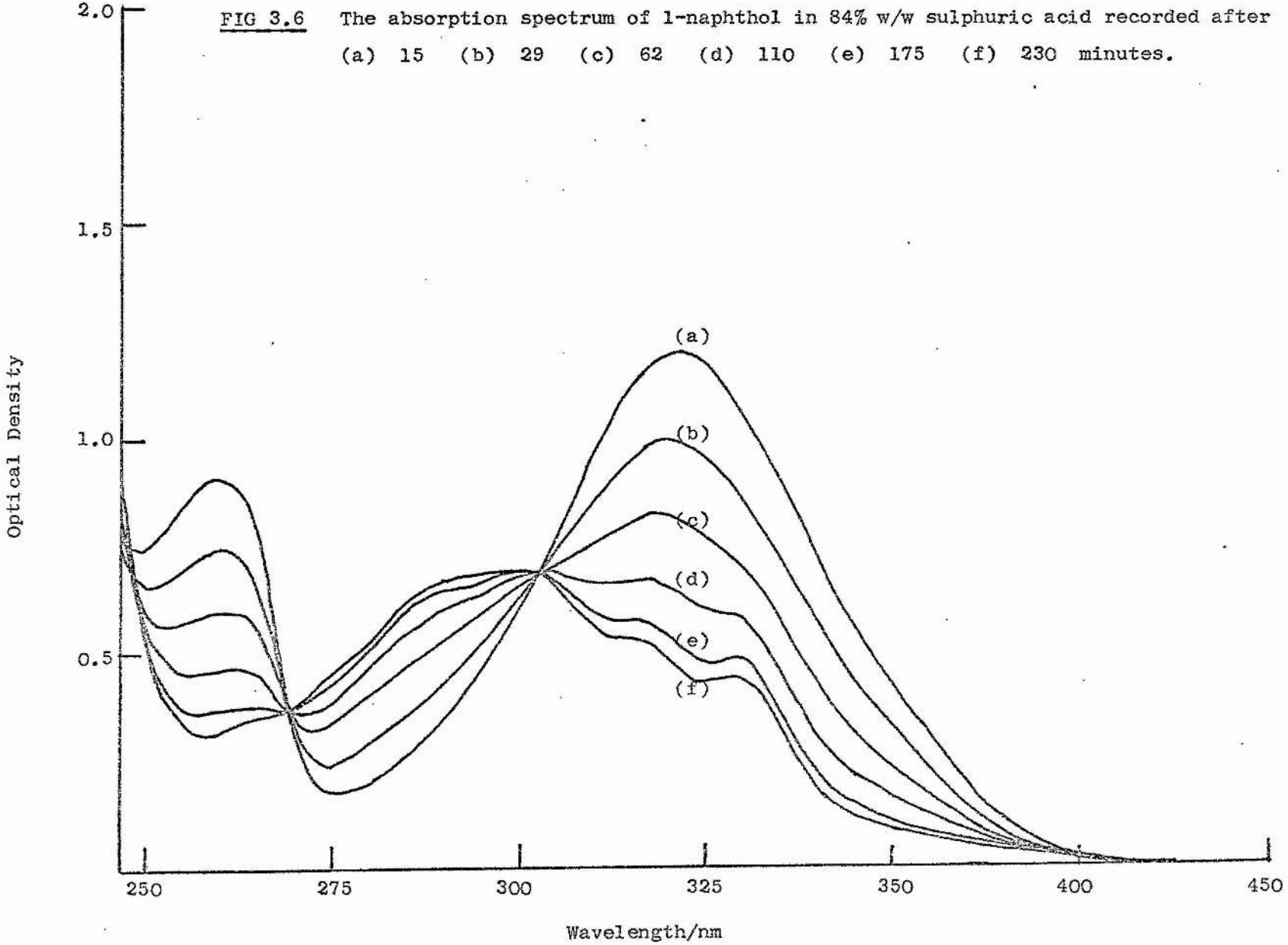
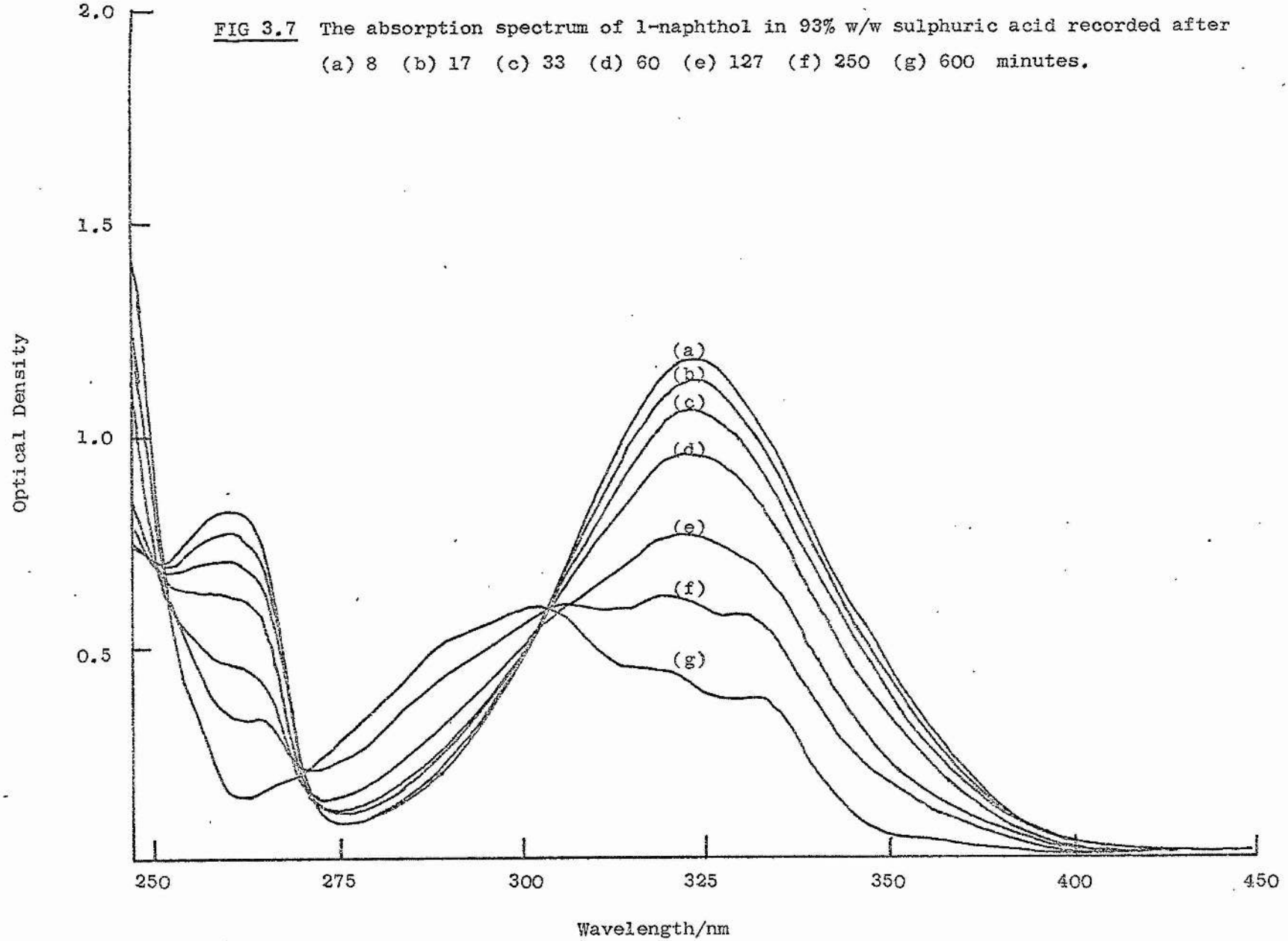


FIG 3.7 The absorption spectrum of 1-naphthol in 93% w/w sulphuric acid recorded after (a) 8 (b) 17 (c) 33 (d) 60 (e) 127 (f) 250 (g) 600 minutes.



obtained from 1-naphthol in concentrated sulphuric acid. Further evidence was obtained when 1-naphthol-4-sulphonic acid was dissolved in strong sulphuric acid and the u.v. spectrum followed with time (Fig. 3.8.). The 1-naphthol-4-sulphonic acid underwent isomerization to a mixture of 2- and 4-sulphonic acids. 1-Naphthol-2-sulphonic acid also isomerized in strong sulphuric acid (Fig. 3.9.).

(d) The Species Formed from 1-Naphthol in Strong Acids Immediately After Mixing.

The spectra obtained immediately after 1-naphthol had been dissolved in 98% w/w sulphuric acid and 70% w/w perchloric acid are identical (Figs. 3.4 and 3.5). It is proposed that 1-naphthol is protonated in these acids, and the long wavelength band (maximum = 322 nm) in Figs 3.4 and 3.5 is attributed to the protonated species.

(e) The Position of Protonation of 1-Naphthol in Strong Acid

It is now well established that benzene and its derivatives form proton-addition compounds, commonly called σ complexes or benzenonium ions, in strongly acidic media.[66] Kresge, Chiang and Hakka[67] showed by nmr and uv spectra that the conjugate acids of 1.3.5 trihydroxybenzene and its ethers are benzenonium ions.

The nmr spectrum of 1-naphthol in 70% w/w perchloric acid and 98% w/w sulphuric acid was recorded using a Varian H.A.100 spectrometer with the tetramethylammonium ion as an internal reference. The spectrum was similar in sulphuric acid and perchloric acid. The spectrum shows a complicated pattern of peaks at low field, but a single (slightly broad) peak at δ = 4.6 ppm. This single peak is sharper in 98% w/w sulphuric acid than 70% w/w perchloric acid. The low field pattern of peaks remained stable with time, whereas the intensity of the high field peak

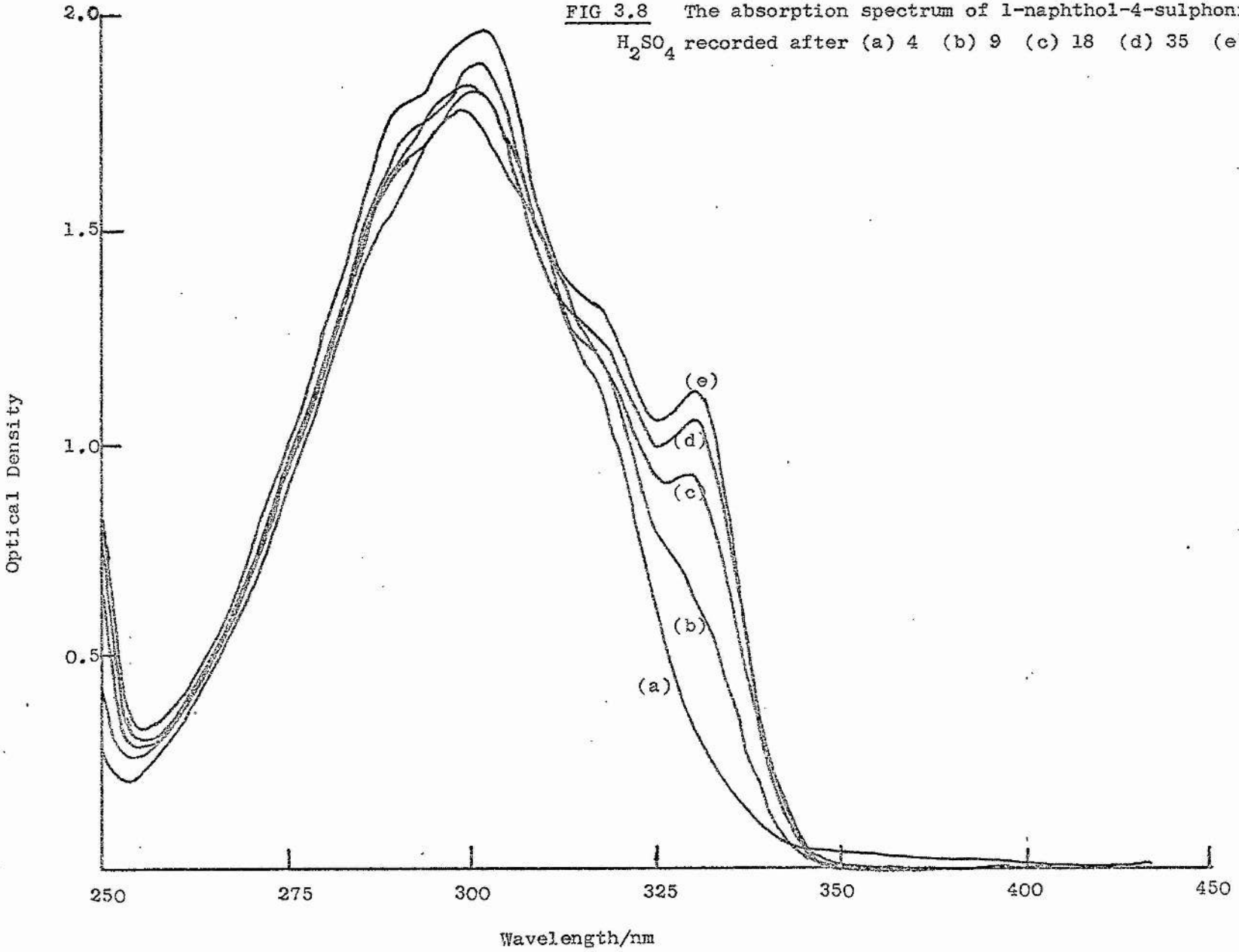
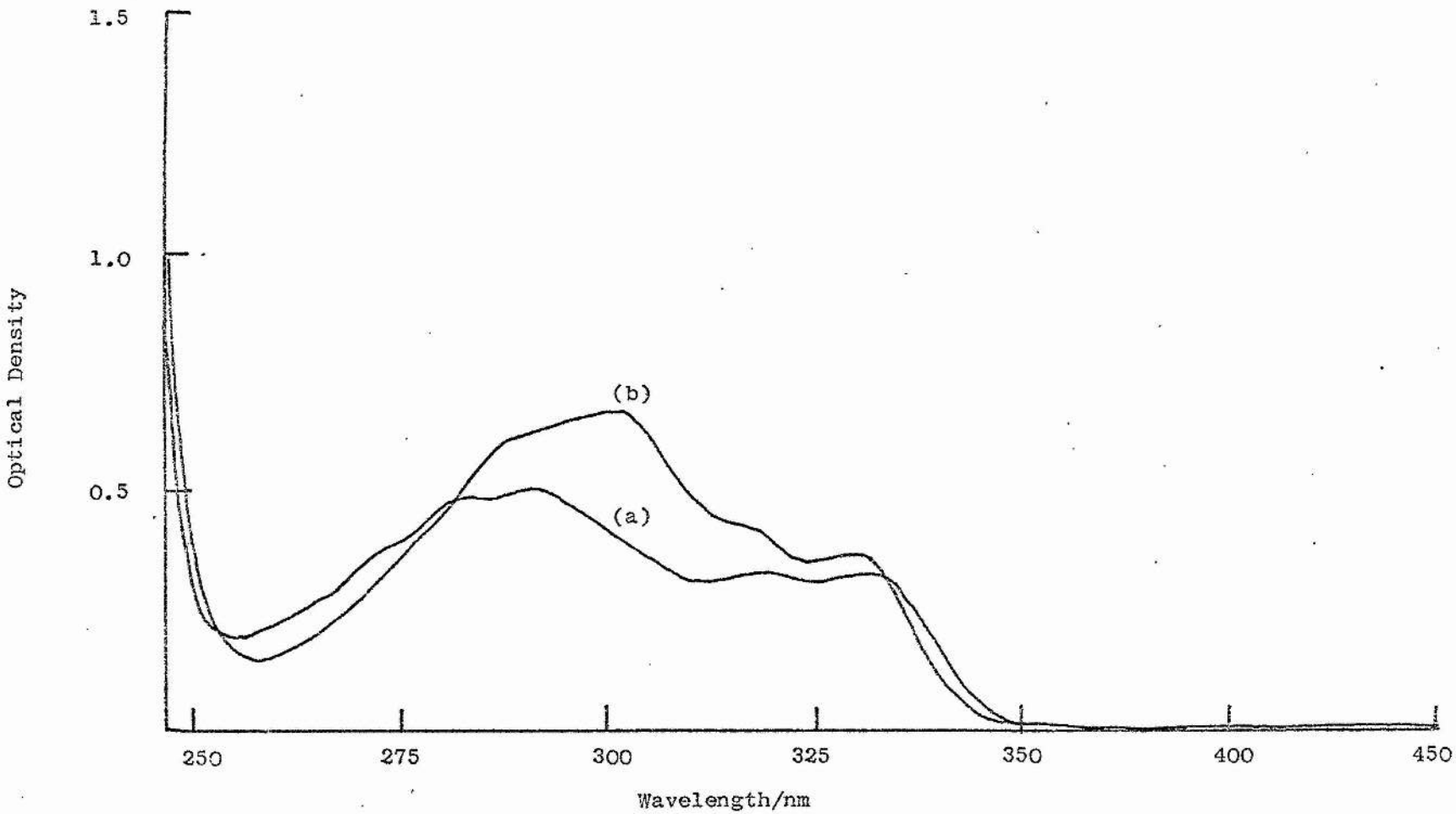


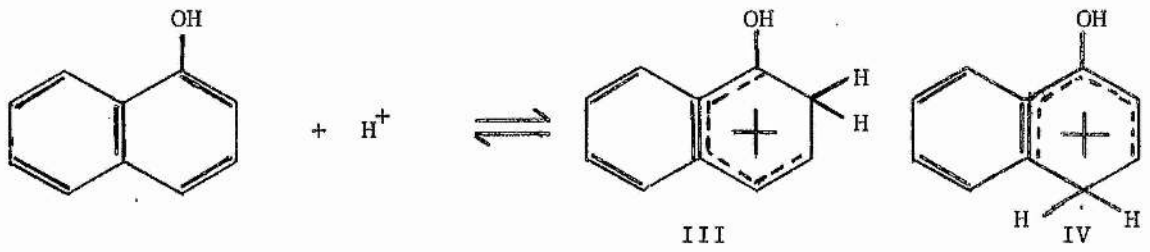
FIG 3.8 The absorption spectrum of 1-naphthol-4-sulphonic acid in 88% w/w H_2SO_4 recorded after (a) 4 (b) 9 (c) 18 (d) 35 (e) 75 minutes.

FIG 3.9 The absorption spectrum of 1-naphthol-2-sulphonic acid in 88% w/w sulphuric acid recorded after (a) 3 minutes (b) 23 minutes.



decreased with time.

It is proposed that 1-naphthol forms a 'benzenonium' ion i.e.



This is as expected since protonation can be regarded as electrophilic attack.

The hydroxyl group exchanges rapidly with the solvent and is not observable as a separate nmr signal. The carbon protons, on the other hand, have lifetimes of the order of seconds in 70% w/w perchloric acid. They therefore give broadened nmr lines[67]. As the acid strength is increased, the rate of exchange of the carbon protons with the solvent becomes even slower[67], and the nmr signals become sharper.

The single peak at high field in the nmr spectrum of 1-naphthol can be assigned to the methylene protons of III and IV, and the complicated pattern of peaks can be assigned to the other ring protons. The signal due to the methylene protons decreases with time, which implies that the protonated 1-naphthol is disappearing. The rate of disappearance is also of the same order as the rate of disappearance of the protonated species shown by the ultra-violet absorption spectra (Figs 3.6 and 3.7).

It was found that below approx. 70% w/w sulphuric acid, 1-naphthol does not protonate or sulphonate. Thus it appears that in sulphuric acid of > 70% w/w 1-naphthol is protonated to some extent, and that it is slowly sulphonating also. The site of protonation for 1-naphthol is a carbon atom in the naphthalene ring and not the hydroxyl group.

(f) The $pK(S_o)$ for 1-Naphthol in Strong Sulphuric Acid Solution

The position of equilibrium of acid-base reactions in dilute aqueous solution is approximately governed by hydrogen ion concentration according to equation 3.1.

$$\log \frac{C_{BH^+}}{C_B} = \log I = pK_{BH^+} + \log C_{H^+} \qquad 3.1$$

However this is seldom, if ever, true in concentrated acids. This situation led to the invention of acidity functions, h, (or $H = -\log h$), which preserve the simple acidity dependence of equation 3.1 as expressed in equation 3.2.

$$\log I = pK_{BH^+} + \log h \qquad 3.2$$

According to equation 3.2, plots of log I against log h should be linear and of unit slope, if the acidity function employed governs the particular protonation reaction being examined.

Sulphuric acid solutions of strength 71.5% w/w to 88.74% w/w were prepared by weighing out amounts of standardised acid. 25 cm^3 of each acid was taken and brought to 25°C by means of a thermostated water bath. 0.05 cm^3 of a stock solution of 1-naphthol in A.R. methanol was added with a Lang-Levy pipette. The amount of liquid which this pipette delivered had been checked previously to see how reproducible it was. The acid solution was then mixed, poured into a 1 cm quartz cell and placed in the thermostated cell holder of the Unicam S.P. 500 spectrophotometer. The optical density of the solution at 330 nm was measured 1 minute after mixing. A reference solution of exactly the same acid strength was employed for each determination of optical density.

1-Naphthol was added as a small aliquot of the stock solution in methanol, to the acid solutions, since this was the quickest and most

convenient method. The methanol concentration of 0.2% has no effect on the spectrum of 1-naphthol in sulphuric acid.

The optical densities at various acid strengths are shown in Table 3.2.

TABLE 3.2

The Optical Density of 1-Naphthol at Various Acid Strengths

Acid Strength % w/w	$-H_o$	$-H_c$	O.D. at 330 nm	I	log I
71.50	6.16	9.64	0.055	0.05314	-1.2746
72.75	6.36	9.91	0.093	0.09328	-1.0302
74.57	6.64	10.31	0.186	0.2058	-0.6865
76.40	6.93	10.71	0.369	0.5118	-0.2909
77.57	7.12	10.97	0.530	0.9464	-0.0239
77.96	7.18	11.06	0.584	1.154	0.0622
78.48	7.26	11.165	0.692	1.740	0.2400
79.05	7.35	11.30	0.785	2.574	0.4106
79.44	7.41	11.38	0.799	2.745	0.4386
80.54	7.59	11.62	0.910	5.056	0.7038
81.68	7.73	11.87	0.965	7.720	0.8876
82.73	7.93	12.10	1.012	12.97	1.1130
83.79	8.10	12.34	1.035	18.82	1.2747
84.86	8.27	12.57	1.050	26.25	1.4191
85.65	8.40	12.75	1.100		
87.97	8.765	13.27	1.090		
88.00	8.77	12.27	1.090		
88.74	8.89	13.43	1.080		

Indicator ratios (I) were calculated using equation 3.3

$$I = \frac{C_{BH^+}}{C_B} = \frac{A}{(A_{BH^+} - A)} \qquad 3.3$$

where A_{BH^+} is the absorbance of a solution sufficient to convert the 1-naphthol completely into its protonated form, and A is the absorbance

of a less acidic solution containing both the free base and its conjugate acid. H_o and H_c refer to acidity functions. The H_o values shown in Table 3.2 were taken from Ryabova et al[68] who used mainly primary amines as indicators. The H_c values were taken from Reagan[69] whose acidity function is based principally on hydrocarbon indicators. These two acidity functions are shown graphically in Fig 3.10.

The actual H_o values used for this work were interpolated from the graph of the Ryobova data for 70% w/w ⟶ 90% w/w sulphuric acid shown in Fig 3.11. Reagan, however, gives H_c data to 80% w/w sulphuric acid only. These values were extrapolated to 90% w/w as shown in Fig 3.12, and the H_c values used in this work were interpolated from this graph.

Plots of log I against H_o and H_c are shown in Fig 3.13 and 3.14. Both graphs show good straight lines; when log I is plotted against H_o a slope of 1.12 is obtained, whereas when plotted against H_c a slope of 0.96 is obtained. Thus it appears that H_c, rather than H_o, governs the protonation reaction of 1-naphthol. This is further evidence for 1-naphthol being protonated on a carbon atom in the naphthalene ring.

Plots of optical density at 330 nm (from Table 3.2) against the usual measures of acid strength (weight %, M, H_o, and H_c) are sigmoid in shape, as expected for 1-naphthol being protonated. The plot of optical density against $-H_c$ is shown in Fig 3.15.

The H_c acidity scale therefore was the scale used to measure the $pK(S_o)$ for the protonation of 1-naphthol in sulphuric acid by use of the equation

$$pK(S_o) = H_c + \log \frac{\varepsilon_M - \varepsilon}{\varepsilon - \varepsilon_I} \qquad 3.4$$

FIG 3.10 The acidity functions H_o and H_c for aqueous sulphuric acid.

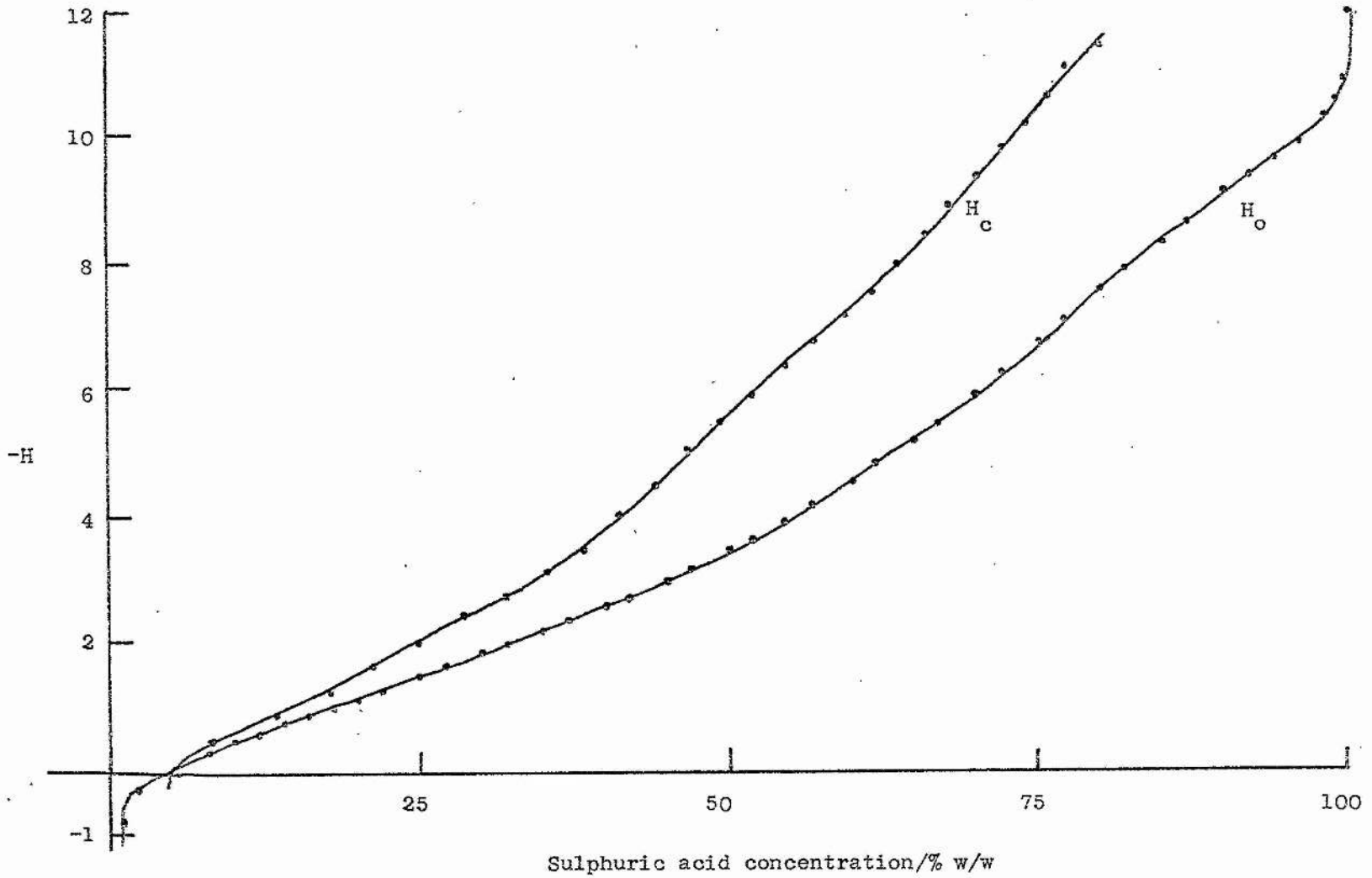


FIG 3.11 The acidity function H_o for 70% w/w - 90% w/w H_2SO_4

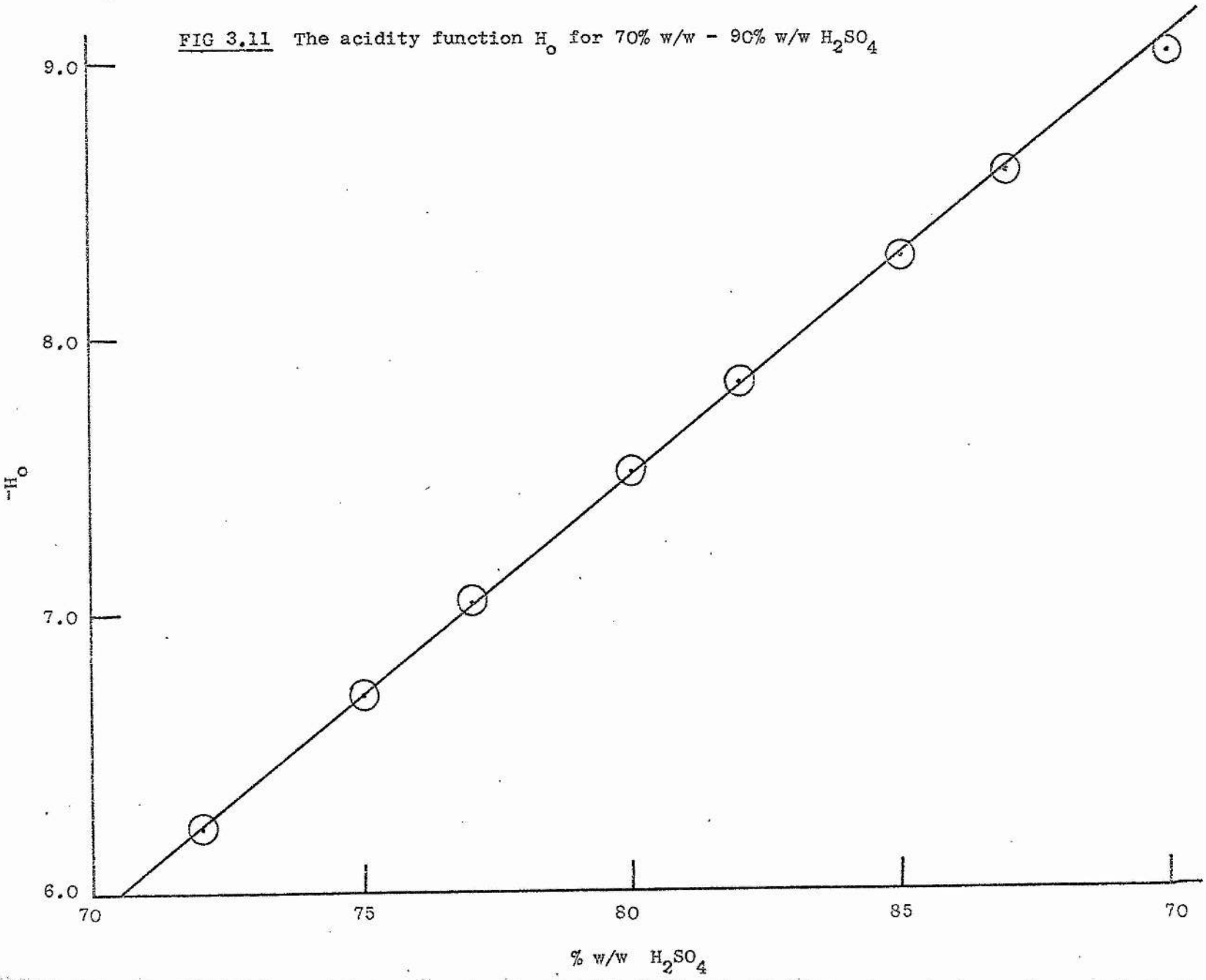


FIG 3.12 Extrapolation of the H_c data to 90% w/w sulphuric acid.

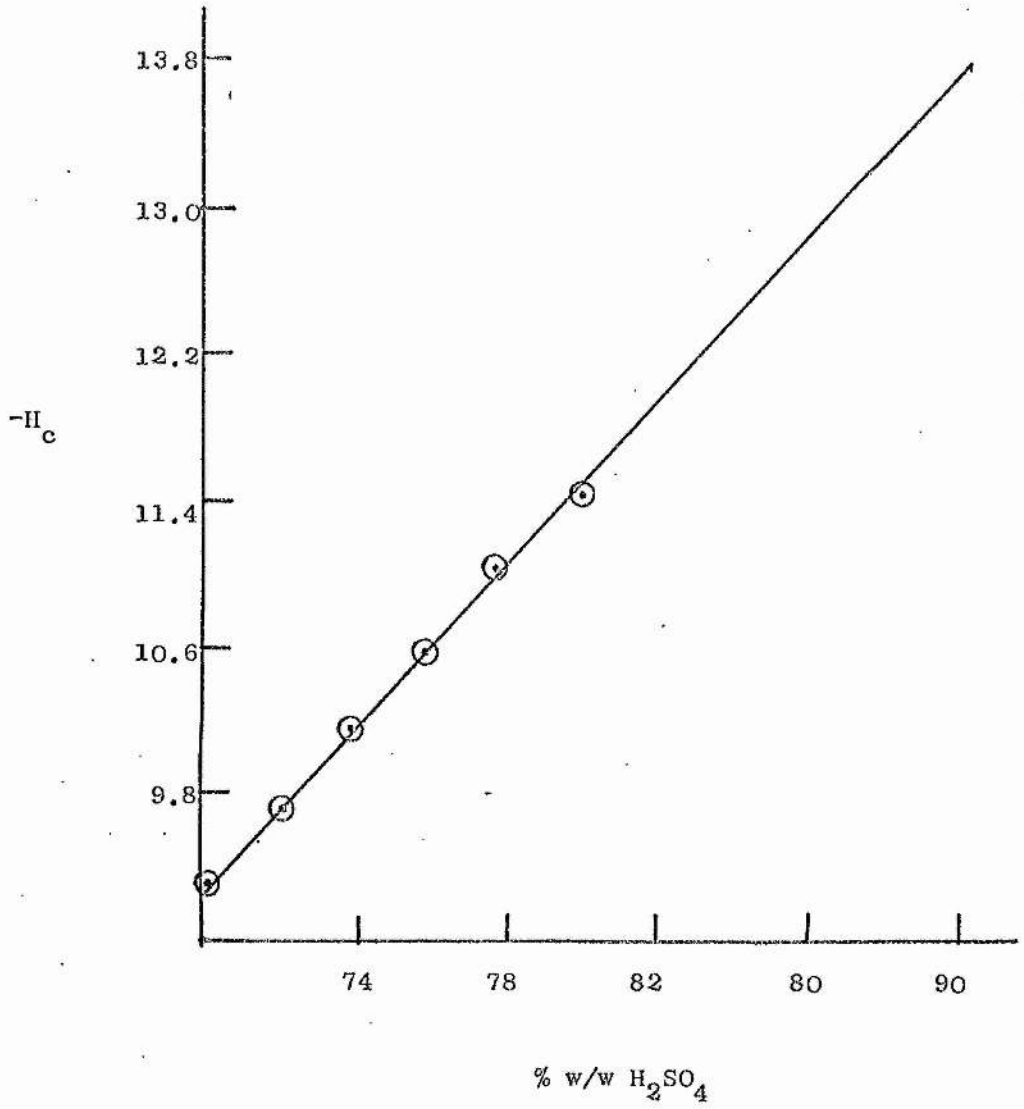


FIG 3.13 Plot of log I against H_o for 1-naphthol.

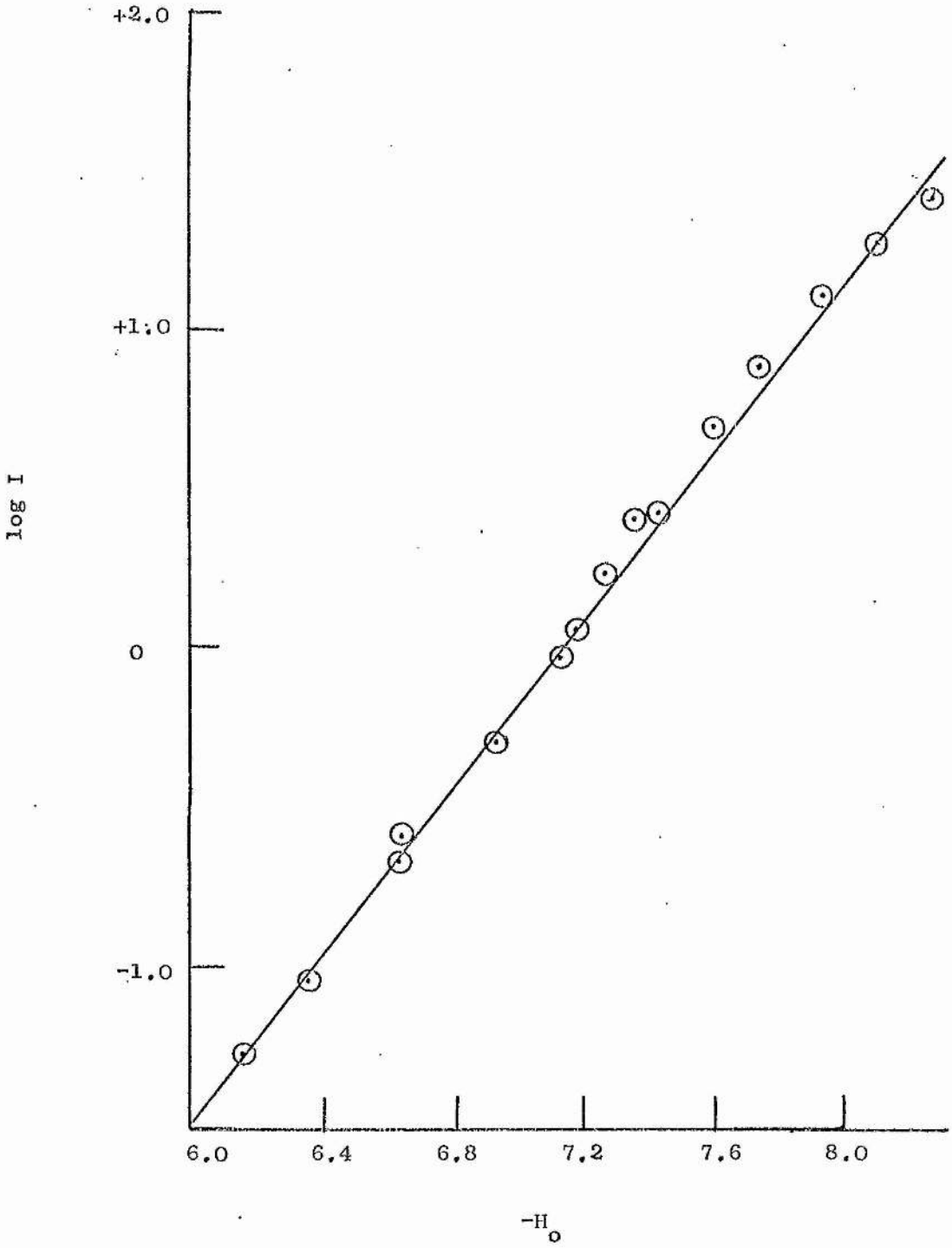


FIG 3.14 Plot of log I against H_c for 1-naphthol.

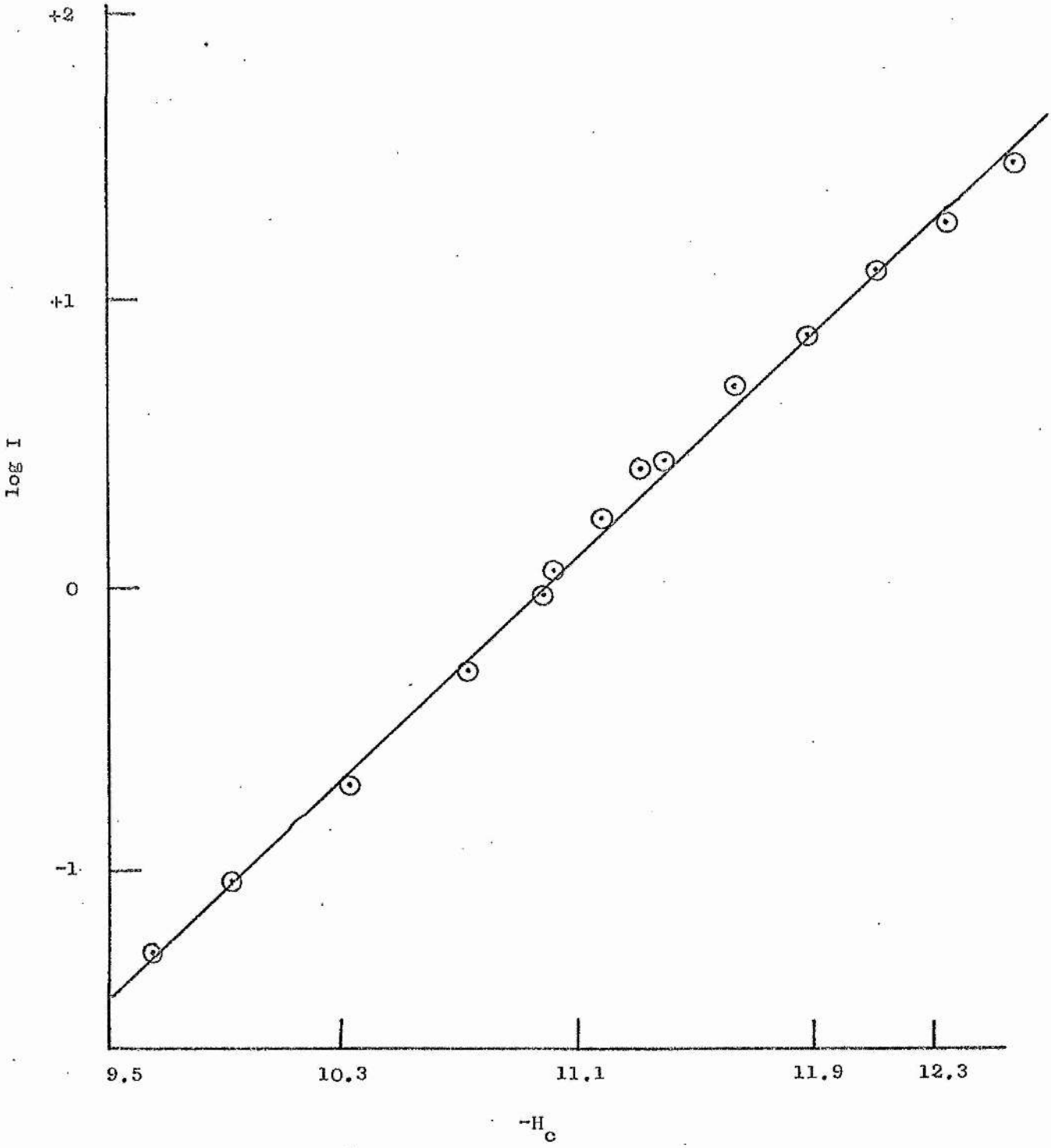
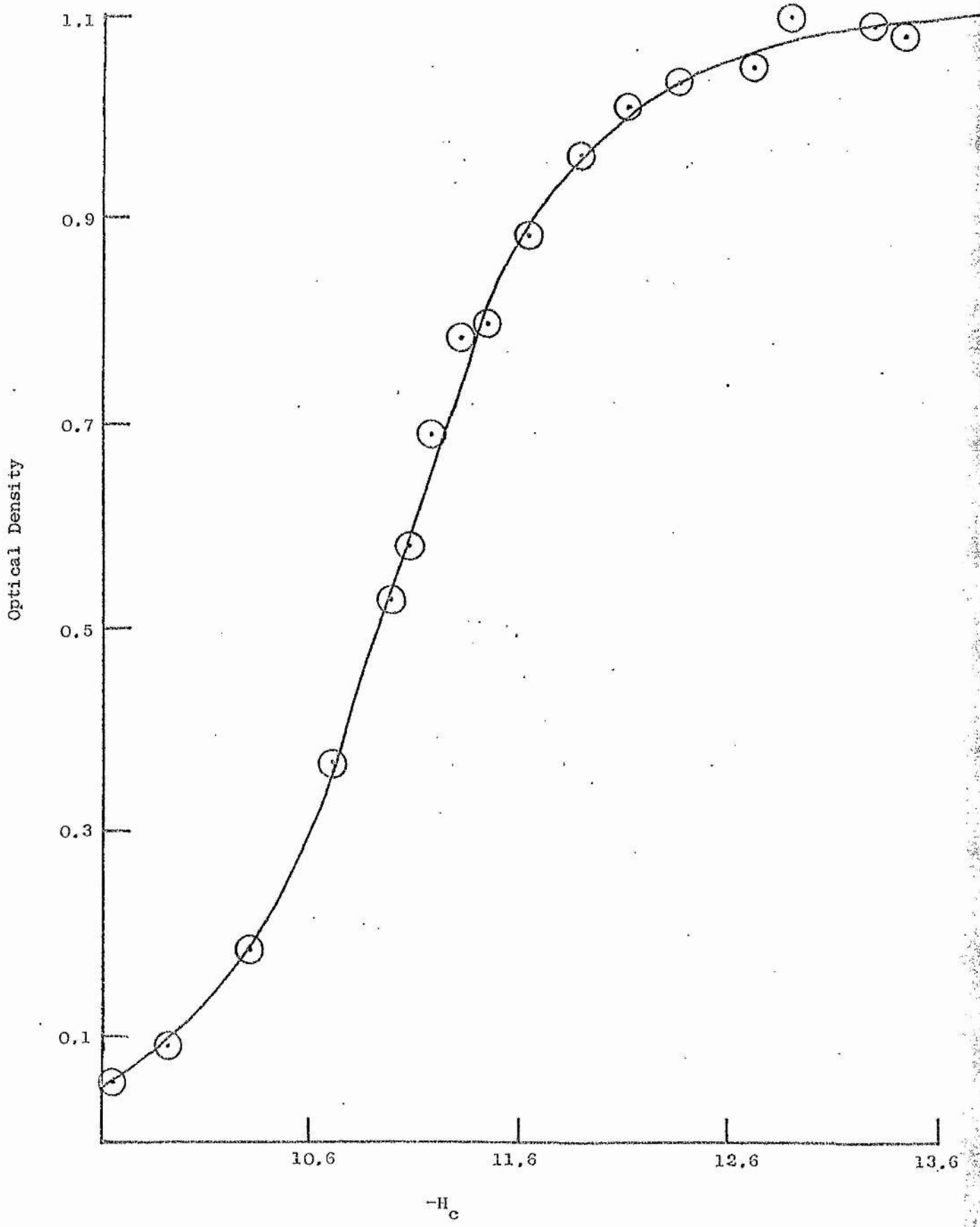


FIG 3.15 The plot of optical density of 1-naphthol at 330 nm against $-H_c$.



where ε_I is the extinction coefficient of 1-naphthol at the analytical wavelength, ε_M is the extinction coefficient of protonated 1-naphthol at the same wavelength, and ε is the extinction coefficient of the mixture of the two forms at the same wavelength. Since the same concentrations and cell-thicknesses were used, equation 3.4 may be written with optical densities (d) replacing extinction coefficients (ε).

i.e.

$$pK(S_o) = H_c + \log \frac{d_M - d}{d - d_I} \qquad 3.5$$

The data used to determine the $pK(S_o)$ of 1-naphthol are shown in Table 3.3.

Table 3.3

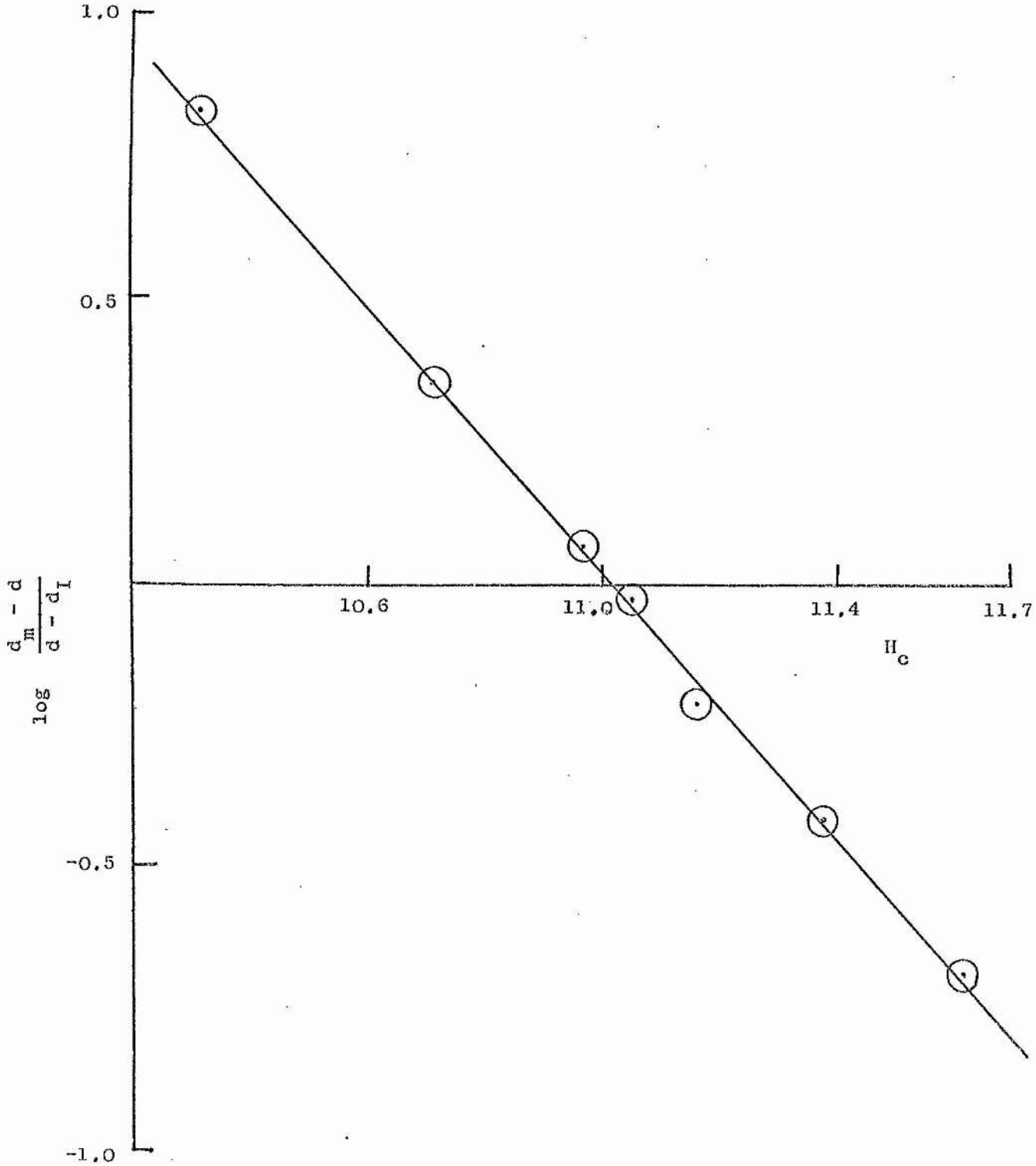
Determination of the ionization constant of 1-naphthol in strong sulphuric acid solution

$-H_c$	Optical Density at 330 nm	$\frac{d_M - d}{d - d_I}$	$\log \frac{d_M - d}{d - d_I}$	$pK(S_o)$
10.31	0.186	$\frac{0.9115}{0.136}$	0.8262	11.14
10.71	0.369	$\frac{0.7185}{0.319}$	0.3526	11.06
10.97	0.530	$\frac{0.5575}{0.480}$	0.0651	11.04
11.06	0.584	$\frac{0.5035}{0.534}$	-0.0255	11.03
11.165	0.692	$\frac{0.3955}{0.642}$	-0.2103	10.95
11.38	0.799	$\frac{0.2885}{0.749}$	-0.4143	10.97
11.62	0.910	$\frac{0.0178}{0.860}$	-0.6853	10.93

This gives a $pK(S_o)$ of -11.02 ± 0.12 at 25°C.

If H_c is plotted against $\log \frac{d_m - d}{d - d_I}$ a straight line is obtained with an intercept of $pK(S_o)$. This is shown for 1-naphthol in Fig 3.16, the intercept being -11.02 on the H_c scale.

FIG 3.16 The graphical determination of pK (S_o) for the protonation of 1-naphthol.



Thus the $pK(S_o)$ for the protonation of 1-naphthol is -11.02 ± 0.12 at 25^oC.

This estimate of the $pK(S_o)$ is regarded as being reliable, although 1-naphthol undergoes sulphonation at the sulphuric acid concentrations used. The reaction is slow enough, even in the strongest acid used (see Figs 3.6 and 3.7) for the effect on the 1-naphthol concentration after one minute to be negligible.

(g) The Fluorescence of Protonated 1-Naphthol

The fluorescence spectra (corrected) of 1-naphthol in aqueous solutions of pH 0 and 14 are shown in Figs 3.17 and 3.18.

Solutions of 1-naphthol in perchloric and sulphuric acid were examined immediately after mixing in the hope of observing the fluorescence of the protonated species. Little fluorescence was observed with solutions of 1-naphthol in 70-72% w/w perchloric acid, or from a solution in 88.74% sulphuric acid. It was concluded that the fluorescence of protonated 1-naphthol must be very weak or that protonated 1-naphthol does not fluoresce in aqueous acidic solutions.

(h) The Transient Absorption Spectrum of Protonated 1-Naphthol

An attempt was made to measure the transient absorption of 1-naphthol in sodium hydroxide. The spectrum obtained was weak and diffuse as Porter and Jackson[32] reported.

To measure the transient absorption spectrum of a freshly prepared solution of 1-naphthol in strong acid proved to be a difficult problem. However a simple and fairly efficient method was used. An aliquot of a stock solution of 1-naphthol in ethanol was introduced into the quartz cell (Fig 2.3) and the ethanol evaporated off at a water pump. The quartz cell was then connected

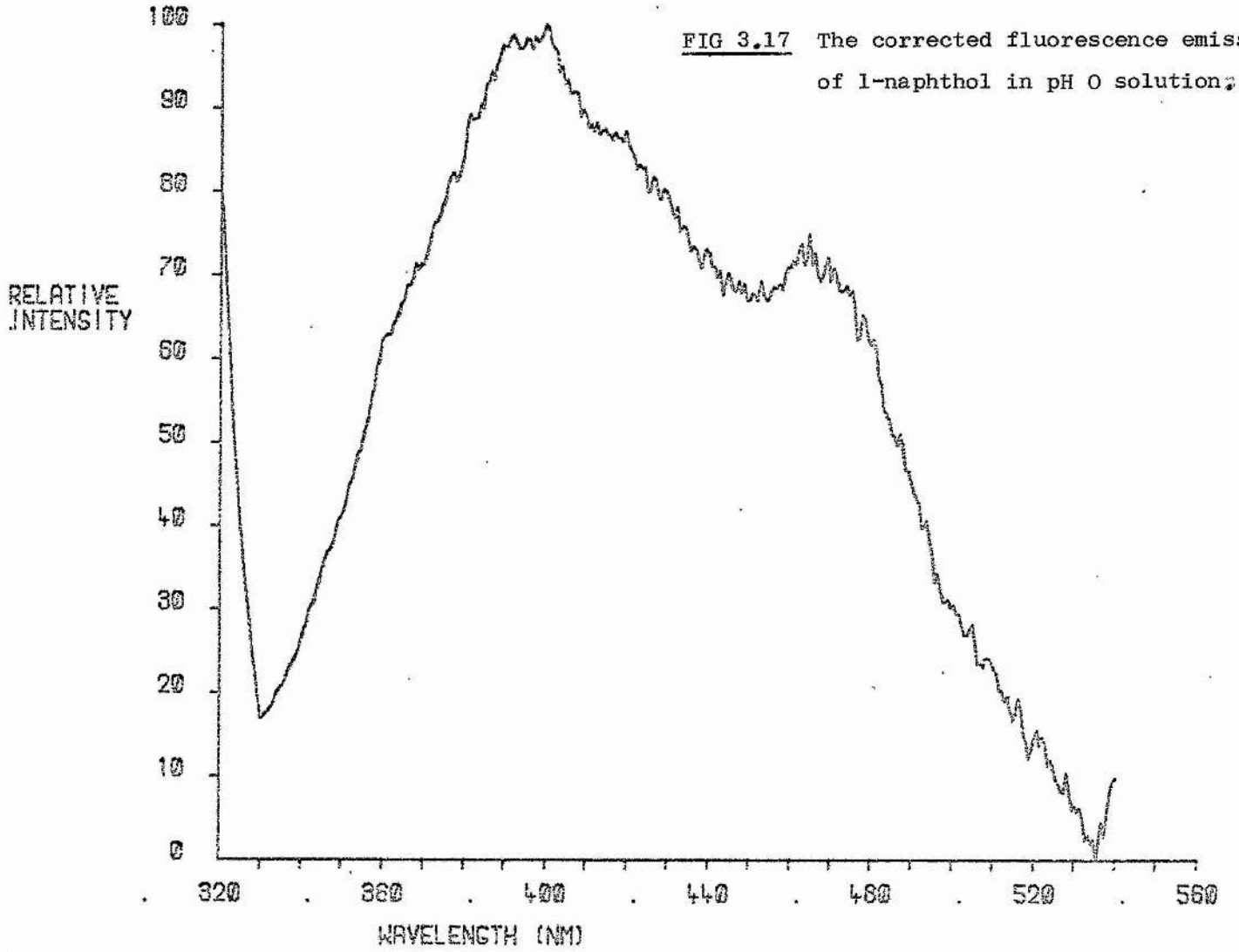


FIG 3.17 The corrected fluorescence emission spectrum of 1-naphthol in pH 0 solution.

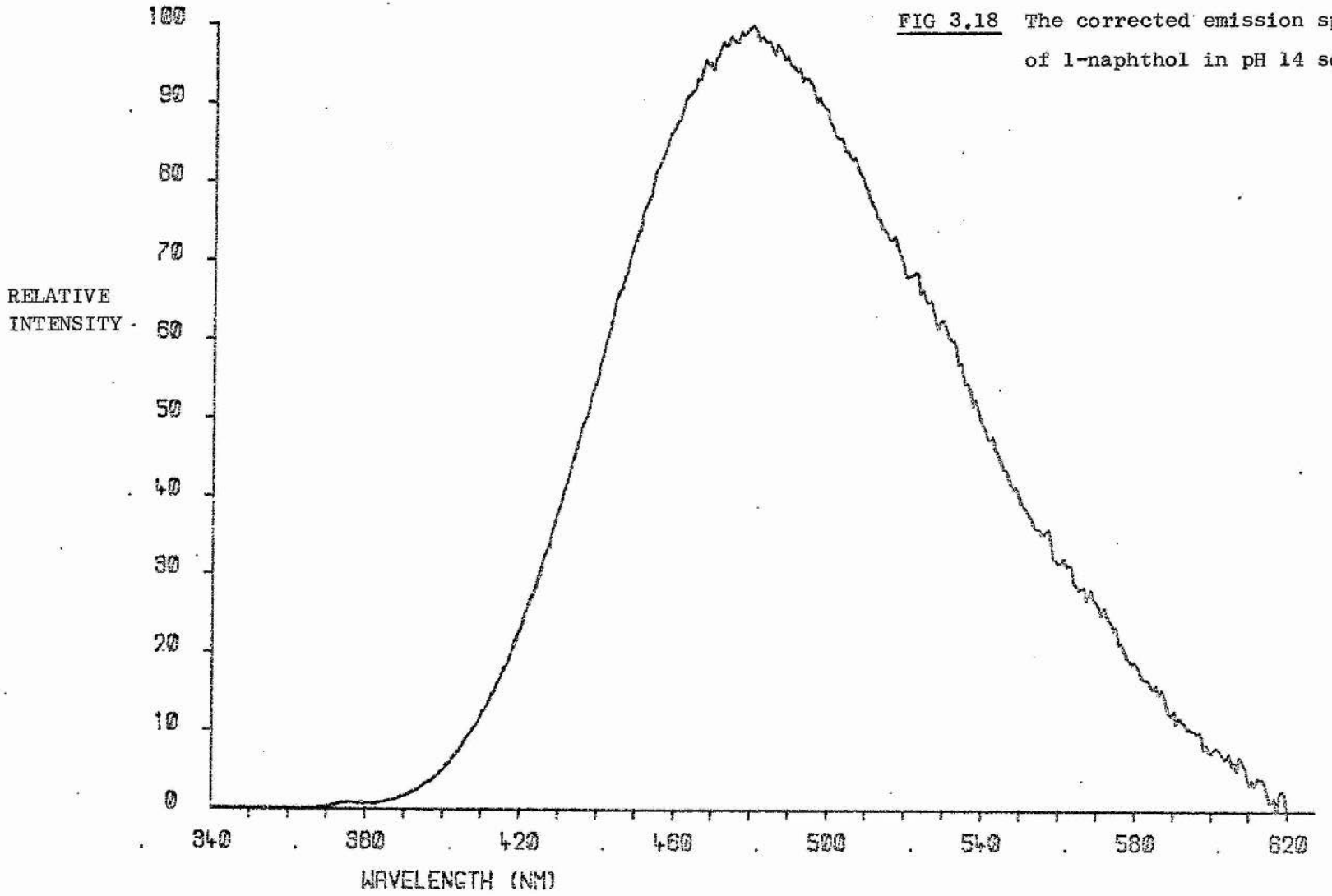


FIG 3.18 The corrected emission spectrum of 1-naphthol in pH 14 solution.

to the reservoir (Fig 2.3) which contained freshly degassed sulphuric acid. The quartz cell was surrounded by liquid nitrogen and then evacuated. The sulphuric acid was given one more freeze-pump cycle to ensure that it was thoroughly outgassed and then poured into the cell, whereupon the 1-naphthol dissolved. The measurement of the transient absorption spectrum of 1-naphthol was completed twenty minutes after the time of mixing.

Protonated 1-naphthol shows a very weak triplet-triplet absorption spectrum, if any, since the spectrum obtained was diffuse with a maximum O.D. of 0.3 only.

(i) The Transient Absorption Spectrum of Sulphonated 1-Naphthol in Strong Sulphuric Acid Solutions

Solutions of 1-naphthol in sulphuric acid of strength greater than 70% w/w (i.e. an acid strength capable of sulphonating the 1-naphthol), were prepared. Previous work had shown that no transients were obtained with solutions of 1-naphthol in sulphuric acid below 70% w/s.

When these solutions were flashed, strong transient absorption spectra were observed. However the transient absorption spectrum observed 10 μs after flashing a solution of 1-naphthol in 85% w/w sulphuric acid, was quite different from that observed 200 μs after flashing. This is shown by Fig 3.19. When the intensities of these absorption spectra were followed with varying acid strength, the results shownin Table 3.4 were obtained.

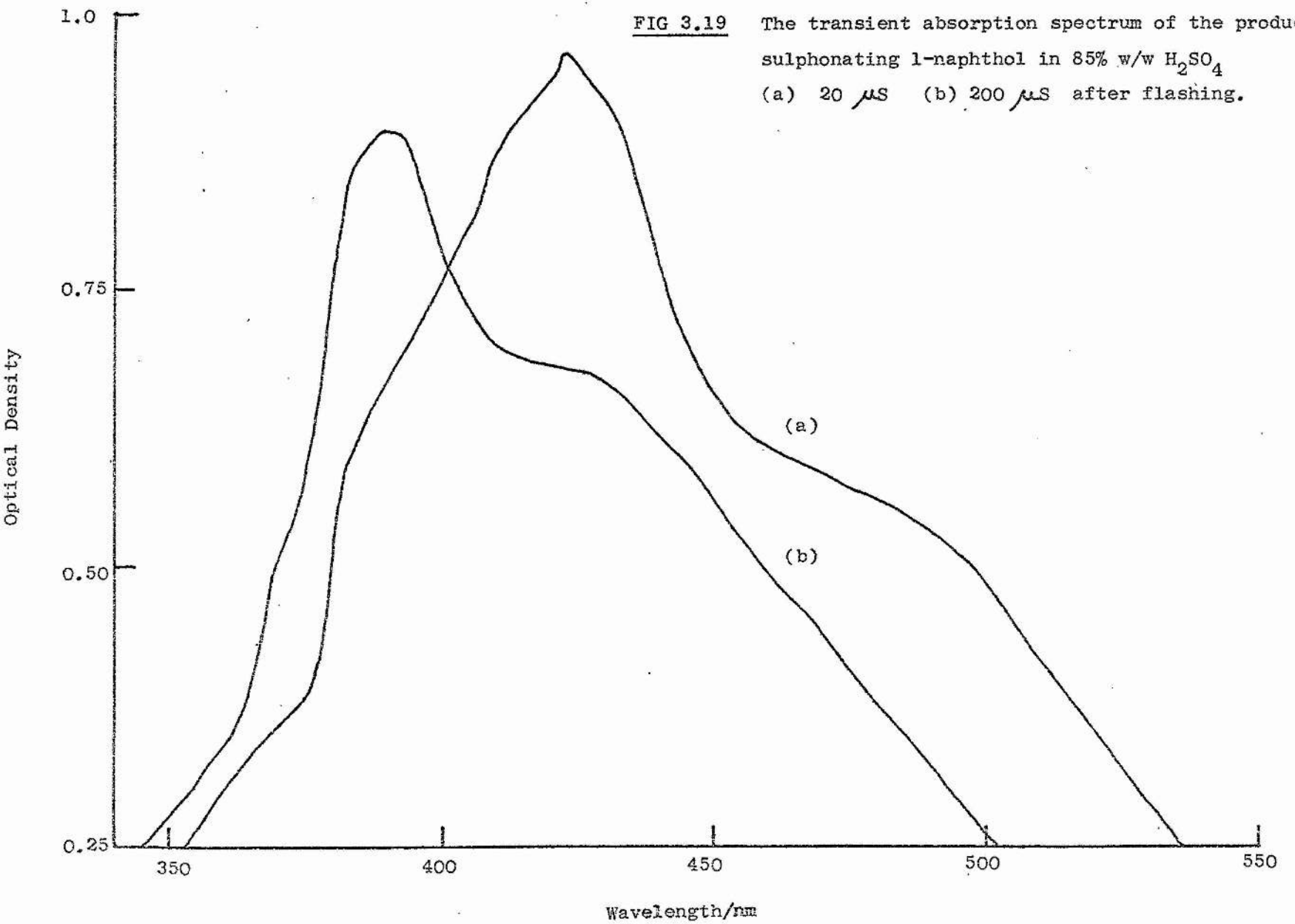


FIG 3.19 The transient absorption spectrum of the products of sulphonating 1-naphthol in 85% w/w H_2SO_4
(a) 20 μS (b) 200 μS after flashing.

Table 3.4

Optical Density Measurements of the Transient Absorption Spectrum of 1-Naphthol-Sulphonic Acids in Conc. Sulphuric Acid.

Acid Strength % w/w	Optical Density of Transient Absorption at 430 nm	390 nm
71.50	0.30	0.25
77.57	0.60	0.55
79.44	1.00	0.89
83.63	0.95	0.85
84.46	0.98	0.925
88.75	0.83	0.80

When the transient absorption spectra of sulphonated 1-naphthol in sulphuric acid are examined in further detail the following facts appear. The transient species, whose absorption has a maximum at approx. 430 nm, has disappeared 2 ms after flashing. The transient whose absorption has a maximum at approx. 390 nm is formed as the other transient disappears, and disapppears 10 ms after flashing. This is shown by Fig 3.20.

The long-lived transient species is formed in its greatest concentration 65 μs after flashing.

1-Naphthol-2-sulphonic acid, which isomerises in strong sulphuric acid to give a mixture of 1-naphthol-2- and -4-sulphonic acids, gives exactly the same transient absorption spectrum as 1-naphthol, when flashed in 88% w/w H_2SO_4. The spectrum obtained from 1-naphthol-2-sulphonic acid in 88% w/w H_2SO_4 also changes with time in exactly the same way as that of 1-naphthol in strong sulphuric acid.

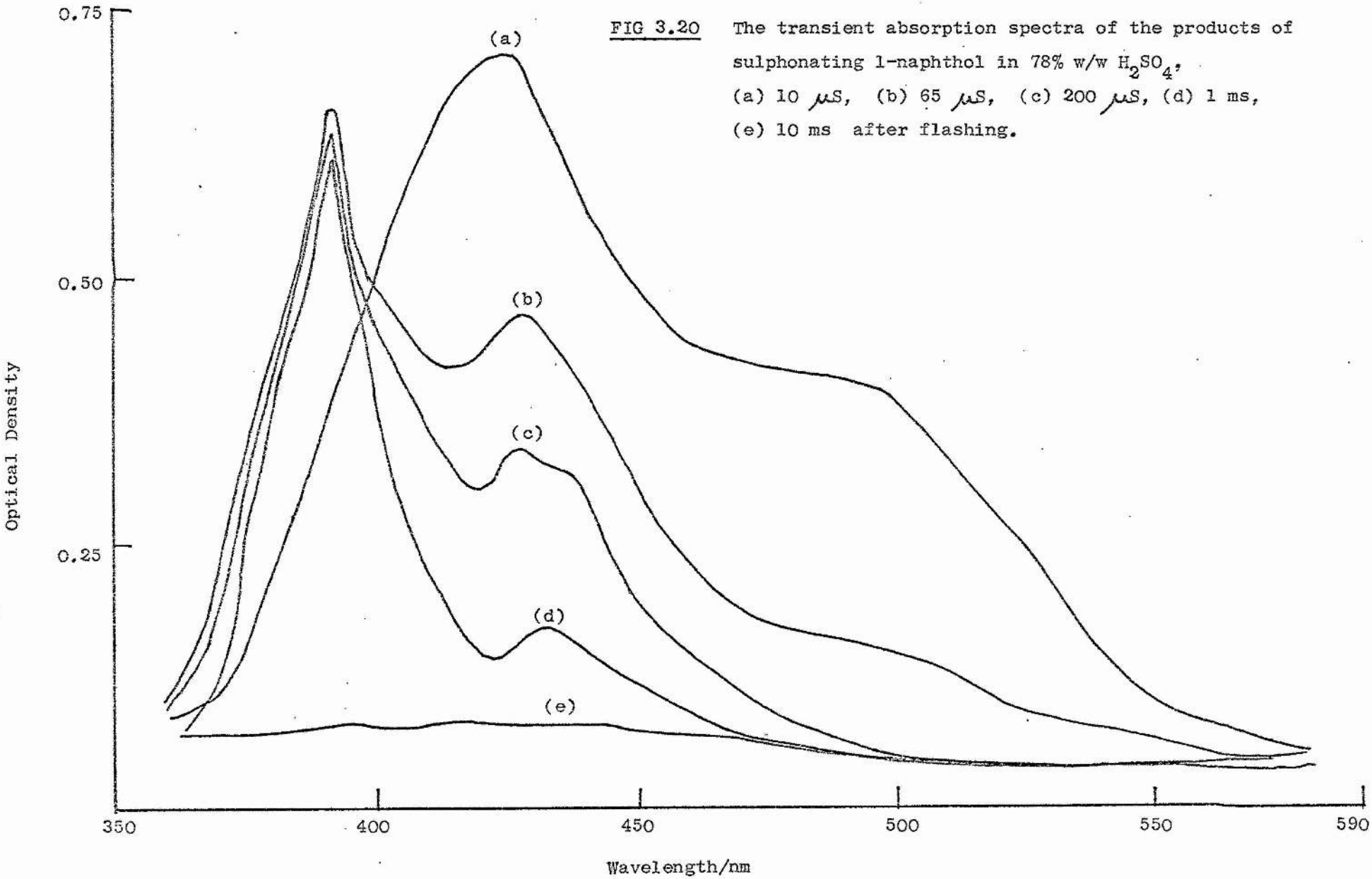
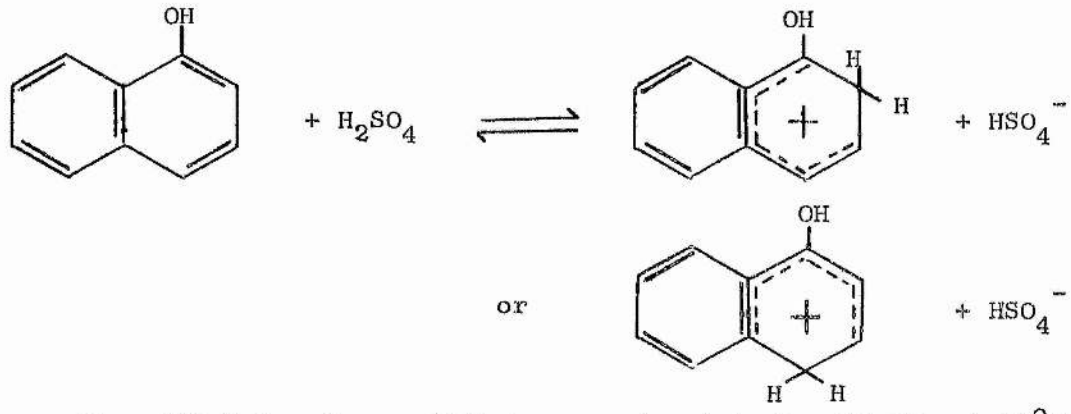


FIG 3.20 The transient absorption spectra of the products of sulphonating 1-naphthol in 78% w/w H_2SO_4, (a) 10 μs, (b) 65 μs, (c) 200 μs, (d) 1 ms, (e) 10 ms after flashing.

(j) Discussion

No triplet-triplet absorption spectrum was found for 1-naphthol in acidic solution up to 70% w/w H_2SO_4. Therefore no determination of $pK(T_1)$ was possible, and no evidence was found for Daudel's theory that the $pK(T_1)$ should be very different from the $pK(S_o)$ for an α, electron donating, substituent of naphthalene.

1-Naphthol protonates in strong sulphuric and perchloric acids (Chapter 3.e.):



The $pK(S_o)$ for the equilibrium was found to be -11.02, at 25°C, on the H_c acidity scale which was found to govern the protonation of 1-naphthol. This is hardly surprising since Reagan based the acidity scale principally on hydrocarbon indicators, and protonation of 1-naphthol occurs at a carbon atom in the naphthalene ring (Chapter 3.e). 1-Naphthol and related compounds could possibly be used as indicators for extending Reagan's acidity scale.

It seems that sulphuric acid of 70% w/w or greater concentration is needed before 1-naphthol will either sulphonate or protonate. Protonated 1-naphthol will not undergo sulphonation, since sulphonation is usually regarded as an electrophilic process[113], and so it is uncharged 1-naphthol that is sulphonated. There is some controversy about which species sulphonates which compounds in aqueous sulphuric acid[70]. Let us consider that SO_3 is the species responsible for the sulphonation

of 1-naphthol in aqueous sulphuric acid. The mechanism for sulphonation would then be of the following form

$$ArH + SO_3 \rightleftharpoons Ar\overset{+}{<}\begin{matrix}H\\ SO_3^-\end{matrix}$$

$$Ar\overset{+}{<}\begin{matrix}H\\ SO_3^-\end{matrix} + HSO_4^- \longrightarrow ArSO_3^- + H_2SO_4$$

$$ArSO_3^- + H_2SO_4 \longrightarrow ArSO_3H + HSO_4^-$$

where ArH = 1-naphthol.

If SO_3 is the sulphonating agent, then the rate of sulphonation will increase as the logarithm of the activity of SO_3, ($\log a_{SO_3}$), increases.

Now $$H_2SO_4 \rightleftharpoons SO_3 + H_2O$$

$$\therefore \log K = \log a_{SO_3} + \log a_{H_2O} - \log a_{H_2SO_4}$$

For a change in acid concentration

$$0 = \triangle \log a_{SO_3} + \triangle \log a_{H_2O} - \triangle \log a_{H_2SO_4}$$

$$\text{i.e.} \triangle \log a_{SO_3} = \triangle \log a_{H_2SO_4} - \triangle \log a_{H_2O}$$

Therefore for a change from 70% w/w sulphuric acid to 80% w/w.

$$\triangle \log a_{SO_3} = -(1.914 - 3.533) + (2.276 - 1.332)$$

$$= \underline{2.56}$$

and for a change from 80% to 90%

$$\triangle \log a_{SO_3} = -(0.602 - 1.914) + (3.638 - 2.276)$$

$$\triangle \log a_{SO_3} = \underline{2.67}$$

Values of activities are taken from Giauque et al[71] . Thus as the sulphuric acid concentration is increased from 70 to 80% w/w, the log a_{SO_3} increase is 2.56 compared with an increase of $-H_c$ of 2.1, and for a sulphuric acid concentration change from 80 to 90% w/w the log a_{SO_3} increase is 2.67, compared with an increase in H_c of 2.3. Log a_{SO_3}, therefore, changes more rapidly than "log a_{H^+}" and so as the sulphuric acid concentration increases, the sulphonating effect of the medium increases more rapidly than the rapidly increasing protonating effect.

This explains how 1-naphthol becomes progressively more sulphonated as the sulphuric acid strength increases, although the amount of the uncharged 1-naphthol species undergoing sulphonation actually decreases.

Transient absorption spectra were obtained for a mixture of 1-naphthol-2- and -4-sulphonic acids in strong sulphuric acid. The intensity of both the short-lived and long-lived species increased with increasing acid strength. (Table 3.4) These transient absorption spectra were quite different from that obtained for 1-naphthol-2-sulphonate in aqueous solutions of low pH, which had a maximum absorption at 406 nm approx (see Chapter 4). 1-Naphthol-4-sulphonate in aqueous solution of low pH has an extremely weak transient absorption spectrum. That is, the spectrum obtained in strong sulphuric acid is not what one would expect from a simple mixture of 1-naphthol-2- and -4-sulphonic acids. It appears therefore that, a radical is also formed when the sulphonated 1-naphthol is flashed in strong acid and that this radical is formed from the short lived triplet species. More investigation is clearly required before a definite hypothesis regarding the behaviour of 1-naphthol-2- and -4-sulphonic acids in strong sulphuric acid when flashed can be made.

CHAPTER 4

1-NAPHTHOL-2-SULPHONATE AND 1-NAPHTHOL-4-SULPHONATE

1. ACID-BASE PROPERTIES

(a) Introduction

The $pK(S_o)$ of 1-naphthol-2-sulphonate has been measured previously by potentiometric methods[72], ultraviolet absorption spectrometry[73,74], and fluorescence spectrometry[74]. Potentiometric methods[75,76], ultraviolet absorption spectrometry[73,74] and fluorescence spectrometry[74] have also been used to measure the $pK(S_o)$ of 1-naphthol-4-sulphonate. Tanizaki et al[77] have shown how the absorption spectrum of 1-naphthol-4-sulphonate, in aqueous solutions, changes with pH.

The relation between fluorescence intensity of the 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate ions and hydrogen ion concentration was observed in 1926[78], and this relationship has recently been used to measure pK(So) for these two compounds[74]. 1-Naphthol-4-sulphonic acid, which is sometimes known as Neville-Winther acid, has also been used as a fluorescent indicator[79,80]. However, the $pK(S_1)$ values for 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate have never been measured.

Breitschwerdt and Weller[81,82] have used a flash method to convert 1-naphthol-4-sulphonate (ROH), in neutral or weakly acidic solution into the RO^- ion, through its excited state. Relaxation to the equilibrium composition was followed spectroscopically, and the rate of the reaction

$$RO^- + H_3O^+ \longrightarrow ROH + H_2O$$

was thus determined. The $T \leftarrow T$ absorption spectra of 1-naphthol-2- and -4-sulphonates have not been given previously and $pK(T_1)$ values have never been measured.

(b) Purity of 1-naphthol-2- and -4-sulphonates.

Samples of 1-naphthol-2-sulphonate (Potassium salt) and 1-naphthol-4-sulphonate (sodium salt) were obtained from Eastman Kodak. A carbon, hydrogen analysis of the commercial sample of 1-naphthol-2-sulphonate was performed. This commercial sample was then boiled with activated charcoal, recrystallised five or six times from water, and a further carbon hydrogen analysis was performed. The results are shown in Table 4.1.

TABLE 4.1

The results of carbon hydrogen analysis for 1-naphthol-2-sulphonate (potassium salt).

	C% w/w	H% w/w
Theoretical composition	45.78	2.69
Commercial sample	44.53	2.68
Purified Sample	45.75	2.68

The recrystallised salt was taken as being pure $C_{10}H_7SO_3K$. Thin layer chromatography[83] was used to ensure that the recrystallised salt contained only the -2-sulphonate isomer of 1-naphthol. Silica gel plates, which had been activated for 1 hour at 120°C, were used and a mixture of methylene chloride, concentrated ammonia and methanol (80:6:30) was used as a solvent system. The chromatogram was allowed to run for three hours, and then the plate was observed under ultra-violet light. Only one spot was visible.

The ultra-violet absorption spectrum of the recrystallised salt agreed well with the spectrum given by Daglish[62] for 1-naphthol-2-sulphonate. The recrystallised 1-naphthol-2-sulphonate (potassium salt) was therefore taken as being pure and used as such.

A carbon hydrogen analysis was also performed on the commercial sample of 1-naphthol-4-sulphonate (sodium salt), and a sample that had

been boiled with activated charcoal, recrystallised five or six times from water, and dried overnight in an oven at 120°C. The results of these analyses are shown in Table 4.2.

TABLE 4.2

The results of carbon hydrogen analyses for 1-naphthol-4-sulphonate (sodium salt)

	C% w/w	H% w/w
Theoretical composition	48.78	2.87
Commercial sample	33.49	2.30
Purified sample	45.35	3.02

If 1-naphthol-4-sulphonate has a molecule of water attached, then the theoretical carbon and hydrogen composition is 45.45% w/w C and 3.02% H_2. The results of the analysis performed on the purified 1-naphthol-4-sulphonate are in close agreement with these calculated results. The purified product, therefore has the formula $C_{10}H_7SO_3Na.H_2O$.

The ultra violet absorption spectrum of this purified sample agreed well with the spectrum assigned to 1-naphthol-4-sulphonate by Daglish[62], but the sample was found to contain traces of 1-naphthol-2-sulphonate by thin layer chromatography. A silica column was prepared and the sample of recrystallised 1-naphthol-4-sulphonate salt placed on it. The column was eluted with a mixture of methylene chloride, concentrated ammonia and methanol (80:6:30) and a separation of the two naphthol sulphonates was achieved. The sample collected after the separation on the silica column was taken as being pure 1-naphthol-4-sulphonate and used in all the work described here.

(c) Absorption spectroscopy: determination of $pK(S_o)$.

i) 1-Naphthol-2-sulphonate.

The absorption spectra of 1-naphthol-2-sulphonate in dilute

hydrochloric acid (1 M) and sodium hydroxide are shown in Fig 4.1 and characterize the spectra of the naphthol form (ROH) and the naphtholate ion (RO^-). The $pK(S_o)$ was determined by following the optical density of aqueous solutions of 1-naphthol-2-sulphonate with varying pH[84]. $pK(S_o)$ values were calculated from the following equation

$$pK = pH + \log \frac{d_{(RO^-)} - d}{d - d_{(ROH)}} \qquad (4.1)$$

where $d_{(RO^-)}$ and $d_{(ROH)}$ are the optical densities of the naphtholate ion and naphthol forms of 1-naphthol-2-sulphonate respectively, and d is the optical density of the mixture of the ROH and RO^- forms at the same wavelength. All measurements of optical density were made at 345 nm, since the greatest difference in optical density between the ROH and RO^- forms is observed at this wavelength.

Several solutions with constant sulphonate concentration, but differing pH values, were prepared and the optical densities at 345 nm were measured. The differing pH values of these solutions were obtained using buffers. The concentration of these buffers was very small (Ionic strength, I, = 0.0004), however, since buffers of the same concentration were used in the determination of $pK(S_1)$ (See Chapter 4.1.d) to avoid quenching effects.

The $pK(S_o)$ values shown in Table 4.3 were calculated with $d_{RO^-} = 0.745$ and $d_{ROH} = 0.004$.

TABLE 4.3

Calculation of $pK(S_o)$ values of 1-naphthol-2-sulphonate from ultra-violet absorption measurements.

pH	d	$d_{(RO^-)}-d$	$d-d_{(ROH)}$	$\log \frac{d_{RO^-} - d}{d - d_{(ROH)}}$	$pK(S_o)$
8.95	0.144	0.601	0.140	+0.6328	9.58
9.04	0.169	0.576	0.165	+0.5429	9.58
9.07	0.220	0.525	0.216	+0.4857	9.56
9.39	0.309	0.436	0.305	+0.1552	9.55
9.51	0.340	0.405	0.336	+0.0812	9.59
9.62	0.370	0.375	0.366	+0.0105	9.63
9.79	0.474	0.271	0.470	-0.2391	9.56

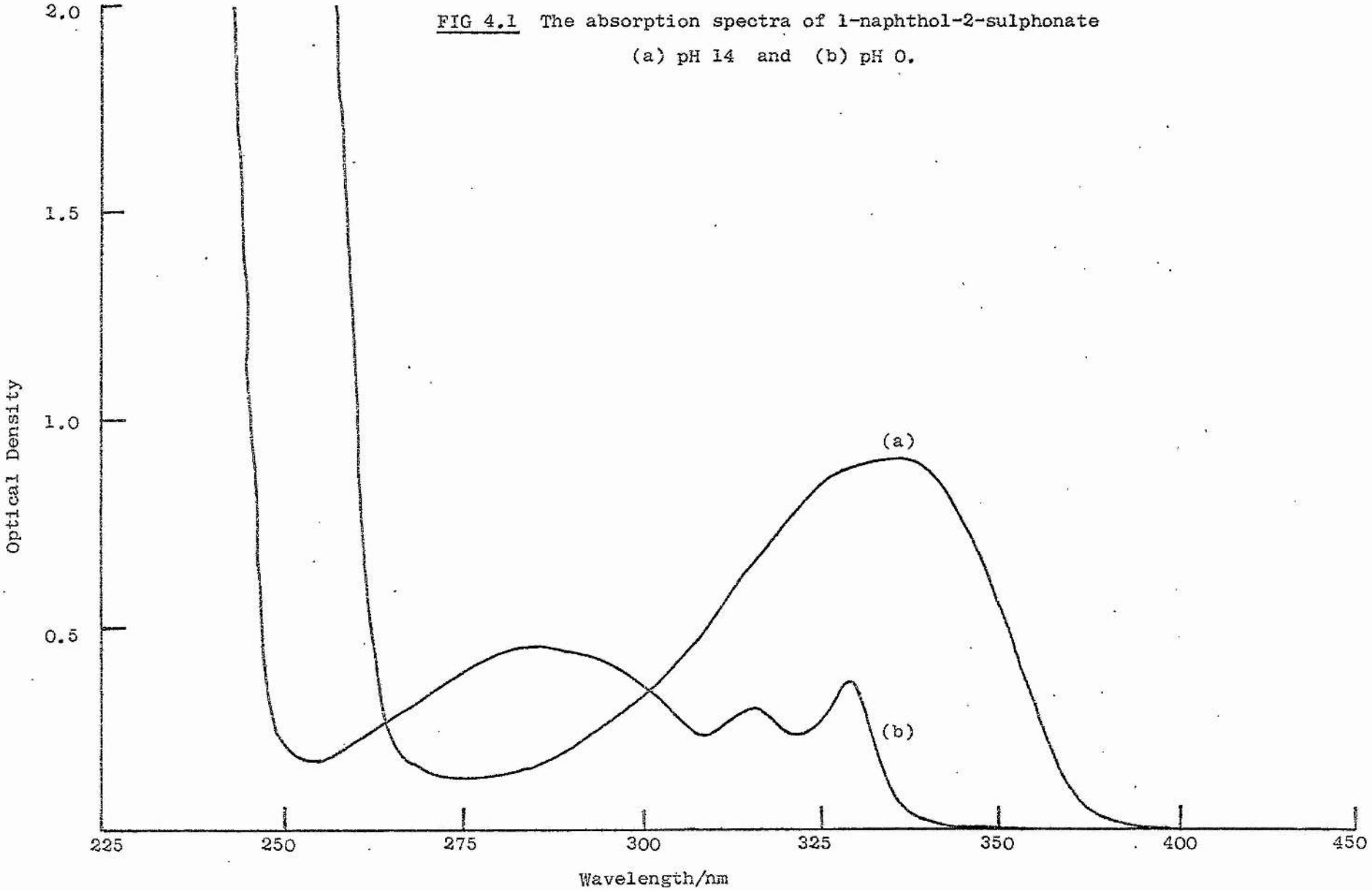


FIG 4.1 The absorption spectra of 1-naphthol-2-sulphonate (a) pH 14 and (b) pH 0.

Thus the $pK(S_o)$ of 1-naphthol-2-sulphonate = $\underline{9.58 \pm 0.05}$.
This agrees satisfactorily with values of 9.41 (I = 0.01)[74], 9.62[72] (thermodynamic dissociation constant), and 9.47 (I = 0.02)[73] quoted previously. In the Förster Cycle calculations which follow, a value of 9.58 is used for the $pK(S_o)$ of 1-naphthol-2-sulphonate.

ii) 1-Naphthol-4-sulphonate.

The absorption spectra of the ROH and RO^- forms of 1-naphthol-4-sulphonate, in solutions of different pH values, are shown in Fig 4.2. The $pK(S_o)$ was determined in exactly the same way as for 1-naphthol-2-sulphonate. The $pK(S_o)$ values shown in Table 4.4 were calculated with $d_{RO^-} = 0.815$ $d_{ROH} = 0.000$. Optical densities were measured at 345 nm.

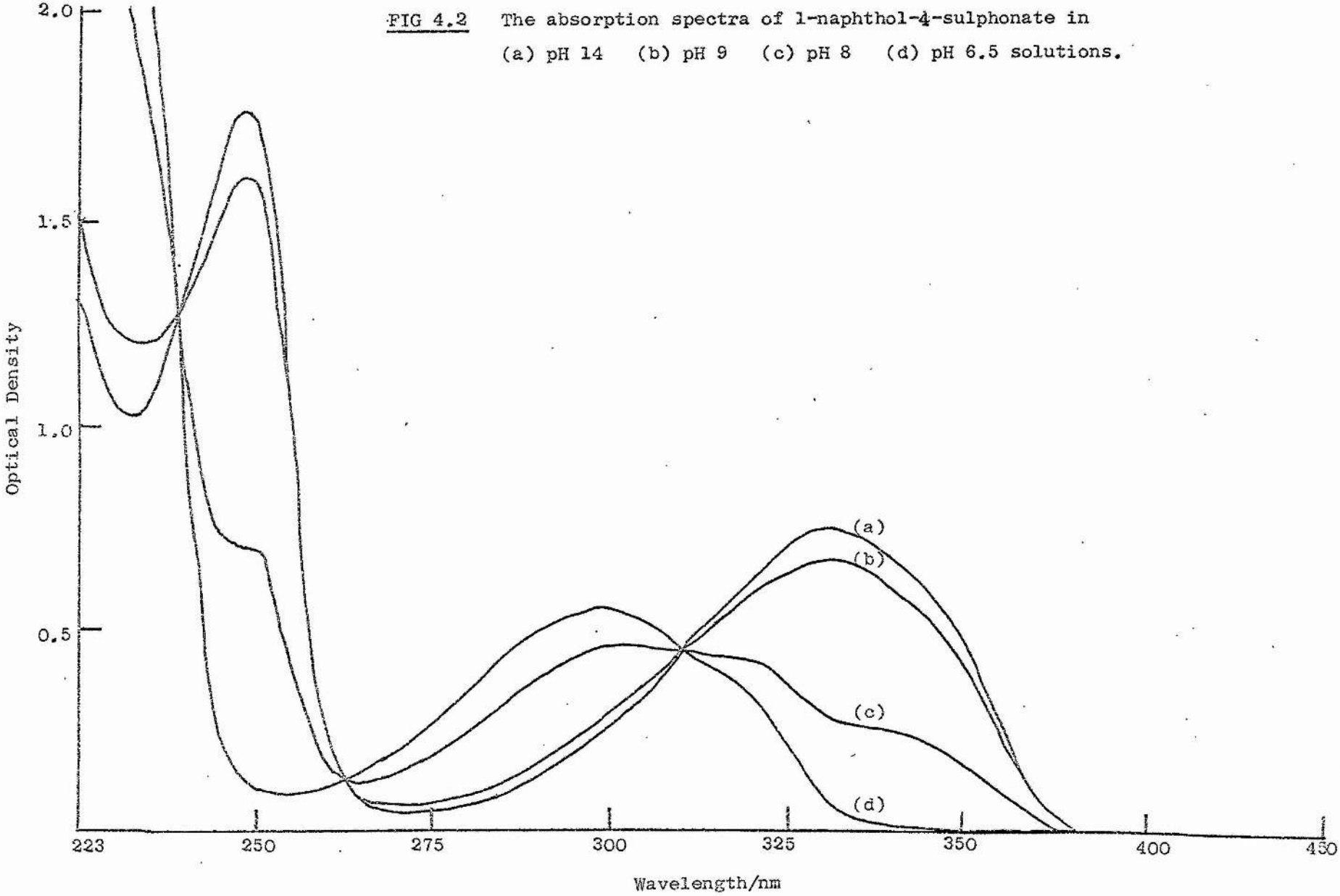
TABLE 4.4

Calculation of the $pK(S_o)$ values of 1-naphthol-4-sulphonate from ultra-violet absorption measurements

pH	d	$d_{RO^-}-d$	$d-d_{(ROH)}$	$\log \frac{d_{RO^-}-d}{d-d_{ROH}}$	$pK(S_o)$
7.00	0.776	0.039	0.776	+1.2988	8.30
7.24	0.7405	0.0745	0.7405	+0.9973	8.23
7.66	0.649	0.166	0.649	+0.5900	8.25
8.20	0.442	0.373	0.442	+0.0737	8.27
8.38	0.358	0.457	0.358	-0.1060	8.27
8.66	0.257	0.558	0.257	-0.3367	8.32

Thus the $pK(S_o)$ of 1-naphthol-4-sulphonate = $\underline{8.27 \pm 0.05}$.
This also agrees satisfactorily with values of 8:32 (thermodynamic dissociation constant)[75], 8.27 (I = 0.01)[74], 8.20[76], 8.47 (thermodynamic dissociation constant)[73] quoted previously. In the Förster Cycle calculations which follow later in this chapter, a value of 8.27 is used for the $pK(S_o)$ of 1-naphthol-4-sulphonate.

FIG 4.2 The absorption spectra of 1-naphthol-4-sulphonate in (a) pH 14 (b) pH 9 (c) pH 8 (d) pH 6.5 solutions.



(d) Fluorescence spectroscopy: determination of $pK(S_1)$.

i) 1-Naphthol-2-sulphonate.

The corrected fluorescence spectra of 1-naphthol-2-sulphonate in hydrochloric acid (1 M) and sodium hydroxide (1 M) are shown in Figs 4.3 and 4.4.

Fig 4.5 shows the fluorescence intensity curves of 1-naphthol-2-sulphonate, in aqueous solutions, at various pH values. The $(ROH)^*$ and $(RO^-)^*$ forms have fluorescence maxima at 350 nm and 450 nm respectively and there is an isoemissive point at 394 nm. It follows that both these emissions originate from excitation of the "neutral", ROH, form of 1-naphthol-2-sulphonate, because the corrected fluorescence excitation spectra are identical with the absorption spectrum of 1-naphthol-2-sulphonate.

The change in fluorescence emission, due to a protolytic reaction in the excited state, occurs in solutions of much lower pH values than those in which the ground state protonation of RO^- occurs, showing that 1-naphthol-2-sulphonate is a stronger acid in the excited state.

The $pK(S_1)$ for 1-naphthol-2-sulphonate was expected to be sensitive to ionic strength changes. For this reason solutions of 1-naphthol-2-sulphonate were made up to a constant ionic strength of 0.05. Sodium acetate/acetic acid, and sodium formate/formic acid buffers were used to prepare solutions of pH 2.7 to pH 5.8, and a perchloric acid/sodium perchlorate mixture was used to prepare solutions of low pH values. The concentration of 1-naphthol-2-sulphonate used for the fluorescence intensity measurements was 2.10^{-6} M, to avoid the inner filter effect, and the excitation wavelength was 328 nm.

The variation in fluorescence intensity of the $(ROH)^*$ and $(RO^-)^*$ forms of 1-naphthol-2-sulphonate with the pH of solution is shown graphically in Fig 4.6.

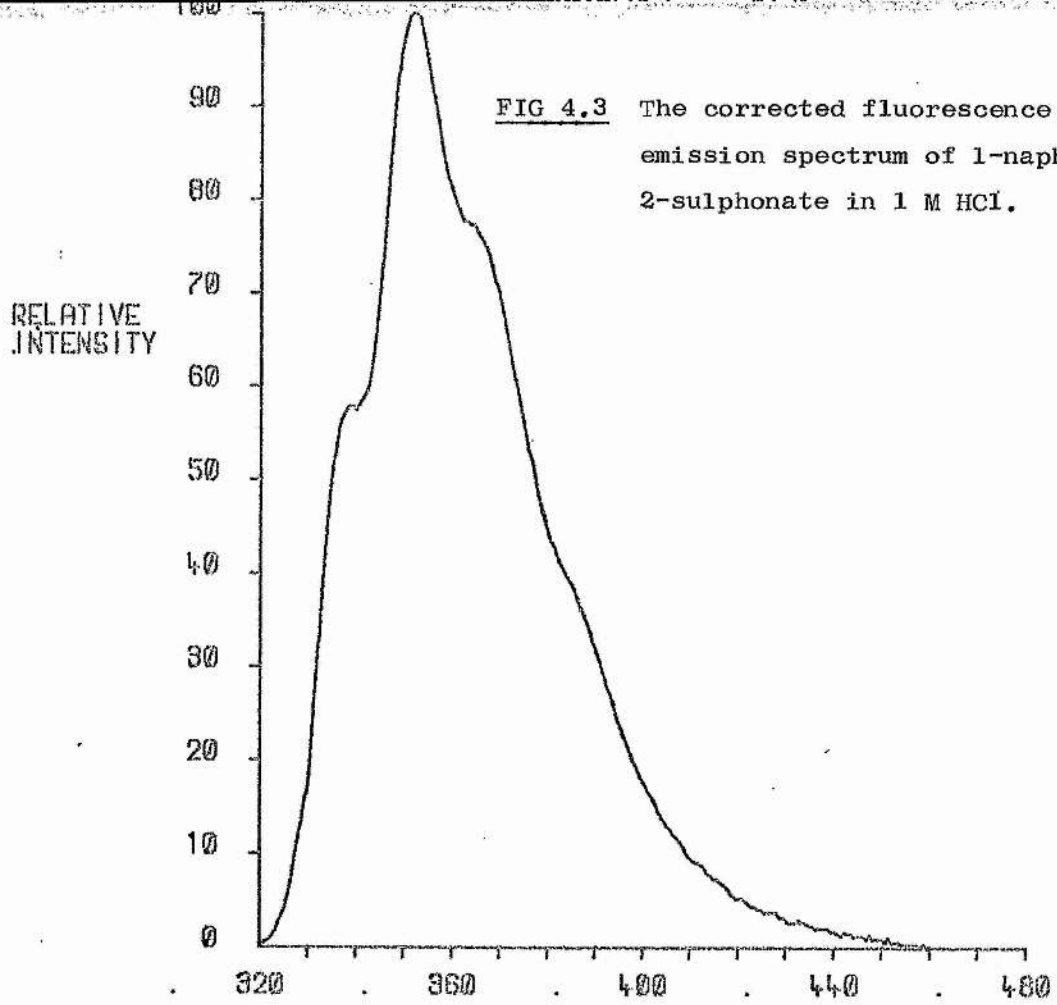


FIG 4.3 The corrected fluorescence emission spectrum of 1-naphthol-2-sulphonate in 1 M HCl.

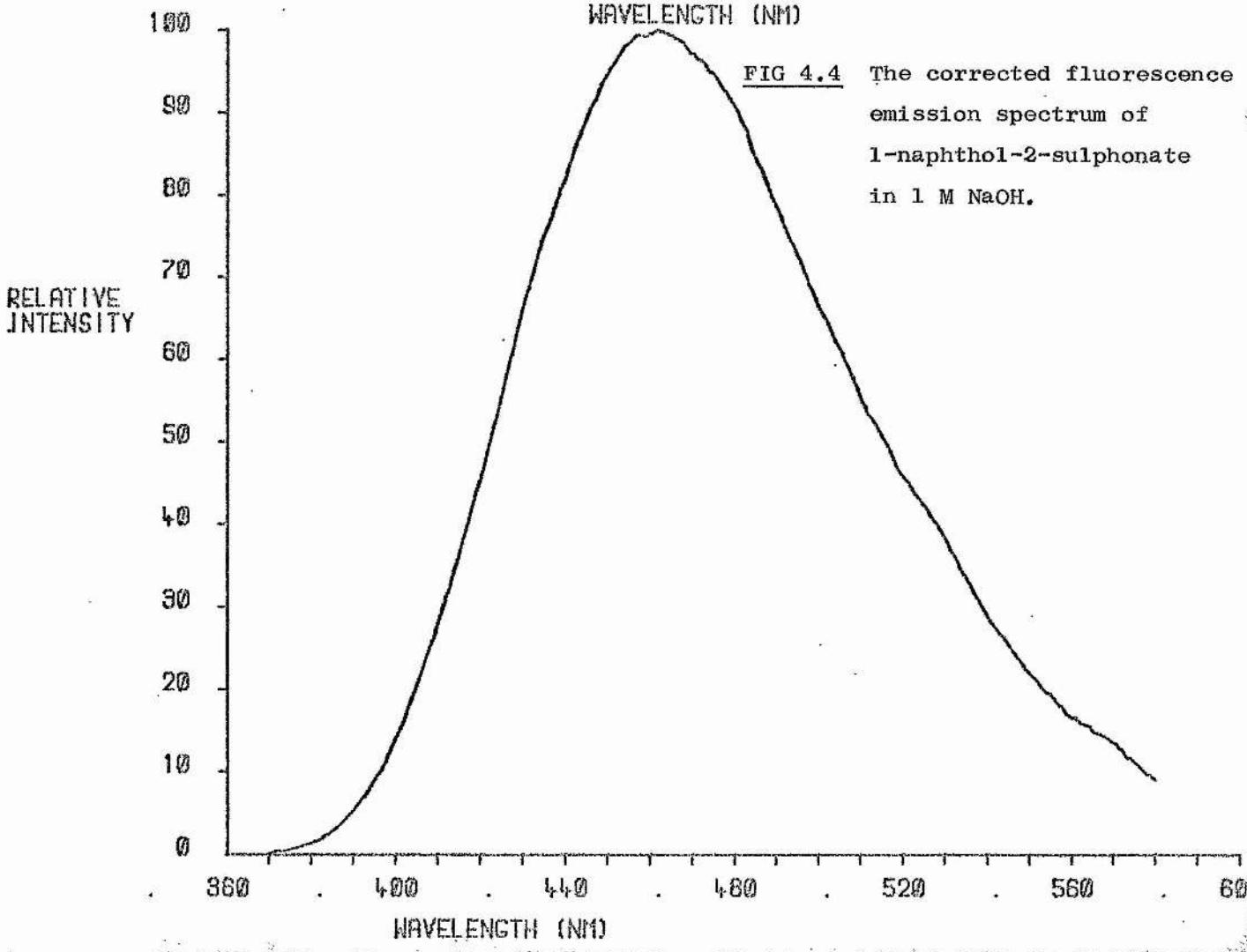


FIG 4.4 The corrected fluorescence emission spectrum of 1-naphthol-2-sulphonate in 1 M NaOH.

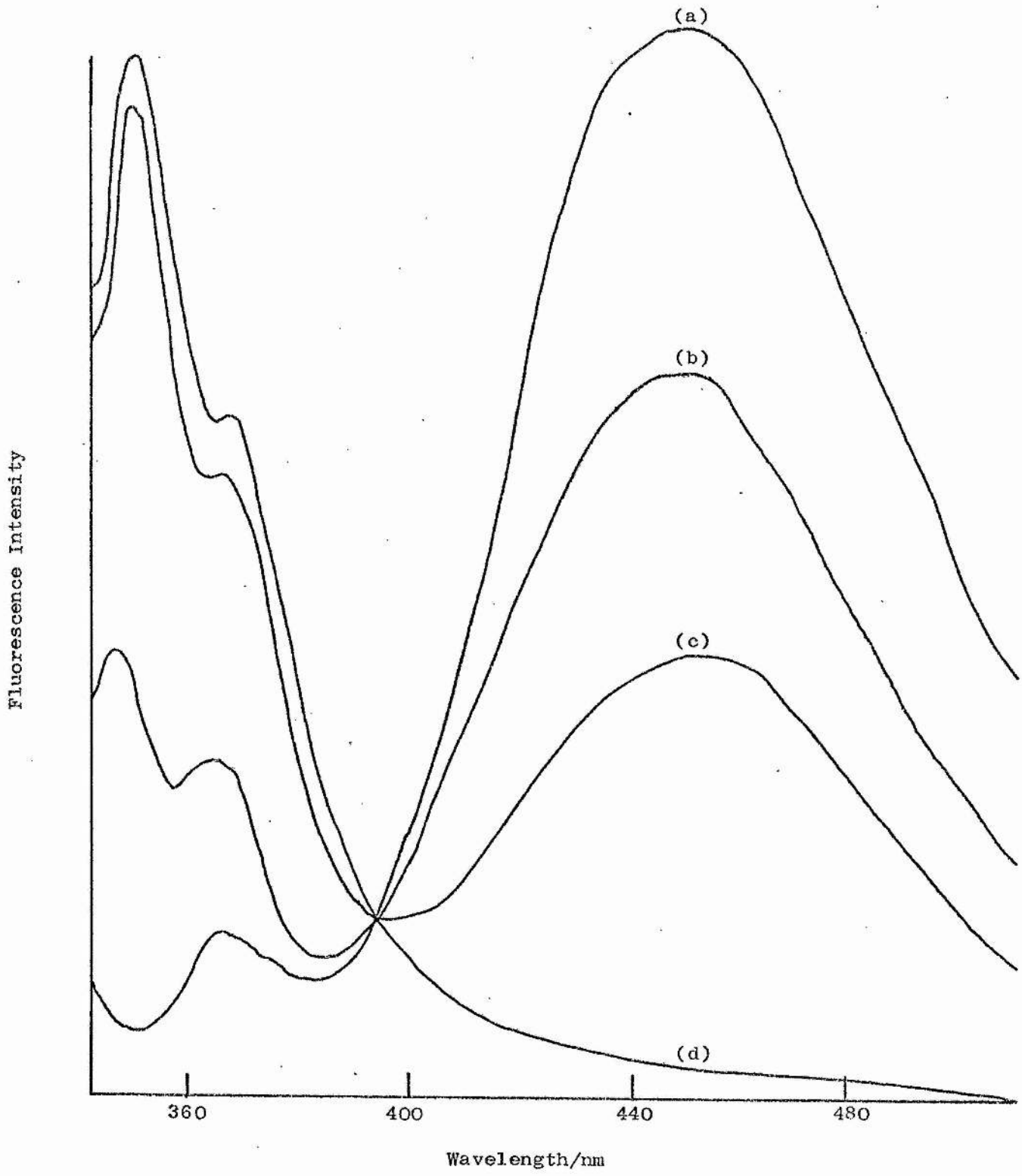
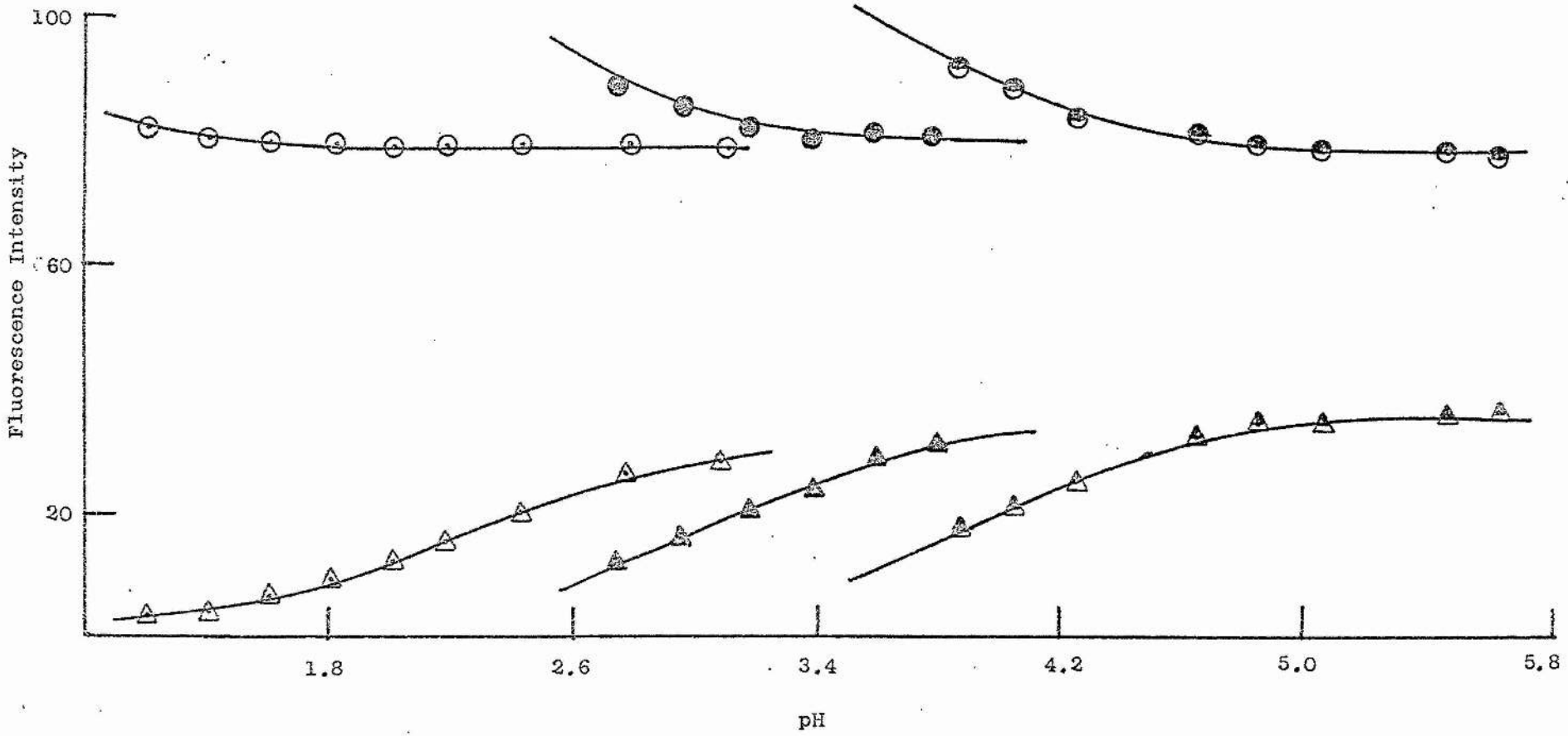


FIG 4.5 Fluorescence intensity curves of 1-naphthol-2-sulphonate in aqueous solutions at various pH values. (Excited at 330 nm) (a) pH 11.8 (b) pH 9.0 (c) pH 8.0 (d) pH 0.

FIG 4.6 The fluorescence intensity of 1-naphthol-2-sulphonate as a function of pH, ○ = $(ROH)^*$ form, △ = $(RO^-)^*$ form, ○, △ correspond to $HClO_4/NaClO_4$ solutions, ◍, ◭ correspond to HCOOH/NaCOOH solutions and ⊖, ▲ correspond to CH_3COOH/CH_3COONa solutions.



The presence of formic acid, acetic acid, formate ions and acetate ions will affect the equilibrium concentrations of $(RO^-)^*$ and (RH^*) only in so far as they affect the pH value and activity coefficients. However if fluorescence occurs before the equilibrium is established the presence of these acids and bases can produce profound changes in the rates of reactions involved in the equilibrium, and hence they can alter the intensities of fluorescence of $(RO^-)^*$ and $(ROH)^*$. The kinetics of these protolytic reactions in the excited state have been worked out by Weller[25,30].

If information is to be obtained about the excited state equilibrium,

$$(ROH)^* + H_2O \rightleftharpoons (RO^-)^* + H_3O^+ \qquad (4.2)$$

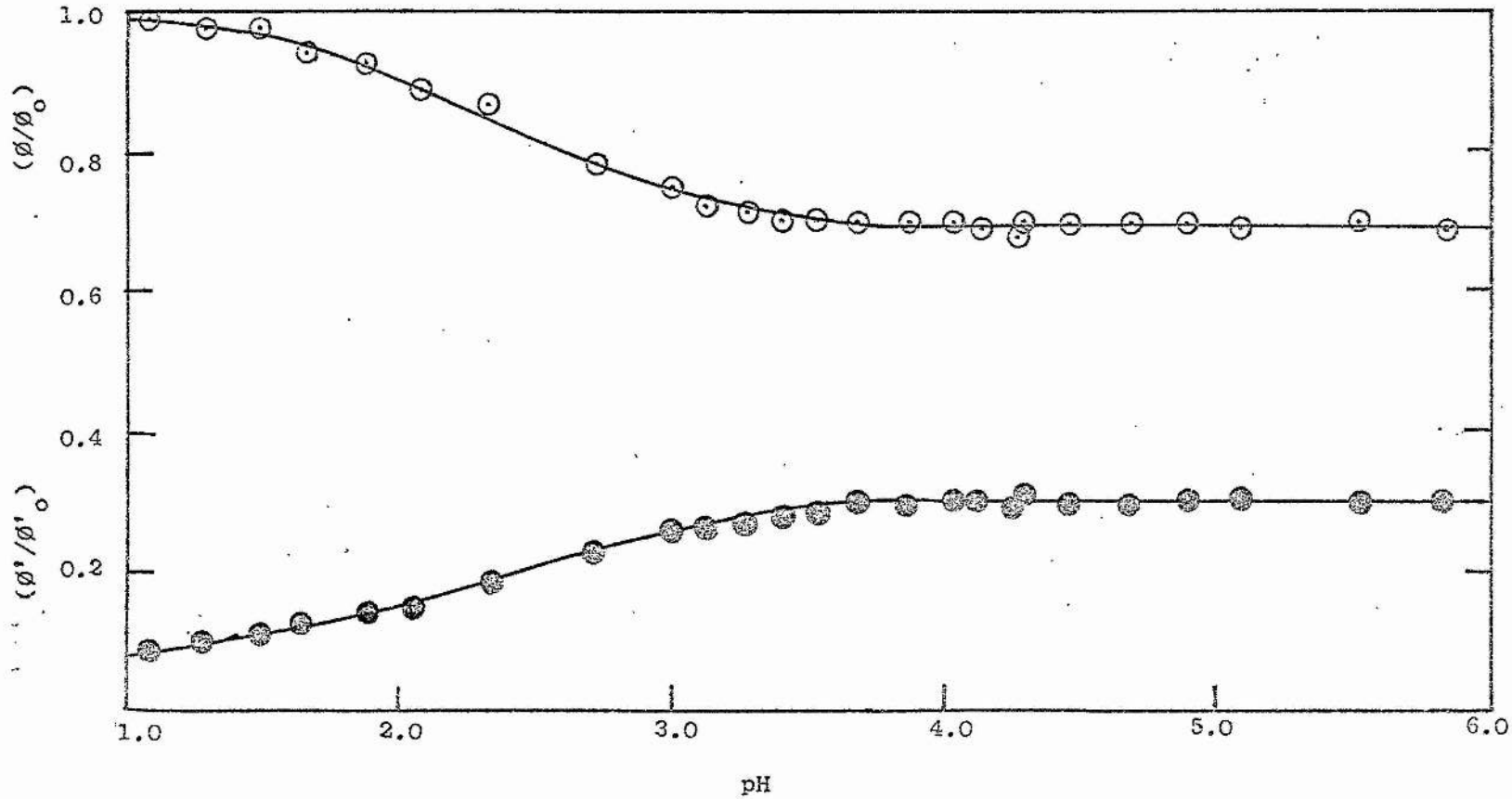
then the solutions used to measure the fluorescence intensities should be unbuffered, or the concentration of buffer should be so small that the following equilibrium can be neglected

$$(ROH)^* + B^- \rightleftharpoons (RO^-)^* + HB \qquad (4.3)$$

It was found that if the ionic strength of the buffers was reduced to 0.0004 then the equilibrium process 4.3 had little effect on the fluorescence intensities of $(ROH)^*$ and $(RO^-)^*$. This is shown by Fig 4.7, which was compiled from measurements of fluorescence intensities of solutions of 2-naphthol in buffers of ionic strength 0.0004. The pH of these solutions was measured immediately after the fluorescence intensity had been recorded. The values of $\phi/\phi_o = 0.70$ and $\phi'/\phi'_o = 0.30$ for the flat parts of the curves are in good agreement with the values of 0.73 and 0.28 obtained by Weller[25], where ϕ/ϕ_o and ϕ'/ϕ'_o refer to the relative fluorescence intensities, and ϕ_o and ϕ'_o the maximum intensities of the $(ROH)^*$ and (RO^-) forms.

The $pK(S_1)$ of 1-naphthol-2-sulphonate was investigated therefore, by preparing solutions of the sulphonate in buffers of ionic strength

FIG 4.7 The relative fluorescence intensity of 2-naphthol in water as a function of pH. Open circles indicate the relative intensity of naphthol fluorescence ($\emptyset/\emptyset_o$); filled circles indicate the relative intensity of naphtholate fluorescence ($\emptyset'/\emptyset'_o$).



0,0004 for pH values 2,7 to 5,8. Solutions of lower pH values were prepared by addition of the appropriate amount of perchloric acid. Solutions were again excited with light of wavelength 328 nm and a concentration of 2.10^{-6} M 1-naphthol-2-sulphonate was used. The fluorescence intensities of $(ROH)^*$ and $(RO^-)^*$ obtained are shown in Table 4.5 and are presented graphically in Fig 4.8. Once again the pH of the solutions was measured immediately after the fluorescence intensity had been recorded.

The fact that the $(ROH)^*$ fluorescence doesn't increase with decreasing pH until a pH value of 1,8 is reached, whereas the $(RO^-)^*$ fluorescence begins decreasing with decreasing pH at pH = 4,2, is strange. This phenomenon was investigated and the results obtained are described in Chapter 5. Therefore the variation of the intensity of the $(RO^-)^*$ fluorescence with pH was used to investigate the excited state equilibrium 4.2. A plot of the relative intensity of the naphtholate fluorescence against the pH of solution is shown in Fig 4.9. The values of $\emptyset'/\emptyset'_o$ plotted in Fig 4,9 are taken from Table 4.5.

(ii) 1-Naphthol-4-sulphonate.

The fluorescence intensity of 1-naphthol-4-sulphonate in aqueous acidic solutions is extremely weak. The corrected fluorescence spectrum of the 4-sulphonate ion in an acidic ethanol solutions is shown in Fig 4.10(a) and Fig 4.10(b) shows the corrected fluorescence spectrum of 1-naphthol-4-sulphonate in sodium hydroxide solution.

The $pK(S_1)$ of 1-naphthol-4-sulphonate was investigated by preparing solutions of the sulphonate in buffers of ionic strength 0,0004. Solutions of low pH were prepared by the addition of the appropriate amount of perchloric acid, and solutions of high pH were prepared by the addition of sodium hydroxide. The concentration of 1-naphthol-4-sulphonate used was 6.10^{-6} M, to avoid inner filter effects,

TABLE 4.5

Fluorescence intensities of the $(ROH)^*$ and $(RO^-)^*$ forms of 1-naphthol-2-sulphonate in aqueous solutions of varous pH values.

pH	Fluorescence Intensity at 350 nm i.e. $(ROH)^*$ ie Ø	Fluorescence Intensity at 450 nm ie $(RO^-)^*$ ie Ø'	$Ø'/Ø'_o$
0.22	80.00	1.25	0.009
0.39	76.00	1.25	0.009
0.69	73.00	1.75	0.012
0.93	72.00	2.00	0.014
1.08	72.00	3.00	0.021
1.28	71.50	3.40	0.024
1.48	71.00	4.50	0.031
1.68	70.00	6.00	0.042
1.88	70.50	7.75	0.054
2.10	70.00	9.50	0.066
2.39	70.00	12.40	0.086
2.60	70.00	15.25	0.106
2.81	70.25	17.50	0.121
2.96	70.00	19.00	0.132
3.07	70.00	20.75	0.145
3.20	69.25	21.75	0.151
3.32	70.00	23.00	0.160
3.45	70.00	24.00	0.166
3.56	69.50	24.50	0.170
3.75	70.00	25.00	0.173
3.95	70.00	26.00	0.180
4.24	70.00	26.50	0.184
4.15	70.00	26.50	0.184
4.30	70.00	26.50	0.184
4.48	70.50	27.00	0.187
5.07	70.00	26.50	0.184
5.82	70.00	26.75	0.186
14.00	1.00	144.20	1.000

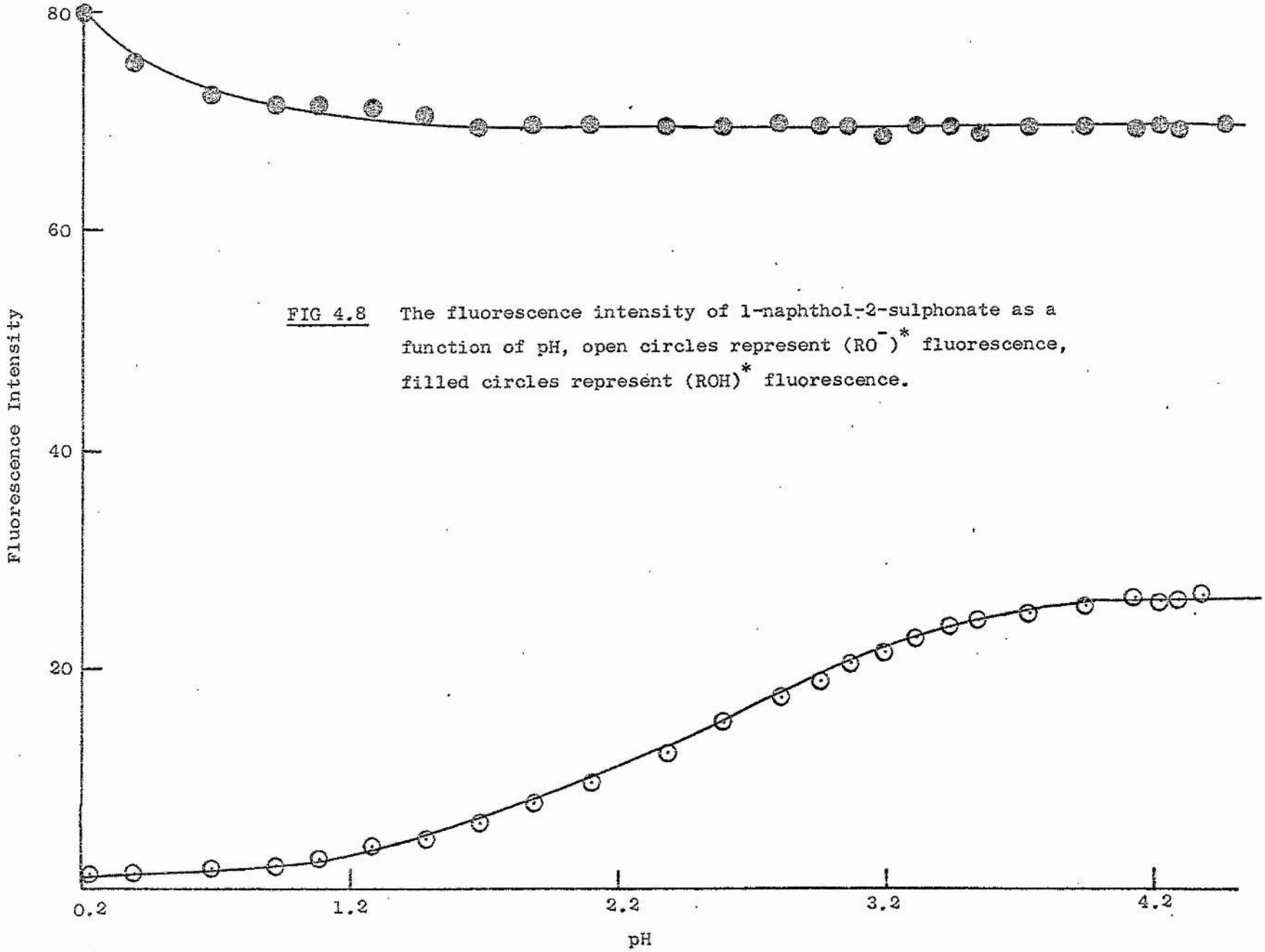
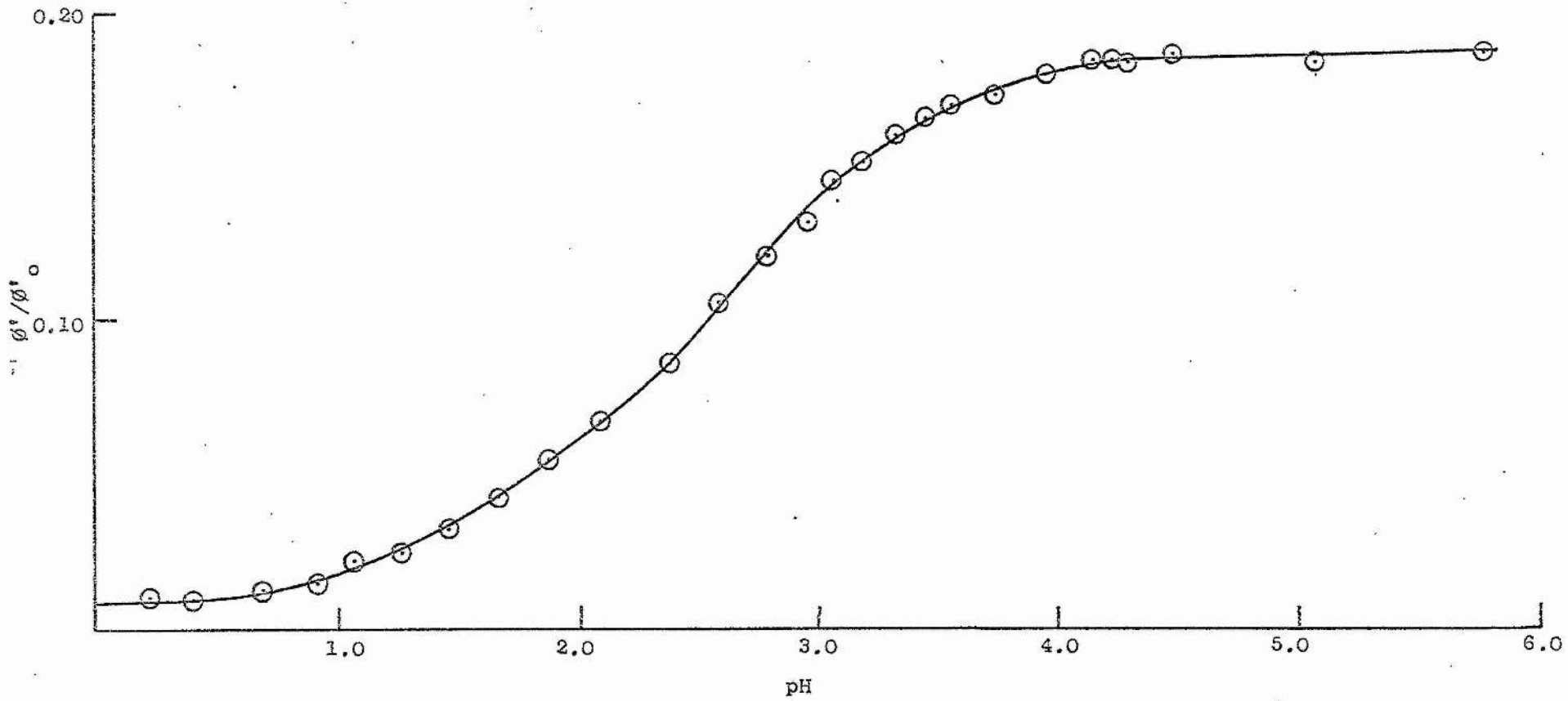


FIG 4.8 The fluorescence intensity of 1-naphthol-2-sulphonate as a function of pH, open circles represent $(RO^-)^*$ fluorescence, filled circles represent $(ROH)^*$ fluorescence.

FIG 4.9 The relative fluorescence intensity of the $(RO^-)^*$ form of 1-naphthol-2-sulphonate as a function of pH.



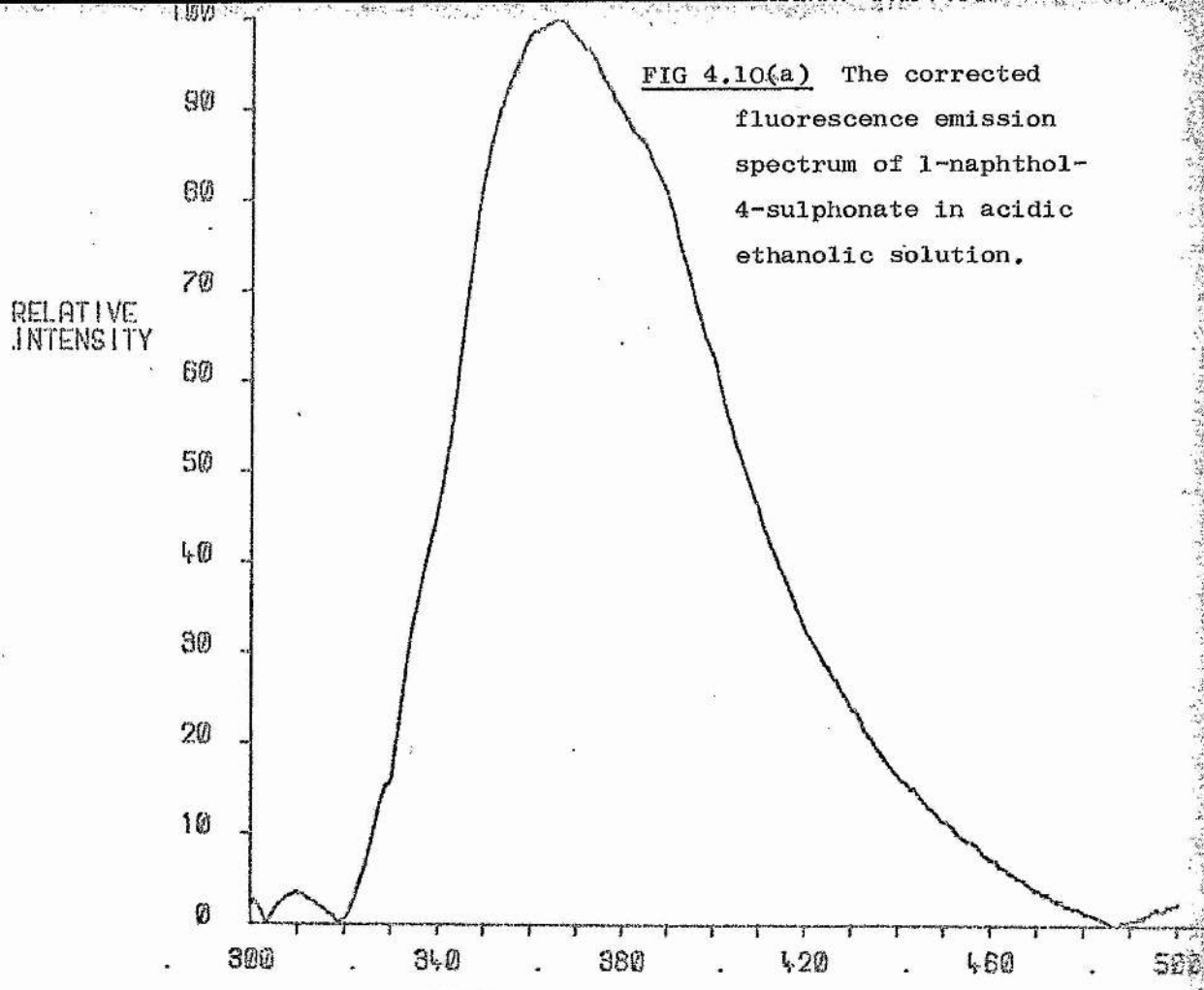


FIG 4.10(a) The corrected fluorescence emission spectrum of 1-naphthol-4-sulphonate in acidic ethanolic solution.

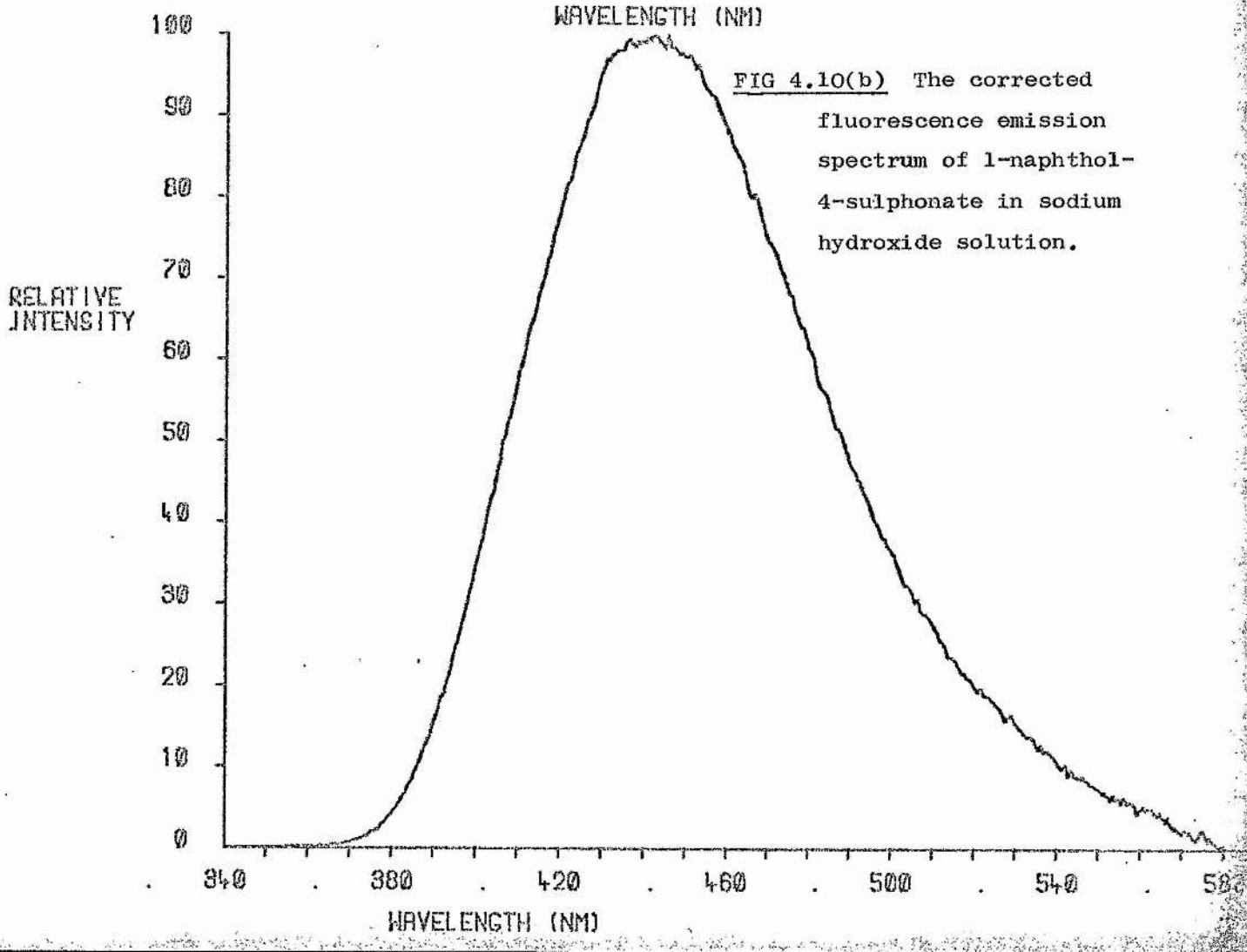


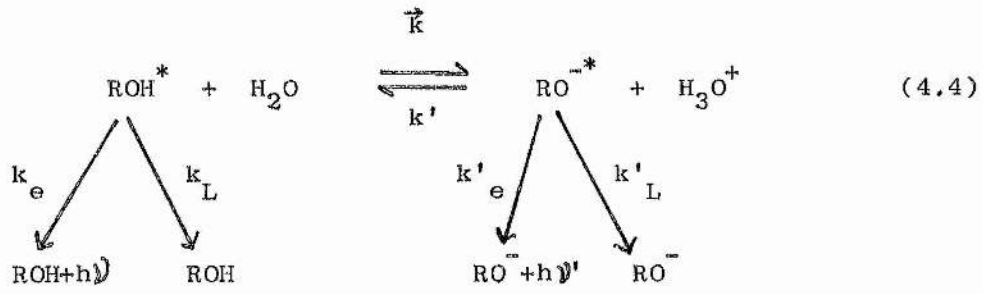
FIG 4.10(b) The corrected fluorescence emission spectrum of 1-naphthol-4-sulphonate in sodium hydroxide solution.

and all solutions were excited with light of wavelength 320 nm. Because the fluorescence of the naphthol $(ROH)^*$ form is so weak in aqueous solutions, fluorescence intensity measurements were made at 430 nm only i.e, only the intensity of $(RO^-)^*$ form was investigated with varying pH. The results obtained are shown in Table 4.6 and are presented graphically in Fig 4.11. The right hand inflection in Fig 4.11 is due to the ground state $pK(S_o)$ at 8.27. Thus the RO^- form is excited as the pH is increased rather than the ROH^- form of 1-naphthol-4-sulphonate, and the fluorescence from the $(RO^-)^*$ form increases.

(iii) The approximate $pK(S_1)$ of 1-naphthol-2- and -4-sulphonate.

Fluorescence life-times for the two naphthol sulphonates were not obtained, unfortunately. Attempts to measure lifetimes were made using the repetitive spark ("pulsed flash") technique described by Birkes and Munro[85]. The apparatus used has been described previously[86]. Although fluorescence lifetimes for compounds such as quinine sulphate in 1 M sulphuric acid (τ = 20 ns) were obtained using the apparatus, the fluorescence intensity and lifetimes of the naphthol sulphonates were of the same order as the intensity and lifetime of the spark ($\sim$ 9 ns), making fluorescence lifetime measurements impossible by this method.

Approximate values for $pK(S_1)$ can be obtained in two ways, however. Weller[25] has given the kinetics of the equilibrium,



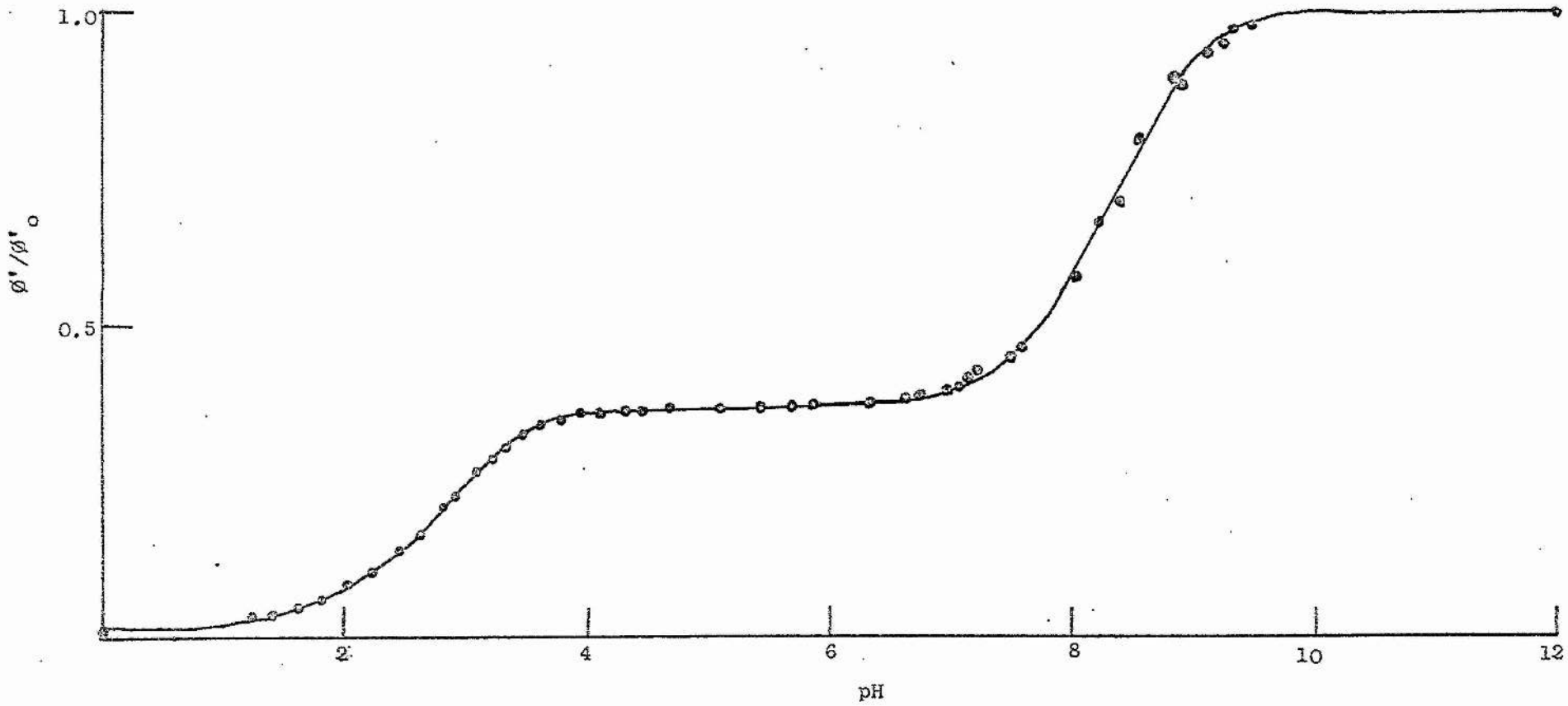
(4.4)

TABLE 4.6

The fluorescence intensities of the $(RO^-)^*$ form of 1-naphthol-4-sulphonate in aqueous solutions of various pH values.

pH	Fluorescence intensity at 430 nm ie $(RO^-)^*$ ie Ø'	Ø'/Ø'$_o$	pH	Fluorescence intensity at 430 nm ie $(RO^-)^*$ ie Ø'	Ø'/Ø'$_o$
0	0.06	0.006	5.67	35.25	0.371
1.24	2.60	0.027	5.88	35.50	0.374
1.42	3.20	0.034	6.32	35.75	0.376
1.61	4.20	0.044	6.60	36.00	0.379
1.79	5.50	0.058	6.69	36.50	0.384
2.01	7.80	0.082	6.99	37.50	0.395
2.23	10.00	0.105	7.05	38.00	0.400
2.45	13.00	0.137	7.15	39.50	0.416
2.61	15.20	0.160	7.20	40.10	0.422
2.80	19.75	0.208	7.48	42.50	0.447
2.91	21.25	0.224	7.56	44.00	0.463
3.08	25.00	0.263	8.02	54.75	0.576
3.22	26.60	0.280	8.20	62.50	0.658
3.33	28.80	0.303	8.35	66.00	0.695
3.47	30.50	0.321	8.55	75.90	0.799
3.61	32.00	0.337	8.85	84.80	0.893
3.78	32.75	0.345	8.90	84.50	0.899
3.94	33.90	0.357	9.11	88.50	0.932
4.11	34.00	0.358	9.24	90.20	0.949
4.30	34.25	0.361	9.33	92.50	0.977
4.45	34.50	0.363	9.49	93.20	0.981
4.65	35.00	0.368	12.00	95.00	1.000
5.07	34.75	0.366	13.00	95.00	1.000
5.40	35.25	0.371			

FIG 4.11 The relative fluorescence intensity of the $(RO^-)^*$ form of 1-naphthol-4-sulphonate as a function of pH.



where $\vec{k}$ is the pseudounimolecular rate constant of the forward reaction, k_e and k'_e are the unimolecular rate constants of fluorescence and k_L and k'_L are the unimolecular rate constants of radiationless deactivation. Using the steady state method Weller[25] worked out the following relationships for the ratios of fluorescence intensities ϕ/ϕ_o and ϕ'/ϕ'_o

$$\phi/\phi_o = \frac{1 + k'\tau'}{1 + \vec{k}\tau + k'\tau'} \qquad (4.5)$$

and

$$\phi'/\phi'_o = \frac{\vec{k}\tau}{1 + \vec{k}\tau + k'\tau'} \qquad (4.6)$$

where τ and τ' are the fluorescence lifetimes of the $(ROH)^*$ and $(RO^-)^*$ forms respectively. Now k' varies with the H_3O^+ concentration as follows

$$k' = \overleftarrow{k}\, C_{H_3O^+} \qquad (4.7)$$

where $\overleftarrow{k}$ is the bimolecular rate constant of the back reaction. For small H_3O^+ concentrations $k'\tau'$ can be neglected and equations 4.5 and 4.6 are reduced to

$$(\phi/\phi_o)_{const.} = \frac{1}{1 + \vec{k}\tau} \qquad (4.8)$$

and

$$(\phi'/\phi'_o)_{const.} = \frac{\vec{k}\tau}{1 + \vec{k}\tau} \qquad (4.9)$$

where $(\phi/\phi_o)_{const.}$ and $(\phi'/\phi'_o)_{const.}$ refer to the flat parts of the curve in Fig 4.9 and 4.11 respectively (that is between pH 4.0 and 7.0 approx.).

Now the equilibrium constant K is given by

$$K = \frac{\vec{k}}{\overleftarrow{k}} = \frac{\vec{k}}{k'} \cdot C_{H_3O^+} \qquad (4.10)$$

$$\text{or} \quad pK(S_1) = pH + \log \frac{k'}{\vec{k}} \qquad (4.11)$$

$$\text{or} \quad pK(S_1) = pH + \log \frac{k'\tau'}{\vec{k}\tau} + \log \frac{\tau}{\tau'} \qquad (4.12)$$

Equation (4.12) becomes

$$pK(S_1) = pH + \log \frac{\gamma}{\gamma'} \qquad (4.13)$$

when $\vec{k}\gamma = k'\gamma'$, and equation 4.6 becomes

$$\phi'/\phi'_o = \frac{\vec{k}\gamma}{1 + 2\vec{k}\gamma} = \frac{(\phi'/\phi'_o)_{const.}}{1 + (\phi'/\phi'_o)_{const.}} \qquad (4.14)$$

If the pH where $\phi'/\phi'_o = \frac{(\phi'/\phi'_o)_{const.}}{1 + (\phi'/\phi'_o)_{const.}}$ is known

then by substituting this value of pH in equation (4.13), an approximate value of $pK(S_1)$ can be obtained. If $(\phi'/\phi'_o)_{const.}$ is known we can also determine $\vec{k}\gamma$ from equation 4.9. These calculations were made for both 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate and the results obtained are listed in Table 4.7.

Table 4.7

$\vec{k}\gamma$ values and $pK(S_1) - \log \gamma/\gamma'$ values for 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate.

	$(\phi'/\phi'_o)_{const.}$ ‡	pH ‡‡	$\vec{k}\gamma$	$pK(S_1) - \log \gamma/\gamma'$
1-naphthol-2-sulphonate	0.185	3.26	0.2270	3.26
1-naphthol-4-sulphonate	0.368	3.12	0.5832	3.12

‡ values are taken from Fig 4.9 and Fig 4.11

‡‡ this pH refers to the value of pH where $\phi'/\phi'_o = \frac{(\phi'/\phi'_o)_{const.}}{1 + (\phi'/\phi'_o)_{const.}}$ taken from Figs 4.9 and 4.11.

Consider equation 4.6

$$\phi'/\phi'_o = \frac{\vec{k}\gamma}{1 + \vec{k}\gamma + k'\gamma'} \qquad (4.6)$$

$$\therefore \quad \phi'/\phi'_o = \frac{\vec{k}\tau}{1 + \vec{k}\tau + \overleftarrow{k}\tau' C_{H_3O^+}} \qquad (4.15)$$

$$\therefore \quad \phi'_o/\phi' = 1/\vec{k}\tau + 1 + \frac{\overleftarrow{k}\tau'}{\vec{k}\tau} C_{H_3O^+} \qquad (4.16)$$

Thus a plot of ϕ'_o/ϕ' against the H_3O^+ concentration will give a slope of $\frac{\overleftarrow{k}\tau'}{\vec{k}\tau}$ and an intercept on the ordinate axis of $1 + 1/\vec{k}\tau$. A value of $\vec{k}\tau$ can be found from the intercept, and by taking the logarithm of the slope,

i.e.
$$\log \frac{\overleftarrow{k}\tau'}{\vec{k}\tau} = \log \frac{\overleftarrow{k}}{\vec{k}} + \log \tau'/\tau$$

$$= pK(S_1) - \log \tau/\tau'$$

a value of $pK(S_1) - \log \tau/\tau'$ can be obtained for each compound.

Plots of ϕ'_o/ϕ' against $C_{H_3O^+}$ were made for both 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate and these are shown in Fig 4.12. The plot for 1-naphthol-2-sulphonate is made using the data in Table 4.8 and the plot for the -4-sulphonate is made using the data in Table 4.9.

Table 4.8

The information used in the plot of ϕ'_o/ϕ' against $C_{H_3O^+}$ for 1-naphthol-2-sulphonate $\phi'_o = 144.2$

pH	$C_{H_3O^+}$	Fluorescence intensity of the $(RO^-)^*$ form i.e. ϕ'	ϕ'_o/ϕ'
2.39	0.004074	12.40	11.63
2.60	0.002514	15.25	9.46
2.81	0.001548	17.50	8.24
2.96	0.001096	19.00	7.58
3.07	0.000851	20.75	6.95
3.20	0.000631	21.75	6.63
3.32	0.000479	23.00	6.26

FIG 4.12 Plots of ϕ'_o/ϕ' against H_3O^+ concentration for the $(RO^-)^*$ forms of 1-naphthol-2- and -4-sulphonates.

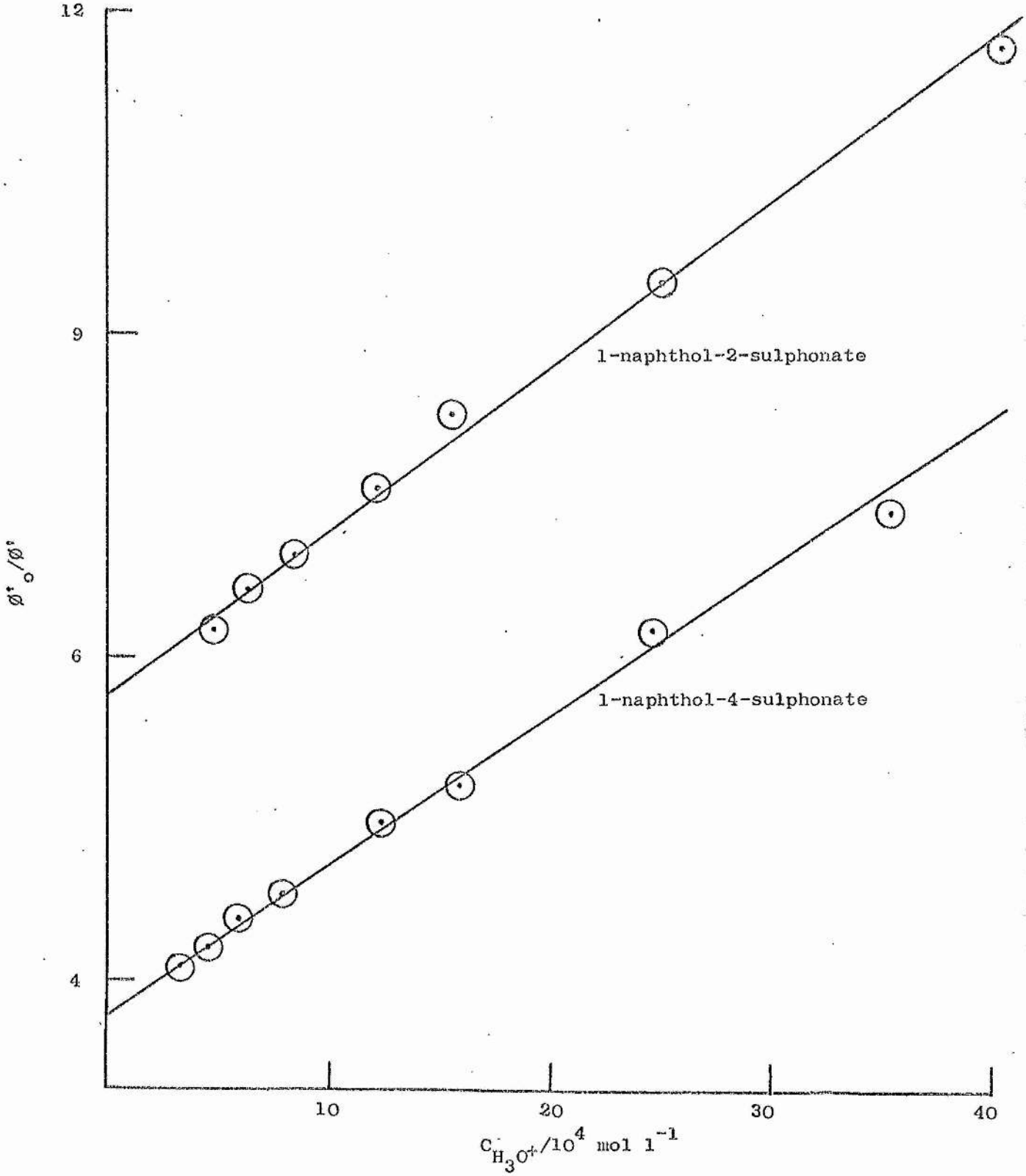


Table 4.9

The information used in the plot of ϕ'_o/ϕ' against $C_{H_3O^+}$ for 1-naphthol-4-sulphonate ϕ'_o = 95.00

pH	$C_{H_3O^+}$	Fluorescence intensity of the $(RO^-)^*$ form i.e. ϕ'	ϕ_o'/ϕ'
2.45	0.003548	13.00	7.31
2.61	0.002455	15.20	6.25
2.80	0.001585	19.75	4.81
2.91	0.001230	21.25	4.47
3.08	0.000832	25.00	3.80
3.22	0.000603	26.60	3.57
3.33	0.000468	28.80	3.30
3.47	0.000339	30.50	3.11

The results of the intercepts on the ordinate and the slopes of the graphs of ϕ'_o/ϕ' against $C_{H_3O^+}$ are shown in Table 4.10

Table 4.10

$\vec{k}\tau$ values and $pK(S_1)$ - log τ / τ' values for 1-naphthol-2- and -4-sulphonate obtained from Fig 4.12.

	Intercept	Slope	$\vec{k}\tau$	$pK(S_1)$-log τ/τ'
1-naphthol-2-sulphonate	5.65	1626	0.2149	3.21
1-naphthol-4-sulphonate	2.70	1381	0.5882	3.14

(e) Flash spectroscopy: determination of $pK(T_1)$.

The transient absorption spectra of 1-naphthol in aqueous solution are very weak and diffuse (See Chapter 3). However, well characterized

transient absorption spectra were observed for 1-naphthol-2-sulphonate in aqueous acidic and alkaline solutions, and for 1-naphthol-4-sulphonate in aqueous alkaline solutions.

(i) 1-Naphthol-2-sulphonate.

1-Naphthol-2-sulphonate shows a strong transient absorption spectrum in sodium hydroxide solution (See Fig 4.13). The long wavelength absorption band, with a maximum at 525 nm, is assigned to the (RO^-) triplet molecule. The short wavelength absorption band, with a maximum at 405 nm, is attributed to the naphthoxyl radical of 1-naphthol-2-sulphonate since this band is also observed in the transient absorption spectrum of 1-naphthol-2-sulphonate in aqueous acidic solutions, and is very similar to the absorption band assigned to the naphthoxyl radical of 1-naphthol by Porter and Land[87].

The $pK(T_1)$ of 1-naphthol-2-sulphonate was estimated by watching the disappearance of the band assigned to the triplet (RO^-) as the pH of the solutions used for the determination was lowered. Solutions of 1-naphthol-2-sulphonate (5.10^{-5} M) were prepared in buffered solutions of constant ionic strength (I = 0.05), except for one solution of high pH which was prepared by addition of the appropriate amount of sodium hydroxide. Ultra-violet absorption spectra of these solutions, taken before and after flashing, showed >10% decomposition after 5 flashes. The measurements of optical density were therefore made at the shortest delay (10 μs) between the photolytic and spectrographic flashes, and measurements which had been made on solutions that had been flashed once only were used.

The method used to estimate the $pK(T_1)$ has been given previously[32]. If $[T_{max}]$ is the optical density of the (RO^-) form at the extreme pH where only triplet RO^- can be assumed present, and [T] is the optical density, measured at the same wavelength, at an intermediate pH, then

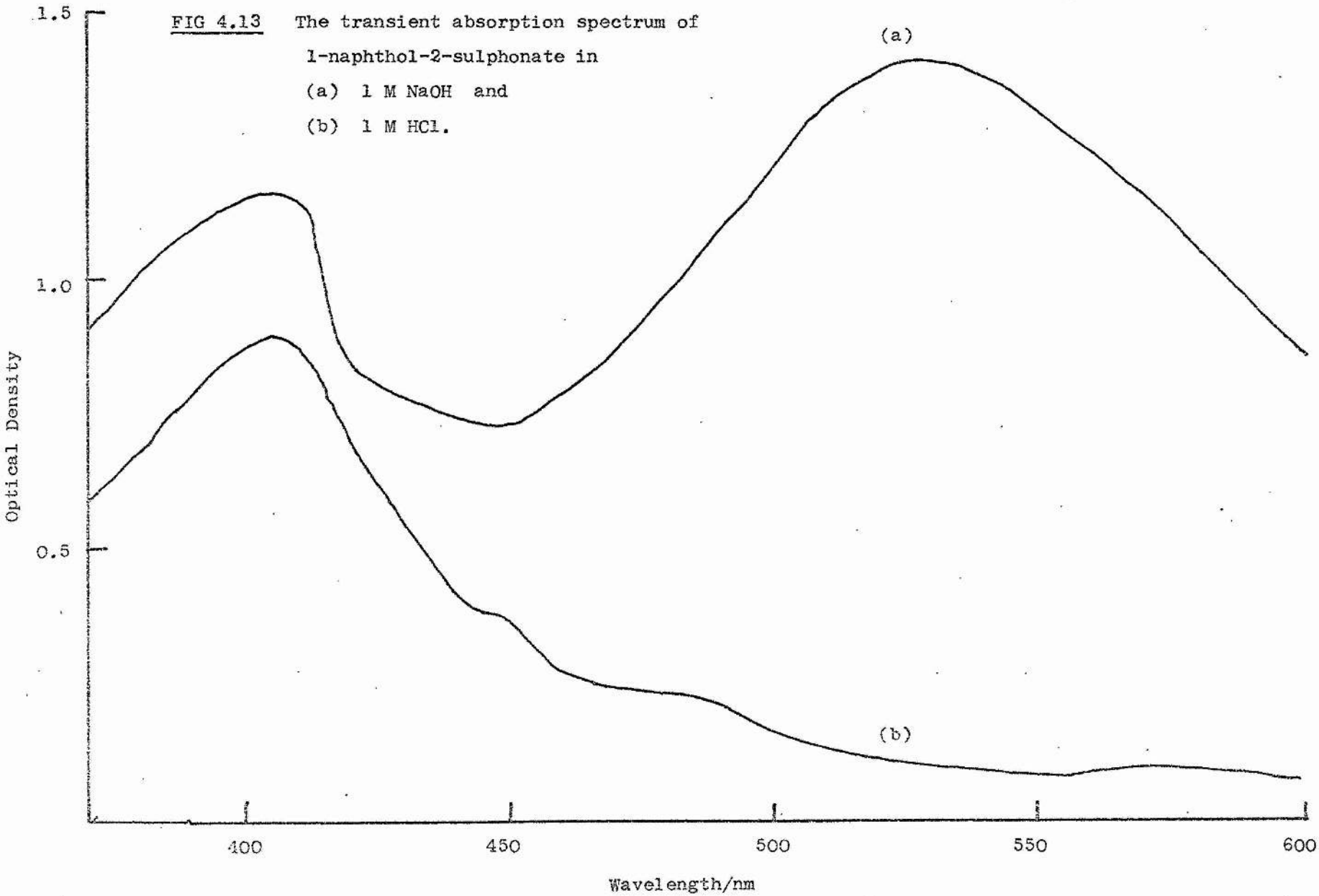


FIG 4.13 The transient absorption spectrum of 1-naphthol-2-sulphonate in (a) 1 M NaOH and (b) 1 M HCl.

$$[T_{max}] = \varepsilon_{RO^-} C.l \qquad (4.17)$$

$$\text{and } [T] = \varepsilon_{RO^-} C_{RO^-} l + \varepsilon_{ROH} C_{ROH} l \qquad (4.18)$$

where ε = extinction coefficient, C = concentration and l = path length

$$\text{If} \quad C_{RO^-} + C_{ROH} = C \qquad (4.19)$$

$$\text{then} \quad \frac{[T]}{[T_{max}]} = \frac{\varepsilon_{RO^-} C_{RO^-} + \varepsilon_{ROH} (C - C_{RO^-})}{\varepsilon_{RO^-} C} \qquad (4.20)$$

When C_{RO^-} is zero, (4.20) becomes

$$\frac{[T]}{[T_{max}]} = \frac{\varepsilon_{ROH} C}{\varepsilon_{RO^-} C} = \frac{\varepsilon_{ROH}}{\varepsilon_{RO^-}} . \qquad (4.21)$$

At the pK when $C_{ROH} = C_{RO^-}$

$$\frac{[T]}{[T_{max}]} = \frac{(1 + \varepsilon_{ROH}/\varepsilon_{RO^-})}{2} \qquad (4.22)$$

In a plot of $[T]/[T_{max}]$ against pH, $\varepsilon_{ROH}/\varepsilon_{RO^-}$ can be read off directly from equation 4.21, and substitution in equation 4.22 gives the value of $[T]/[T_{max}]$ at the pH equivalent to the pK. In this method no assumption is made about extinction coefficients, but the total amount of triplet formed is taken to be constant over the range investigated.

The optical density measurements of the RO^- triplet of 1-naphthol-2-sulphonate, taken at 525 nm, are given in Table 4.11.

Table 4.11

The optical densities of the RO^- triplet of 1-naphthol-2-sulphonate at various pH values.

pH	O.D.	$[T]/[T_{max}]$
12.70	1.285	1.000
10.87	1.280	0.996
10.09	1.257	0.987
9.20	1.151	0.896
7.96	0.910	0.708
7.43	0.600	0.467
7.04	0.500	0.389
5.82	0.286	0.223
5.01	0.200	0.156
3.63	0.160	0.125
2.10	0.150	0.117

Fig 4.14 shows the plot of $[T]/[T_{max}]$ against pH for 1-naphthol-2-sulphonate. From the graph $\varepsilon_{ROH}/\varepsilon_{RO^-} = 0.12$, and substitution of this in equation 4.22 gives $[T]/[T_{max}] = 0.56$ and therefore a $pK(T_1)$ of 7.50.

∴ the $pK(T_1)$ of 1-naphthol-2-sulphonate = 7.50 at 20°C.

(ii) 1-Naphthol-4-sulphonate.

1-Naphthol-4-sulphonate shows a very weak diffuse transient absorption spectrum in 1 M hydrochloric acid solution. The transient absorption spectrum in sodium hydroxide solution is somewhat stronger however, but not as strong as the corresponding transient absorption of 1-naphthol-2-sulphonate, although the two spectra are very similar. The short wavelength absorption band, with a maximum at 400 nm, is assigned to the naphthoxyl radical of 1-naphthol-4-sulphonate and the long wavelength band (max = 533 nm approx) is attributed to the triplet (RO^-) molecule of 1-naphthol-4-sulphonate.

The $pK(T_1)$ was estimated by watching the disappearance of the RO^- triplet absorption band of 1-naphthol-4-sulphonate as the pH was lowered. Solutions of 1-naphthol-4-sulphonate (10^{-4} M) were prepared in buffered solutions of constant ionic strength (I = 0.05), and measurements of optical density were made 10 μs after flashing. All measurements were made on solutions that had been flashed once only.

The optical density measurements of the RO^- triplet of 1-naphthol-4-sulphonate, taken at 550 nm are shown in Table 4.12.

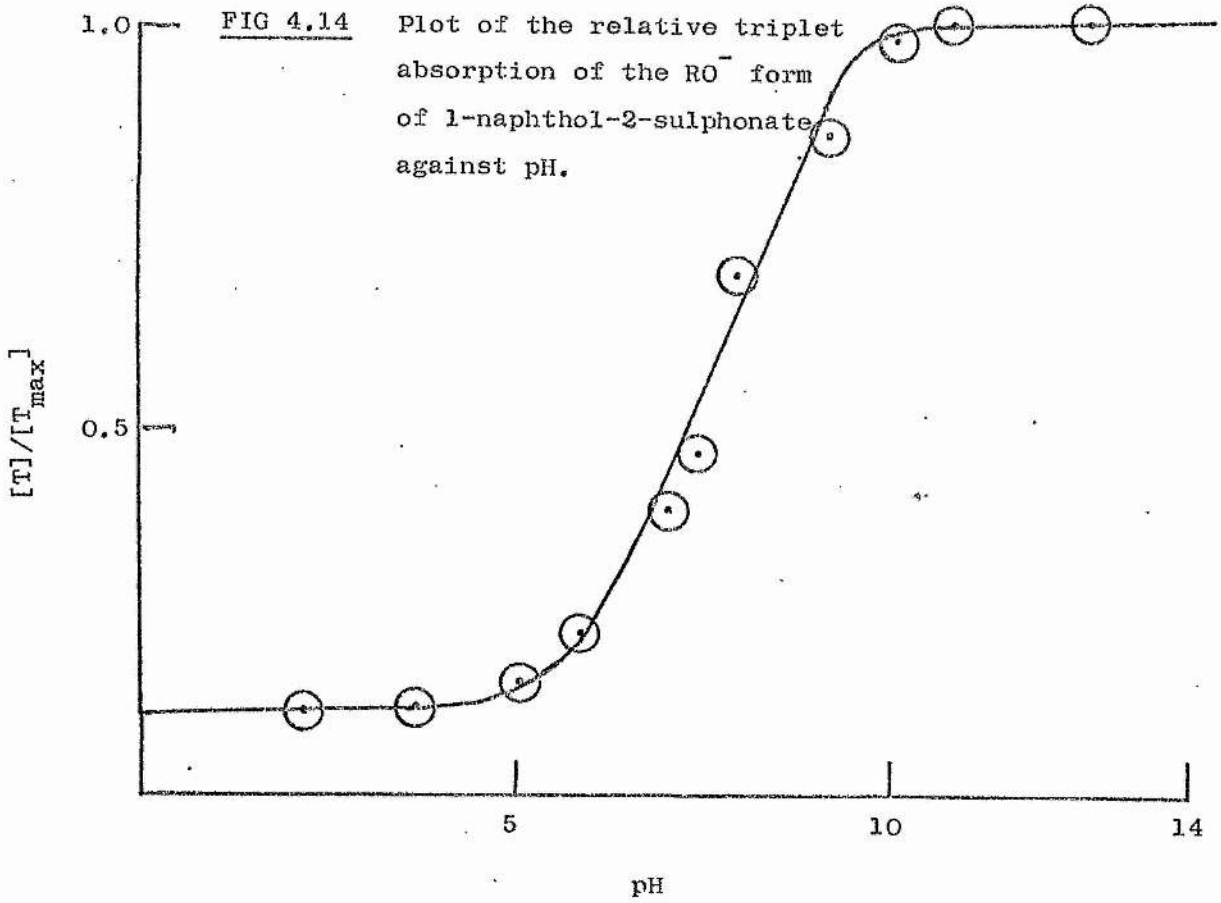


FIG 4.14 Plot of the relative triplet absorption of the RO^- form of 1-naphthol-2-sulphonate against pH.

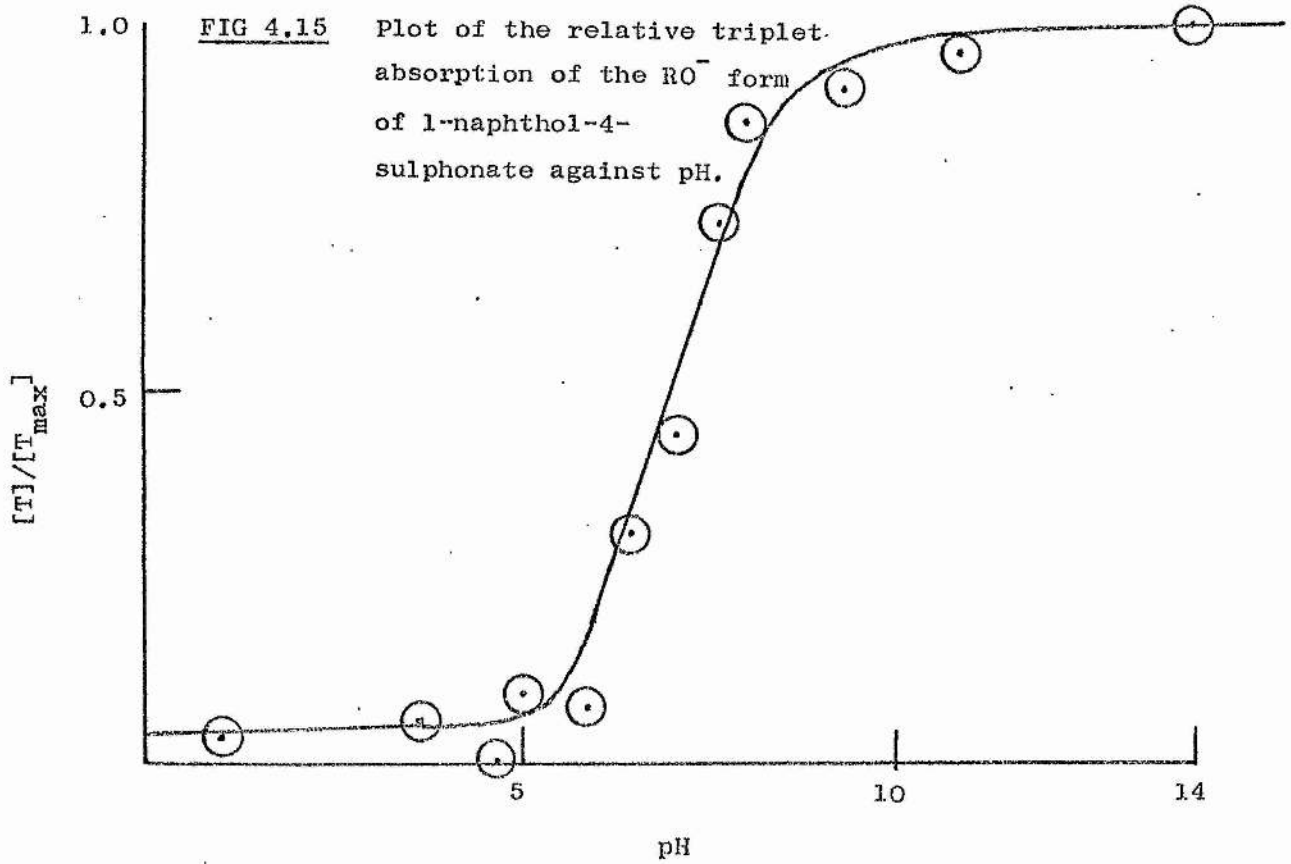


FIG 4.15 Plot of the relative triplet absorption of the RO^- form of 1-naphthol-4-sulphonate against pH.

FIG 4.16 The transient absorption spectra of 1-naphthol-4-sulphonate in 1 M NaOH.

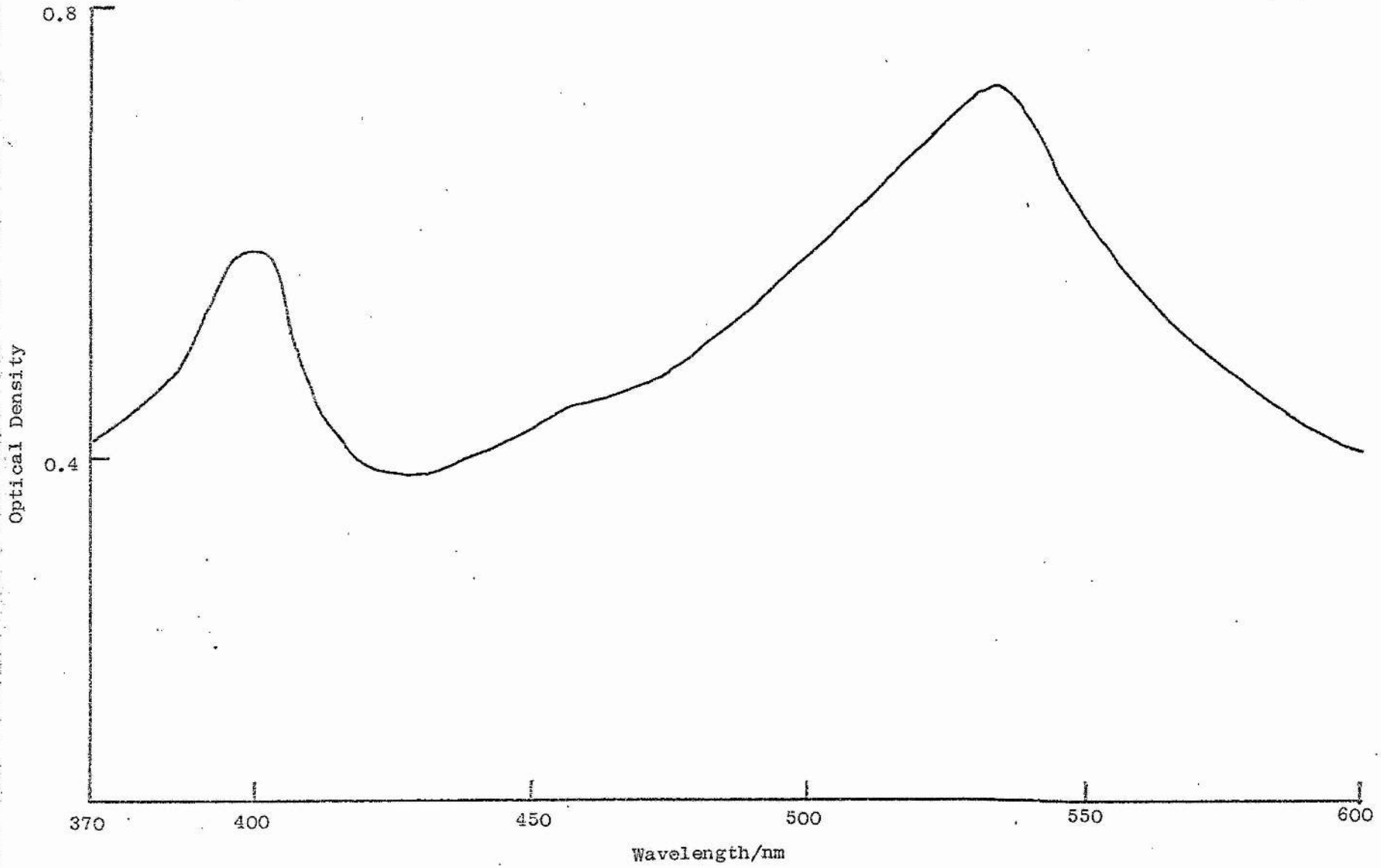


Table 4.12

The optical densities of the RO^- triplet of 1-naphthol-4-sulphonate in solutions of various pH.

pH	O.D.	$[T]/[T_{max}]$
13.97	0.549	1.00
10.82	0.527	0.960
9.27	0.500	0.910
7.95	0.475	0.865
7.61	0.400	0.729
7.04	0.242	0.441
6.41	0.170	0.309
5.85	0.040	0.073
5.00	0.050	0.091
4.61	0.000	0.000
3.59	0.030	0.055
0.95	0.018	0.033

Fig 4.15 shows the plot of $[T]/[T_{max}]$ against pH for 1-naphthol-4-sulphonate. From the graph $\varepsilon_{ROH}/\varepsilon_{RO^-} = 0.04$, therefore $[T]/[T_{max}] = 0.52$ giving a $pK(T_1)$ of 7.05.

∴ the $pK(T_1)$ of 1-naphthol-4-sulphonate = 7.05 at 20°C.

(f) Förster Cycle Calculations.

i) $pK(T_1)$ determination.

The corrected phosphorescence emission spectra of 1-naphthol-2-sulphonate in sodium hydroxide (1 M) and perchloric acid (1 M) are shown in Figs 4.17 and 4.18 respectively, and the corresponding spectra of 1-naphthol-4-sulphonate are shown in Figs 4.19 and 4.20. Table 4.13 gives the spectral data used in the Förster cycle calculations,

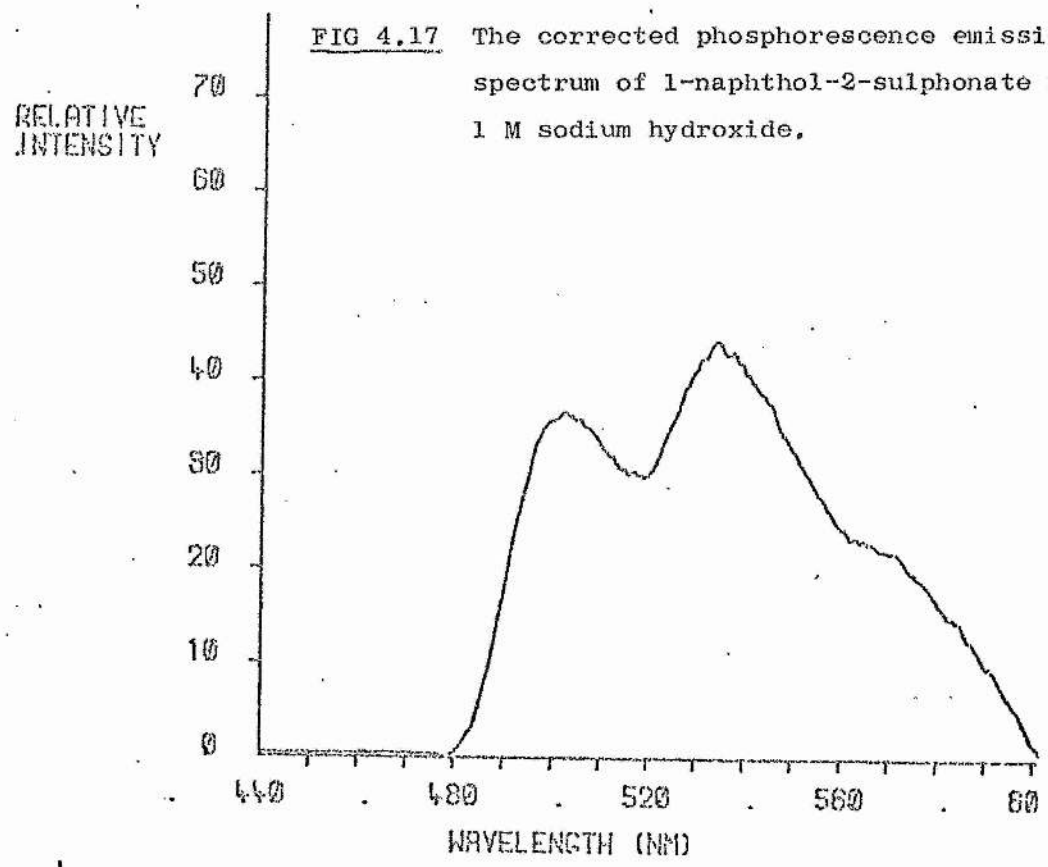


FIG 4.17 The corrected phosphorescence emission spectrum of 1-naphthol-2-sulphonate in 1 M sodium hydroxide.

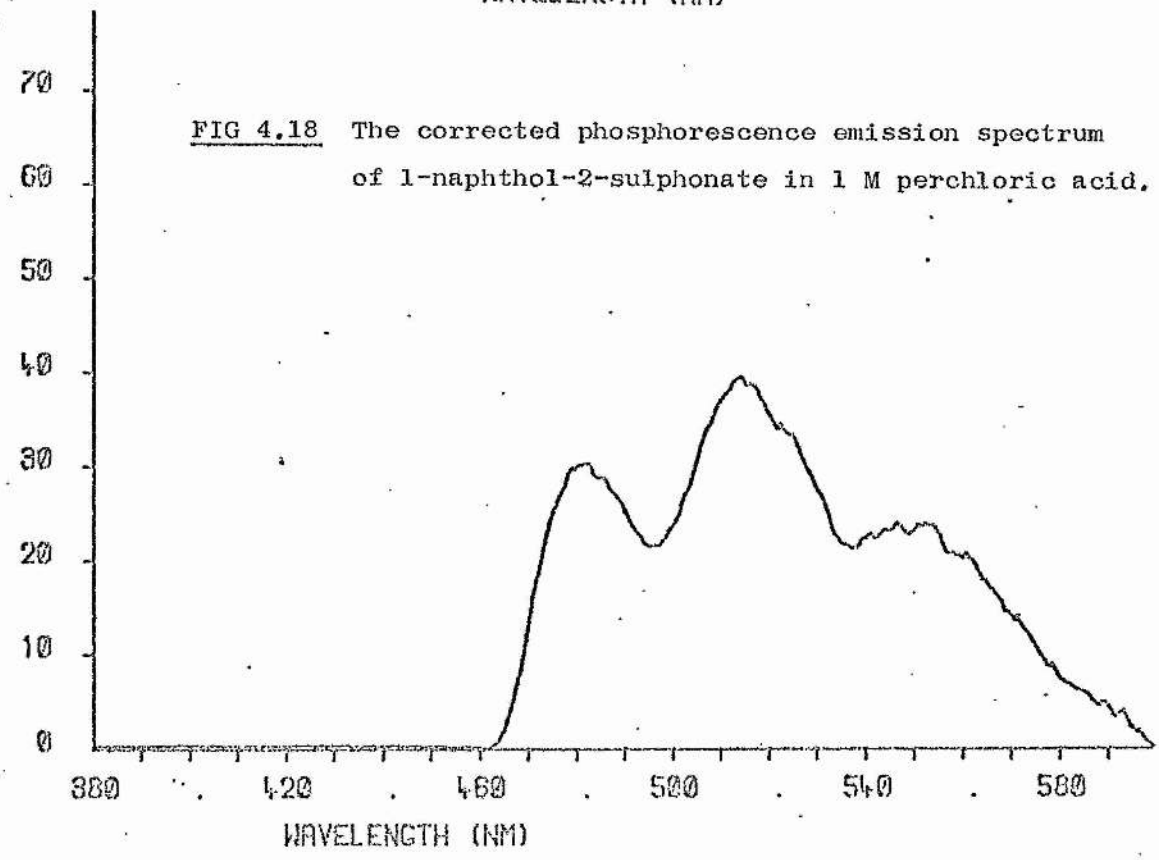


FIG 4.18 The corrected phosphorescence emission spectrum of 1-naphthol-2-sulphonate in 1 M perchloric acid.

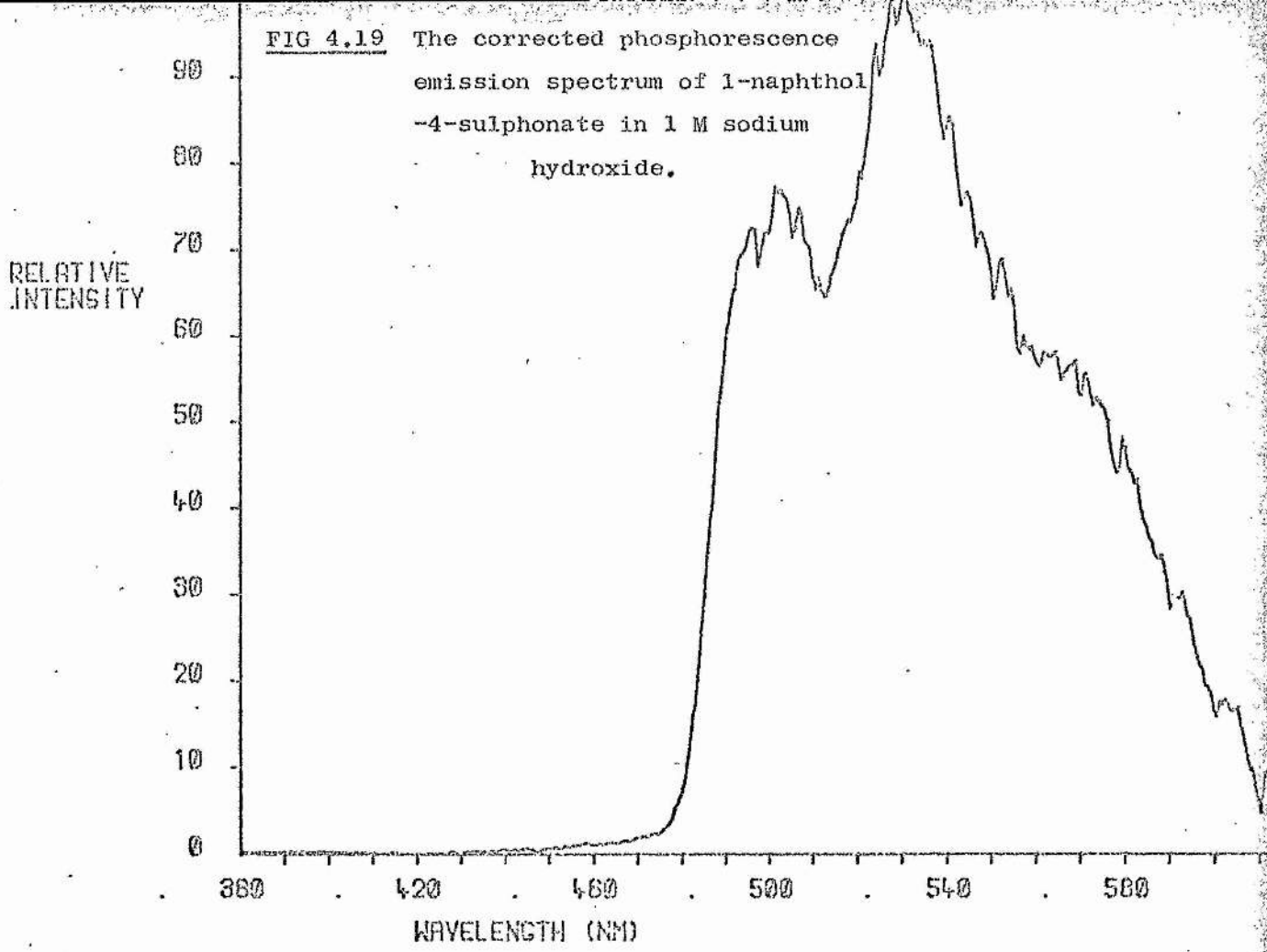


FIG 4.19 The corrected phosphorescence emission spectrum of 1-naphthol-4-sulphonate in 1 M sodium hydroxide.

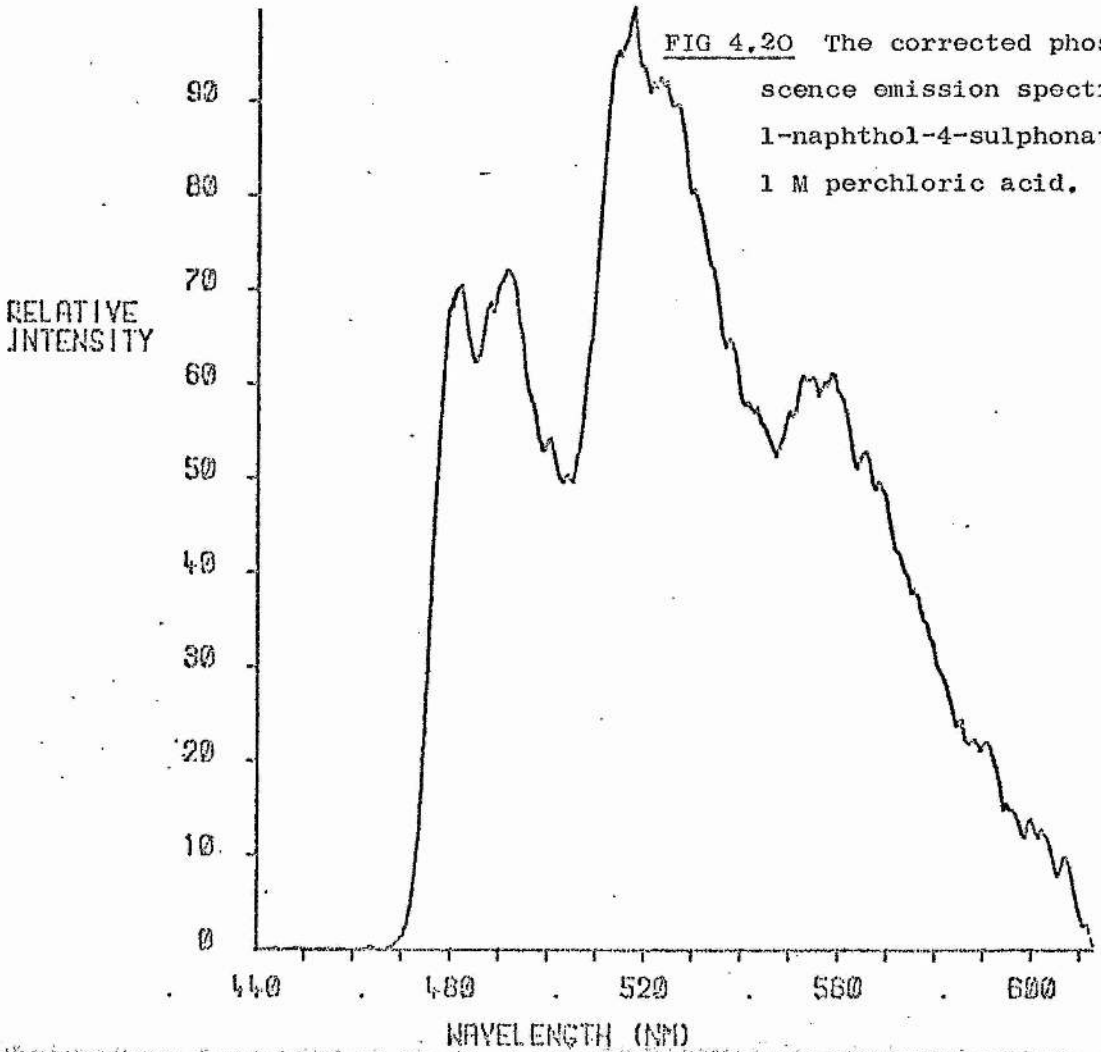


FIG 4.20 The corrected phosphorescence emission spectrum of 1-naphthol-4-sulphonate in 1 M perchloric acid.

and the $pK(T_1)$ values calculated.

Table 4.13

$pK(T_1)$ values of 1-naphthol-2- and -4-sulphonates based on Förster Cycle Calculations

	$\bar{\nu}_{max}$ ROH form (cm^{-1})	$\bar{\nu}_{max}$ RO^- form (cm^{-1})	$\Delta\bar{\nu}$ cm^{-1}	$pK(T_1)$ Förster Cycle	$pK(T_1)$ Flash photolysis
1-naphthol-2-sulphonate	18 190	17 690	500	8.51	7.50
1-naphthol-4-sulphonate	18 000	17 750	250	7.74	7.05

ii) <u>$pK(S_1)$ determination.</u>

Table 4.14 gives the spectral data used in the Förster Cycle calculations and the $pK(S_1)$ values calculated.

Table 4.14

$pK(S_1)$ values of 1-naphthol-2- and -4-sulphonates based on Förster Cycle Calculations.

	absorption		fluorescence	
	$\bar{\nu}_{max}$ ROH form (cm^{-1})	$\bar{\nu}_{max}$ RO^- form (cm^{-1})	$\bar{\nu}_{max}$ ROH form (cm^{-1})	$\bar{\nu}_{max}$ RO^- form (cm^{-1})
1-naphthol-2-sulphonate	30 490	29 850	27 560 26 130	21 580
1-naphthol-4-sulphonate	31 250	30 300	27 280 26 000	22 625

	Average $\Delta\bar{\nu}$ (cm^{-1})	$pK(S_1)$ Forster Cycle	$pK(S_1) - \log \tau/\tau'$ Fluorescence
1-naphthol-2-sulphonate	3 310 2 595	2.52 4.04	3.24
1-naphthol-4-sulphonate	2 802 2 442	2.29 3.06	3.13

Values of 9.58, amd 8.27 are used for the $pK(S_o)$ of 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate respectively in the Förster Cycle calculations. In Table 4.14 two values of $\tilde{\nu}_{max}$ for the ROH form are listed for each sulphonate. This is because the fluorescence spectra of these sulphonates in acid solution show slight inflections at long wavelengths and there was considerable difficulty therefore in deciding upon the maximum of the long wavelength emission band. The inflections and the clearly defined maxima were used in the calculations and two $pK(S_1)$ values were calculated for each compound.

(g) Discussion.

The acidity constants determined for 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate are shown in Table 4.15.

Table 4.15

The acidity constants of 1-naphthol-2- and -4-sulphonates.

	$pK(S_o)$	phosphorescence $pK(T_1)$	flash photolysis $pK(T_1)$	Forster Cycle $pK(S_1)$	Fluorescence $pK(S_1)$-$\log \frac{Y}{Y-Y'}$	$\vec{k}_{YY}$
1-naphthol-2-sulphonate	9.85	8.51	7.50	2.52 4.04	3.24	0.22
1-naphthol-4-sulphonate	8.27	7.74	7.05	2.29 3.06	3.13	0.59

The T⇐ T absorption spectrum of 1-naphthol-4-sulphonate in sodium hydroxide (Fig 4.16) is weaker than the T⇐T spectrum of 1-naphthol-2-sulphonate in sodium hydroxide, although the two spectra are very similar in shape. The sample of the -4-sulphonate used contained some of the -2-sulphonate before it was purified. There is therefore the possibility that the sample of purified 1-naphthol-4-sulphonate still contained traces of -2-sulphonate, and the T⇐T absorption spectrum obtained was a result of this impurity. However the results obtained

from the flash photolysis investigation show that the $pK(T_1)$ values are a half unit apart, the 1-naphthol-4-sulphonate being a stronger acid in its triplet state than the -2-sulphonate. Phosphorescence measurements also show that the 1-naphthol-4-sulphonate is a stronger acid in its triplet state than the -2-sulphonate and the $pK(T_1)$ values obtained are 0.7 unit apart. It was concluded that the spectrum shown in Fig 4.16 could confidently be attributed to the triplet $\leftarrow$ triplet absorption of 1-naphthol-4-sulphonate. 1-Naphthol-4-sulphonate, like 1-naphthol, shows very weak fluorescence and transient absorption spectra in aqueous acidic media, whereas the fluorescence of 1-naphthol-2-sulphonate in aqueous acidic solution is as strong as the fluorescence observed in aqueous alkaline solution, and the transient absorption of the naphthoxyl radical of 1-naphthol-2-sulphonate is observed in acidic solutions. This is discussed in more detail in Chapter 5.

Whilst fluorescence lifetimes have not been obtained for either of the compounds studied because of their low fluorescence intensities, certain assumptions can be made, and hence approximate $pK(S_1)$ values can be put forward. If the lifetimes of the $(RO^-)^*$ and $(ROH)^*$ forms are of the same order then $\log \tau / \tau'$ will be very small and the $pK(S_1)$ of 1-naphthol-2-sulphonate will be 3.24 approx and the $pK(S_1)$ of 1-naphthol-4-sulphonate will be 3.13 approx. The lifetimes of the $(RO^-)^*$ and ROH^* forms of the naphthol-sulphonates might be expected to be very similar to those of the corresponding forms of 1-naphthol. There is some doubt, however, about the value of the lifetime of the ROH form of 1-naphthol. Weller[28] gives $\tau = 13$ ns and $\tau' = 8.4$ ns for 1-naphthol, i.e. the two lifetimes are of the same order approximately. Rosenberg and Brinn[88] have used a single photon counting apparatus recently to measure the fluorescence lifetimes of 1-naphthol. In contrast to Weller they found that the fluorescence

lifetime of the ROH form (τ) was very small for 1-naphthol, 2-chloro-1-naphthol, and 4-chloro-1-naphthol. They found τ for these three compounds to be < 1 ns, and τ' (the lifetime of the RO^- form) to be 8.2 ns for 1-naphthol, 10.2 ns for 2-chloro-1-naphthol and 9.0 ns for 4-chloro-1-naphthol.

Lifetimes τ and τ' of this order would make a considerable difference (as much as 1 unit) to the approximate $pK(S_1)$ values of 1-naphthol-2- and -4-sulphonates i.e. $pK(S_1) = 4.24$ approx and $pK(S_1) = 4.13$ approx.

However there can be no doubt that the ordering of the pK values for 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate is

$$pK(S_o) > pK(T_1) \gg pK(S_1)$$

i.e. the difference between $pK(T_1)$ and $pK(S_1)$ is quite large for the two 1-naphthol sulphonates, and $pK(T_1)$ is quite close to the $pK(S_o)$. Bertron, Chalvet, and Daudel[15] thought that for derivatives of naphthalene which have an electron-donating substituent in the α position, the difference between $pK(S_1)$ and $pK(T_1)$ would be small, and that $pK(T_1)$ would be quite far away from $pK(S_o)$. (See Chapter 3.a.)

1-Naphthol-2- and -4-sulphonic acids exist as sulphonates i.e. RSO_3^- ions in aqueous solutions in the region of pH 0-14. The $-SO_3^-$ group has a Hammett substituent constant, σ, very close to zero. It is therefore neither a strong electron donor nor a withdrawer of electrons. These sulphonates are therefore examples of naphthalene derivatives containing an electron donating substituent in the α position, and the ordering of the pK values obtained for the ground, first excited singlet, and first excited triplet states does not agree with the proposals of Daudel et al.

2. THE PHOTOCHEMICAL REACTION OF 1-NAPHTHOL-2-SULPHONATE AND 1-NAPHTHOL-4-SULPHONATE IN ALKALINE SOLUTION.

(a) Introduction.

When treated with alkali at high temperature naphthalene sulphonic acids yield the corresponding naphthols[89] and naphthol sulphonic acids yield dihydroxy compounds. However there is nothing recorded about the reaction of 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate in alkaline solution at room temperature.

(b) The reaction of 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate in sodium hydroxide solutions at room temperature.

Solutions of 1-naphthol-2- and -4-sulphonates (10^{-4} M approx.) in aqueous sodium hydroxide are stable when they are kept in the dark. If they are exposed to daylight, however, the solutions become yellow and their ultraviolet absorption spectra change with time. See Fig 4.21. The ultraviolet absorption spectra of the products of these reactions are shown for both 1-naphthol-2- and -4-sulphonates in Fig 4.22.

A solution of 1-naphthol-2-sulphonate (10^{-4} M) in alcoholic sodium hydroxide (1 M) was also quite stable when kept in the dark. When this solution was exposed to daylight, its ultraviolet absorption spectrum also changed with time. This change of absorption spectrum with time was similar to that obtained when solutions of 1-naphthol-2-sulphonate in aqueous sodium hydroxide were exposed to daylight, although the alcoholic solution did not become yellow.

(c) 1-Naphthol-2-sulphonate in water at room temperature.

Solutions of 1-naphthol-2-sulphonate (10^{-4} M) in water are stable when kept in the dark and when they are exposed to daylight. Yellowing is observed, however, and the absorption spectrum of the solution changes

FIG 4.21 The absorption spectrum of 1-naphthol-2-sulphonate in 1 M sodium hydroxide solution, which is exposed to daylight, after (a) 4 minutes
(b) 15 minutes
(c) 30 minutes
(d) 53 minutes
(e) 72 minutes
(f) 120 minutes

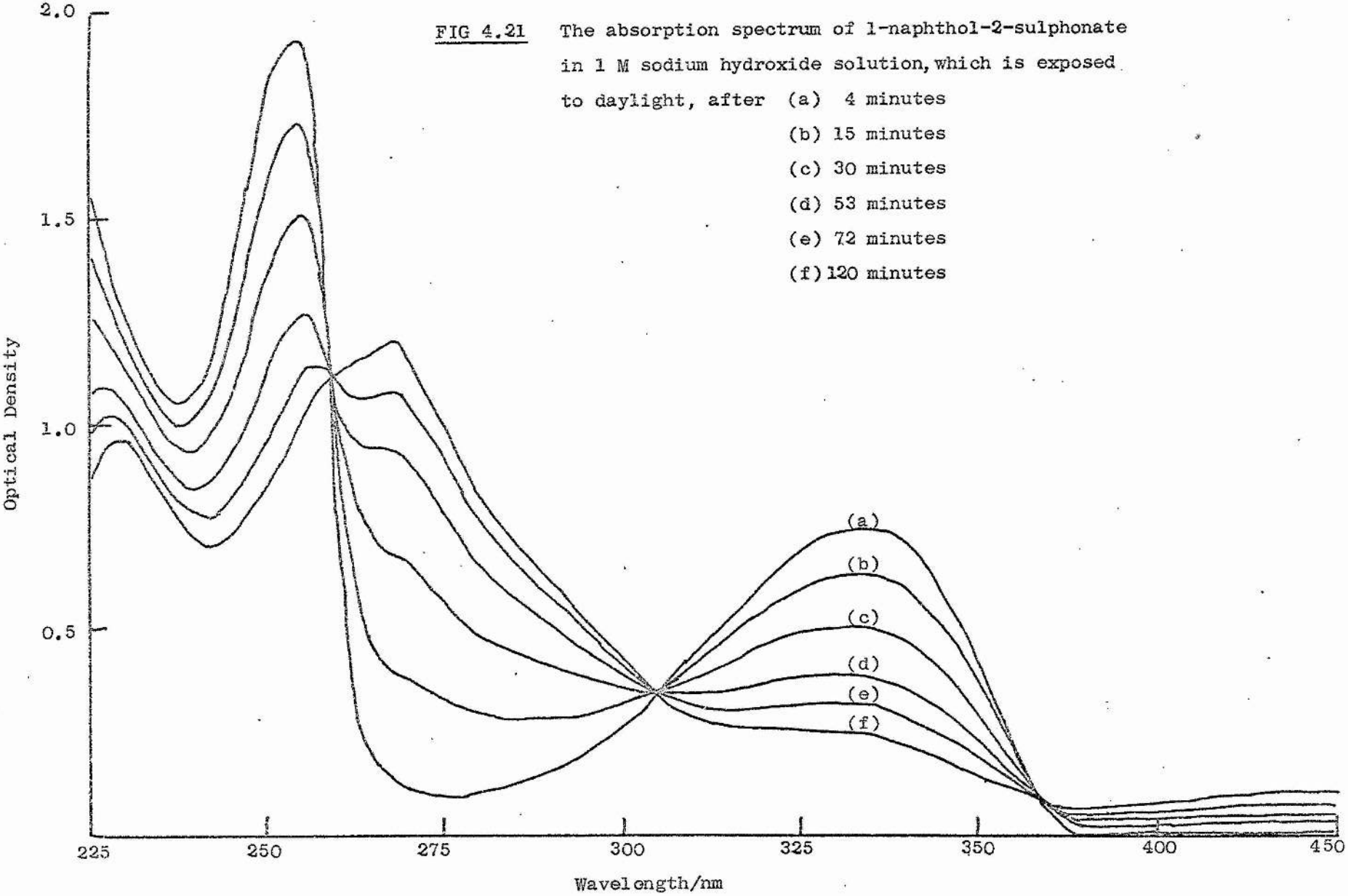
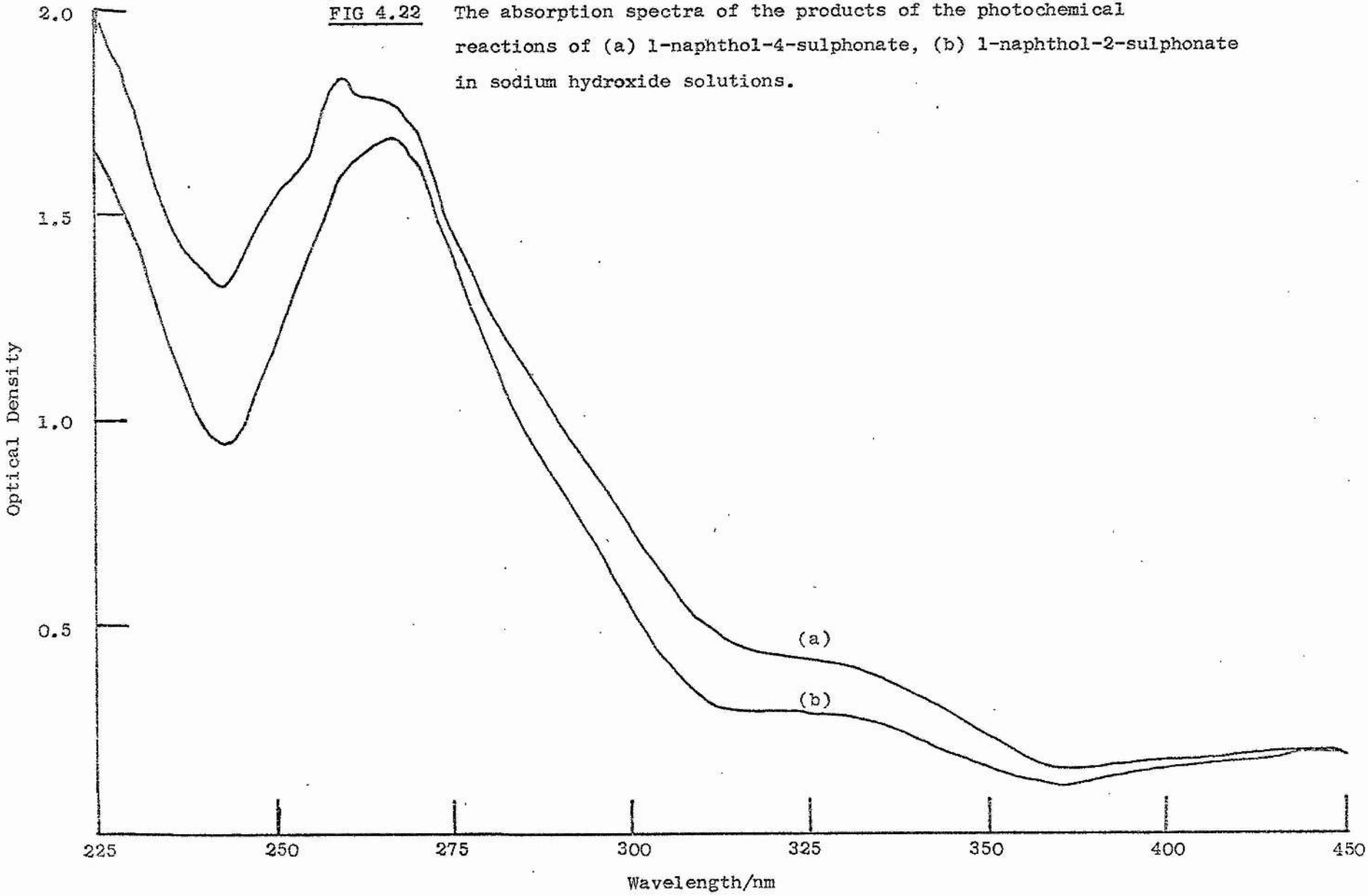


FIG 4.22 The absorption spectra of the products of the photochemical reactions of (a) 1-naphthol-4-sulphonate, (b) 1-naphthol-2-sulphonate in sodium hydroxide solutions.



with time when the solution is irradiated with a xenon lamp.

(d) The effect of oxygen on the reaction of 1-naphthol-2-sulphonate in sodium hydroxide solution.

A solution of 1-naphthol-2-sulphonate (10^{-4} M) was prepared in aqueous sodium hydroxide. The solution was halved and one half degassed by the freeze-pump-thaw method. The two halves were then irradiated with the same intensity of light from a xenon lamp.

The solution which had been degassed showed little change in its ultraviolet absorption spectrum even after twelve hours continuous irradiation, whereas the solution that contained dissolved oxygen showed a great change in its absorption spectrum, and had become quite yellow, after 10 minutes irradiation.

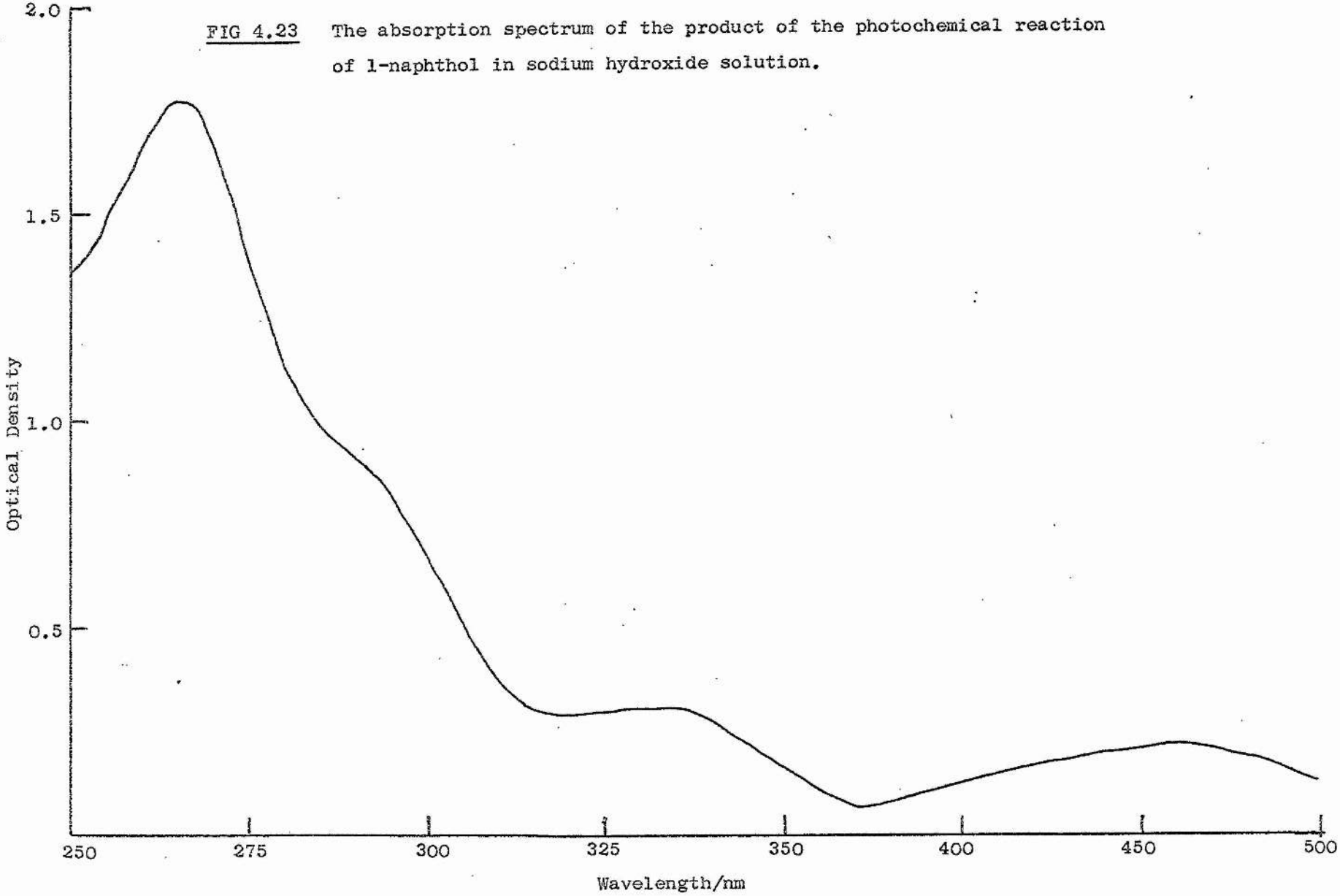
(e) 1-Naphthol in sodium hydroxide solution at room temperature.

Solutions of 1-naphthol in sodium hydroxide are quite stable when they are kept in the dark. However they also become yellow when exposed to daylight. The absorption spectrum of a solution of 1-naphthol in sodium hydroxide also changes with time in the same way as a solution of 1-naphthol-2- or -4-sulphonate in sodium hydroxide; and the product of the reaction of 1-naphthol in sodium hydroxide has an absorption spectrum (see Fig 4.23) which is similar to the spectra of the reaction products of 1-naphthol-2- and -4-sulphonates in sodium hydroxide solutions.

(f) Discussion.

1-naphthol-2-sulphonate, 1-naphthol-4-sulphonate and 1-naphthol undergo a photochemical reaction in aqueous solutions. This is shown by the fact that all aqueous solutions of these compounds are stable when they are kept in the dark. Solutions in sodium hydroxide undergo a reaction when exposed to daylight, and a solution of 1-naphthol-2-

FIG 4.23 The absorption spectrum of the product of the photochemical reaction of 1-naphthol in sodium hydroxide solution.



sulphonate undergoes a similar reaction when irradiated with ultraviolet light. The absorption bands of 1-naphthol-2-sulphonate in sodium hydroxide solution extend to 365 nm, whereas in water only light of 340 nm wavelength can be absorbed. Hence ultraviolet light is required for 1-naphthol-2-sulphonate to react in water whereas daylight suffices for the reaction in sodium hydroxide solution.

El'tsov et al[90] described the photochemical desulphonation of aromatic sulphonic acids for the first time. Irradiation of sodium-1-naphthalene sulphonate in aqueous solutions at pH 1 to 13 gave naphthalene, and 4-amino-1-naphthalene sulphonate (at pH 7 to 13) gave 1-naphthylamine in 1 to 5% yields.

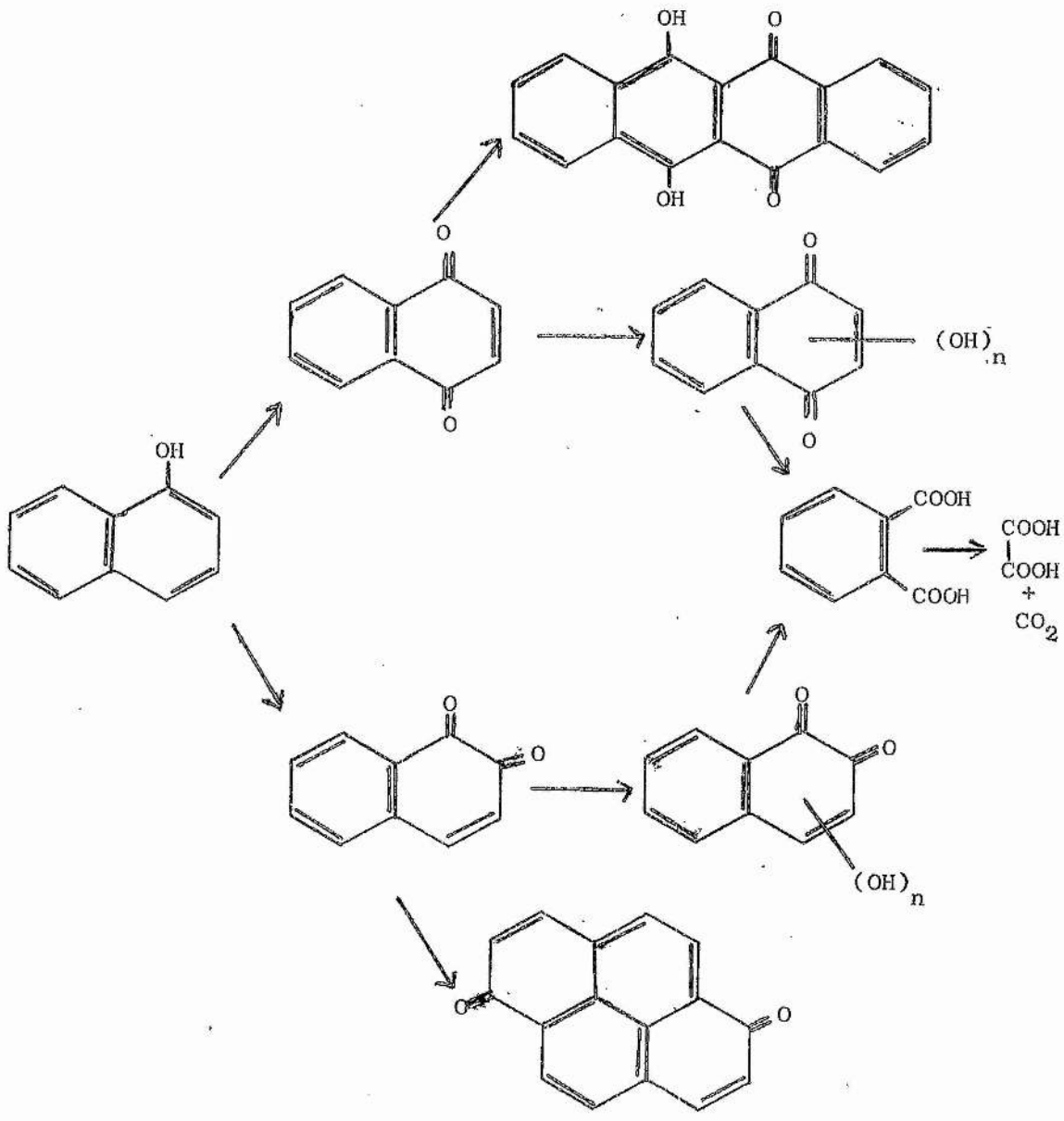
Clark and Stonehill[91] irradiated solutions of anthraquinone-2-sulphonate in aqueous solutions at pH > 10.5, and obtained β-hydroxy derivatives. Between pH 9 and 60% w/w sulphuric acid a mixture of α and β hydroxy derivatives was found. However when anaerobic solutions of anthraquinone-2-sulphonate were irradiated similar hydroxylated products were obtained.

Although there might be some photochemical desulphonation of solutions of 1-naphthol-2- and -4-sulphonates in aqueous solutions, it seems that this cannot be the main reaction since a similar reaction was observed with 1-naphthol. Clark and Stonehill obtained similar products on irradiating aerobic and anaerobic solutions. In contrast the reaction of 1-naphthol-2-sulphonate in aqueous solutions goes extremely slowly in anaerobic solutions when compared with the rate of the reaction in aerobic solutions. It was felt, therefore, that 1-naphthol, 1-naphthol-2-sulphonate, and 1-naphthol-4-sulphonate were not undergoing a similar reaction to that described for anthraquinone-2-sulphonate by Clark and Stonehill.

The irradiation of phenols, cresols and dihydroxybenzenes in oxygenated aqueous solution has been studied in detail[92]. A multitude

of products deriving from homolytic carbon-carbon coupling, carbon oxygen coupling and hydroxylation reactions is formed under these conditions. Kawasaki[93] has found that in an alkaline medium, 1-naphthol is easily oxidised by oxygen to form 1:2-naphthaquinone and 1:4 naphthaquinone as intermediates which are further oxidised to form phthalic acid in good yield along with a small amount of 9,10-dihydroxynaphthacenequinone, hydroxy naphthalenes, oxalic acid and 3,8 pyrenequinone.

Thus



Considerable difficulty was encountered in trying to isolate the photochemical reaction products of 1-naphthol-2- and -4-sulphonates in aqueous solutions and no information was gathered about these products. However the reaction of 1-naphthol in sodium hydroxide appeared to be very similar to that of the naphthol sulphonates and the products formed from the reaction of all three compounds had similar absorption spectra. Thus it would appear that the photochemical reaction of 1-naphthol-2- and -4-sulphonates in aqueous solutions will form sulphonated derivatives of the products shown in the preceding reaction scheme.

Having noticed this reaction of 1-naphthol-2- and -4-sulphonates during the preliminary investigation of the acid-base properties of these compounds, quantitative measurements of optical density, fluorescence intensity or triplet absorption in aqueous solutions were taken immediately using freshly prepared solutions, or if this was not possible, solutions which had not been exposed to light of any form.

CHAPTER 5

THE EFFECT OF VARIOUS SOLUTES ON THE FLUORESCENCE INTENSITY OF 1-NAPHTHOL-2- AND -4-SULPHONATES IN AQUEOUS ACIDIC SOLUTIONS.

(a) Introduction

While following the variation in fluorescence intensity with changing pH, a strange phenomenon was observed with 1-naphthol-2-sulphonate (See Fig 5.5). The fluorescence intensity of the RO^{--} ion varied as expected with pH. That is, from pH 5.8 to pH 4.8 a region of constant fluorescence intensity was observed, as one might expect if there was incomplete equilibrium in the excited state. The fluorescence intensity decreased from pH 4.2, to lower values of pH. This is very similar to the results for 2-naphthol described by Weller[28].

The ROH fluorescence intensity however, instead of increasing, remained constant from pH 5.8 till pH 1.6, where it increased as the pH was lowered to pH 1.0. It was decided to investigate the fluorescence intensity of ROH in increasing acidity.

(b) The variation of fluorescence intensity with increasing acid strength for 1-naphthol sulphonic acids.

Measurements were made of the fluorescence intensity of 1-naphthol-2-sulphonic acid in increasing hydrochloric acid and perchloric acid concentration, and the results are shown graphically in Figs 5.1 and 5.2. The effects on the fluorescence spectrum of 1-naphthol-2-sulphonic acid as the perchloric acid concentration is increased are shown in Fig 5.3. There is no change in the shape of the fluorescence spectrum as the acid strength is increased. There is a slight

FIG 5.1 Fluorescence of 1-naphthol-2-sulphonic acid in (a) perchloric acid
(b) hydrochloric acid

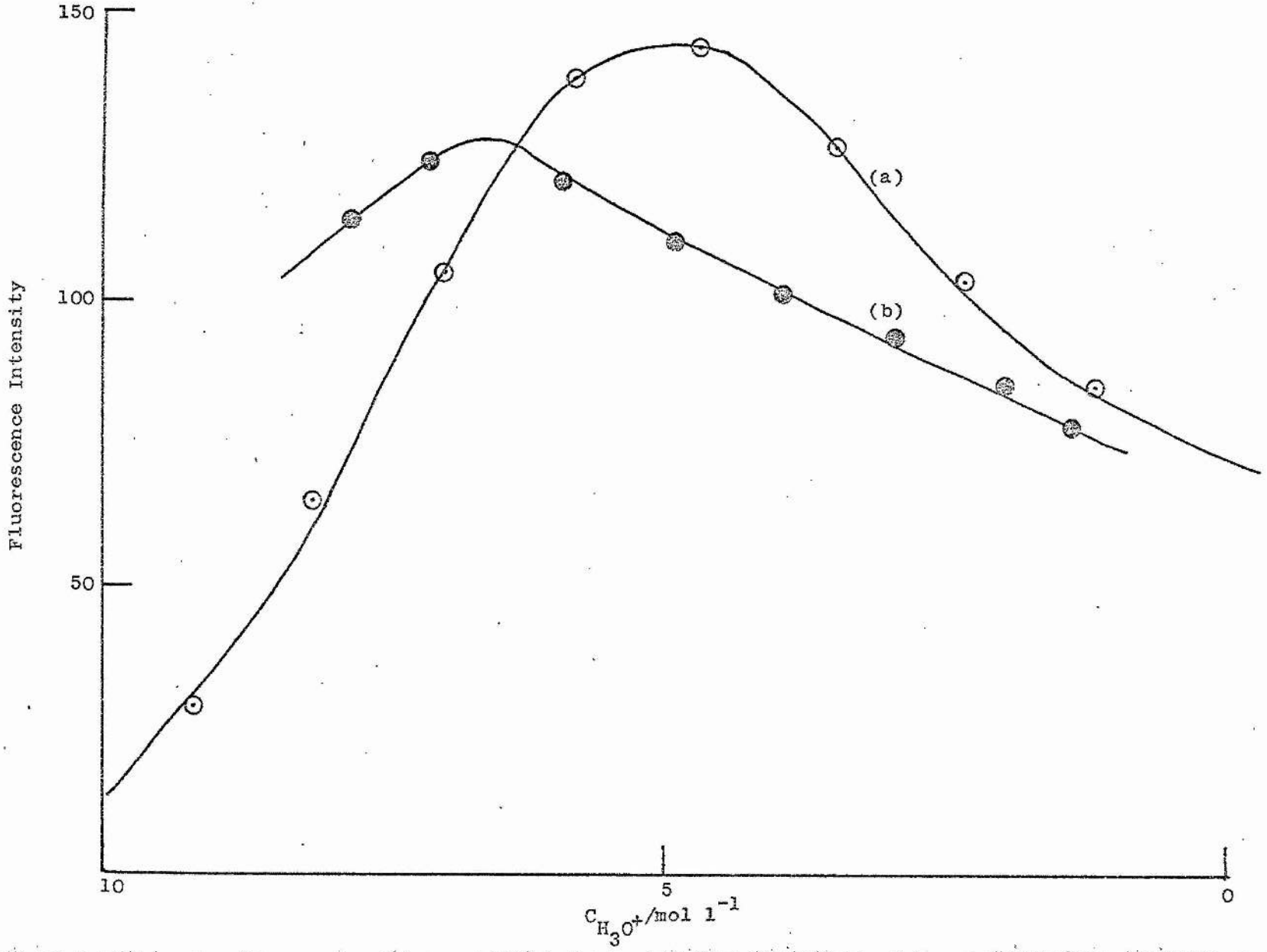


FIG 5.2 Fluorescence of 1-naphthol-2-sulphonic acid in (a) perchloric acid
(b) hydrochloric acid

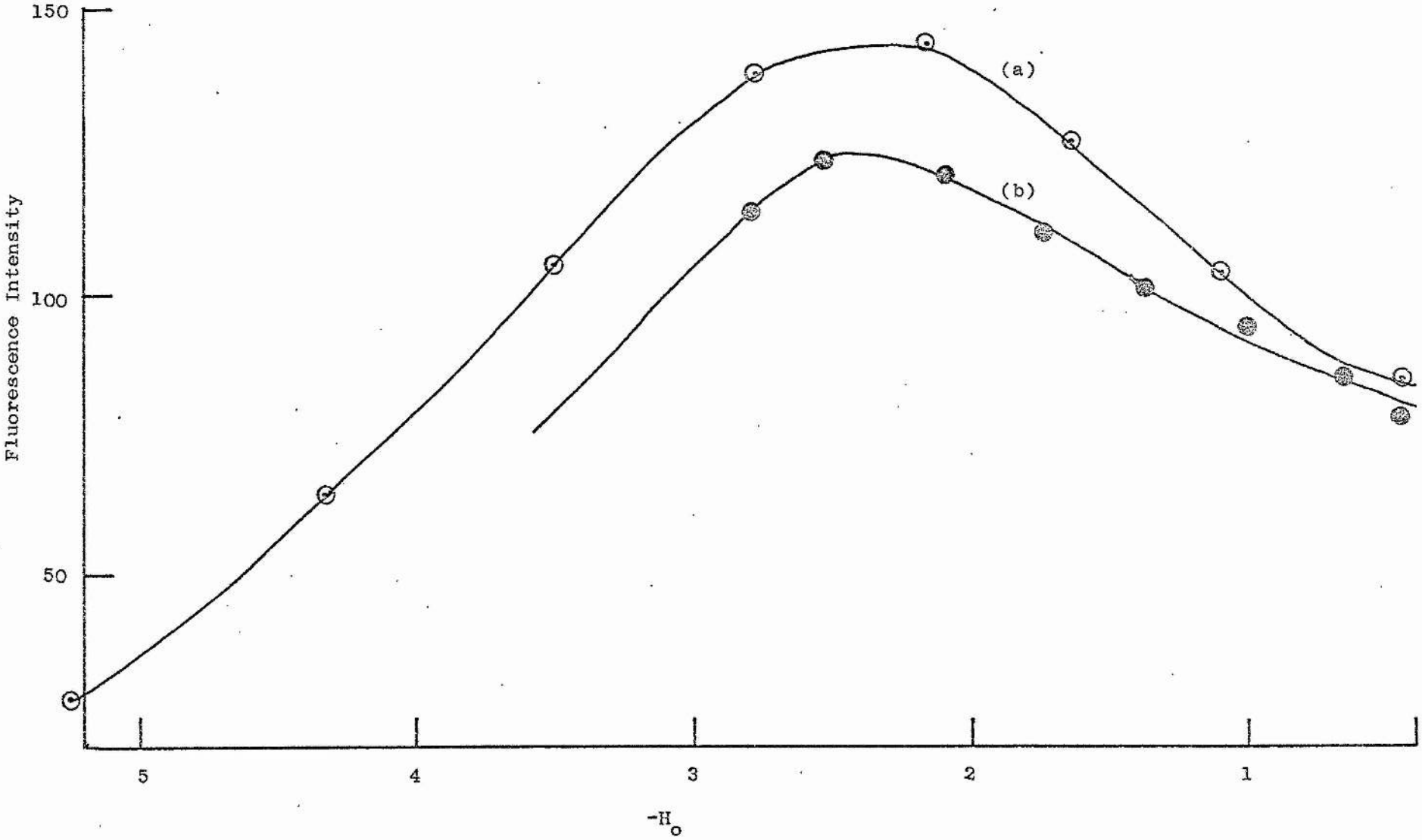
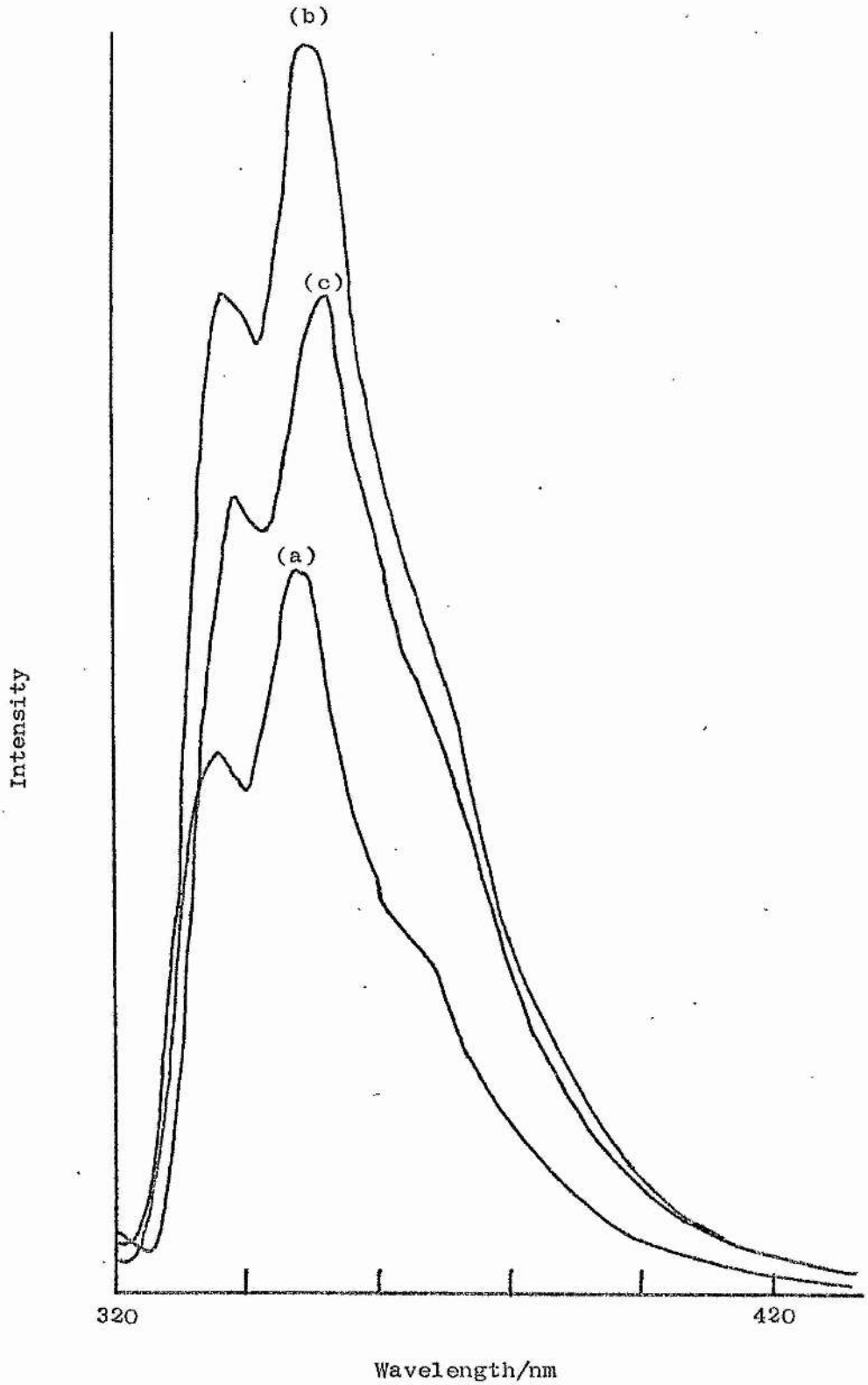


FIG 5.3 The fluorescence spectrum of 1-naphthol-2-sulphonic acid in (a) 1.16 M perchloric acid (b) 5.80 M perchloric acid (c) 8.12 M perchloric acid.

Excitation Wavelength = 310 nm.



shift however, but this shift is by no means large enough to account for the variation of fluorescence intensity at 350 nm with acid strength, as shown in Fig 5.1 and 5.2. This striking variation in fluorescence intensity can be seen as a real phenomenon in Fig 5.3. The ground state absorption spectrum of 1-naphthol-2-sulphonic acid also showed no marked change up to 9 M except a slight solvent shift as the perchloric acid concentration was increased.

Yakatan and Schulman[94] found that protonation of the 1- and 2-naphthalene sulphonates failed to shift their absorption and fluorescence spectra, and attributed this to negligible conjugation between the site of protonation and the aromatic system. Rohatgi and Singh[95] found that changes in acidity had no effect on the absorption spectra of 1- and 2-anthracene sulphonates, and only a very small effect on the fluorescence spectra of these compounds. Fierz and Weissenbach[96] gave $pK(S_o)$ values of 0.74 and 0.60 for the 1- and 2-naphthalene sulphonic acids and these appear reasonable.

Rohatgi and Singh found changes in the absorption and fluorescence spectra for the protonation of the neutral naphthalene sulphonic acids and their determinations yielded $pK(S_1)$ values of -3.7 for the 1- isomer and -5.1 for the 2-isomer, and $pK(S_o)$ values of -10.6 and -8.3. These values correspond to the following equilibrium

$$RSO_3H + H^+ \rightleftharpoons RSO_3H_2^+$$

but I feel that these pK values possibly refer to the protonation of the naphthalene ring rather than the SO_3H group. Accordingly Rohatgi and Singh found that, at acidities greater than H_o -2, the fluorescence of naphthalene-1-sulphonic acid diminished and shifted to the red. A corresponding change in the fluorescence of naphthalene-2-sulphonic acid occurred beginning at $H_o < -3$.

By comparison it seems possible that the decrease in fluorescence

intensity which begins at H_o approximately -2.4 for 1-naphthol-2-sulphonic acid, is due to the protonation of the neutral species in the excited state. Further evidence for the formation of a protonated species is shown in Fig 5.4 i.e. 1-naphthol-4-sulphonic acid also exhibits a decrease in fluorescence intensity, but the decrease begins at H_o approximately - 1.5.

The increase in fluorescence from solutions of low pH to solutions of acidity, H_o-2.5 and H_o-1.5 for both 1-naphthol-2- and -4-sulphonic acids, is still unexplained however.

Fig 5.5 shows graphically the variation of fluorescence intensity with acid concentration from pH 6.0 to H_o-5.0 for 1-naphthol-2-sulphonic acid. The graph is compiled from the data shown in Table 5.1.

The following relation

$$\phi/\phi_o + \phi'/\phi'_o = 1 \qquad (5.1)$$

where ϕ is the fluorescence intensity of the ROH species, ϕ' is the fluorescence intensity of the RO^- species, and ϕ_o and ϕ'_o are the maximum fluorescence intensities of the respective forms, can be applied to the range of acid strength where equilibrium is not completely established in the excited state viz from $[H^+] = 10^{-4}$ M to 10^{-6} M. Values of ϕ ϕ' and ϕ'_o are taken from Table 5.1.

Thus $$70/\phi_o + \frac{26}{144.2} = 1$$

$$\therefore \phi_o = 85.4$$

The maximum fluorescence intensity of the ROH species, as determined by calculation, is 85.4 (on the arbitary practical scale used to record the fluorescent intensities of Table 5.1 and Fig 5.5), and one might expect this intensity to have been reached by an $[H^+]$ of 10^o molar. From Fig 5.5 the maximum fluorescence intensity is

FIG 5.4 The variation of fluorescence intensity with acid concentration
(a) 1-naphthol-2-sulphonic acid (b) 1-naphthol-4-sulphonic acid.

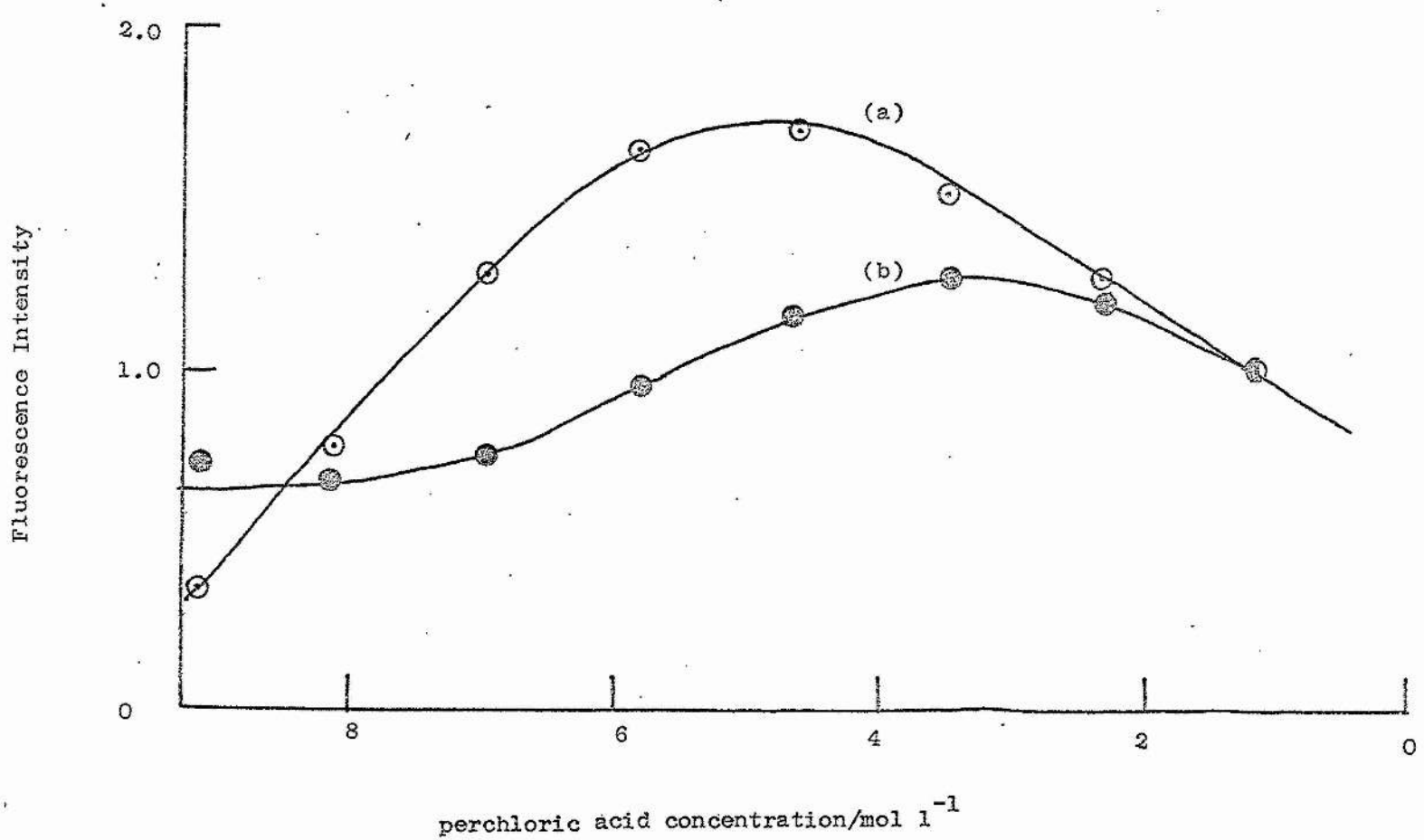


FIG 5.5 The variation of the fluorescence intensity of 1-naphthol-2-sulphonic acid with acid concentration (a) the ROH form (b) the RO^- form.

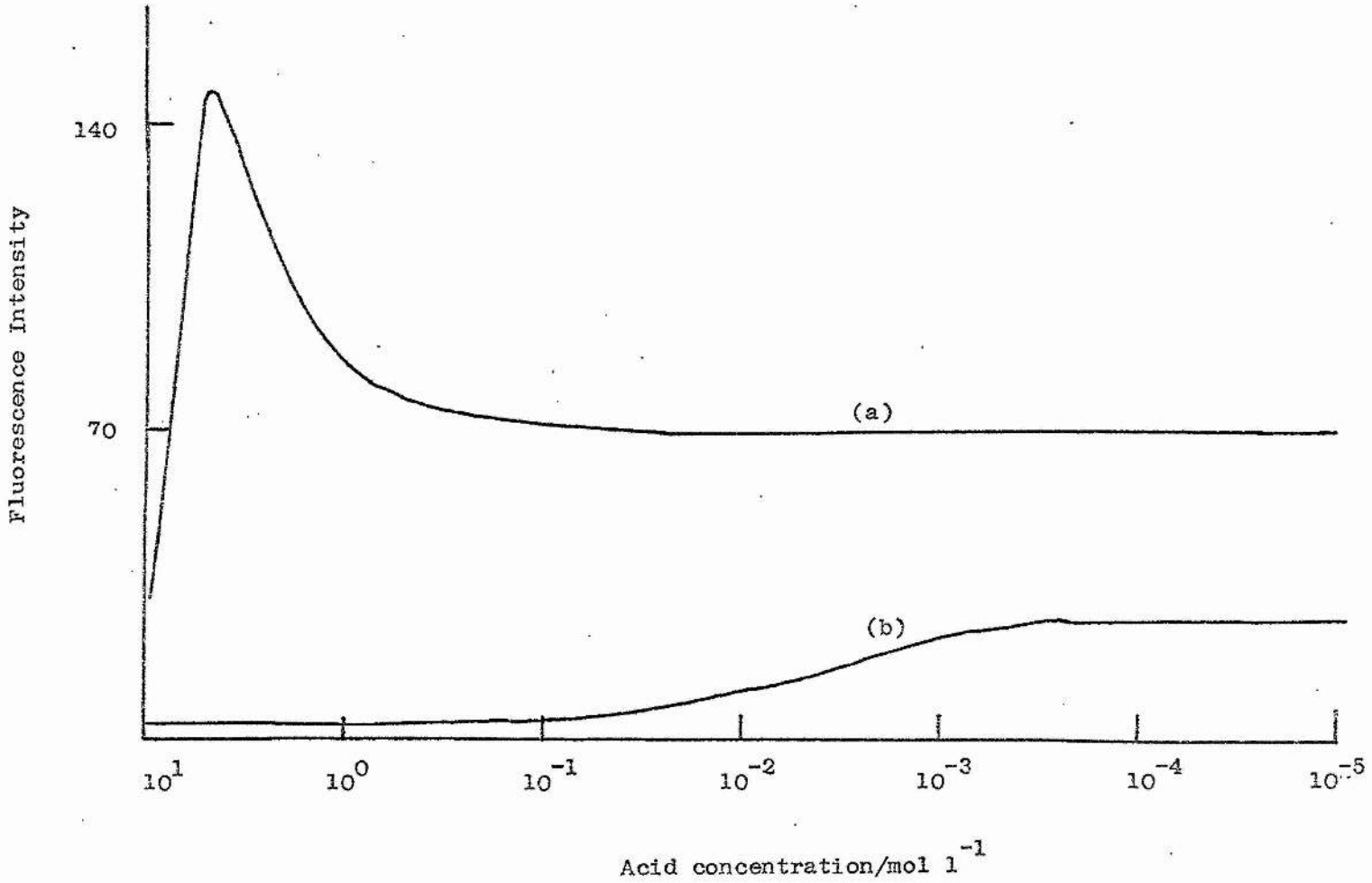


TABLE 5.1

Fluorescence intensity of ROH and RO^- forms of 1-naphthol-2-sulphonate as a function of acid concentration

Excitation Wavelength = 329 nm

Concentration of H^+ in moles/litre	ROH fluorescence 350 nm	RO^- fluorescence 450 nm	Concentration of H^+ in moles/litre	ROH fluores. 350 nm	RO^- fluores. 450 nm
$1.51.10^{-6}$	70.00	26.75	$8.51.10^{-3}$	70.00	9.50
$4.27.10^{-6}$	70.50	26.75	$1.32.10^{-2}$	70.50	7.75
$8.511.10^{-6}$	70.00	26.50	$2.09.10^{-2}$	70.00	6.00
$1.32.10^{-5}$	70.00	26.50	$3.24.10^{-2}$	71.00	4.50
$2.00.10^{-5}$	70.50	26.50	$5.25.10^{-2}$	71.50	3.40
$3.31.10^{-5}$	70.50	27.00	$8.32.10^{-2}$	71.50	3.00
$5.01.10^{-5}$	70.00	26.50	$1.18.10^{-1}$	72.0	2.0
$7.08.10^{-5}$	70.00	26.50	$2.04.10^{-1}$	73.0	1.75
$1.12.10^{-4}$	70.00	26.00	$4.07.10^{-1}$	76.0	1.25
$1.18.10^{-4}$	69.00	25.00	$6.02.10^{-1}$	80.0	1.25
$1.78.10^{-4}$	70.00	25.00	$1.17.10^{0}$	84.25	1.00
$2.75.10^{-4}$	69.50	24.50	$2.33.10^{0}$	102.7	1.00
$3.55.10^{-4}$	70.00	24.00	$3.48.10^{0}$	126.00	0.80
$4.79.10^{-4}$	70.00	23.00	$4.66.10^{0}$	143.60	0.75
$6.31.10^{-4}$	69.25	21.75	$5.81.10^{0}$	138.20	0.70
$8.511.10^{-4}$	70.00	20.75	$6.98.10^{0}$	104.10	0.60
$1.55.10^{-3}$	70.25	17.50	$8.12.10^{0}$	64.50	0.50
$4.07.10^{-3}$	70.00	12.40	$9.2.10^{0}$	29.30	0.50

In 1 N NaOH

RO^- fluorescence intensity = 144.2

given as 145 at an $[H^+]$ of 5.2 10^0 molar.

It is possible that the ROH species is quenched by H_3O^+ ions and this could account for the fluorescence intensity of the ROH species remaining constant for such a wide range of acid strength at the lower acidities. However no explanation could be found in these terms for the great <u>increase</u> in intensity from $[H^+] = 10^{-1}$ M to $[H^+] = 5.2$ M. Therefore the following experiments were performed in an effort to shed further light on this unusual behaviour.

N.B. The fluorescence intensity of 2-naphthol was measured in increasing perchloric acid concentration. The ground state absorption spectrum changed above 7 M perchloric acid, and so the fluorescence intensity was not measured at a higher acid strength. The results are given in Table 5.2.

Table 5.2

The effect of increasing perchloric acid molarity on the fluorescence intensity of 2-naphthol.

Excitation Wavelength = 330 nm.

Molarity of $HClO_4$	Fluorescence Intensity at 354 nm
0.2	74.25
1.16	60.50
2.32	51.75
3.48	30.50
4.65	14.50
5.80	4.05

The fluorescence intensity is found to decrease rapidly with increasing perchloric acid strength, in marked contrast to the results obtained with 1-naphthol-2- and -4-sulphonic acids. The results obtained for 2-naphthol are as expected for strong acid quenching.

(c) The variation of fluorescence intensity with increasing sodium perchlorate molarity.

The fluorescence spectra of the following compounds have been described in Chapters 3 and 4. 1-Naphthol-2-sulphonate (Figs 4.3 and 4.4), 1-naphthol-4-sulphonate (Figs 4.10(a) and (b)) and 1-naphthol (Figs 3.17 and 18). The ground state absorption spectrum, and the corrected fluorescence and fluorescence excitation spectra for naphthalene-2-sulphonate are given in Fig 5.6 and Fig 5.7.

Solutions of each of these compounds in 0.928 M perchloric acid and various sodium perchlorate concentrations were prepared. The fluorescence intensity of each solution was measured at room temperature. The results are shown graphically in Fig 5.8.

Fig 5.6

The ultraviolet absorption spectrum of naphthalene-2-sulphonate in 1 M $HClO_4$

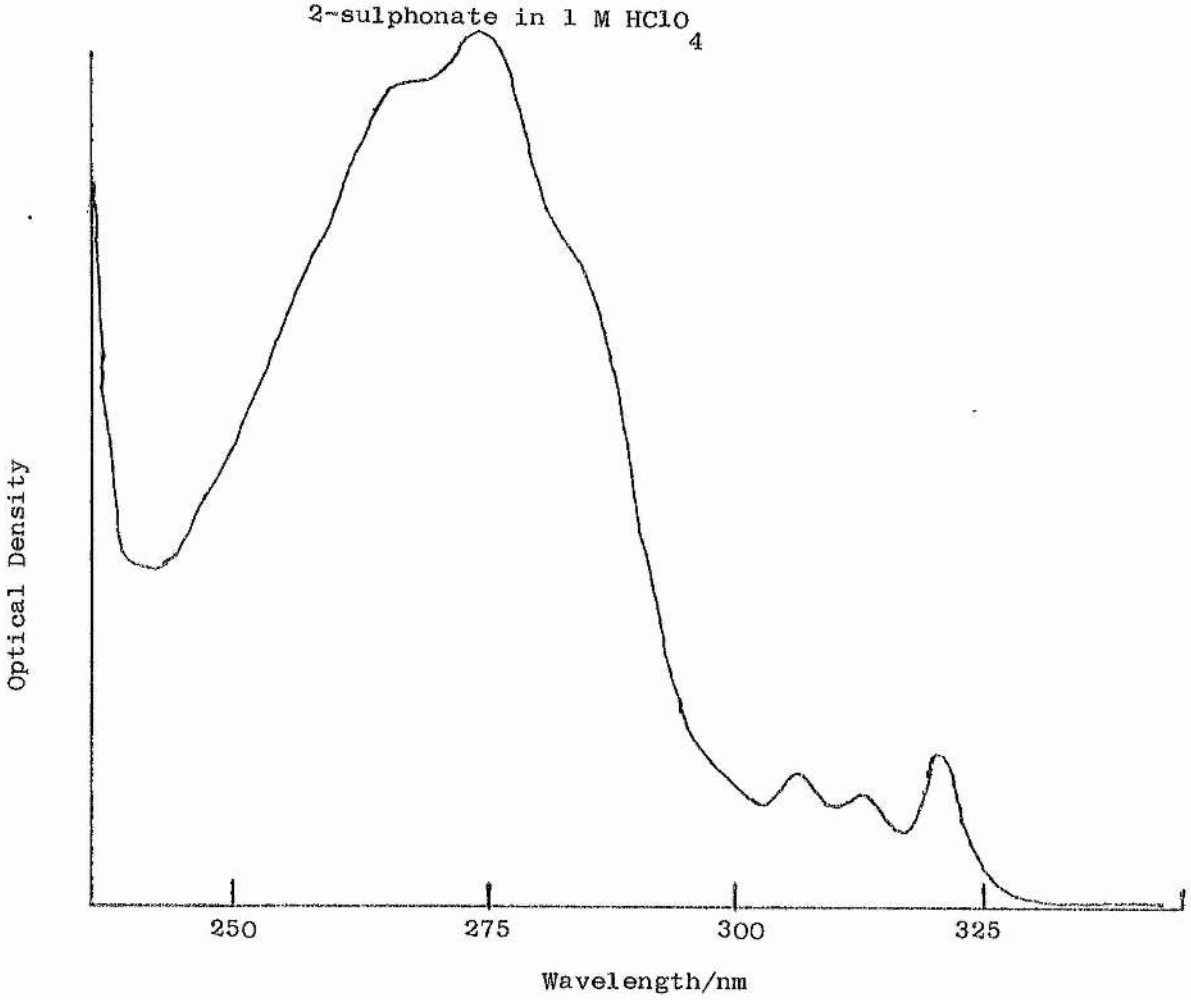
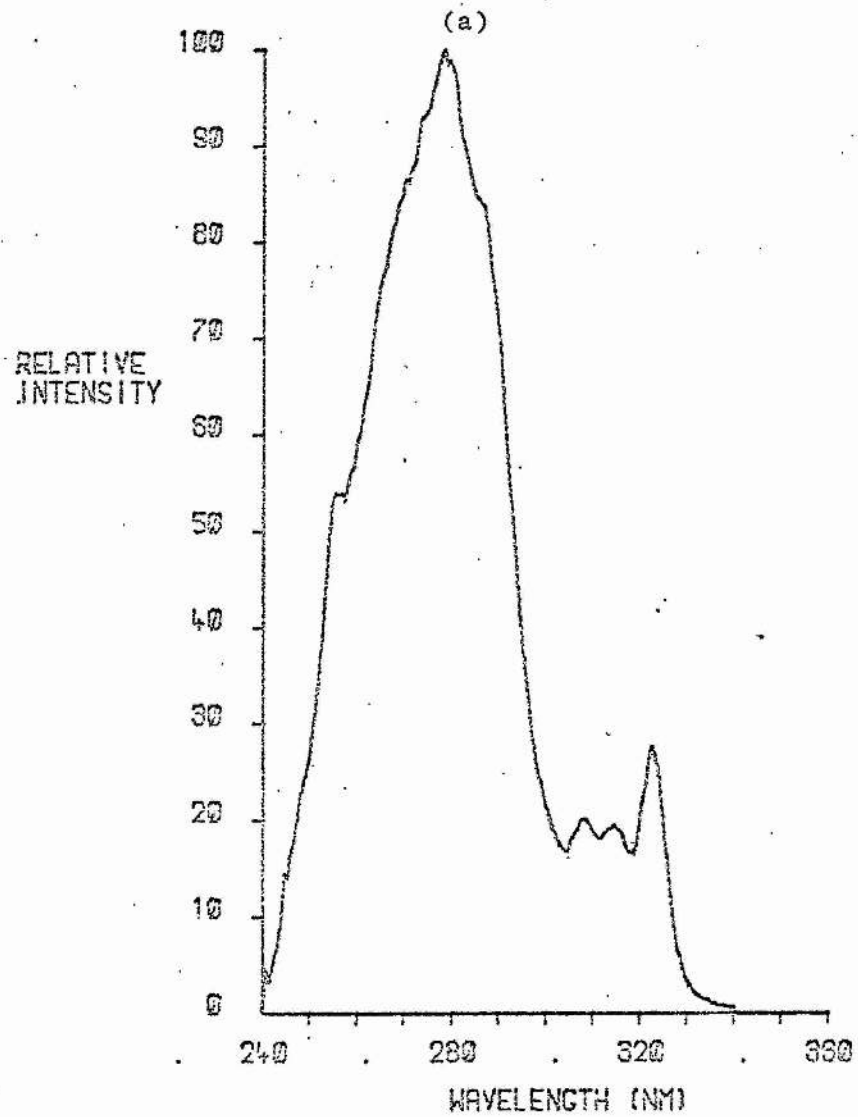


FIG 5.7 Naphthalene-2-sulphonate in aqueous solutions (a) corrected fluorescence excitation spectrum
(b) corrected fluorescence emission spectrum.



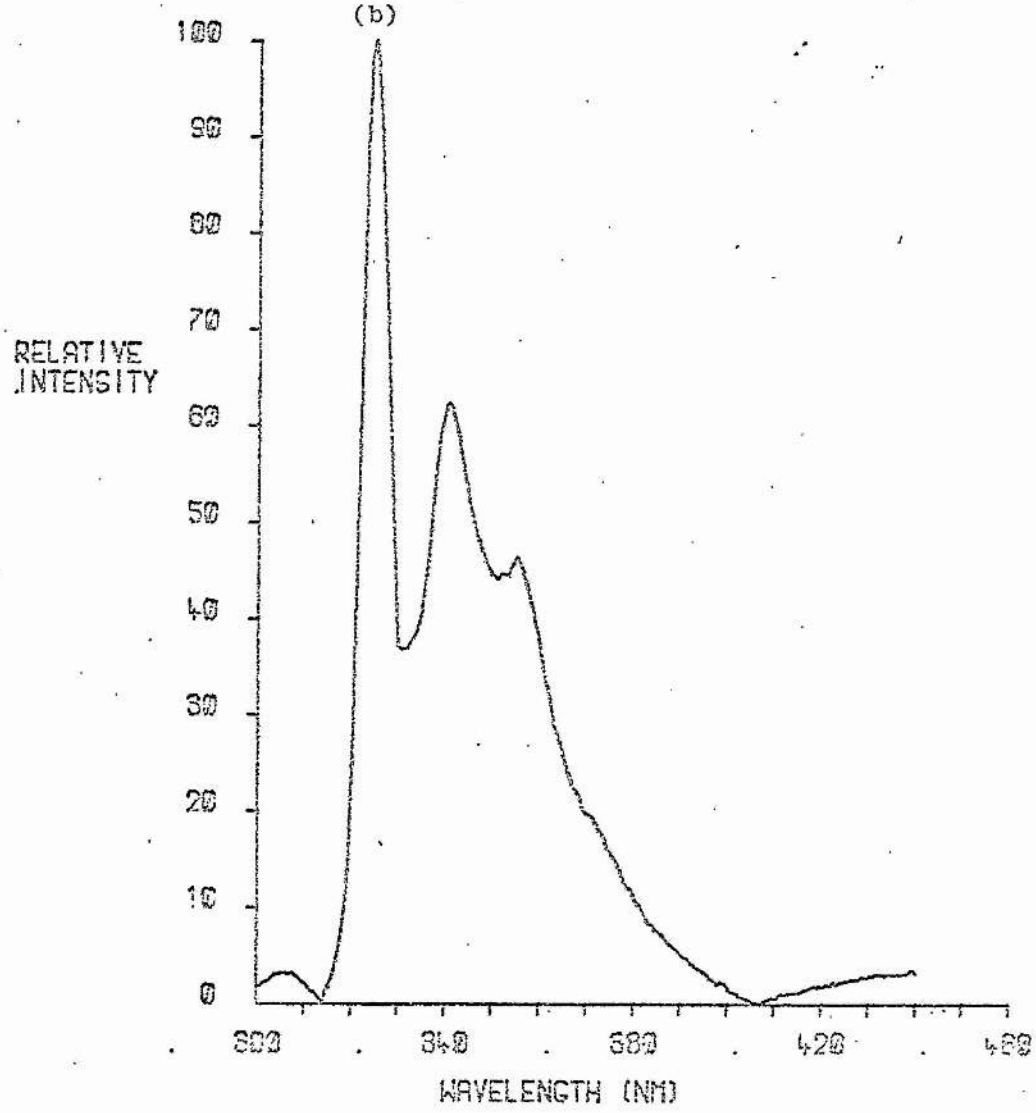
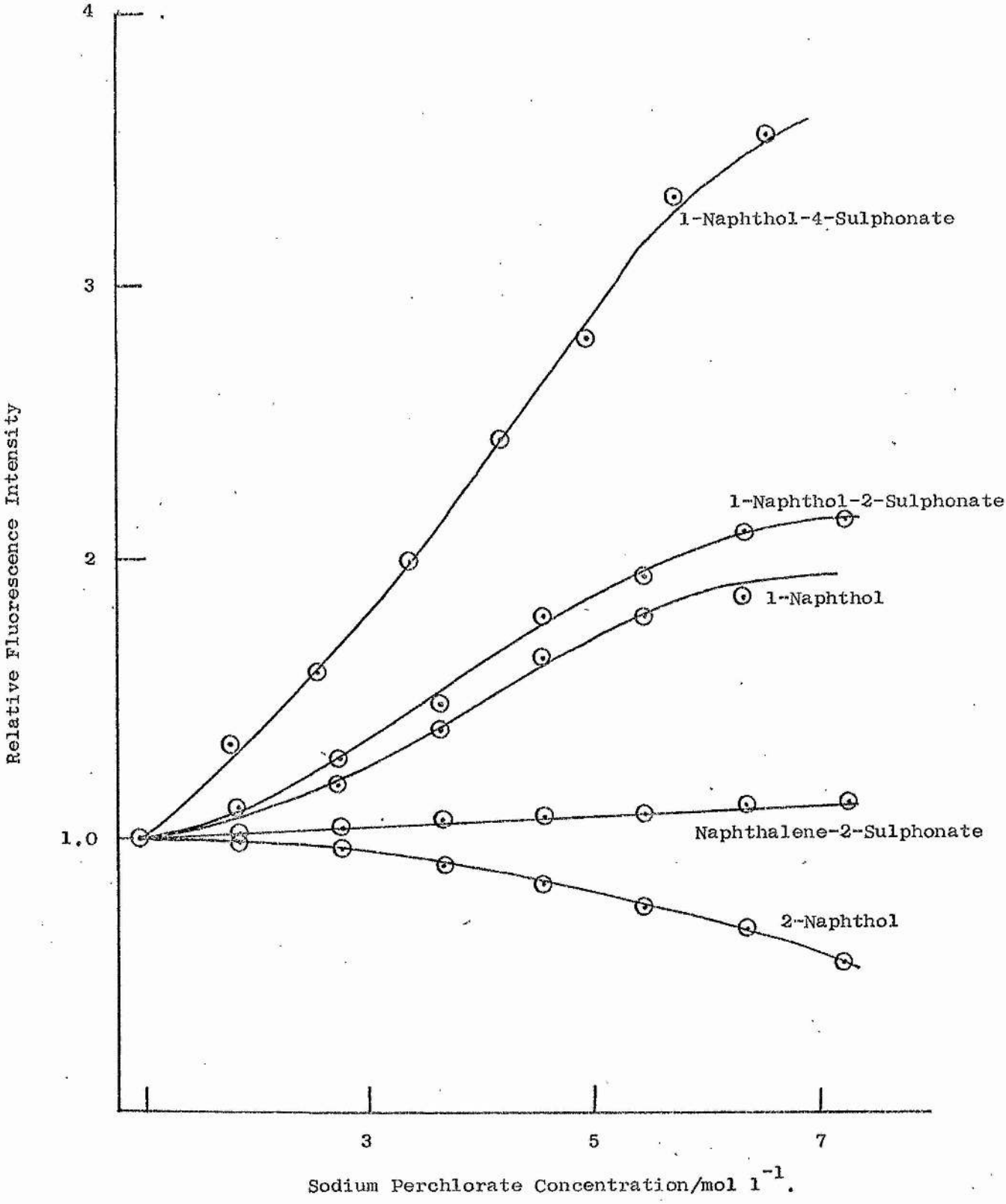


FIG 5.8 Variation of fluorescence intensity with sodium perchlorate concentration (in 0.928 M $HClO_4$).



For each compound, the results obtained were normalised by regarding as unity the fluorescence intensity of a solution where the concentration of ClO_4^- ion was 0.928 M. This enabled a comparison to be made of the effect of increasing the ClO_4^- ion concentration for each compound.

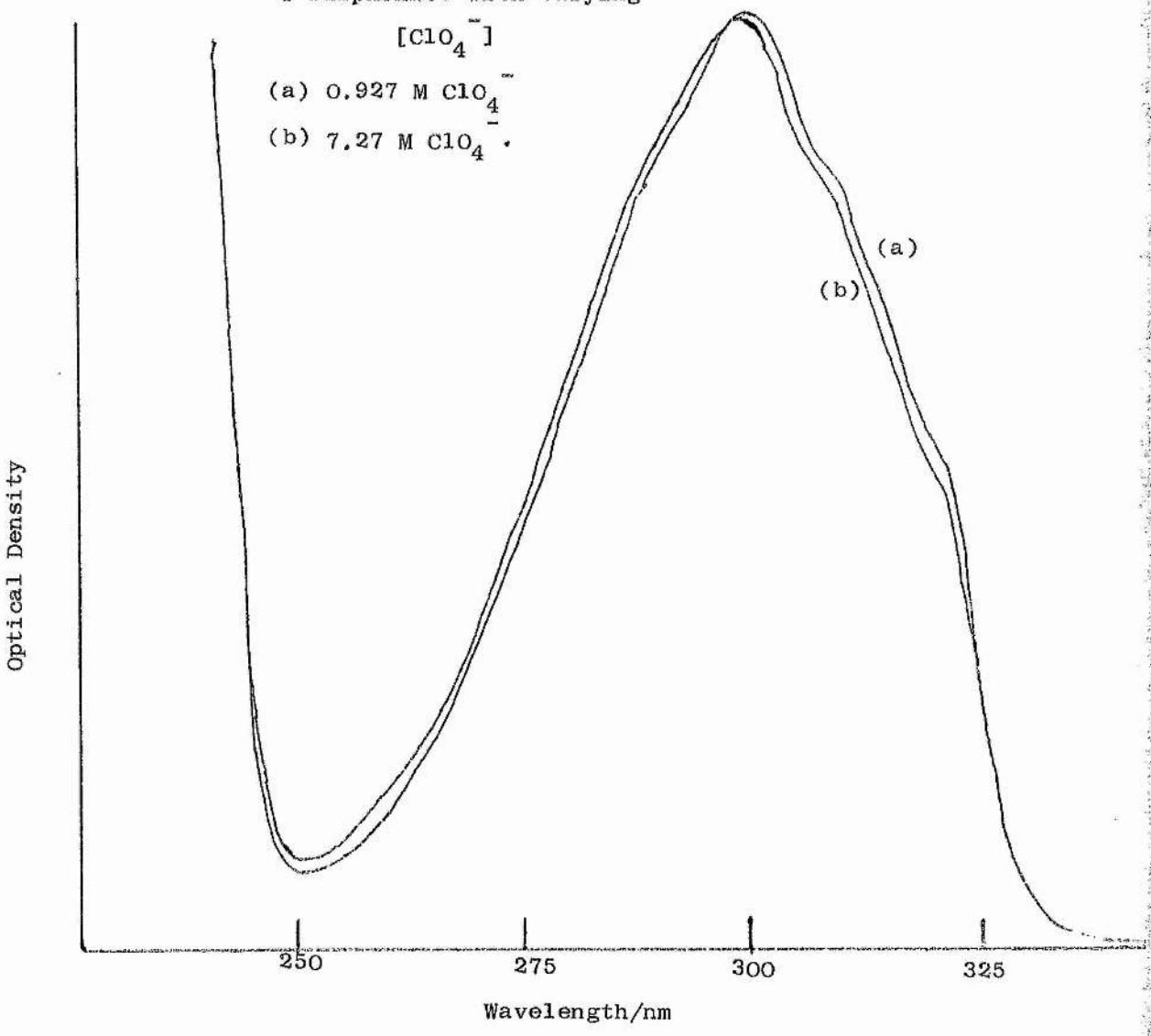
The addition of perchlorate ion, even up to 7 molar, had little effect upon the ground state absorption spectra of any of the compounds investigated. A slight blue solvent shift was seen for the majority of compounds studies, as shown for 1-naphthol-4-sulphonate in Fig 5.9.

Fig 5.9

The U.V. absorption spectrum of 1-naphthol-4-sulphonate with varying $[ClO_4^-]$

(a) 0.927 M ClO_4^-

(b) 7.27 M ClO_4^-.



The addition of sodium perchlorate had little effect on the form of the fluorescence spectra either. A slight solvent shift only was observed, as seen in Fig 5.10 and Fig 5.11.

The solvent shifts, in the U.V. spectrum and the fluorescence spectrum, are much too small to account for the increase in fluorescence intensity as shown by 1-naphthol-2-sulphonate etc. or the expected decrease in fluorescence intensity as shown by 2-naphthol. The anomalous increase in fluorescence intensity is shown clearly as a real effect by Figs 5.10 and 5.11.

(d) The variation of fluorescence intensity with the addition of methanol, ethanol and n-propanol.

Solutions of 1-naphthol-2-sulphonate were prepared in 0.928 M perchloric acid, with different amounts of methanol, ethanol and n-propanol added. The results are shown graphically in Fig 5.12, for the variation of fluorescence intensity with the amount of alcohol added.

Solutions of 1-naphthol-4-sulphonate were also made up in 0.928 M perchloric acid with different amounts of ethanol added. The results of how the fluorescence intensity of 1-naphthol-4-sulphonate varied with the amount of ethanol added, and the results obtained, for 1-naphthol-2-sulphonate, were normalised. That is the fluorescence intensity of the solution of each compound that had no ethanol added was taken as being unity. This enabled a comparison of the effect of ethanol on the fluorescence intensity of each compound to be made, and this comparison is shown graphically in Fig 5.13.

The effect of adding ethanol to solutions of 1-naphthol-2- and -4-sulphonates was a slight red solvent shift in the ultraviolet absorption spectra. Little effect (apart from intensity)

FIG 5.10 The fluorescence spectrum of 1-naphthol-2-sulphonate in (a) 0.928 perchloric acid solution and (b) 0.928 M perchloric acid solution containing sodium perchlorate (7.27 mol l^{-1}).

Excitation Wavelength = 330 nm.

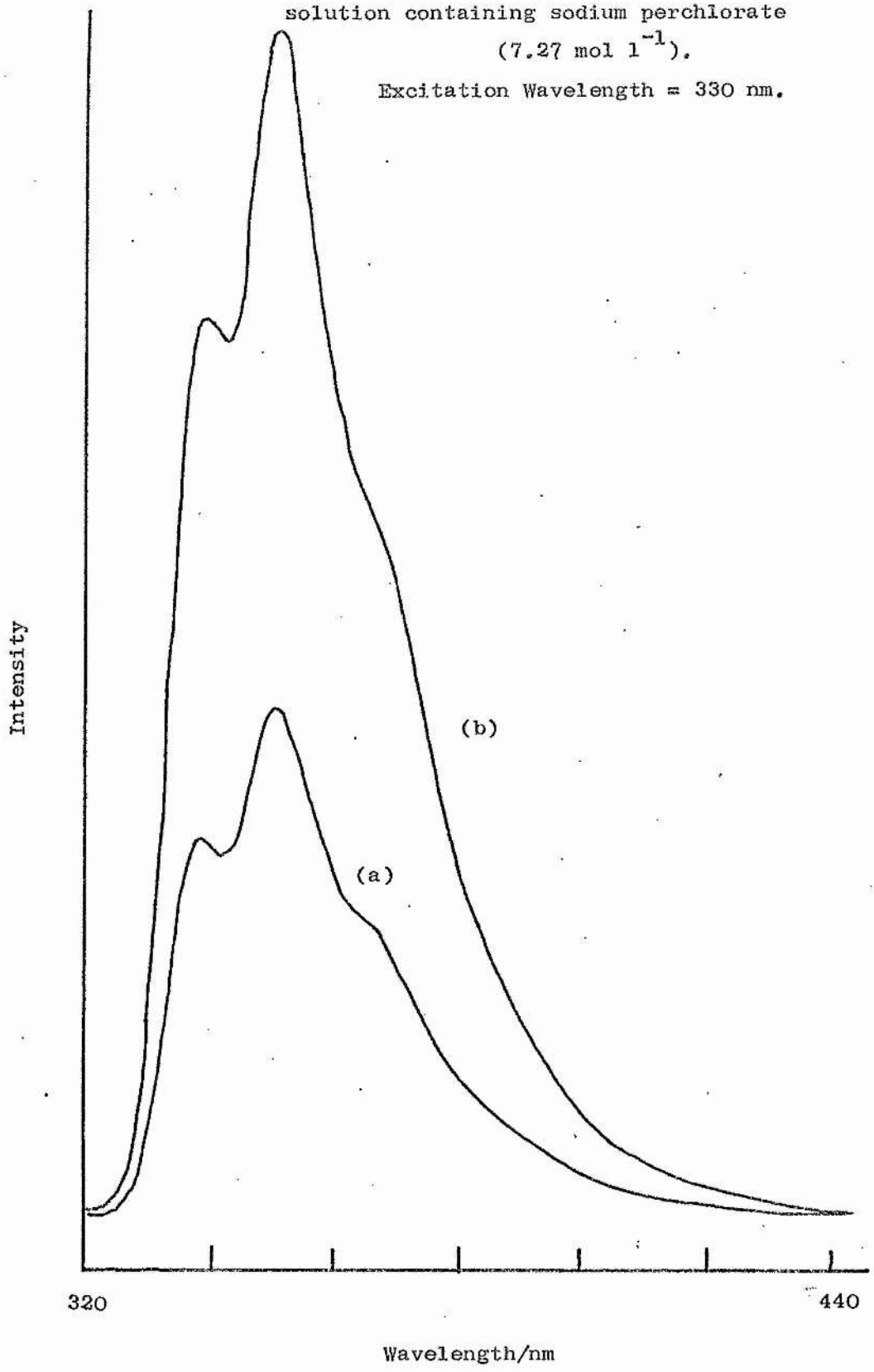


FIG 5.11 The fluorescence spectrum of 2-naphthol in
(a) 0.928 M perchloric acid solution and
(b) 0.928 M perchloric acid solution containing sodium perchlorate (7.27 mol l^{-1}).
Excitation Wavelength = 330 nm.

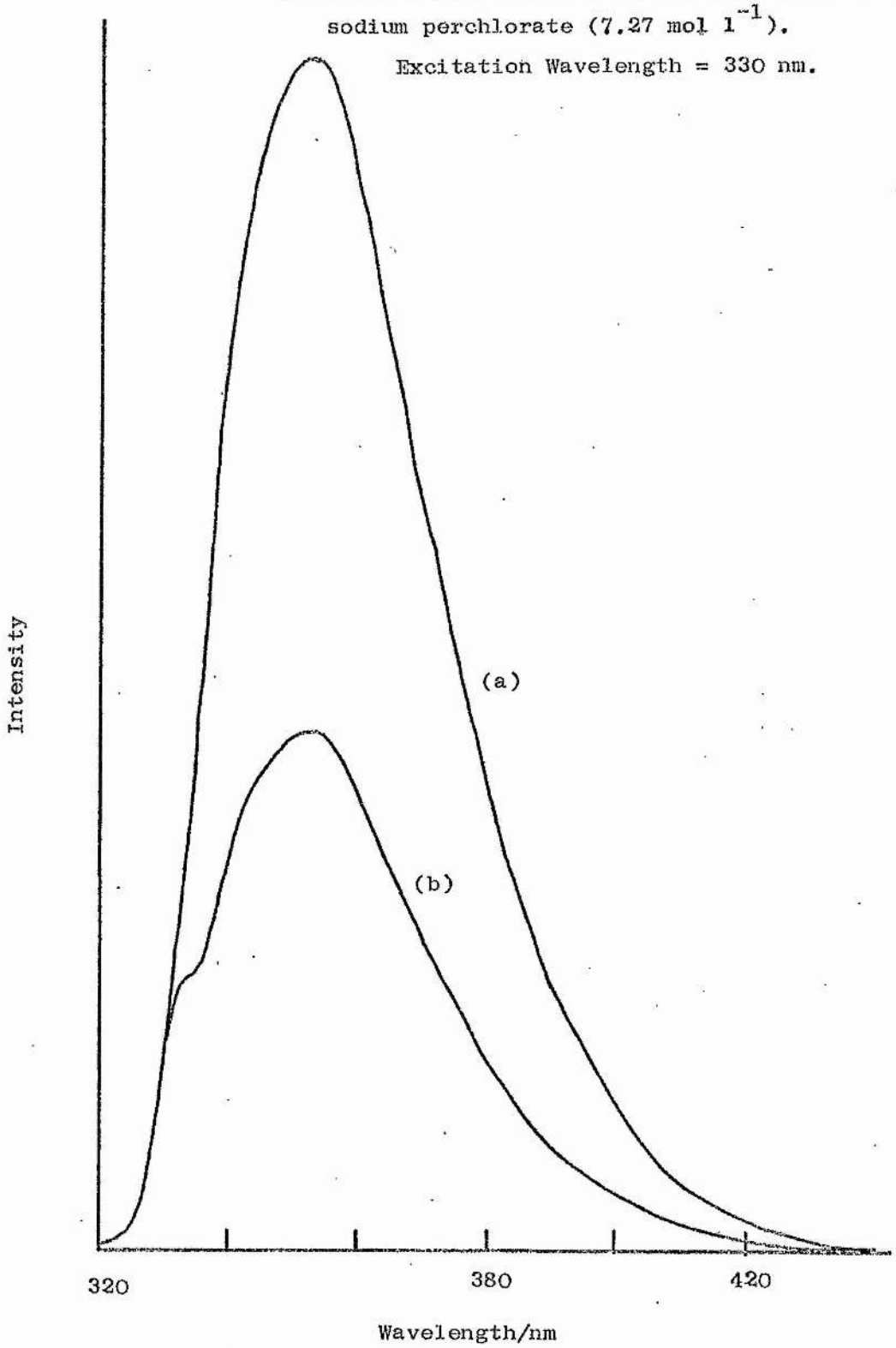


FIG 5.12 The effect of alcohols on the fluorescence intensity of 1-naphthol-2-sulphonate in 0.928 M perchloric acid.

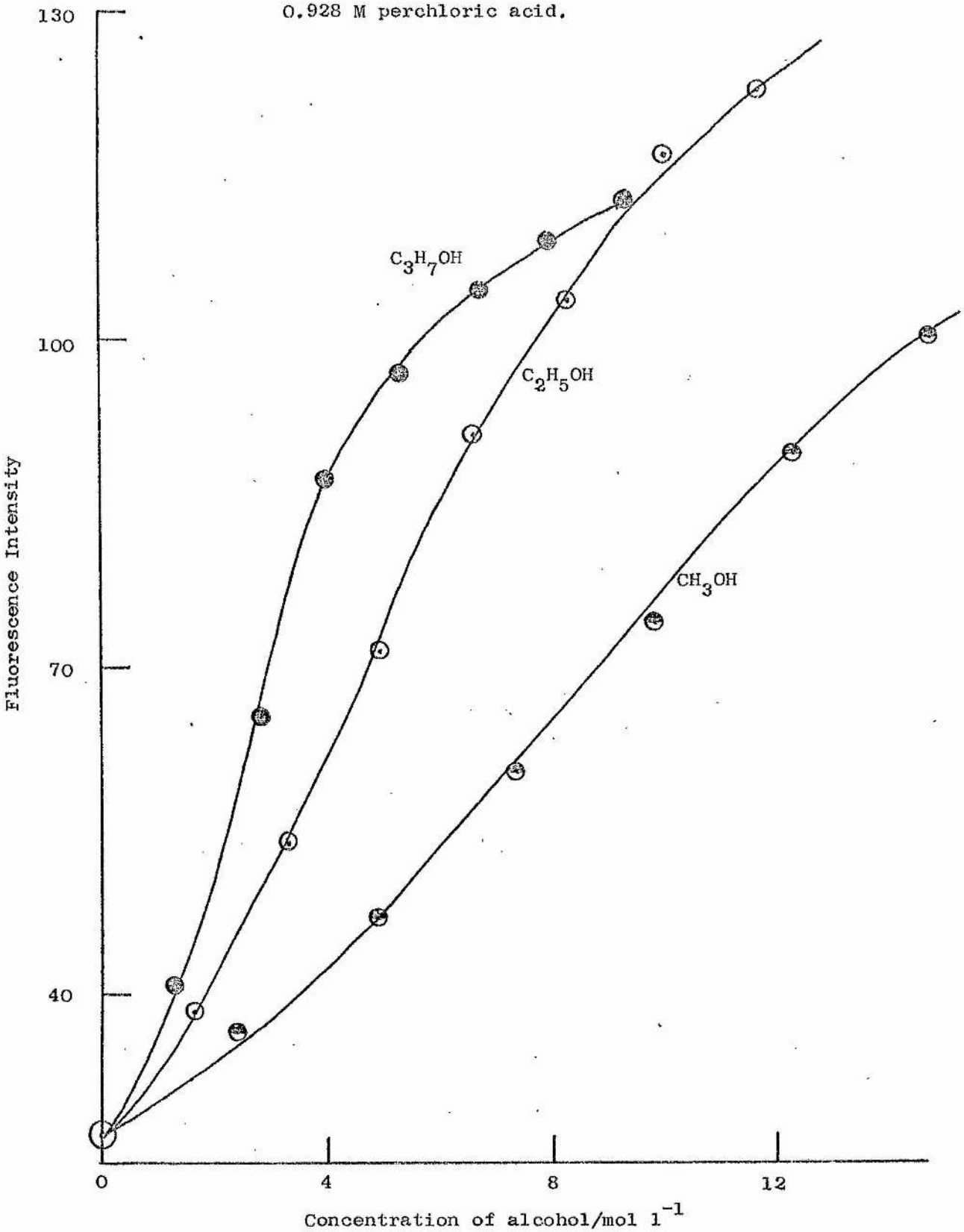


FIG 5.13 The effect of ethanol on the fluorescence intensity of 1-naphthol-2- and -4-sulphonates. in 0.928 M perchloric acid.

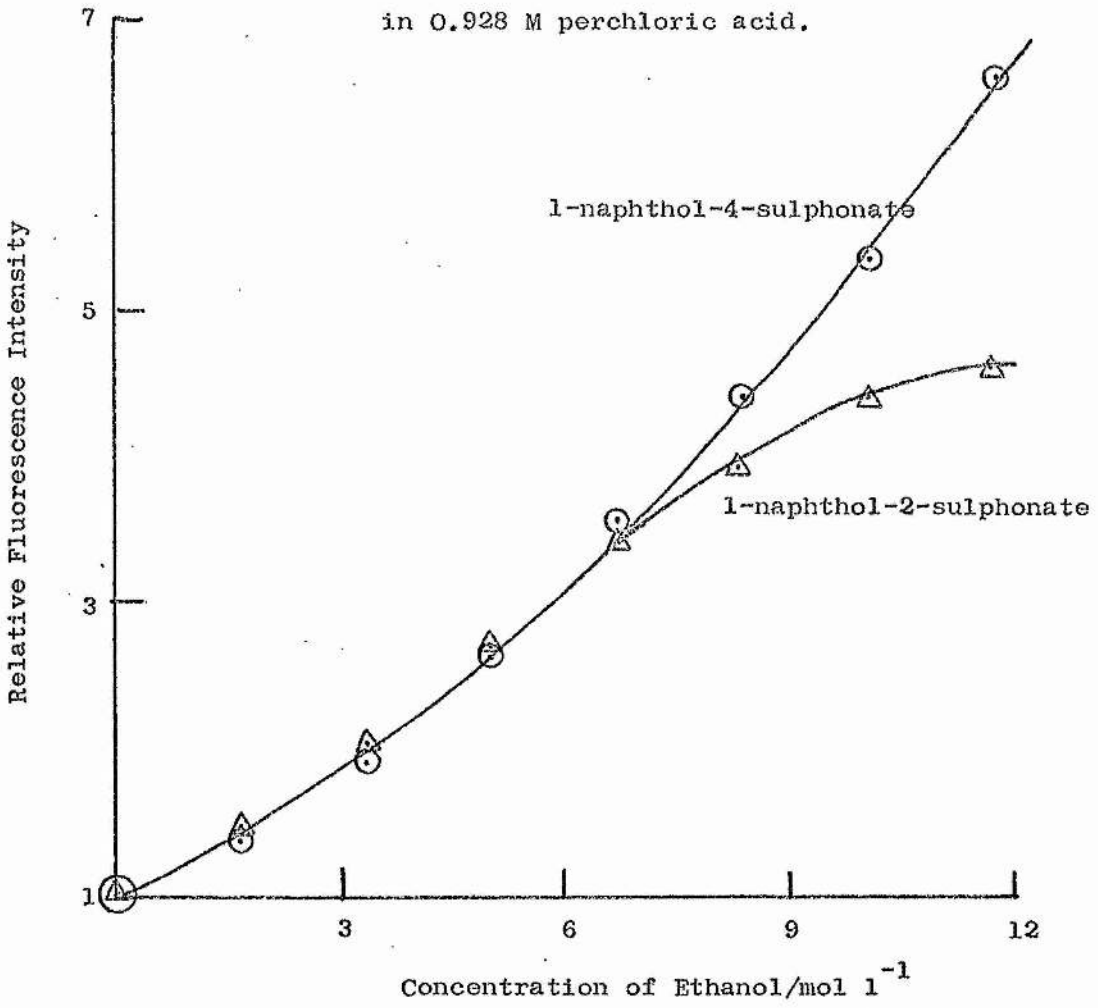
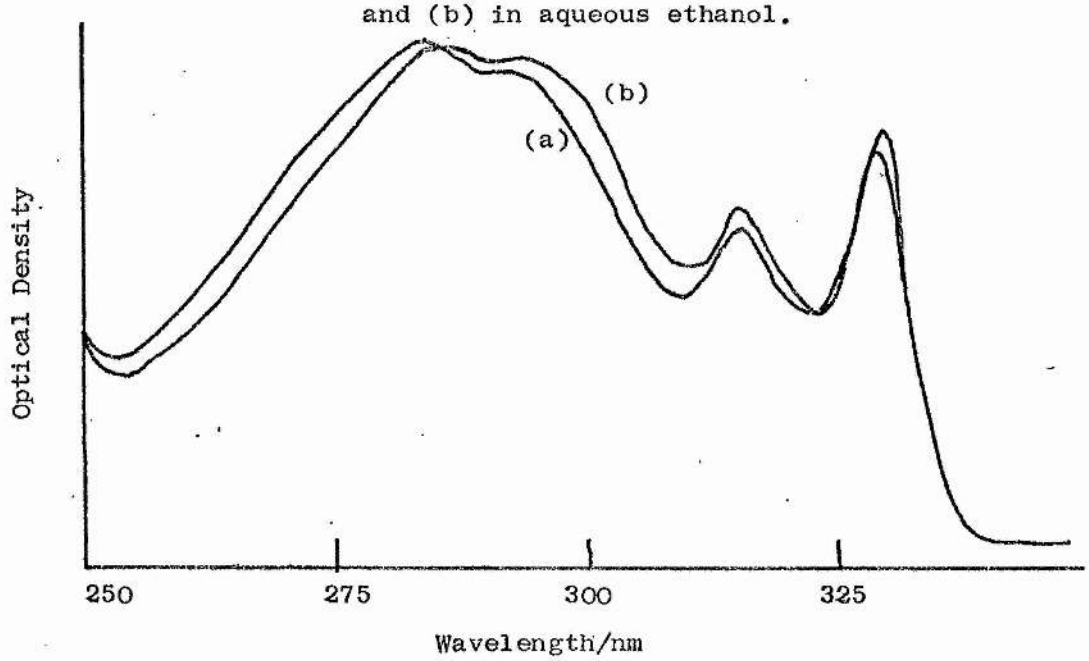


FIG 5.14 The effect of ethanol on the absorption spectrum of 1-naphthol-2-sulphonate; (a) in water and (b) in aqueous ethanol.



was observed on the fluorescence spectra. This is shown in Fig 5.14, 5.15 and 5.16. In fact Fig 5.15 and 5.16 show the effect of ethanol on the fluorescence intensity as being a strong, real, effect.

(e) The variation of fluorescence intensity with the addition of sodium tetrafluoroborate and sodium chloride.

The fluorescence intensities of solutions of 1-naphthol-2- and -4-sulphonates in 0.928 M perchloric acid with various amounts of sodium tetrafluoroborate added were measured. Sodium tetrafluoroborate was used since BF_4^- is a large anion like ClO_4^-. The results were normalised as described previously and are shown graphically in Fig 5.17. The solutions were prepared just prior to recording the intensity, to minimize the effects of hydrolysis of the tetrafluoroborate ion.

The effect of the addition of sodium chloride on fluorescence intensity was investigated for 1-naphthol-2-sulphonate only. The results were normalised and compared with the effect of perchlorate ion and ethanol on the fluorescence intensity of 1-naphthol-2-sulphonate in Fig 5.18.

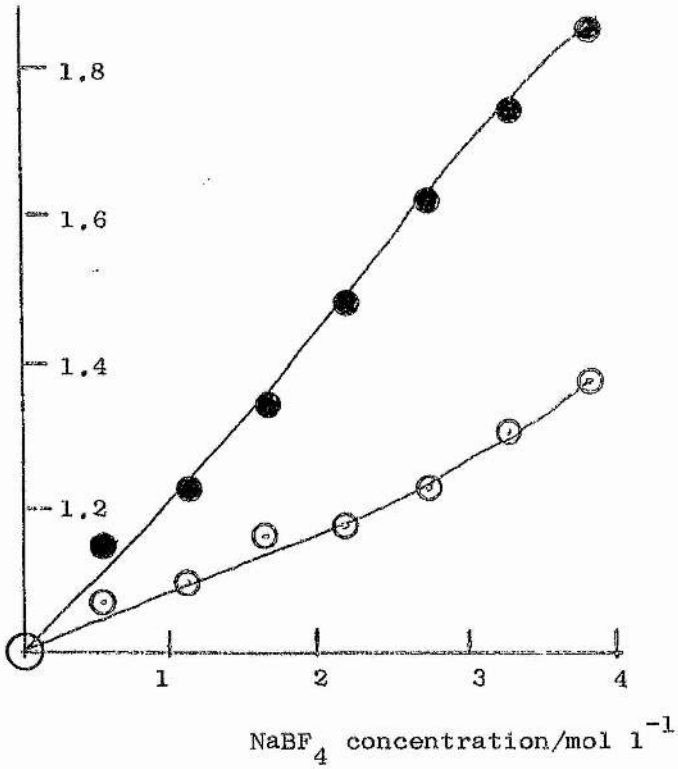


Fig 5.17
The fluorescence intensity of 1-naphthol-2- and -4-sulphonates with addition of $NaBF_4$.

FIG 5.15 The fluorescence spectrum of 1-naphthol-2-sulphonate in (a) 0.928 M perchloric acid solution and (b) 0.928 M perchloric acid solution containing ethanol (11.69 mol l^{-1}). Excitation Wavelength = 330 nm.

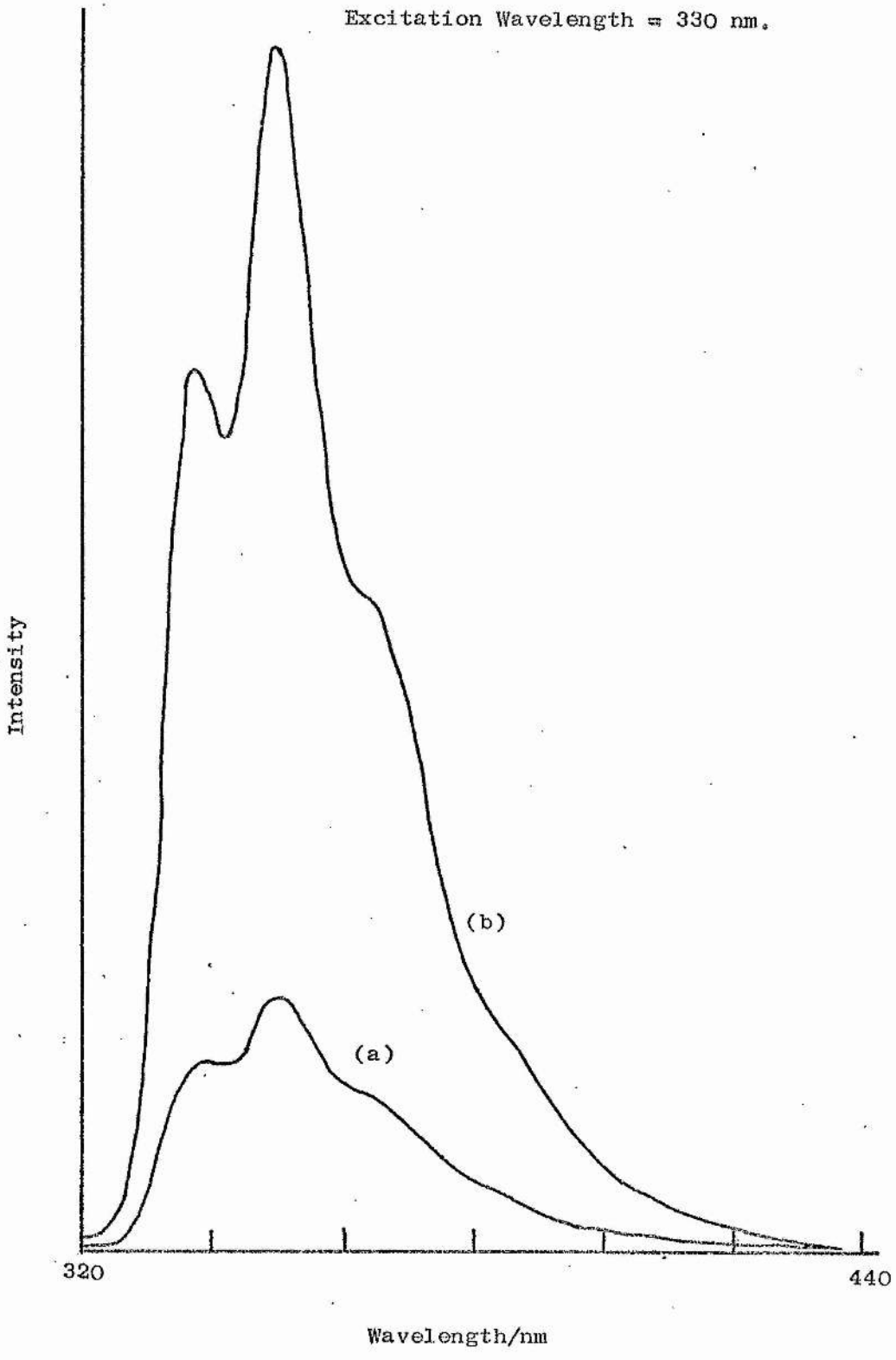


FIG 5.16 1-Naphthol-4-sulphonate in (a) 0.928 M perchloric acid and (b) 0.928 M perchloric acid containing ethanol (11.69 mol l^{-1}). Excitation Wavelength = 320 nm.

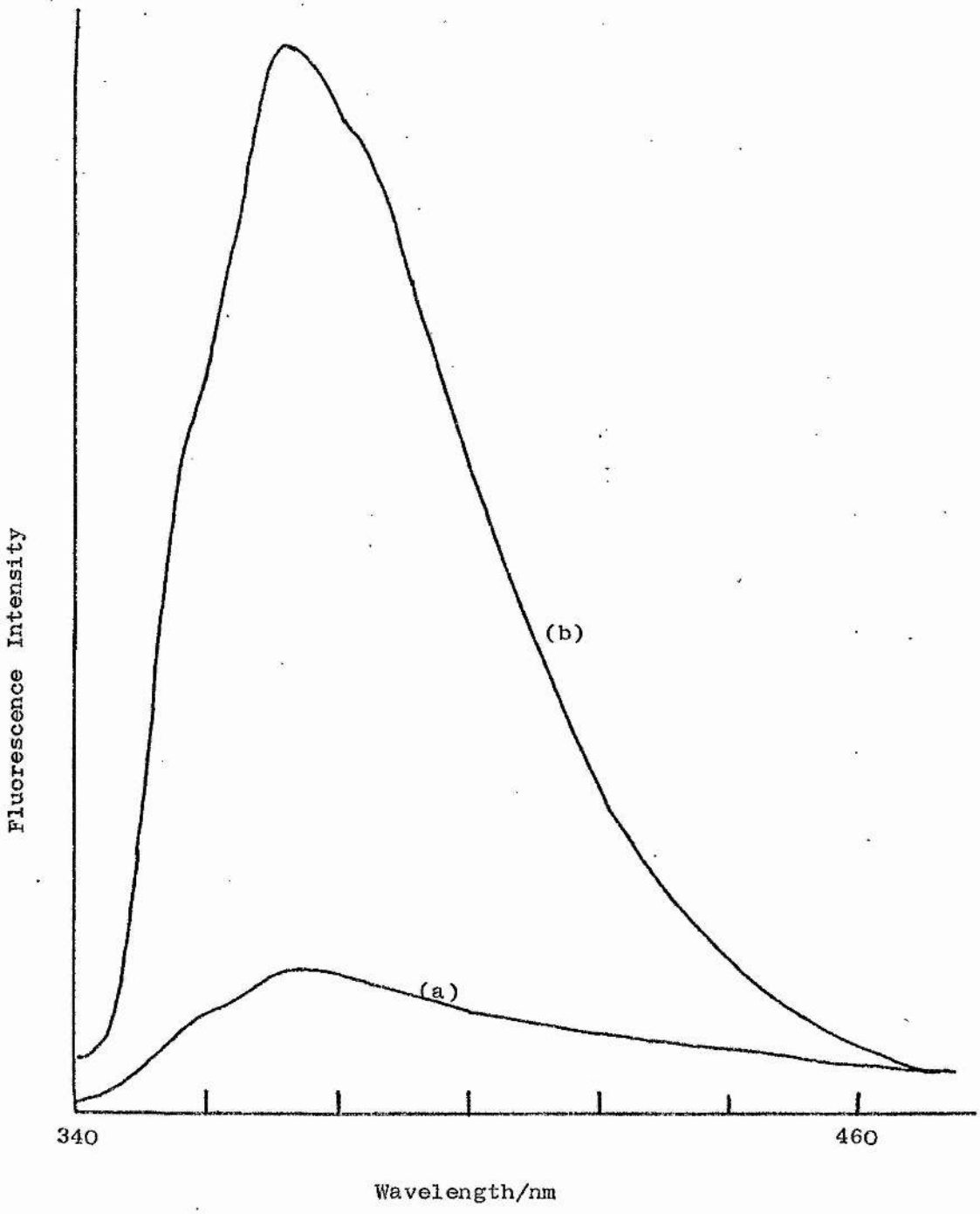
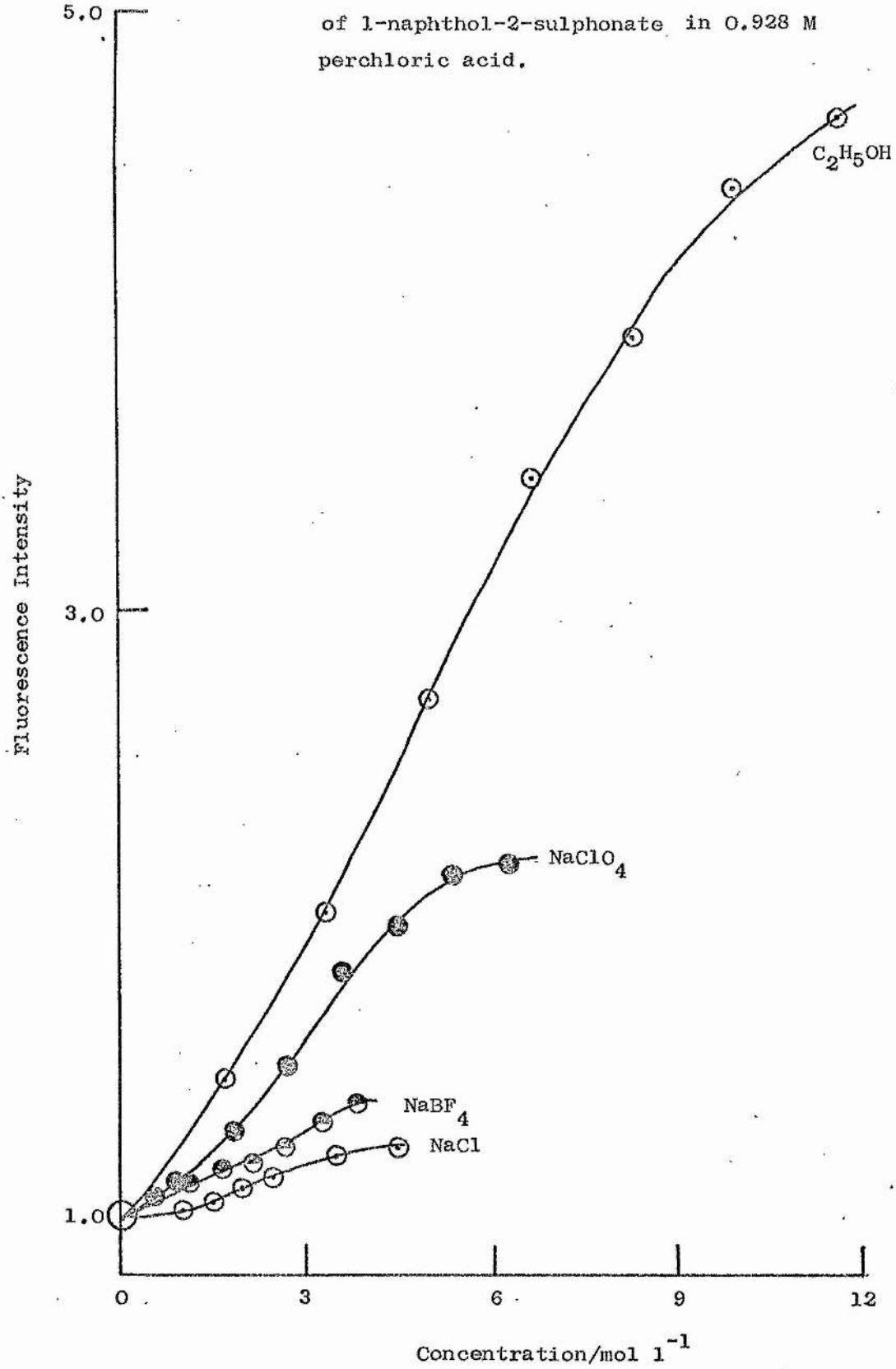


FIG 5.18 The effect of sodium chloride, sodium tetrafluoroborate, sodium perchlorate and ethanol on the fluorescence intensity of 1-naphthol-2-sulphonate in 0.928 M perchloric acid.



(f) The variation of fluorescence intensity with temperature for 1-naphthol-2- and -4-sulphonates.

The fluorescence intensity measurements were made using the controlled temperature cell holder accessory of the Perkin Elmer Hitachi MPF-2A Spectrophotometer. The fluorescence cell was allowed to equilibriate and the emission at right angles to the incident light was recorded. Measurements of fluorescence intensity with decreasing temperature were made for 1-naphthol-2- and -4-sulphonates, and 2-naphthol. The results, normalised for comparison, are shown graphically in Fig 5.19.

(g) The effect of dissolved oxygen on the fluorescence intensity of 1-naphthol-2-sulphonate.

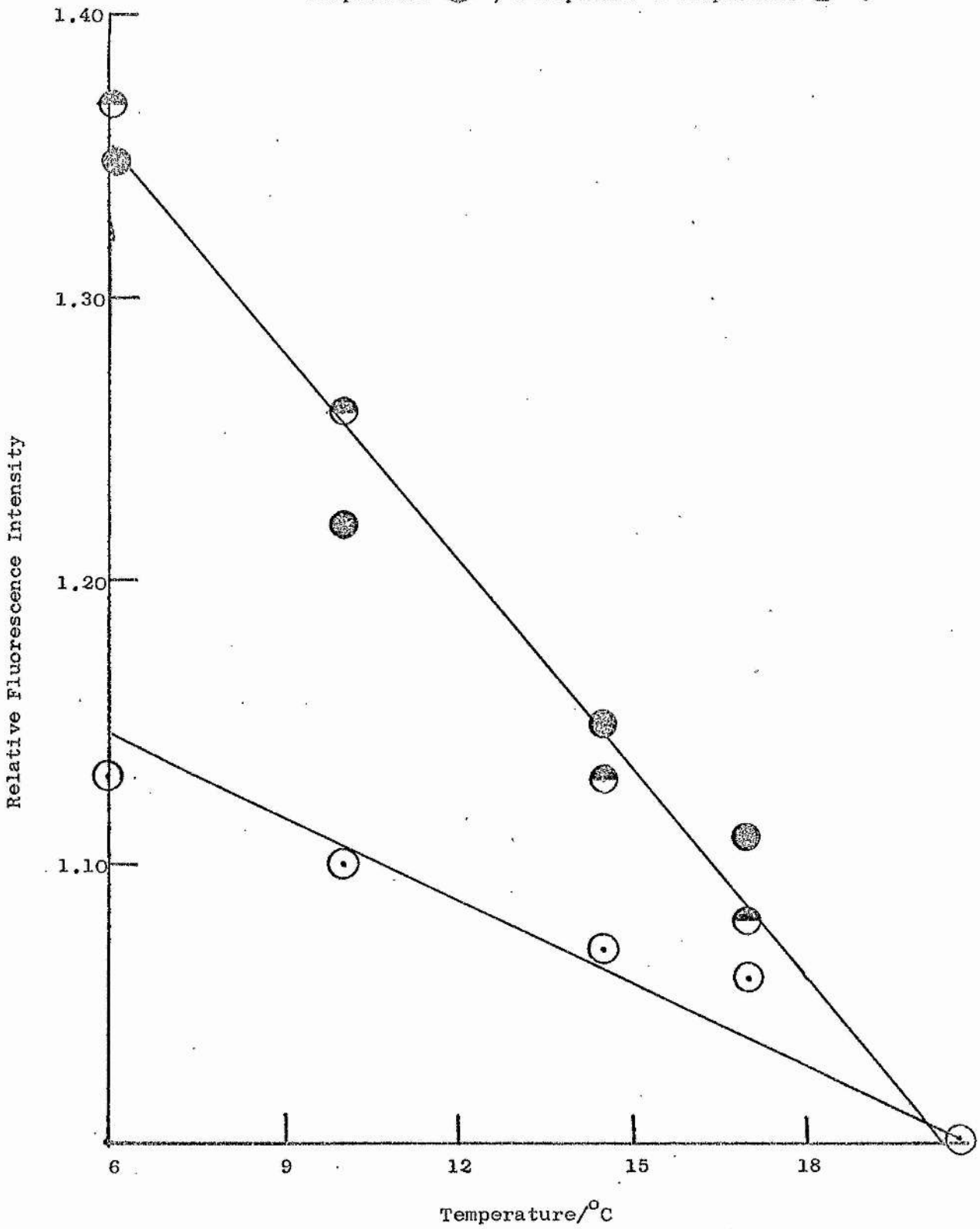
A solution of 1-naphthol-2-sulphonate in 0.928 M perchloric acid was prepared. The solution was halved and one half degassed by the freeze-pump-thaw technique. The intensity of fluorescence of the two solutions measured at the same wavelength is compared in Table 5.3. The fluorescence intensity was recorded on an arbitary scale.

Table 5.3

The fluorescence intensity of an aerobic and anaerobic solution of 1-naphthol-2-sulphonate in 0.928 M perchloric acid.

	Intensity at 350 nm
Degassed solution	50
Non-degassed solution	50

FIG 5.19 The effect of temperature on the fluorescence intensity of 2-naphthol ⊙ , 1-naphthol-2-sulphonate ● , 1-naphthol-4-sulphonate ◒ .



(h) The effect of added sodium perchlorate on the strength of the transient absorption spectrum of 1-naphthol-2-sulphonate in acid solution.

Two solutions of 1-naphthol-2-sulphonate in 0.928 M perchloric acid were prepared. The concentrations of ClO_4^- ions were 0.928 M and 6.591 M in the two solutions. The two solutions were degassed and their transient absorption spectra recorded using exactly the same procedure. The strengths of the transient absorption at 410 nm (the absorption band assigned to the naphthoxyl radical of 1-naphthol-2-sulphonate in Chapter 4) for the two solutions are recorded in Table 4.

Table 4

The transient absorption of 1-naphthol-2-sulphonate in 0.928 M perchoric acid.

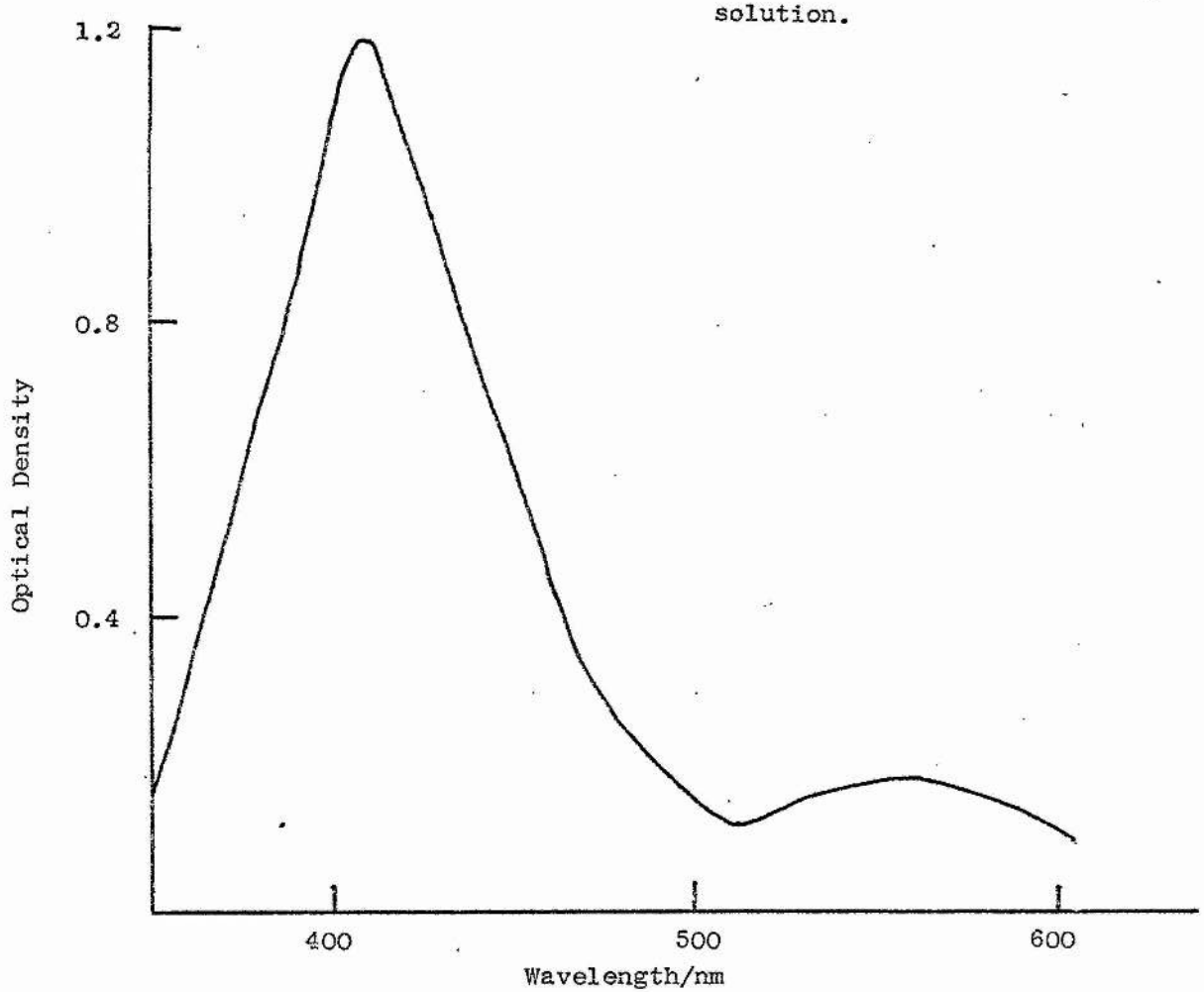
$[ClO_4^-]$/mol l^{-1}	Optical Density at 410 nm
0.928	0.45
6.591	1.15

The transient absorption spectrum of the solution of 1-naphthol-2-sulphonate in 0.928 M perchloric acid containing 6.591 M sodium perchlorate was compiled and is shown in Fig 5.20. This spectrum shows good agreement with the transient absorption of 1-naphthol-2-sulphonate in dilute acid solution shown in Fig 4.13. No solvent shift of the band assigned to the naphthoxyl radical can be detected, although it appears that there is the appearance of a new absorption band at longer wavelengths in Fig 5.20.

(i) Discussion

The concentration of quencher required to quench prompt

FIG 5.20 The transient absorption spectrum of 1-naphthol-2-sulphonate in a 0.928 M H_3O^+ and 6.591 M ClO_4^- solution.



fluorescence appreciably is so high[2] that impurity quenching rarely presents a difficulty. The most likely source of fluorescence quenching is dissolved oxygen, which may have considerably effects on air-saturated solutions of compounds having long fluorescence lifetimes. For example, saturation of a dilute solution of pyrene in cyclohexane with air quenches the fluorescence by a factor of 20[97]. In liquid paraffin and glycerol the degree of quenching is much less owing to the higher solvent viscosities. Hence in some cases the solvent viscosity can have a considerable effect on the intensity of fluorescence. At high concentrations of sodium perchlorate, the viscosity of the solution is greatly increased. However the removal of oxygen is found to have no effect on the fluorescence intensity of 1-naphthol-2-sulphonate (Chapter 5.g), and it follows that the viscosity of the solution is not responsible for the increase in fluorescence with the addition of $NaClO_4$, $NaBF_4$, and NaCl.

There is a lot of evidence for the ClO_4^- [98-104], BF_4^- [101-104], and Cl^- [98,99] ions breaking the structure of water. The situation regarding the effects of alcohols on the structure of water is not quite as clear. Sidorova and Kochnev[105] found that alcohols "promote" the structure of water and the order of effectiveness is

MeOH > EtOH > nPrOH

NMR[106] and dielectric[107] studies suggest also that alcohols tend to stabilise water structure. Horne et al[108], however found contrasting results. They concluded that the addition of alcohol tends to break up the structured regions in liquid water, thus making the liquid more normal i.e. unassociated. The found that

n-PrOH > EtOH > MeOH

was the order of the effectiveness as water structure breakes. Taniewska-Osinska and Growchowski[109] used near infrared spectroscopy

to study the structure of aqueous solutions of alcohols. Their experimental results generally confirmed the view that three regions exist in water-alcohol systems: the stabilization of water by alcohol molecules, the distruction of the water skeleton with a strongly developed heterogeneity, and a destroyed structure of water.

From Fig 5.18 the order of effectiveness for increasing the fluorescence intensity of 1-naphthol-2-sulphonate in 0.928 M $[H^+]$ is

$$EtOH > NaClO_4 > NaBF_4 > NaCl$$

For the same number of mol l^{-1} added, MeOH increases the intensity of fluorescence by approximately the same amount as $NaClO_4$. Thus the order of effectiveness can be written

$$nPrOH > EtOH > MeOH \geq NaClO_4 > NaBF_4 > NaCl$$

If one considers the evidence of Horne et al, this order is the same as one might expect for the effect of solutes on the structure of water. The increased fluorescence intensity of 1-naphthol-2- and -4-sulphonates may therefore be the result of breaking the structure of water by certain solutes.

However the addition of ClO_4^- and BF_4^- ions is known to have the same effect on the structure of water as raising the temperature[102]. If the increase in fluorescence intensity of naphthol sulphonates is due to some "breaking" of water structure effect, one might expect therefore that an increase in temperature would result in an increase in fluorescence intensity, and decreasing the temperature would result in a decrease in fluorescence intensity.

The fluorescence intensity of 1-naphthol-2- and -4-sulphonates increases with decreasing temperature (Chapter 5.7), and the increase is greater than that observed with 2-naphthol. If the hypothesis is accepted that the increase in fluorescence intensity is a result

of "breaking" the structure of water, the increasing fluorescence intensity with decreasing temperature is seen as the resultant of two opposed effects: (i) as the temperature is decreased the water becomes more structured and the fluorescence should therefore decrease (ii) as the temperature decreases, the rates of radiationless conversion and intersystem crossing decrease and therefore the fluorescence intensity should increase.

The comparison with 2-naphthol for the variation of fluorescence intensity with decreasing temperature is not necessarily meaningful, since the effect of temperature on fluorescence intensity is also dependent upon the quantum efficiency of the compound being studied: the fluorescence intensity of a compound with a fluorescence efficiency nearly equal to one will increase negligibly as the temperature is decreased. The fact that the fluorescence intensity of both 1-naphthol-2- and -4-sulphonates increases at the same rate with decreasing temperature is also surprising, since 1-naphthol-2-sulphonate in 0.928 M $HClO_4$ is a far stronger fluorescer than 1-naphthol-4-sulphonate. It would appear, therefore, that the effect of increasing the structure of water, and decreasing the rates of radiationless conversion and intersystem corssing for each compound, coupled with their differences in quantum efficiency, results in approximately the same rate of increasing fluorescence intensity with decreasing temperature!

The ground state absorption spectra of both 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate in aqueous solutions show a red shift with the addition of ethanol and a smaller blue shift on addition of sodium perchlorate. It seems very unlikely that solvent shifts are responsible for the increased fluorescence intensity with the addition of certain solutes. For example, at the excitation wavelength, the solvent shift in going from aqueous solution to 11.7 M

ethanol results in the following increase in absorbance

1-naphthol-4-sulphonate	0.59	⟶ 0.65
1-naphthol-2-sulphonate	0.75	⟶ 0.79

That is, the absorbance of 1-naphthol-4-sulphonate is increased by a factor of 1.10, and that of 1-naphthol-2-sulphonate by a factor of 1.05. These increases in absorbance cannot possibly account for fluorescence increases by factors of 6.6 and 4.6 for the -4- and -2-sulphonates respectively. It seems unlikely that the same fluorescence enhancement effect of ethanol and sodium perchlorate should be caused by opposed solvent shifts anyway.

Presumably the phenolic groups of 1-naphthol, 1-naphthol-2-sulphonate, and 1-naphthol-4-sulphonate are liable to weak hydrogen bonding with solvent water molecules. It is proposed that the excited forms of these compounds lose energy through this bonding with the solvent water i.e. radiationless conversion to the ground state.

The introduction of ethanol, sodium perchlorate and sodium tetrafluoroborate in large quantities reduces the water concentration considerably. If the hydrogen bonding with solvent water molecules is regarded as the simple equilibrium process,

$$N + H_2O \rightleftharpoons N.H_2O \qquad (5.2)$$

where N represents, 1-naphthol, 1-naphthol-2-sulphonate or 1-naphthol-4-sulphonate, then it can be seen that removal of water will favour the species which is not hydrogen bonded. An increased concentration of the excited state of this species, which does not lose some of its energy through the hydrogen bonding to the solvent will therefore account for the increased fluorescence intensity. The variation in fluorescence intensity of 1-naphthol-2-sulphonate with the calculated molarity of water for acidic solutions containing

ethanol, sodium perchlorate, and sodium chloride can be seen in Fig 5.21. From the equilibrium 5.2 it follows that

$$K = \frac{(N.H_2O)}{(N)\ (H_2O)} \qquad (5.3)$$

where K = the formation constant of $N.H_2O$ and $(N.H_2O)$ is the activity of $N.H_2O$ etc. If we assume that the activity coefficients of $N.H_2O$ and N are equal then equation 5.3 can be written as

$$K = \frac{[N.H_2O]}{[N]\ (H_2O)} \qquad (5.4)$$

where $[N.H_2O]$ refers to the concentration of $N.H_2O$ etc. If x is the fraction of N that is converted into the non-fluorescent complex $N.H_2O$

$$K = \left(\frac{x}{1-x}\right) . \frac{1}{(H_2O)} \qquad (5.5)$$

$$\therefore \quad K\ .\ (H_2O) = \left(\frac{x}{1-x}\right) = \left(\frac{1}{1-x}\right) - \frac{(1-x)}{(1-x)}$$

$$\therefore \left(\frac{1}{1-x}\right) = K(H_2O) + 1 \qquad (5.6)$$

If Ø is the fluorescence intensity of 1-naphthol, 1-naphthol-2-sulphonate of 1-naphthol-4-sulphonate in acidic solution, then

$$Ø = k(1-x)\ C^o \qquad (5.7)$$

where k is a constant and C^o is the total concentration of the fluorescer (i.e. $[N] + [NH_2O]$). Thus the fluorescence intensity of the hydrogen bonded form is taken as zero. The maximum fluorescence intensity $Ø_o$ is given by

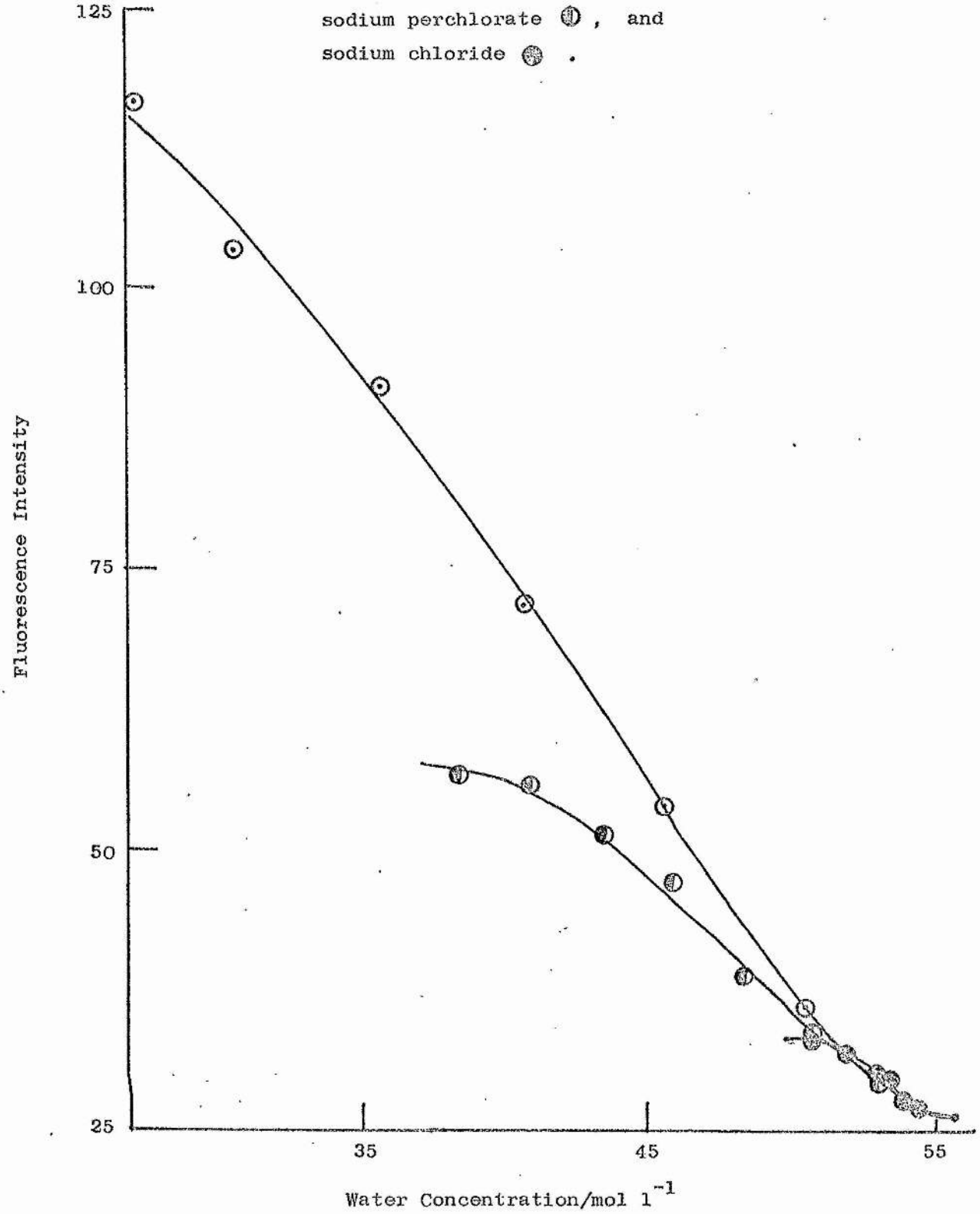
$$Ø_o = k\ C^o \qquad (5.8)$$

$$\therefore \quad \therefore \quad \frac{Ø_o}{Ø} = \frac{1}{(1-x)} ,$$

whence equation 5.6 becomes

$$1/Ø = 1/Ø_o + \left(\frac{K}{Ø_o}\right)\ (H_2O) \qquad (5.9)$$

FIG 5.21 1-Naphthol-2-sulphonate in 0.928 M perchloric acid containing ethanol ⊙, sodium perchlorate ◍, and sodium chloride ◉.



This is a form of the Stern-Volmer equation[110] which is given by equation 5.10

$$\phi_o/\phi = 1 + k(Q) \qquad (5.10)$$

where k is generally known as the Stern-Volmer quenching constant, and Q is a quenching reagent. ϕ_o the fluorescence intensity in the absence of the quenching reagent is not known for 1-naphthol, or 1-naphthol-2- and -4-sulphonates in acidic solutions. Therefore the usual Stern-Volmer plots of ϕ_o/ϕ against quencher concentration were not made. However plots of $1/\phi$ against the quencher concentration should still give straight lines, and plots of this kind are shown in Fig 5.22. The plots of $1/\phi$ against the concentration of water give straight lines at high water concentrations but become curved as the water concentration decreases. It can be seen from equation (5.9) that plots of $1/\phi$ against the activity of water would be more appropriate. Plots of this kind were made for 1-naphthol-2-sulphonate in acidic solutions containing varying amounts of sodium perchlorate or sodium chloride, but the shapes of the curves obtained were exactly the same as those obtained by plotting $1/\phi$ against the water concentration. If two molecules of water were involved in the equilibrium process (5.2) then a graph of $1/\phi$ against the square of the water concentration or activity, would give a straight line, and if three molecules of water were involved, then a plot of $1/\phi$ against the cube of the water concentration or activity should give a stright line. Plots of this kind were made and straight lines were observed at high water concentrations, but they also became curved as the water concentration decreased. It appears therefore that, although water probably does quench the fluorescence of 1-naphthol, 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate in acidic solution (since the fluorescence intensity of these compounds increases as the concentration of water decreases) a point is reached

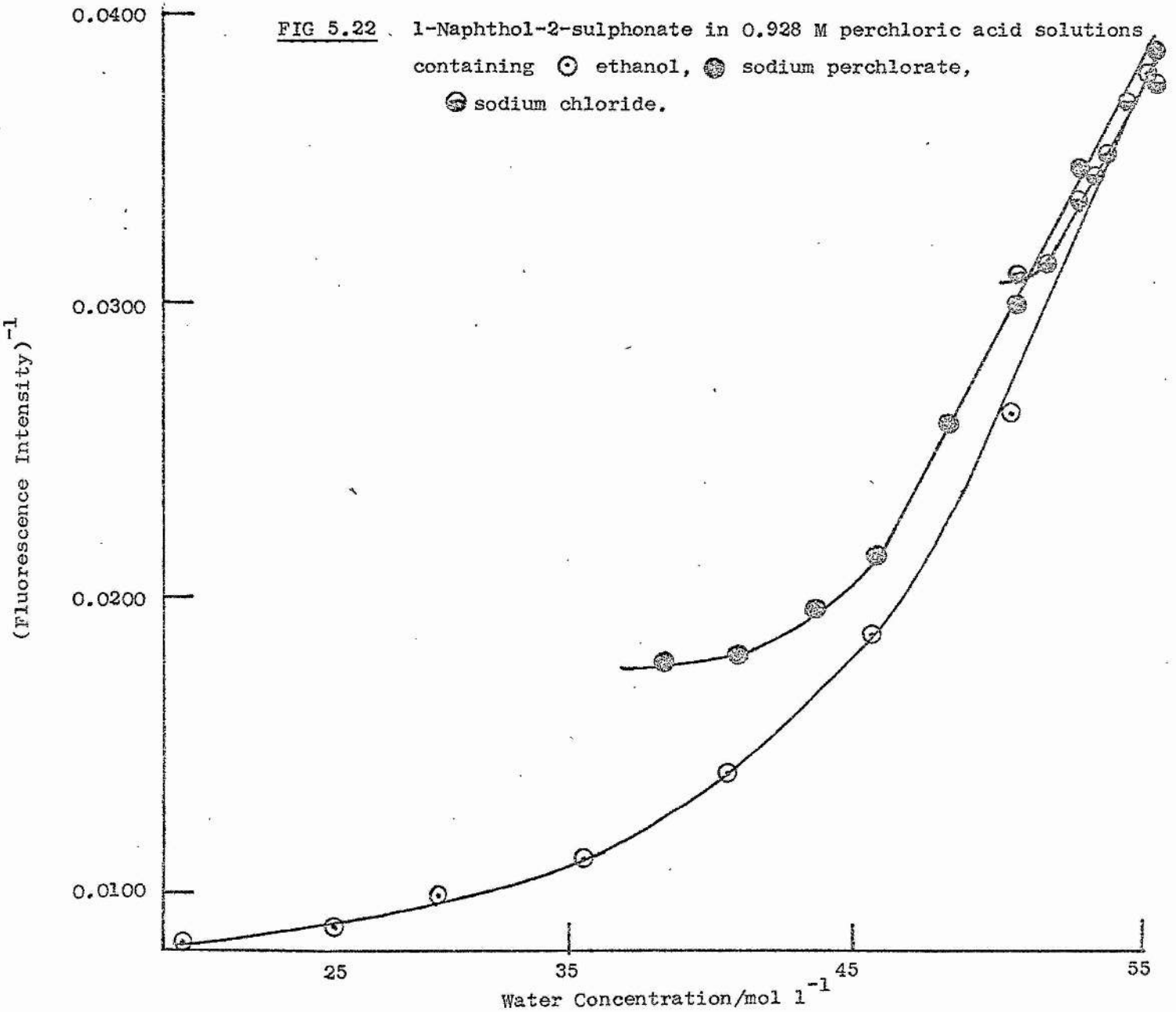


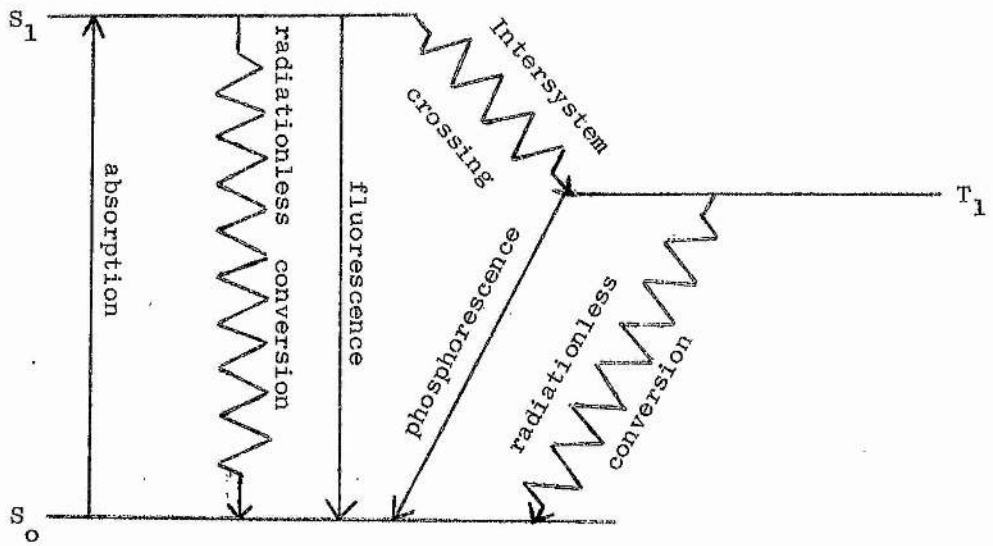
FIG 5.22 1-Naphthol-2-sulphonate in 0.928 M perchloric acid solutions containing ⊙ ethanol, ◉ sodium perchlorate, ◉ sodium chloride.

where the removal of further water has very little effect on the fluorescence intensity, and this point is different depending upon whether the water is replaced by ethanol, sodium perchlorate, or sodium chloride.

Further evidence for the theory that the increase in fluorescence intensity of these compounds is due to the removal of water can be gained from the evidence of chapter 5.h. The addition of sodium perchlorate to a solution of 1-naphthol-2-sulphonate in 0.928 M perchloric acid resulted in an increase of the naphthoxyl radical yield, which is presumably formed through the triplet state of 1-naphthol-2-sulphonate. Thus addition of sodium perchlorate resulted in an increased triplet yield and since the population of the excited singlet state is also increased, the added sodium perchlorate must reduce the rate of radiationless conversion from the first excited singlet state (S_1) to the ground state S_o. Consider the simple Jablonski diagram shown in Fig 5.23.

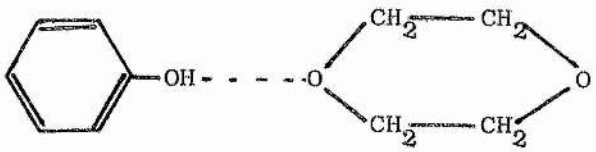
Fig 5.23

Jablonski diagram.



Reduction of radiationless conversion from the first excited singlet state to the ground state, by preventing hydrogen bonding to the solvent, would automatically result in an increased fluorescence intensity. A greater population of the S_1 state would also result in more intersystem crossing, an increased population of the T_1 state, and hence a greater yield of the naphthoxyl radical. I.P. Garland, working in our laboratory, has subsequently confirmed that the yield of the naphthoxyl radical of 1-naphthol-2-sulphonate increases steadily as the sodium perchlorate concentration is increased to 6 M. These experiments eliminate the possiblity that the increased fluorescence intensity might be due to an inhibition of the intersystem crossing which would of course have resulted in a decreased triplet yield and hence a decreased naphthoxyl radical yield.

Nagakura and Baba[111], and Weller[27] have shown that compounds such as phenol, 2-naphthol and 3-hydroxypyrene show red shifts of their absorption spectra when dissolved in proton acceptor solvents such as dioxane, as compared with their spectra in aliphatic hydrocarbons. They attributed these spectral shifts to the formation of hydrogen-bonded complexes of the type

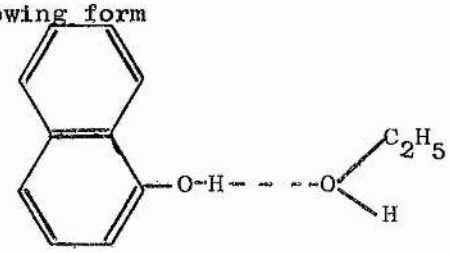


(5,11)

If the hydrogen bonding of 1-naphthol, 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate with solvent water molecules is of this type, then a red shift of the absorption spectra of these compounds when dissolved in water as compared with their absorption spectra in aliphatic hydrocarbons, would be expected also. 1-Naphthol-2-sulphonate and 1-naphthol-4-sulphonate are insoluble in aliphatic

hydrocarbons, whereas 1-naphthol is soluble. However there is no observed shift in the absorption spectrum of 1-naphthol when dissolved in water as compared with its absorption spectrum in cyclohexane; but 1-naphthol shows a red shift of its absorption spectrum when dissolved in ethanol as compared to its spectrum in cyclohexane, and the two naphthol sulphonates both show red shifts in going from water to ethanol. These solvent shifts and lack of solvent shifts can be explained.

1-naphthol, 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate are hydrogen bonded to ethanol and the hydrogen bonding is of the following form



(5,12)

This is shown by the red solvent shift of the absorption spectrum of 1-naphthol in ethanol as compared with its spectrum in cyclohexane. Presumably the S_1 states of 1-naphthol and its sulphonates do not lose energy through this hydrogen bonding to ethanol in the same way as energy is lost through hydrogen bonding to water. This is probably because water is such an associated liquid that the energy of the S_1 state can be gradually lost as it is passed through the "chains" of water molecules.

Water is a stronger base than ethanol[112], and one might expect it therefore to form stronger hydrogen bonds (of the type shown in 5,11 and 5,12) than ethanol with 1-naphthol, 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate. This in turn should be shown by a larger red shift of the absorption spectrum of 1-naphthol in water, compared with its spectrum in cyclohexane, than the red shift of the absorption spectrum in ethanol. However no red shift

is observed for 1-naphthol in changing from cyclohexane to water.

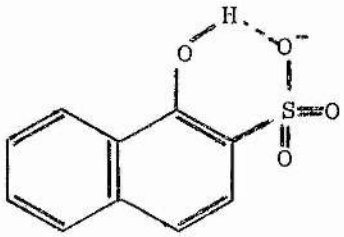
The low wavenumber absorption band of 1-naphthol is an $a_{\pi} \leftarrow 1$ transition. If in water, the ground state hydrogen-bonds at the lone pair electron site as well as hydrogen bonding of the type shown in 5.11 and 5.12 occurring, then the failure of changing from cyclohexane to water to shift the ground state absorption spectrum of 1-naphthol can be explained. Hydrogen-bonding of the type shown in 5.11 and 5.12 would shift the absorption spectrum to longer wavelengths. Promotion of a lone pair electron into the π electron system would reduce hydrogen-bonding at the lone pair electron site in the excited state. Thus a change from cyclohexane to water would reduce the energy of the ground state to a greater degree than that of the excited state and the absorption spectrum would shift to shorter wavelengths. It is therefore proposed that in water hydrogen bonding of the type shown in 5.11 and 5.12 as well as hydrogen bonding at the lone pair electron site occurs with 1-naphthol and the 1-naphthol sulphonates. The two opposed shifts which result from changing from cyclohexane to water cancel one another and therefore no shift is observed.

It seems likely that the increased fluorescence intensity of 1-naphthol, 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate is due to the reduction of the water concentration by the addition of solutes in large quantities. The S_1 state of these compounds loses energy through hydrogen bonds to the solvent water, presumably the hydrogen-bonds of type 5.11 and 5.12 since the RO^- forms of these compounds, which are quite strong fluorescers, would also be likely to undergo hydrogen-bonding of the type which is proposed to occur at the lone pair electron site of the -OH group. However the effect of the solutes on the structure of water may be involved also, since the order of the ability of these solutes

to break the structure of water is exactly the same as their ability to increase the fluorescence intensity of 1-naphthol-2-sulphonate in acidic solutions.

Both 1-naphthol and 1-naphthol-4-sulphonate exhibit very weak fluorescence and transient absorption spectra in aqueous acidic solutions, whereas in alkaline solutions they both show quite strong fluorescence and 1-naphthol-4-sulphonate has a moderately strong transient absorption spectrum. 1-Naphthol-2-sulphonate, however, has a strong transient absorption spectrum in alkaline solutions and a moderately strong absorption in acidic solutions. The -2-sulphonate shows strong fluorescence, of approximately the same intensity, in alkaline or acidic solutions.

Intra-molecular hydrogen bonding is proposed to explain these differences between 1-naphthol-2-sulphonate and 1-naphthol and its -4-sulphonate i.e.



In this way hydrogen bonding between the phenolic group and solvent water molecules will be much less for 1-naphthol-2-sulphonate than for 1-naphthol and 1-naphthol-4-sulphonate, where there is no intramolecular hydrogen bonding. Therefore the first excited singlet state of 1-naphthol-2-sulphonate will not lose as much energy through radiationless conversion to the ground state (via hydrogen bonding to solvent water molecules) and therefore will exhibit more fluorescence, the triplet yield will be increased and hence the strength of the transient absorption spectrum.

It is interesting to note that 2-naphthol has strong fluorescence, of approximately equal intensity, in acidic and alkaline solutions, and shows strong triplet ⟵ triplet absorptions in acidic and alkaline solutions also. This would imply, therefore, that radiationless conversion to the ground state from the first excited singlet state is quite small for 2-naphthol. This then implies that the first excited singlet state of 2-naphthol does not lose energy through the hydrogen bonds between the phenolic group and solvent water in the same way as the S_1 state of 1-naphthol, or that 2-naphthol does not exhibit hydrogen bonding in aqueous acidic solutions to the same extent as 1-naphthol. However the acid strengths of 1-naphthol and 2-naphthol are similar in the ground and first excited singlet states, and one would expect, therefore, that in aqueous acidic solutions they both exhibit hydrogen bonding to the same extent.

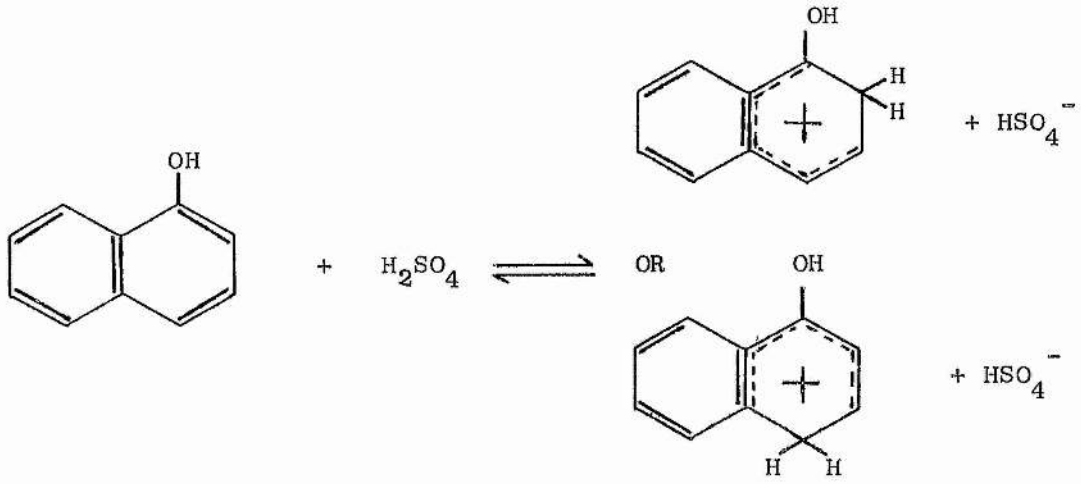
Thus at present it would appear that the S_1 state of 1-naphthol, and 1-naphthol-2- and -4-sulphonates is quenched by water in aqueous acidic solutions. This quenching process does not occur with 2-naphthol. Removal of water by introduction of solutes in large quantities increases the fluorescence intensity of 1-naphthol and its sulphonates, and also increases their triplet yields. The hydrogen bonding of the phenolic group of these compounds with solvent water molecules is responsible for quenching the S_1 state and the hydrogen bonding is of the type shown in 5,11 and 5,12. However the effect of these solutes on the structure of water may be involved also, since the order of the ability of the solutes to break the structure of water is exactly the same as their ability to increase the fluorescence intensity of 1-naphthol-2-sulphonate in acidic solutions.

Further investigation is clearly needed before the increase in fluorescence intensity of 1-naphthol and the naphthol sulphonates in aqueous acidic solutions can be fully explained. For example, an investigation of the effect of added solutes on the fluorescence intensity of 1-methoxynaphthalene-2- and -4-sulphonates in aqueous solutions would determine whether the S_1 state of 1-naphthol-2- and -4-sulphonates is deactivated by hydrogen bonding, of the type shown in 5.11 and 5.12, to solvent water molecules. Further work using sulphonic acid derivatives of 2-naphthol might also confirm the difference in excited state properties of 1-naphthol and 2-naphthol that is shown by the results already obtained in this work.

CHAPTER 6

CONCLUSIONS

1-Naphthol protonates in concentrated perchloric and sulphuric acids, and protonation occurs at a carbon atom in the naphthalene ring. i.e.



The $pK(S_o)$ for the equilibrium was found to be -11.02 on the H_c acidity scale, which was found to govern the protonation of 1-naphthol. No fluorescence or transient absorption were detected for protonated 1-naphthol.

1-Naphthol undergoes sulphonation in concentrated sulphuric acid to form a mixture of 1-naphthol-2-sulphonic acid and 1-naphthol-4-sulphonic acid. Strong transient absorption spectra were observed when this mixture of sulphonic acids in sulphuric acid were flashed. It appeared that a radical was formed from a short-lived triplet species. Although a transient absorption spectrum of 1-naphthol in aqueous solutions has never been observed, the transient absorption of the naphthoxyl radical of the 1-naphthol-2- and -4-sulphonates was observed when these sulphonates were flashed in aqueous solutions. The triplet-triplet absorptions of

the (RO^-) triplet forms of these two naphthol sulphonates were also detected and this enabled determinations of $pK(T_1)$ to be made. Values of $pK(S_o)$ and $pK(S_1)$ were also determined for these two compounds and are shown in Table 5.1.

Table 5.1

Acidity constants of 1-naphthol-2- and -4-sulphonates.

	$pK(S_o)$	Phospho-rescence $pK(T_1)$	Flash photolysis $pK(T_1)$	Forster Cycle $pK(S_1)$	Fluore-scence $pK(S_1)$ $-\log \Upsilon/\Upsilon'$	$\vec{k}_\Upsilon$
1-Naphthol-2-sulphonate	9.58	8.51	7.50	2.52 4.04	3.24	0.22
1-Naphthol-4-sulphonate	8.27	7.74	7.05	2.29 3.06	3.13	0.59

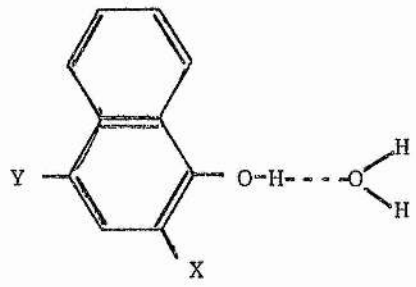
Thus the acidity constants of 1-naphthol-2- and -4-sulphonates can be described in the following way,

$$pK(S_o) > pK(T_1) >> pK(S_1)$$

i.e. the difference between $pK(T_1)$ and $pK(S_1)$ is quite large, and $pK(T_1)$ is quite close to $pK(S_o)$. This is in contrast, however, with the results of quantum mechanical calculations performed by Bertran, Chalvet, and Daudel[15], which suggested that for derivatives of naphthalene which have an electron-donating substituent in the α position, the difference between $pK(S_1)$ and $pK(T_1)$ would be small and that $pK(T_1)$ would be quite far away from $pK(S_o)$.

1-Naphthol, when irradiated in alkaline medium is easily oxidised by oxygen to form phthalic acid, in good yield, with small amounts of 9,10-dihydroxynaphthacenequinone, hydroxy naphthalenes, oxalic acid and 3,8-pyrene quinone[93]. A similar reaction is observed with 1-naphthol-2- and -4-sulphonates in alkaline medium.

The introduction of certain solutes in large quantities to aqueous acidic solutions of constant concentration of 1-naphthol, 1-naphthol-2-sulphonate or 1-naphthol-4-sulphonate, results in an increase in the fluorescence intensity and triplet yield of these compounds. This is attributed to the fact that (i) introduction of these solutes in such large quantities reduces the water concentration of the solutions and (ii) the S_1 states of 1-naphthol and the 1-naphthol-sulphonates are deactivated by hydrogen bonding to solvent water molecules in the following way,



where X and Y can be SO_3^- or H. No increase in fluorescence intensity is observed when similar solutes are added to 2-naphthol.

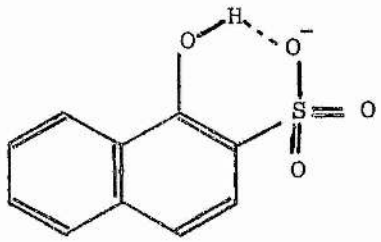
However it is by no means certain that the removal of water molecules is the only factor involved in the increases in fluorescence intensity and triplet yield observed with 1-naphthol, 1-naphthol-2-sulphonate and 1-naphthol-4-sulphonate. The effect of the solutes on the structure of water may be involved also, since the order of the ability of these solutes to break the structure of water is exactly the same as that of

their ability to increase the fluorescence intensity of 1-naphthol-2-sulphonate in acidic solutions.

Both 1-naphthol and 1-naphthol-4-sulphonate exhibit very weak fluorescence and transient absorption spectra in aqueous acidic solutions, whereas 1-naphthol-2-sulphonate exhibits strong fluorescence and a moderately strong transient absorption spectrum.

Intramolecular bonding is proposed to explain these differences between 1-naphthol-2-sulphonate and 1-naphthol and its -4-sulphonate

i.e.



In this way hydrogen bonding between the phenolic group and solvent water molecules is much less for 1-naphthol-2-sulphonate than for 1-naphthol and 1-naphthol-4-sulphonate where there is no intramolecular bonding. This results in a greater population of the S_1 and T_1 states of 1-naphthol-2-sulphonate and therefore the fluorescence and transient absorptions observed are stronger than those observed for 1-naphthol and 1-naphthol-4-sulphonate.

APPENDIX I

PROGRAM SPEKC.

PROGRAM TO EVALUATE TRANSIENT ABSORPTION SPECTRA.

INPUT DATA.
THE SET OF WAVELENGTH REFERENCE CARDS COMMENCE THE CARD INPUT FOLLOWED BY.....
CARD 1 - PLATE NUMBER (I3)
CARDS 2-4 - TITLE
CARD 5 - NUMBER OF BANDS ON PLATE. (MAXIMUM 13)
CARD 6 - OPTICAL DENSITIES OF FILTERS. (20F4.0)
(IN INCREASING ORDER OF MAGNITUDE)

PAPER TAPE.
RESULTS IN SAME ORDER AS CARD 7 WITH EXPTAL. SPEC. LAST.
(EACH BAND TERMINATED WITH 99 +00000 0CRLF)

A PUNCHED CARD OUTPUT OF THE TRANSIENT SPECTRUM IS PRODUCED.

```
      SUBROUTINE GETPTF(IFILE)
      INTEGER CHAR/Z40404040/,CR/Z0D404040/,CARD(80)
      I=0
      REWIND IFILE
    1 CALL READPT(3,1,CHAR)
      CALL FASCI(CHAR)
      IF(CHAR.EQ.CR) GO TO 2
      I=I+1
      CARD(I)=CHAR
      GO TO 1
    2 CALL VALID(CARD,I,IVAL)
      IF(IVAL.EQ.1) GO TO 4
      WRITE(IFILE,3)(CARD(K),K=1,I)
    3 FORMAT(80A1)
    4 CALL READPT(3,1,CHAR)
      REWIND IFILE
      RETURN
      END
```

PROGRAM SPEKC (continued)

```
      DIMENSION ITIT(60),DENS(15),NC(350),V(350),NR(350),VAL(13,350),
     1RESULT(350),NO(15),WAVEL(300)

      IFILE=8
      WAVEL(1)=650.0
      READ(5,10)(WAVEL(J),J=2,276)
   10 FORMAT(16F5.0)
      WRITE(6,500)
      READ(5,20)KODE
   20 FORMAT(I3)
      WRITE(6,500)
      READ(5,30)ITIT
   30 FORMAT(20A4)
      READ(5,40)NUM
   40 FORMAT(I2)
      WRITE(6,500)
      NUMD=NUM-1
      READ(5,50)(DENS(J),J=1,NUMD)
   50 FORMAT(20F4.0)
      WRITE(6,500)
      M=0
   55 N=0
      M=M+1
   60 N=N+1
      CALL GETPTF(IFILE)
      READ(IFILE,70)NC(N),V(N),NR(N)
   70 FORMAT(I2,1X,F6.0,1X,I1)
      IF(NC(N)-90)60,60,80
   80 NO(M)=N-1
      NN=NO(M)
      WRITE(6,500)
      DO 90 N=1,NN
   90 VAL(M,N)=ABS(V(N)*0.0001)
      IF(M-NUM)55,100,100
  100 CONTINUE

            ALL DATA READ.

      WRITE(6,500)
  500 FORMAT(1HO,10X,' PROGRAM READING CHECK.')
      LOWVAL=1000.0
      DO 110 M=1,NUM
      IF(NO(M).LT.LOWVAL)LOWVAL=NO(M)
  110 CONTINUE

            SMALLEST DATA SET FOUND.

      DO 170 N=1,LOWVAL
      M=1
      IF(VAL(NUM,N)-VAL(M,N))120,120,130
  120 RESULT(N)=DENS(1)
      GO TO 170
```

PROGRAM SPEKC (continued)

```
130 M=M+1
    IF(M.GT.NUMD)GO TO 150
    IF(VAL(NUM,N)-VAL(M,N))160,140,130
140 RESULT(N)=DENS(M)
    GO TO 170
150 M=M-1
    RESULT(N)=DENS(M)
    GO TO 170
160 M1=M
    M2=M1-1
    D=VAL(M1,N)-VAL(M2,N)
    D1=VAL(M1,N)-VAL(NUM,N)
    RATIO=D1/D
    RESULT(N)=DENS(M1)-RATIO*(DENS(M1)-DENS(M2))
170 CONTINUE

          EXPERIMENTAL SPECTRUM FOUND.

    WRITE(6,300)
300 FORMAT(1H1,40X,'MICRODENSITOMETER DATA.')
    WRITE(6,310)
310 FORMAT(1H ,40X,'----------------- -----')
    WRITE(6,320)ITIT
320 FORMAT(1H0,10X,3(20A4/))
    WRITE(6,330)KODE
330 FORMAT(1H0,25X,'PLATE NUMBER ',I3)
    WRITE(6,340)
340 FORMAT(1H0,'LAMDA',30X,'OPTICAL DENSITIES.',48X,'EXPT.',5X,'ABS',3
   1X,'LAMDA')
    WRITE(6,350)
350 FORMAT(1H ,1X,'(NM)',96X,'SPEC.',5X,'SPEC.',3X,'(NM)')
    WRITE(6,360)(DENS(J),J=1,NUMD)
360 FORMAT(1H+,8X,12(F5.2,2X))
    WRITE(6,365)
365 FORMAT(1H ,'    ')
    DO 380 N=1,LOWVAL
    WRITE(6,370)WAVEL(N),(VAL(M,N),M=1,NUMD)
370 FORMAT(1H ,F6.1,2X,12(F5.2,2X))
    WRITE(6,375)VAL(NUM,N),RESULT(N),WAVEL(N)
375 FORMAT(1H+,99X,F7.3,5X,F5.3,2X,F5.1)
380 CONTINUE
    WRITE(7,376)KODE,LOWVAL
376 FORMAT(I3,2X,I3)
    WRITE(7,377)ITIT
377 FORMAT(20A4)
    WRITE(7,378)(RESULT(N),N=1,LOWVAL)
378 FORMAT(16F5.3)
    STOP
    END
```

APPENDIX II

PROGRAM SPEKD.

PLOTTING PROGRAM FOR TRANSIENT ABSORPTION SPECTRA.

INPUT DATA.

THE SET OF WAVELENGTH REFERENCE CARDS COMMENCE THE INPUT DATA FOLLOWED BY A CARD GIVING THE NUMBER OF SPECTRA TO BE PLOTTED (I2) AND FINALLY THE PUNCHED CARD OUTPUT FROM SPEKC.

```
      DIMENSION WAVEL(300),ITIT(60),DENS(300)
      WAVEL(1)=650.0
      READ(5,10)(WAVEL(J),J=2,276)
   10 FORMAT(16F5.0)
      READ(5,20)NDATA
   20 FORMAT(I2)
      DO 999 I=1,NDATA
      READ(5,30)KODE,N
   30 FORMAT(I3,2X,I3)
      READ(5,40)ITIT
   40 FORMAT(20A4)
      READ(5,50)(DENS(J),J=1,N)
   50 FORMAT(16F5.3)
      XD=25.0
      YMIN=0.0
      YMAX=1.5
      YL=5.0
      YD=0.25
      XMAX=650.0
      XMIN=325.0
      XL=6.5

      CALL PLOT(1,XMIN,XMAX,XL,XD,YMIN,YMAX,YL,YD)
      CALL PLOT(99)

      DO 70 IJ=350,650,50
      XX=IJ-22
      CALL PLOT(90,XX,-0.075)
      WRITE(3,60)IJ
   60 FORMAT(4X,I3,100X)
   70 CALL CHAR(0.1,10)
      CALL PLOT(99)

      CALL PLOT(90,400.0,-0.15)
      WRITE(3,80)
   80 FORMAT(15HWAVELENGTH (NM),100X)
      CALL CHAR(0.1,10)
      CALL PLOT(99)
```

```
      DO 100 K=10,160,25
      IY=K-10
      YY=IY
      YZ=YY*0.01
      CALL PLOT(90,225.0,YZ)
      WRITE(3,90)YZ
   90 FORMAT(17X,F4.2,100X)
  100 CALL CHAR(0.1,10)
      CALL PLOT(99)

      CALL PLOT(90,290.0,0.915)
      WRITE(3,105)
  105 FORMAT(7HOPTICAL,100X)
      CALL CHAR(0.1,10)
      CALL PLOT(99)

      CALL PLOT(90,290.0,0.830)
      WRITE(3,106)
  106 FORMAT(7HDENSITY,100X)
      CALL CHAR(0.1,10)
      CALL PLOT(99)

      CALL PLOT(90,425.0,1.6)
      WRITE(3,110)KODE
  110 FORMAT(37HTRANSIENT ABSORPTION SPECTRUM NUMBER ,I3,100X)
      CALL CHAR(0.1,10)
      CALL PLOT(99)

      DO 120 J=7,N
  120 CALL PLOT(90,WAVEL(J),DENS(J))
      CALL PLOT(99)

      CALL PLOT(7)

  999 CONTINUE
      STOP
      END
```

REFERENCES

1. A. Jablonski, Z.Physik, 1935, 94, 38.
2. C.A. Parker, Photoluminescence of Solutions (Elsevier, 1968).
3. M. Kasha, Disc.Faraday Soc., 1950, 9, 14.
4. A.A. Lamola, and G.S. Hammond, J.Chem.Phys., 1965, 43, 2129.
5. J.W. Hilpern, G. Porter, and L. Stief, Proc.Roy.Soc., 1964, A277, 437.
6. G. Porter, Pure Appl.Chem., 1962, 4, 141.
7. G. Porter, and M.R. Wright, Disc.Faraday Soc., 1959, 27, 18.
8. G. Porter, Proc.Roy.Soc., 1950, A200, 284.
9. G. Porter, and M.W. Windsor, Disc.Faraday Soc., 1954, 17, 178.
10. G. Porter, and M.R. Topp, Proc.Roy.Soc., 1970, A315, 163.
11. M. Kasha in W.D. McElroy and B. Glass (Eds.), Light and Life, (The John Hopkins Press 1961).
12. G. Porter and P. Suppan, Trans.Faraday Soc., 1965, 61, 1664.
13. T.S. Godfrey, G. Porter, and P. Suppan, Disc.Faraday Soc., 1965, 39, 194.
14. J. Faure, and J.J. Joussot-Dubien, J.Chem.Phys., 1966, 63, 621.
15. J. Bertrán, O.Chalvet, and R. Daudel, Theoret.Chim.Acta. (Berl.), 1969, 14, 1-16.
16. E. Lippert, Z. Naturforsch, 1955, 109, 541.
17. E. Lippert, Z. Elektrochem, 1957, 61, 962.
18. J.N. Brönsted, Rec.Trav.Chim., 1923, 42, 718.
19. J.N. Brönsted, Z.Phys.Chem., 1934, A169, 52.

20. K. Weber, Z.Phys.Chem., 1931, B15, 18.

21. Th. Förster, Naturwiss., 1949, 36, 186.

22. Th. Förster, Z. Elektrochem., 1950, 54, 42.

23. Th. Förster, Z.Elektrochem, 1950, 54, 531.

24. A. Weller, Z.Physik.Chem., 1955, 3, 238.

25. A. Weller, Z. Elektrochem, 1952, 56, 662.

26. A. Weller, Z.Physik.Chem., 1958, 15, 438.

27. A. Weller, Progress in Reaction Kinetics, Vol. 1, Ch. 7, Pergamon Press, London 1961.

28. A. Weller, Z.Physik.Chem., 1958, 17, 224.

29. N. Trieff, and B.R. Sundheim, J.Phys.Chem., 1965, 69, 2044.

30. A. Weller, J. Elektrochem., 1954, 58, 849.

31. A. Weller, Z.Physik.Chem., 1957, 13, 335.

32. G. Jackson, and G. Porter., Proc.Roy.Soc., 1961, A200, 13.

33. L. Lindqvist, Ark.Kemi, 1960, 16, 79.

34. E. Vander Donckt, Progress in Reaction Kinetics, Vol. 5, Ch.5, Pergamon Press, London 1966.

35. E.L. Wehry, and L.B. Rogers, Spectrochim.Acta., 1965, 21A, 1976.

36. H.H. Jaffé, and H. Lloyd Jones, J.Org.Chem., 1965, 30, 964.

37. S. Nagakura, and H. Baba, J.Amer.Chem.Soc., 1952, 74, 5693.

38. H. Beens, K.H. Grellmann, M. Gurr, and A. Weller, Disc. Faraday Soc., 1965, 39, 183.

39. P. Seiler, and Werthemann, Helvet.Chim.Acta., 1971, 54, 2757.

40. A.C. Hopkinson and P.A.H. Wyatt, J.Chem.Soc.(B), 1967, 1333.

41. G.N. Lewis, D. Lipkin, and T.T. Magel, J.Amer.Chem.Soc., 1941, 63, 3005.

42. G. Porter, Techniques of Organic Chemistry Vol. VIII, Part 2, Ed. Weissberger, (Interscience 1963).

43. A. Knowles, Photo-electric Spectrometry Group, Bull., 1970, No. 19, 567-75.

44. G. Porter, Science, 1968, 160, 1299-1307.

45. G. Porter, and M.R. Wright, J.Chim.Phys., 1958, 55, 705.

46. Perkin Elmer Instruction Manuel, Model MPF-2A, 1970.

47. J.D. Winefordner, and P.A. St. John, Anal.Chem., 1963, 35, 2211.

48. T.M. Shepherd, Chem. and Ind., 1973, 332-334.

49. J.F. Ireland, Ph.D. Thesis, 1972.

50. R. Argauer, and C.E. White, Fluorescence Analysis (Dekker 1970).

51. F.R. Lipsett, J.Opt.Soc.Amer., 1959, 49, 673.

52. C.A. Parker, Anal.Chem., 1962, 34, 502.

53. G.K. Turner, Science, 1964, 146, 183.

54. G.M. Edelman, Rev.Sci.Instr., 1965, 36, 809.

55. H.V. Drushel, A.K. Sommers, and R.C. Cox, Anal.Chem., 1963, 35, 2166.

56. P. Byron, and J.B. Hudson, Talanta, 1968, 15, 714.

57. A. Weller, Z. Elektrochem., 1957, 61, 956.

58. A. Weller, Z.Physik.Chem., 1958, 18, 163.

59. A. Weller, Disc.Faraday Soc., 1959, 27, 28.

60. I. Heilbron (Editor), Dictionary of Organic Compounds, (Oxford University Press 1953).

61. O. Mäkitie, Suomen Kemistilehti B, 1966, 39, 23.

62. C. Daglish, J.Amer.Chem.Soc., 1950, 72, 4859.

63. D.M. Hercules, and L.B. Rogers, Spectrochim.Acta., 1959, 393.

64. I.L. Finar, Organic Chemistry, (Longmans 1961).

65. H.H. Hodgson, and D.E. Hathway, J.Soc.Dyers Colourists, 1947, 63, 109-12.

66. For recent reviews of evidence see (a) D.M. Brouwer, E.L. Mackor, and C. MacLean, in "Carbonium Ions", Ed. Olah and Schleyer (John Wiley 1970), and (b) H.H. Perkampus, Advan.Phys.Org.Chem., 1966, 4, 196.

67. A.J. Kresge, Y. Chiang, and L.E. Hakka, J.Amer.Chem.Soc., 1971, 93, 6167.

68. R.S. Ryabova, I.M. Medvetskaya, and M.I. Vinnik, Russ.J.Phys.Chem., 1966, 40, 182.

69. M.T. Reagan, J.Amer.Chem.Soc., 1969, 91, 5506.

70. H. Cerfontain, Mechanistic Aspects in Aromatic Sulphonation and Desulphonation, (John Wiley 1968).

71. W.E. Giauque, E.W. Hornung, J.E. Kunzler, and T.R. Rubin, J.Amer.Chem.Soc., 1960, 82, 62.

72. O. Mäkitie, Suomen Kemistilehti B, 1964, 37, 17-18.

73. J.T. Van Gemert, Aust.J.Chem., 1969, 22, 1883.

74. O. Mäkitie, R. Petrola, U. Aarnisalo, and J. Mäenpää, Ann.Acad.Sci.Fenn., Ser A2, 1972, 162, 5-15.

75. O. Mäkitie, Suomen Kemistilehti B, 1962, 35, 1-3.

76. H. Zollinger and W. Büchler, Helv.Chim.Acta., 1950, 33, 2002-10.

77. Y. Tanizaki, H. Inoué, and N. Ando, Bull.Chem.Soc. Japan, 1965, 38, 1419-25.

78. L.J. Desha, R.E. Sherrill, and L.M. Harrison, J.Amer.Chem. Soc., 1926, 48, 1493-1500.

79. A.G. Nasini, P. De Cori, Atti. III Congress Naz.Chim. Pura applicata, 1930, 668-78.

80. M. Déribéré, Ann.Chim.Anal.Chim.Appl., 1936, 18, 120.

81. K. Breitschwerdt, and A. Weller, Z.Physik.Chem. (Frankfurt), 1959, 20, 353-62.

82. K. Breitschwerdt, and A. Weller, Z. Elektrochem., 1960, 64, 395-9.

83. V.J.R. de Deyne, J. Chromatogr., 1967, 31, 260.

84. A. Albert, and E.P. Serjeant, Ionization Constants of Acids and Bases (Methuen 1962).

85. J.B. Birks, and I.H. Munro, Progress in Reaction Kinetics Vol. 4, 235 (Pergamon, Oxford, 1967).

86. S. Karamat Hussain, and P.A.H. Wyatt, J.Chem.Soc., Faraday Transactions I, 1970, 68, 130-134.

87. E.J. Land, and G. Porter, Trans.Faraday Soc., 1963, 59, 2016.

88. J.L. Rosenberg, and I. Brinn, J.Phys.Chem., 1972, 76, 3558 - 3562.

89. Eller, Ann., 1869, 152, 275.

90. A.V. El'tsov, O.P. Studzinskii, O.V. Kul'bitskaya, N.V. Ogol'tsova, and L.S. Éfros, J.Org.Chem., U.S.S.R., 1970, 6, 641.

91. K.P. Clark and H.I. Stonehill, J.Chem.Soc., Faraday Trans. I, 1972, 68, 577-591, and 1676-77.

92. H.I. Joschek and S.I. Miller, J.Amer.Chem.Soc., 1966, 88, 3269.

93. Kawasaki Hironobu, Kogyo Kagaku Zasshi, 1965, 68, 675-8.

94. G.J. Yakatan and S.G. Schulman, J.Phys.Chem., 1972, 76, 508.

95. K.K. Rohatgi and B.P. Sinhg, J.Phys.Chem., 1971, 75, 595.

96. H.E. Fierz, and P. Weissenbach, Helv.Chim.Acta., 1920, 3, 305.

97. C.A. Parker, and C.G. Hatchard, Nature 1961, 190, 165.

98. H. Yamatera, B. Fitzpatrick, and G. Gordon, J.Mol.Spectr., 1964, 14, 268-278.

99. K. Buijs, and G.R. Choppin, J.Chem.Phys., 1963, 39, 2035-41.

100. G.E. Walrafen, J.Chem.Phys., 1970, 52, 4176-98.

101. G. Brink, and M. Falk, Can.J.Chem., 1970, 48, 3019.

102. S. Subramanian and H.F. Fisher, J.Phys.Chem., 1972, 76, 84-89.

103. P. Dryjanski, and Z. Kecki, Rocz.Chem., 1970, 44, 1141.

104. G.E. Walrafen, J.Chem.Phys., 1971, 55, 768-92.

105. A.I. Sidorova, and I.N. Kochnev, Tepl.Dvizhenie Mol. Mezhmol. Vzaimodeistvie Zhidk.Rastvorakh, 1969, 168-72.

106. I.V. Matyash, and V.I. Yashkichev, Zh.Strukt.Khim, 1964, 5, 13-16.

107. P.S. Yastremskii, and O.Ya. Samoilov, Zh.Strukt.Khim., 1963, 4, 844-9.

108. R.A. Horne, D.S. Johnson and R.P. Young, J.Phys.Chem., 1968, 72, 866-75.

109. S. Taniewska-Osinka, and R. Grochowski, Lodz.Tow.Nauk. Wydz.III, Acta Chim., 1970, 15, 21-30.

110. P. Stern, and M. Volmer, Phys.Z., 1919, 20, 183.

111. S. Nagakura, and H. Baba, J.Amer.Chem.Soc., 1952, 74, 5693.

112. C.E. Newall and A.M. Eastham, Can.J.Chem., 1961, 39, 1752.

113. H. Cerfontain, Mechanistic Aspects in Aromatic Sulphonation and Desulphonation (John Wiley 1968).