

junctions were read by mercury thermometers. Low cycle fatigue was effected² as described earlier³. The sample wire of known length ($\sim 1\text{M}$) was hung vertically under 1 kg wt in a rotatable iron rod of 0.78 cm dia. One operation of winding and unwinding constituted one cycle. After a few cycles the wire broke at the lower end. Immediately the elongation ΔL was measured. A small piece ($\sim 20\text{ cm}$) was cut at the lower end and its TEP measured. The remaining wire was again subjected to a few cycles of operation and after breaking at the bottom the experiments were repeated.

Figure 1 shows the variation in TEP against the number of cycles each indicating $\Delta L/L$ observed which is a quantity proportional to the dislocation density. According to Brindley⁴

$$\text{TEP} \propto b \ln(x_0/x_n), \quad (1)$$

where x_0 is the initial wire length and x_n the length after n cycles and b is a constant. From (1) it follows that on cold work, TEP should increase on the negative side. The TEP of nickel is $-17.3\ \mu\text{V}/^\circ\text{C}$ and becomes more negative. This explains the general trend of increase in TEP of Ni on cold-worked fatigue.

Now the question arises: why do wires annealed at 290°C and 750°C behave in the opposite manner? According to Friedel⁵ at the recovery temperature (300°C in case of Ni) low angled boundaries are formed while at the recrystallization temperature (600°C for Ni) high angled boundaries are formed.

Such boundaries act as sinks for dislocations which move on cold work from the interior of the grain towards the boundaries. Thus the total dislocation density decreases and so does TEP.

Figure 2 shows the recovery of TEP with time. According to Brindley the softening rate is

$$(-dW/dr) = aW \exp(-Q/kT), \quad (2)$$

Q is the activation energy needed to eliminate the cold work effect. No distinction is made for Q corresponding to different annealing temperatures. Figure 2 shows this to be essential. Samples pre-annealed at different temperatures show different amount of changes in TEP for the same number of cold work cycles. In the present case annealing was first done and then the cold work while in the case of Brindley the processes were in a reversed order.

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PROTOTROPISM IN THIOMORPHOLINE

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HETEROALICYCLIC compounds are familiar as pharmaceuticals¹ and biochemicals². They are strongly basic³ which is ascribed to their nonaromaticity. Piperidine, a six-membered saturated cyclic compound, contains a heteroatom and nitrogen. The presence of a second heteroatom may alter the basic properties and the compound may function as a dual donor⁴. Thiomorpholine, containing nitrogen and sulphur atoms is capable of donating non-bonded electrons available with both the heteroatoms⁵. It may also act as a dual proton acceptor. The prototropism of thiomorpholine is studied and its basicity is discussed here.

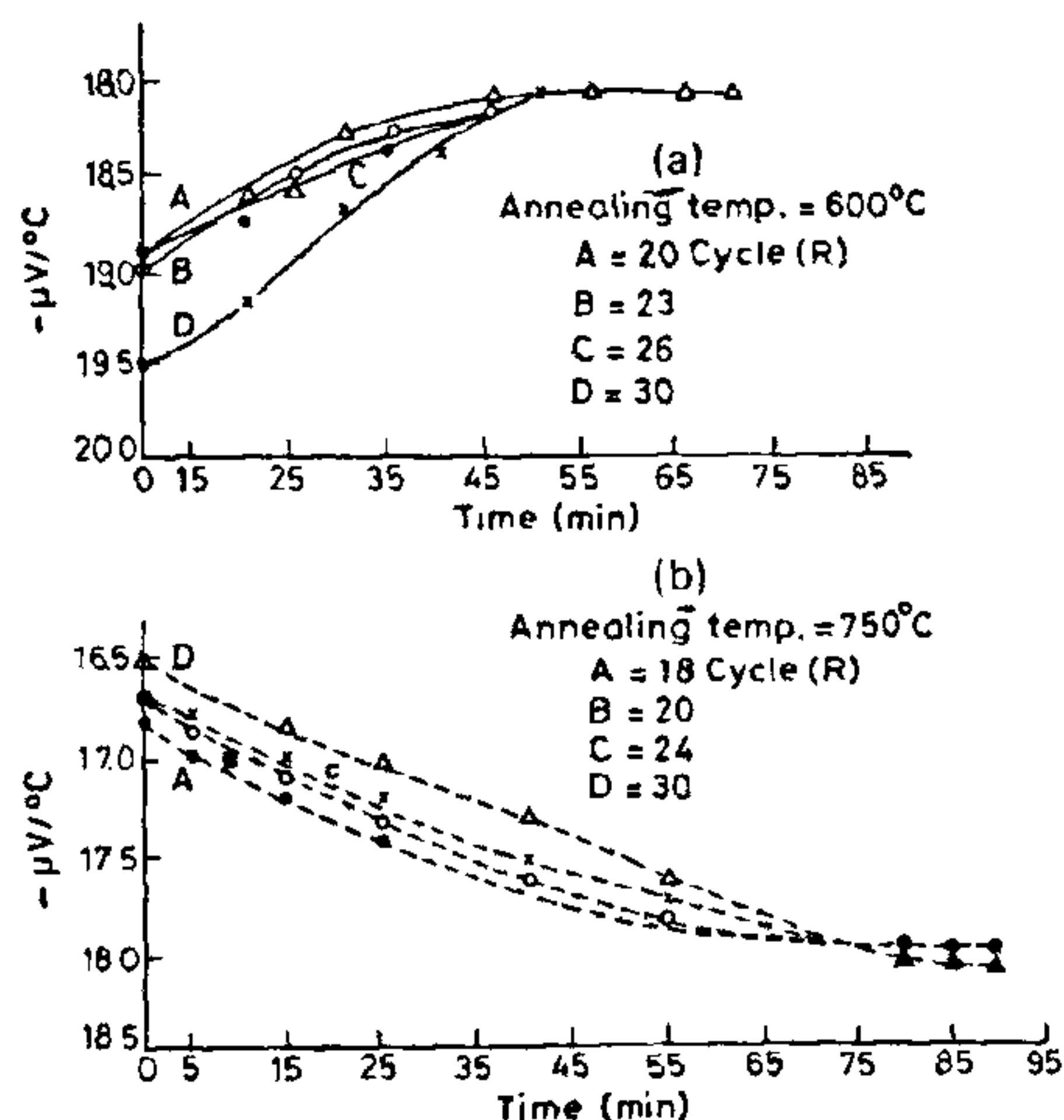


Figure 2. Recovery of thermo-emf in cold worked wires annealed at (a) 600°C , and (b) 750°C .

Thiomorpholine was purchased from Aldrich, USA, and purified by distillation over KOH. Aqueous solutions were prepared and the pH of the test solutions was measured as reported earlier⁶. A stock solution of 0.1 mol dm^{-3} thiomorpholine was prepared. An aliquot of 0.1 ml was delivered into a 10 ml volumetric flask each time and was added with a solution of known pH to make up to the mark. The electronic absorption spectrum was measured using a spectrophotometer (Systronics UV-VIS 108) with matched quartz cells of 1 cm path length. The absorption spectrum in non-aqueous solution was obtained by dissolving the solute in *n*-hexane or methanol and by measuring absorbance of the properly diluted solution.

The electronic absorption spectral data of thiomorpholine are presented in table 1. The molecule is completely saturated and hence $\sigma\sigma^*$ and $n\sigma^*$ transitions are only possible by electronic absorption. The present absorption transition of thiomorpholine in organic solvents is of $n\sigma^*$, the ground state (S_0) of which is generally stabilized in a more polar solvent⁷. This is true as there is a small blue-shift in the absorption maximum of the molecule from a non-polar solvent, *n*-hexane to a relatively polar solvent, methanol or water. Further, there are two non-bonded electronic energy levels in thiomorpholine due to the presence of two heteroatoms. The observed transition may be due to the excitation of a lone pair of nitrogen atom. This can be substantiated as follows: The absorption maximum in piperidine is about 225 nm and is due to a similar transition. The difference in ionization energies of two heteroatoms of thiomorpholine is $\sim 4 \text{ eV}$ and their non-bonded electronic energy levels are therefore separated to some extent. However, because of a probable weak interaction between them, the energy levels are well-placed distantly, leading to a more stabilized non-bonded electronic stage of nitrogen. Thus, the *n*-electrons of nitrogen lead to a higher energy transition and those of

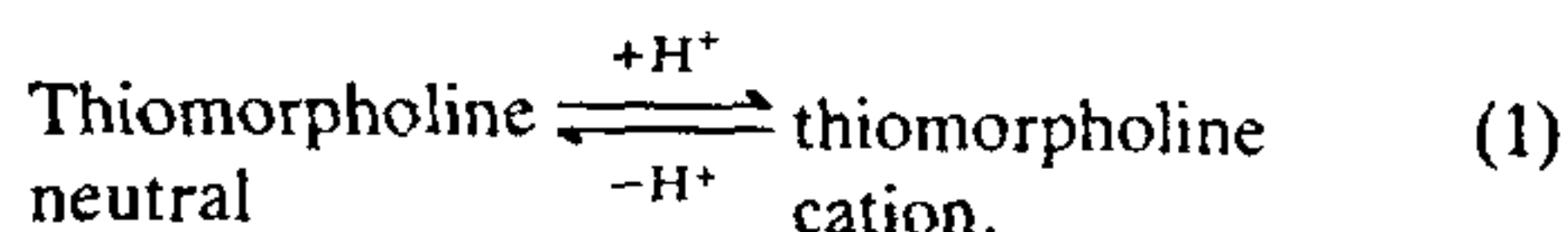
Table 1 Absorption maxima (λ) and molar absorptivity (ϵ) values of thiomorpholine

Solvent	λ , nm	ϵ , $\text{dm}^3/\text{mol}/\text{cm}$
Cyclohexane neat	223	1020
with 1% CF_3COOH	207	850
Methanol neat	220	1010
with 1% H_2SO_4	207	855
Water pH 12	219	980
pH 6	208	870

sulphur to a lower energy transition, in which the latter is not often allowed.

The absorption spectrum of thiomorpholine in *n*-hexane, methanol or in basic aqueous solutions is assigned to the neutral species. The spectral profile is almost identical in the region of pH 13 to 10. However, the absorption maximum is blue-shifted by 11 nm in solutions of $\text{pH} < 9$. This change is attributed to the formation of a monovalent cation. This is further manifested by the resemblance of the band maximum with that of the cyclohexane (205 nm ⁸). In acidic organic solvents, a similar blue-shift is observed (table 1) in comparison with that in neat solvents. The protonation is probably at the nitrogen atom as: (i) The electronegativity of nitrogen is greater than that of sulphur, and (ii) The sulphur atom is generally acidic than the nitrogen atom⁹. The absorption spectrum of the neutral species at pH 12 and that of the cation at pH 6 are depicted in figure 1.

The pK_a value for the prototropic equilibrium (1) calculated spectrophotometrically is found to be 8.84.



For such a prototropic equilibrium in piperidine, piperazine and morpholine, the pK_a values are reported³ to be 11.2, 9.7 and 8.4 respectively. The basicity is reduced from a monoheteroatom contain-

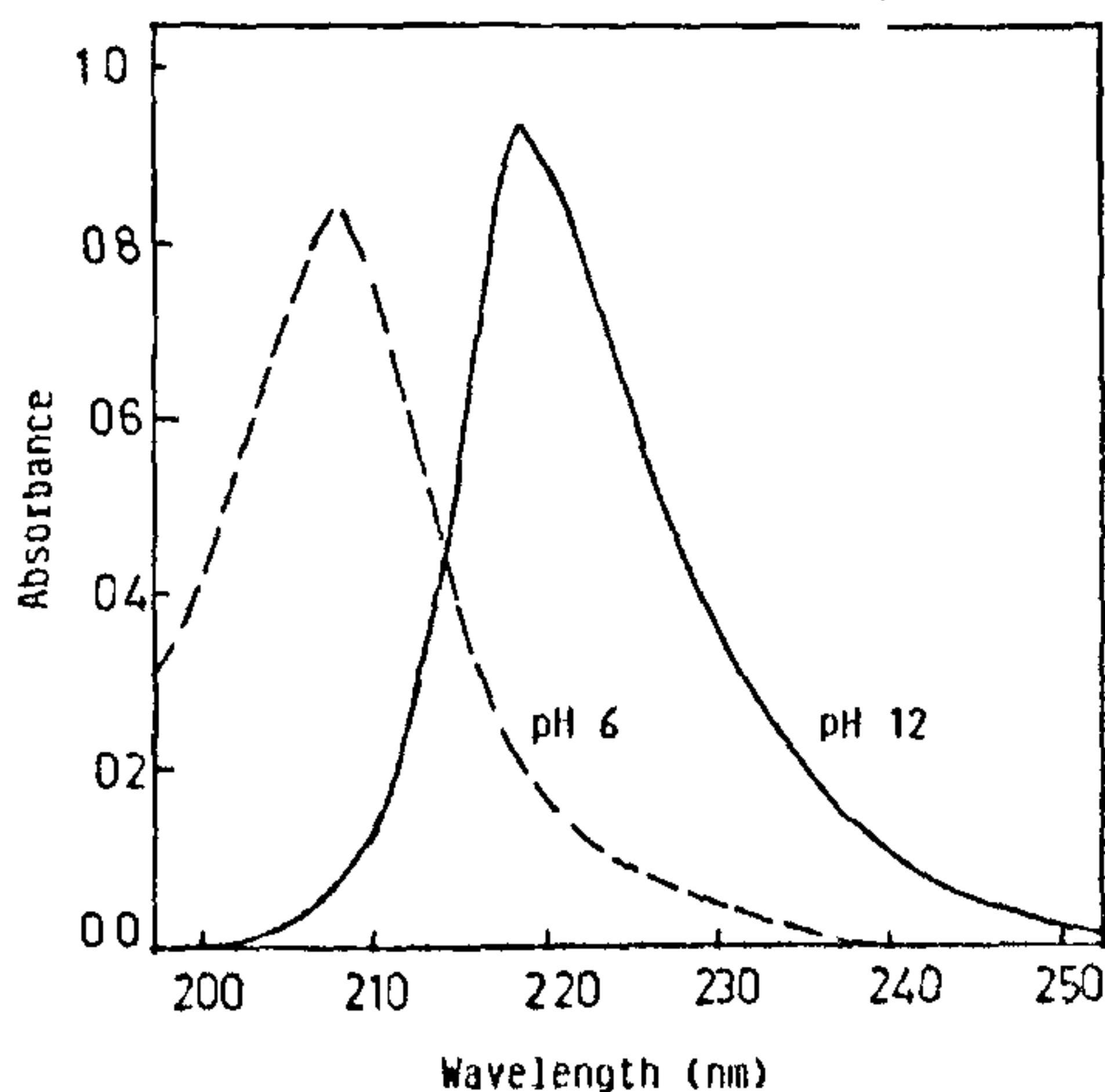


Figure 1. Absorption spectra of thiomorpholine [—, neutral and ---, cation. Concentration = $9.3 \times 10^{-4} \text{ mol dm}^{-3}$].

ing piperidine to compounds having two heteroatoms. This can be attributed to the presence of the second heteroatom in the ring system and possibly through the inductive effect. The pK_a value of thiomorpholine further indicates that its basicity lies between those of piperazine and morpholine. In the case of thiomorpholine and morpholine, the decrease in the basicity is accounted for the existence of two n -electron pairs on the sulphur or oxygen atoms. Between thiomorpholine and morpholine, the former is slightly basic. This can be explained on the basis of: (i) Oxygen being more electronegative than sulphur, and (ii) Sulphur being of larger size than oxygen, as a result of which the lone pair repulsions become slightly less prominent as compared to the perturbation of the lone pair at the nitrogen atom of thiomorpholine.

The basicity of heterocyclic molecules in the excited singlet states cannot be predicted directly owing to the non-fluorescent nature of such molecules. However, in the present case, the Förster cycle method¹⁰ is used to evaluate the pK_a value in the excited singlet state.

$$pK_a(S_1) = pK_a(S_0) - 2.1 \times 10^{-3}(\bar{\nu}_A - \bar{\nu}_B), \quad (2)$$

where $\bar{\nu}_A$ and $\bar{\nu}_B$ are the wavenumbers of the conjugate acid and base respectively. This value of 3.78 indicates that thiomorpholine cation becomes acidic upon excitation, corroborating earlier results in some imidazole derivatives⁶.

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PHASE RULE STUDIES OF BINARY SYSTEMS INVOLVING SULPHOXIDES AND PHENOLS — AN INTERESTING CASE OF COMPOUND FORMATION

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WITH a view to studying the possible interaction between sulphoxides and phenols, the phase diagrams of eight binary systems, each consisting of a sulphoxide and a phenol, have been studied (table 1). The choice of the compounds was restricted as they have to be solids. All the systems except the one with methyl 4-nitrophenyl sulphoxide and *p*-nitrophenol form simple eutectics. Methyl 4-nitrophenyl sulphoxide and *p*-nitrophenol showed the formation of a compound with a congruent melting point at 104°C and an equimolar composition.

Having found from the phase diagram the formation of a compound between methyl 4-nitrophenyl sulphoxide and *p*-nitrophenol, the compound was prepared by mixing the components in 1:1 ratio (molar), melting, thoroughly mixing and solidifying the melt. It could be crystallized from benzene-petroleum ether (b.p. 70–80°C). Attempts to crystallize it from polar solvents like ethanol resulted in its dissociation into individual components. The compound melted at 104°C which is exactly the same as that shown by the phase diagram.

The IR spectrum of the compound and the spectra of the nitrophenol and sulphoxide, from which it is formed, were taken using methylene chloride as solvent. The characteristic bond frequencies are given in table 2. The data confirm the formation of the compound. The sulphoxide has a strong band due to S–O stretching at 1082 cm⁻¹ (Barnard *et al*¹ found a strong band near 1050 cm⁻¹ for sulphoxides). The S→O (or S = O) bond of the sulphoxide gives rise to two S–O bonds (S–OH and S–