II- STUDIES OF SOLID COMPLEXES

1. Preparation of the solid complexes:

Solid complexes of stoichiometric ratio (1:1) were prepared by mixing equimolar quantities of a drug and reagent in hot solutions of dichloroethane or 95 % ethanol. The crystals formed were washed with petroleum ether (40-60) to eliminate moisture and then preserved over silica gel.

2. Elemental analysis:

Elemental analysis (C,H and N) of the prepared charge transfer complexes were done in the micro-analytical center, Cairo university, Giza, Egypt.

3. Absorption spectra of solid complexes:

In this investigation, the nujol mull technique[41] was applied to obtain the electronic absorption spectra of various complexes in the solid state. Thus, the crystal form of the investigated specimen cannot be destroyed (contrary to the case when using the solvent technique). The powder material was mixed well in an agate mortar with nujol oil (BDH) until complete homogeneity. From this mixture transparent windows were made using Whatmann filter paper sheets N$^{o.}$1. In each run a reference window prepared from the nujol without material was used to compensate light scattering.

The electronic absorption spectra were recorded in the range 200-600 nm by the aid of **JASCO** V530 *UV/Vis* spectrophotometer (Japan).

4. IR spectra:

The IR spectra were recorded for the solid state complexes and ligand applying KBr technique using **FT-IR,** Bomem spectrophotometer-*Hartman* and *Braun* MB157 (Canada). For preparing the disc containing the CT complexes, the compound was mixed with the finely powdered KBr to minimize grinding time and hence avoiding the adsorption of the CT complexes on the surface of KBr[42, 43,44], which may lead to its destruction into its original components [45].

5. Melting points:

The melting points were measured by using an ordinary Gallen Kamp tube melting apparatus.

Results & Discussion

Results and discussion

➢ SPECTROPHOTOMETRIC STUDIES OF DRUG COMPLEXES IN SOLUTION

I- Absorption spectra of sulfamethoxazole with reagents I, III and IV:-

In order to investigate the optimum conditions of drug-reagent complex formation, the following studies should be taken in consideration:

1. Effect of pH:

The effect of pH on the complex formation between sulfamethoxazole and reagents o-chloranil, 2,4 dinitrophenol and picric acid (I, III and IV, respectively) was studied in universal buffer solutions of pH range 3.35-11.15. A portion (1.0 mL) of 5.0 $x10^{-3}$ M reagent I or 1.0 mL of 1.0 $x10^{-2}$ M reagent III or IV, 1.0 mL of (200 µg/mL) drug and 3.0 mL buffer of different pH values were mixed well. The volume was completed to 10 mL with bidistilled water. The absorption spectra were recorded using a blank solution prepared in the same way without drug at the same pH value. Illustrative spectra are shown in Figs. (1-a), (2-a) and (3-a) for reagents I, III and IV respectively. Inspection of these figures shows that the optimum pH values giving maximum absorption recommended for subsequent studies of drug-reagent complexes, are 8.23, 5.25 and 11.15 on using reagents I, III and IV, respectively.

2. Determination of λ_{max} of complex species :

For determining the value of λ at which complex species possesses the maximum absorption, the following spectra must be recorded:

A- Spectrum of pure drug 1.0 mL of 200 µg/mL at the optimum pH value using buffer solution at the recommended pH value as a blank.

B- Spectrum of pure reagent 1.0 mL of 5.0×10^{-3} M for reagent I or 1.0 mL of 1.0×10^{-2} M for reagents III and IV at the optimum pH value using the same buffer as a blank.

C- Spectrum of solution mixture of drug (A) and reagent of (B) at the optimum pH value using the same buffer as a blank.

D- Spectrum of solution (C) against (B) as a blank.

The absorption spectra are shown in Figs (1-b), (2-b) and (3-b) for reagents I, III and IV, respectively. Such figures show that the formed complex absorbed maximally at 550, 440 and 450 nm for the three reagents, respectively. These optimal wavelengths are chosen for further investigations.

3. Effect of time and temperature:

The effect of time on complex formation was studied by measuring the absorbance of the complexes at optimum pH against a blank solution of the same pH at various time intervals. Also, the effect of temperature was studied for the same solution by incubating the sample and blank in a water bath at different temperatures (25-45 °C). The absorbance was measured after cooling to room temperature.

The experiments showed that complexes are formed simultaneously after mixing drug and reagent and remain stable for about two hours. Also, it

was found that, increasing the temperature up to 45 °C has a slight effect on the absorbance above which the colour began to fade slowly.

4. Effect of sequence of addition:

The effect of sequence of addition on complex formation was studied by measuring the absorbance of solutions prepared by different sequences of addition against a blank solution prepared in the same manner. Experiments showed that the best sequence of addition is drug-buffer-reagent.

5. Effect of reagent concentration:

To study the effect of reagents I, III and IV concentration on the complex formation, the concentration of drug was kept constant at 200 µg/mL while that of reagent was varied regularly. The resulted spectra showed that 1.0 mL of 5.0×10^{-3} M of reagent I and 1.0×10^{-2} M of reagent III or IV is sufficient for complete complexation.

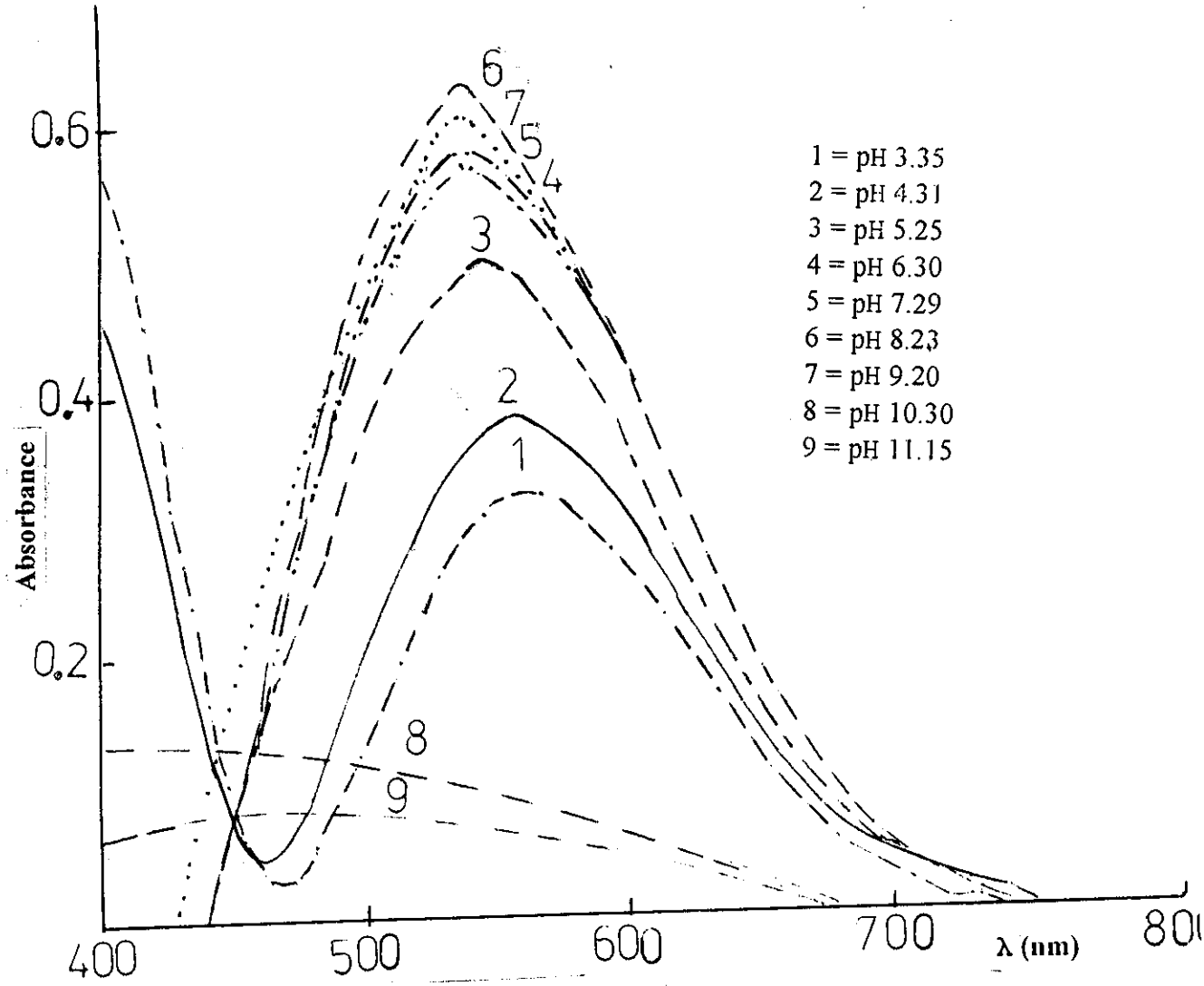

Fig. (1-a) Effect of pH on the absorption spectra of sulfamethoxazole - o-chloranil complex.

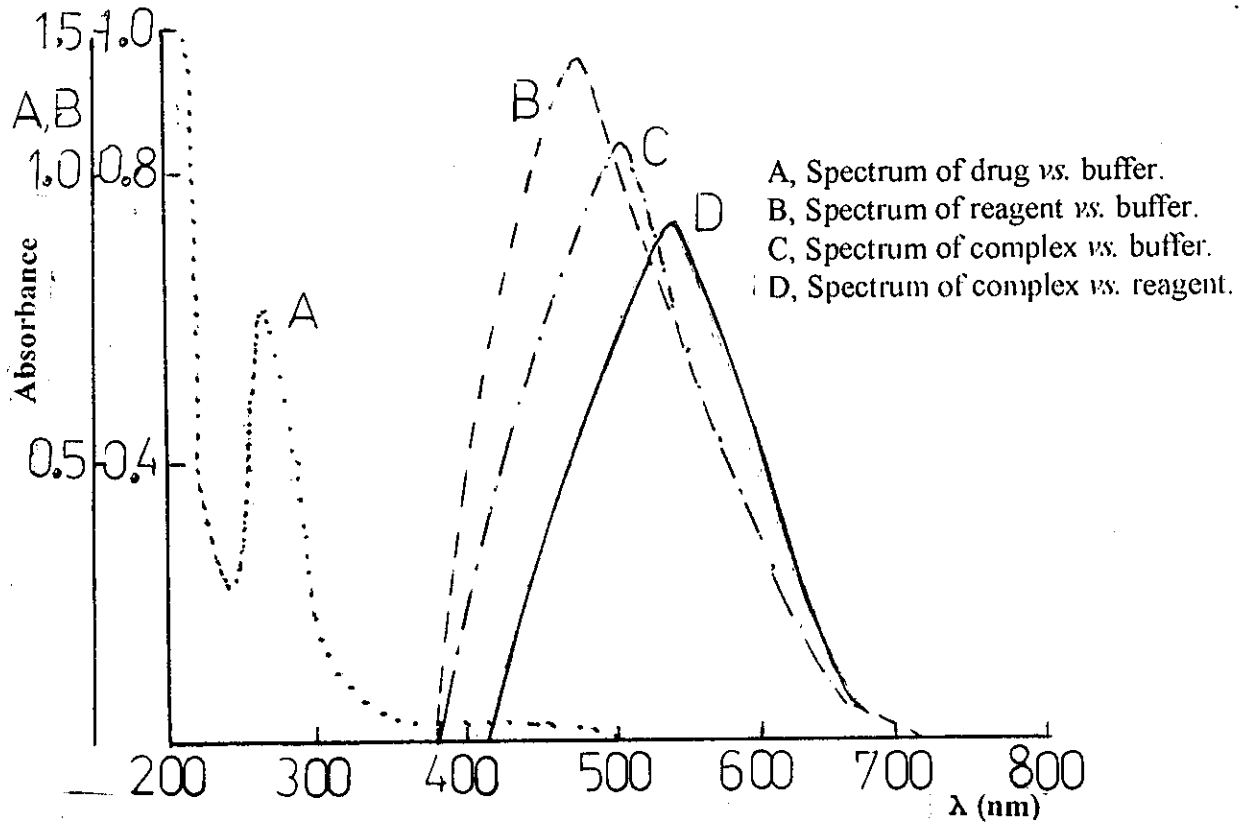

Fig. (1-b) Determination of λ_{max} of sulfamethoxazole- o-chloranil complex at pH 8.23.