
Colorimetric Determination of Menadione Sodium Bisulphate with Chloranilic Acid

U. AJALI, G. B. OKIDE AND U. E. ODO*
Department of Pharmaceutical Chemistry,
University of Nigeria, Nsukka, Nigeria.

Menadione sodium bisulphate was determined colorimetrically with chloranilic acid. It forms instantaneous purple charge transfer complex with chloranilic acid in ethanol-dioxan mixture, which had λ_{\max} at 510 nm. The complexation was maximum at room temperature and at 30 min after mixing the reactants. The molar absorptivity and association constant for the complex were determined to be 147.4 l/mol/cm and 1.32 l/mol, respectively. The standard free energy change for the complex was calculated to be 6.85 kcal/mol. The percentage recovery for the assay of the tablets was 97.6% while the experiment was obtainable at the concentration range of 0.2–1.1 mg % menadione sodium bisulphate.

Charge-transfer complexation is the interaction between electron donor and electron acceptor moieties which are in close proximity. For such interaction to occur there is a jump of a pair of electron initially occupying a molecular orbital in an acceptor in such a way that the excited electrons still remain paired to its original electron partner. The electron donor and acceptor moieties then orient themselves relative to one another in such a way as to make a maximum overlap. Charge-transfer complexation has been thoroughly discussed by Slifkin¹. Charge-transfer complexes can be determined spectrophotometrically through Beer-Lamberts Law². This complexation has been employed in determination of emetine³, piperazine⁴, atropine⁵, aminopenicillins⁶, promethazine hydrochloride⁷, albendazole⁸ and cimetidine⁹.

Menadione, 2-methyl-1,4-naphthoquinone, is a bright yellow crystalline powder with very faint acrid odor or nearly odorless. It is stable in air but is decomposed by light. It melts between 105–107° and is insoluble in water but soluble in alcohol benzene, vegetable oil, chloroform and carbon tetrachloride. It is used in the prophylaxis and treatment of hypoprothrombinemia¹¹. Menadione is assayed by reduction to the corresponding naphthaquinol, which is then

oxidatively titrated with ceric sulphate¹².

This work aims at quantitative determination of menadione sodium bisulphite in dosage forms through charge transfer complexation with chloranilic acid. Stability constant and free energy change for the complex are also determined.

MATERIALS AND METHODS

The reagents used were of analytical grade and were sourced commercially. Chloroform and ethanol were products purchased from May and Baker, England while 1,4-dioxan and p-chloranilic acids were obtained from BDH Chemicals Poole Ltd., England. Menadione sodium bisulphite tablets were products of Vardhman Exports, Mumbai, India. SP8-100 UV spectrophotometer a product of Pye Unicam, England, was used to measure absorbances.

Preparation of solutions:

Five millimoles per liter of chloranilic acid was prepared by dissolving 0.1045 g chloranilic acid in 100 ml of 1,4-dioxan. Other concentrations were obtained by dilution with dioxan. One hundred tablets of menadione sodium bisulphite were pulverized and were extracted with enough quantity of ethanol. The extract was evaporated to dryness to obtain a solid residue, which was decolorized with bone

*For correspondence

charcoal and recrystallised twice in ethanol. The crystalline powder obtained melted at 106°. Five millimoles per liter of menadione sodium bisulphite was prepared by dissolving 0.04305 g of the crystalline powder in ethanol. Other standard solutions were obtained by dilution with ethanol.

Determination of absorption spectra:

Chloranilic acid in dioxan, 2.5×10^{-3} M was scanned in a wavelength range of 200–500 nm against a blank of dioxan. Menadione sodium bisulphite in ethanol, 2.5×10^{-3} M, was scanned in a wavelength range of 200–500 nm against an ethanol blank. Two milliliters of 2.5×10^{-3} M of chloranilic acid was mixed with 3 ml of 2.5×10^{-3} M menadione sodium bisulphite and the mixture was scanned over a wavelength range of 400–600 nm against a mixture of 2 ml of dioxan and 3 ml of ethanol.

Effect of time on menadione sodium bisulphite: chloranilic acid complex formation:

Absorbances of a mixture of 2 ml of 2.5×10^{-3} M chloranilic acid and 2 ml of 2.5×10^{-3} M menadione sodium bisulphite were measured at different time intervals and at 510 nm against a blank of 3:2 ethanol-dioxan mixture.

Effects of temperature on the complex formation;

The absorbances of a mixture of 3 ml of 2.5×10^{-3} M menadione sodium bisulphite and 2 ml of 2.5×10^{-3} M chloranilic acid were measured at different temperatures, and at 510 nm against a blank of 3:2 ethanol-dioxan mixture, after 30 min of mixing the reagents.

Determination of the stoichiometry of the complex:

Job's method of continuous variation was used¹³. Different molar ratios of menadione sodium bisulphite and chloranilic acid mixtures were prepared by mixing different volumes of equimolar, 5.0×10^{-3} mol/l, solutions of chloranilic acid and menadione sodium bisulphite. The absorbances of the mixtures were measured at 510 nm and at room temperature, after 30 min of mixing the reactants. The solvents were mixed in the ratio they occur in the reaction media and were used as blank.

Determination of association constant, molar absorptive free energy change and Beer-Lambert's limit for the complex:

Bensi-Hildebrand method was used¹⁴. Serial volumes (0.4, 0.8, 1.2, 1.6, 2.0, 2.4 ml) of 2.3×10^{-3} M menadione sodium bisulphite were transferred into different tubes and 1.0 ml of 5.0×10^{-3} M chloranilic acid was added to each test tube.

The content of each test tube was mixed and left for 30 min at room temperature. The absorbances of the mixture were measured at 510 nm against a blank of dioxan-ethanol mixture in the ratio they occur in the reaction media. Different concentrations of the complex were prepared and their absorbances measured. A plot of concentrations against absorbances was made and the range of linearity was measured and recorded.

Assay of menadione tablets:

An amount of pulverized menadione sodium bisulphite tablets equivalent to 10 mg of menadione was extracted with ethanol and the solution was made up to 100 ml with ethanol. Known volumes of the filtrate were taken and required amount of chloranilic acid was added to each. The mixtures were allowed to stand for 30 min after mixing the reactants and the absorbances of the mixtures were measured at 510 nm against mixtures of the solvents in the ratio they occur in the reaction media. The percentage recovery was calculated.

RESULTS AND DISCUSSION

Instantaneous golden purple colour was observed on mixing menadione sodium bisulphite in ethanol with chloranilic acid in dioxan. This colour development was as a result of charge transfer complexation, which was supported by the blue shift observed in the spectra detailed in fig. 1. Menadione sodium bisulphite, chloranilic acid and menadione sodium bisulphite-chloranilic acid complex had wavelength of maximum absorbances of 420, 290 and 510 nm, respectively.

The complexation was completed 30 min. after mixing the reactants, as was indicated in fig. 2. Increase in temperature caused an increase in absorbance to a certain limit after which decrease in absorbance was observed. This is shown in fig. 3. Room temperature seems to favour the complex formation. Through Job's method of continuous variation¹³ the stoichiometry for the complex was 3:2 menadione sodium bisulphate:chloranilic acid, shown as fig. 4. This was supported by the intensity of the colour of the complex formed by different proportions of the menadione salt and chloranilic acid, which increased when menadione sodium bisulphite had greater number in a ratio. In this interaction, menadione sodium bisulphate acts as electron donor while chloranilic acid acts as electron acceptor. The Beer-Lambert's range was found to be 0.2-1.1 mg% (w/v) menadione sodium bisulphite.

Benesi-Hildebrand method was used to determine

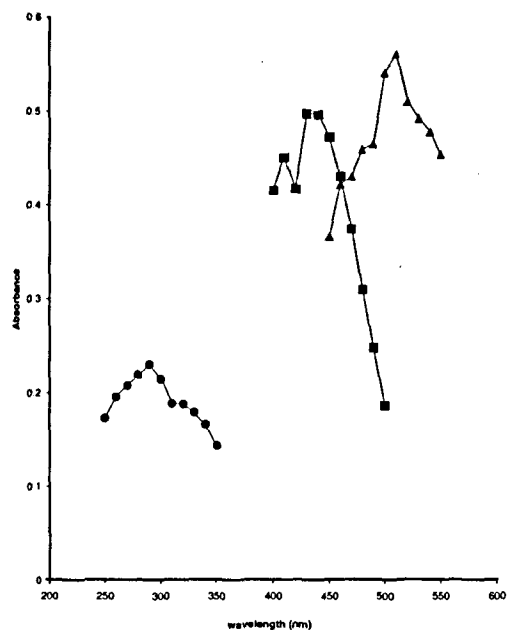


Fig. 1: Absorption spectra of P-chloranilic acid, menadione sodium bisulphite and menadione sodium bisulphite-chloranilic acid complex.

Absorption spectra of menadione sodium bisulphite in ethanol (-●-), chloranilic acid in dioxane (-■-) and menadione sodium bisulphite-chloranilic acid complex in ethanol dioxane mixture (-▲-)

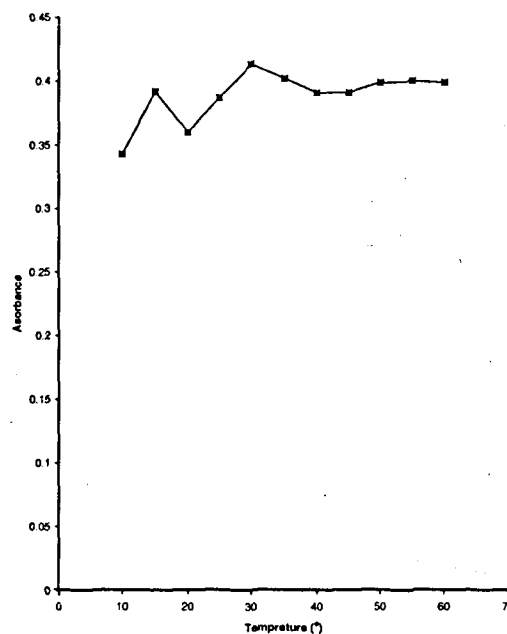


Fig. 3: Effects of temperature on the absorbance of menadione sodium bisulphite-chloranilic acid complex

This shows the absorbances of a mixture of 2.3×10^{-3} M chloranilic acid and 5.0×10^{-3} M menadione sodium bisulphite in a mixture of chloroform and dioxan at different temperatures.

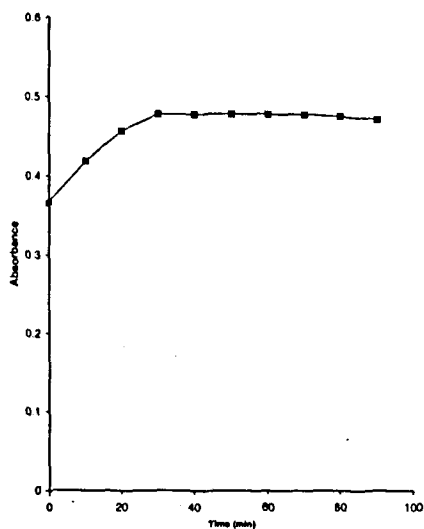


Fig. 2: Absorbance of menadione sodium bisulphite-chloranilic acid complex at different time intervals.

The absorbances of a mixture of 2.3×10^{-3} M of chloranilic acid and 5.0×10^{-3} M of menadione sodium bisulphite in chloroform - dioxan mixture at different time intervals.

associated constant and molar absorptivity. This depends on the fact that one of the component's (chloranilic acid) is in excess so that its concentration is virtually unaltered on formation of a complex. The molar absorptivity and association constant were 1.4738×10^2 M/cm and 1.32 l/mol, respectively. The standard free energy change, ΔG for a complex is related to association constant by Eqn. 1, $\Delta G = -2303 RT \log K$, where R, T and K are universal gas constant, absolute temperature in Kelvin and association constant, respectively.

Using equation 1, ΔG is calculated to be -6.8530 K cal/mol. The complexation is spontaneous and the value is below 30 Kcal/mol. These results supported charge transfer complexation. The mean percentage recovery for the assay tablets was 97.6%. This indicates high degree of accuracy. This method is precise, reproducible and can be employed in assay of menadione sodium bisulphate even in dosage forms. When compared with the ordinary titrimetric method, this method can determine menadione sodium bisulphite at a lower concentration with accuracy.

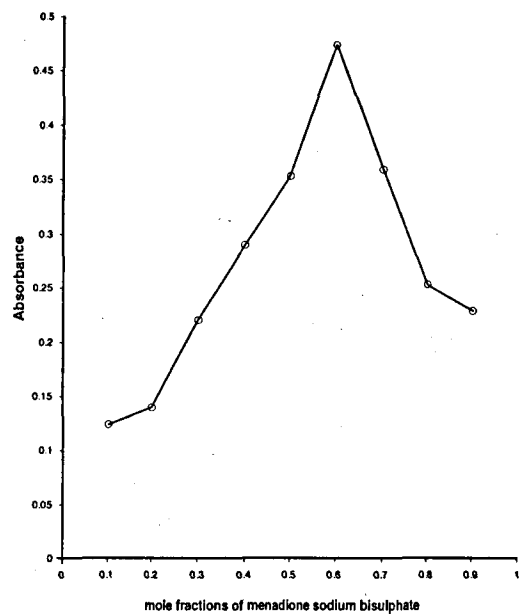


Fig. 4: Job's plot for menadione sodium bisulphate-chloranilic acid complex.

The mole fractions of menadione sodium bisulphite were prepared by mixing different volumes of equi-molar concentrations (5.0×10^{-3} M) of menadione sodium bisulphite in chloroform and p-chloranilic acid in dioxan.

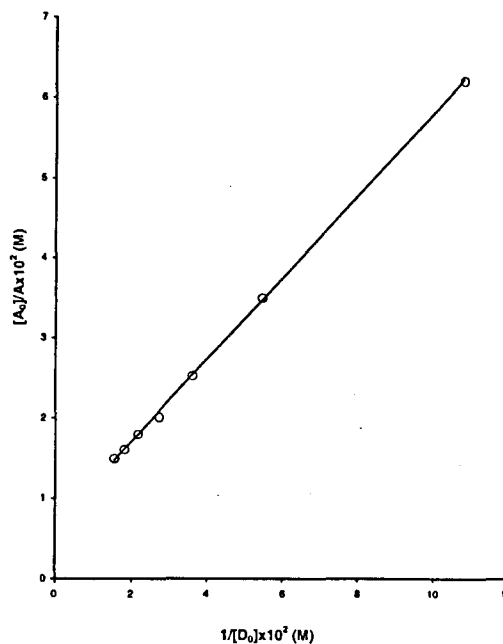


Fig. 5: Benesi-Hildebrand plot for menadione sodium bisulphite-p-chloranilic acid complex.

[A₀], [D₀] and A represent concentration of chloranilic acid, concentration of menadione sodium bisulphite and absorbance, respectively.

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