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Short communication

Schiff bis bases: analytical reagents. II. Spectrophotometric determination of manganese from pharmaceutical forms

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Abstract

By condensing ethyl-*o*-hydroxybenzene with ethylene diamine, and 1-ethyl-salicylidene bis ethylene diamine, a Salen-type Schiff bis base is obtained. These Schiff bis bases present a good capacity of complexing the Mn(II) ions, resulting brown complexes. In this paper, the results of a study concerning the use of the Schiff bis base as reagent in spectrophotometric determination of the Mn(II) is presented. The above mentioned Schiff bis base forms a brown complex with Mn(II) cation, with maximum absorbance at 460 nm, and molar absorbtivity ($\bar{\varepsilon}$) = 9.8×10^4. The complex with Mn(II) presents a maximum stability at pH 6.0. The combination ratio was established by isomolar series method, and it is 1:2 (metal:ligand). The calculated apparent stability constant is $\bar{\beta}_n = 2.943 \times 10^{-5}$. The absorbance is proportional to Mn(II) concentration in the range of 10–70 μg ml^{-1}. In this range, the Lambert–Beer law is respected, the linearity coefficient being 0.9989, S.D. = 0.83, R.S.D. = 0.88 ($n = 7$). In these conditions, the complexation reaction of Mn(II) is interfered by other cations, Fe(II); Fe(III); Ni(II). The results obtained for spectrophotometric determination of Mn(II) using this Schiff base as reagent were successfully applied to pharmaceutical products containing Mn(II) cation.

Keywords: Schiff bis bases reagents; Spectrophotometric determination; Manganese; Pharmaceutical forms

1. Introduction

Schiff bis bases are characterised by their capacity to completely co-ordinate a metal ion, forming chelate rings [1].

Covalent or coordinative binding of Schiff bis base chelates in polymeric chains through metal atom determines their important properties, like, oxygen molecules binding; light energy conversion (photo-redox reactions); catalytic epoxidation of olefins and electrocatalytic properties; electric conductivity; thermic stability [2,3].

By condensing ethyl-*o*-hydroxyphenyl ketone with ethylenediamine, the 1-ethyl-salicylidene bis ethylene diamine (**I**) [4], a Salen-type Schiff bis base is obtained (Fig. 1).

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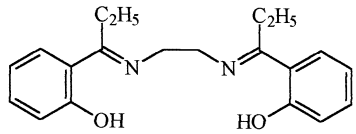

(I)

Fig. 1. Salen-type Schiff bis base obtained.

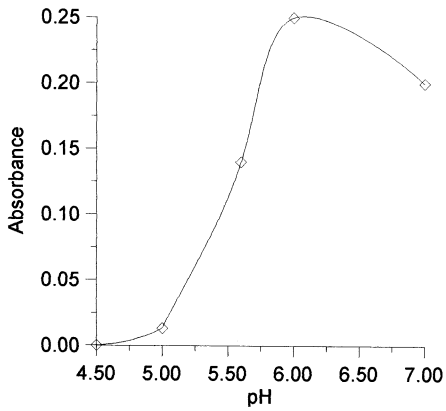

Fig. 2. Influence of pH ([R] = 0.25%; $[Mn^{2+}] = 30$ μg ml^{-1}).

The reagent is a citrine-yellow crystalline powder, m.p. = 138–139 °C, insoluble in water, soluble in ethanol, methanol, very soluble in acetone.

This Schiff bis base has a good capacity of ions Mn^{2+} complexation, with which forms brown complexes.

In this paper, the results of a research concerning Schiff bis base (**I**) utilisation as reagent for manganese spectrophotometric assay is presented. The spectrophotometric method is simple, selective and fast. The complex has a molar absorbtivity $\varepsilon = 9.8 \times 10^4$ at $\lambda_{max} = 460$ nm, greater than other cited reagents, with formaldoxime [5] ($\varepsilon = 1.12 \times 10^4$ at 460 nm); with tetrasodium hydroxycalix-4-arene-*p*-sulfonate [6] ($\varepsilon = 8.46 \times 10^4$ at 510 nm); with antipyryl-*p*-methoxyphenylmethane [7] ($\varepsilon = 10.4 \times 10^4$ at 450 nm); with diantipyryl (*p*-methoxy) phenylmethane [8] ($\varepsilon = 5.45 \times 10^4$ at 450 nm); with rhodamine 6G [9] ($\varepsilon = 6.5 \times 10^4$ at 525 nm). Only neotetrazolium chloride [10] is superior ($\varepsilon = 9.1 \times 10^5$ at 240 nm).

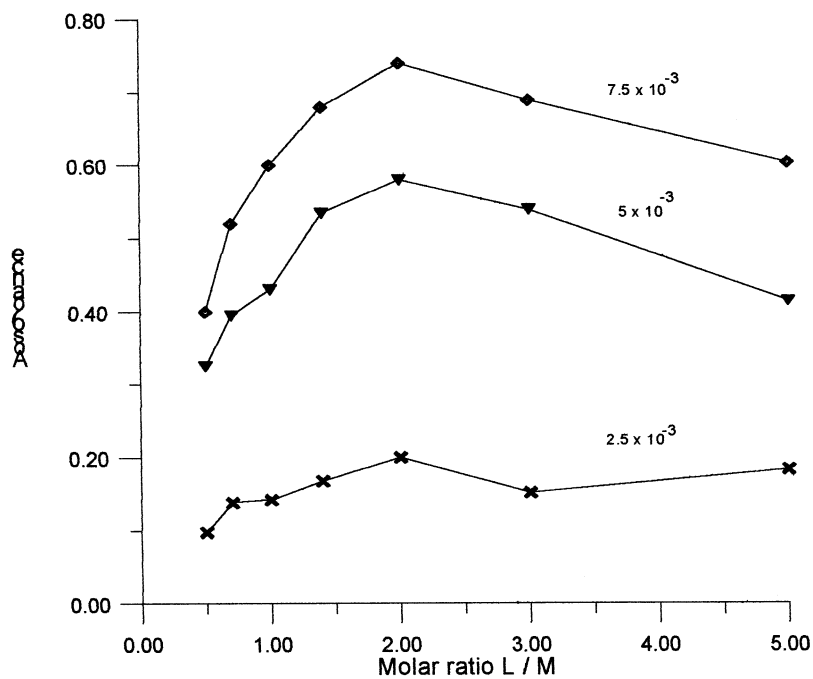

Fig. 3. Molar ratio L/Mn(II).

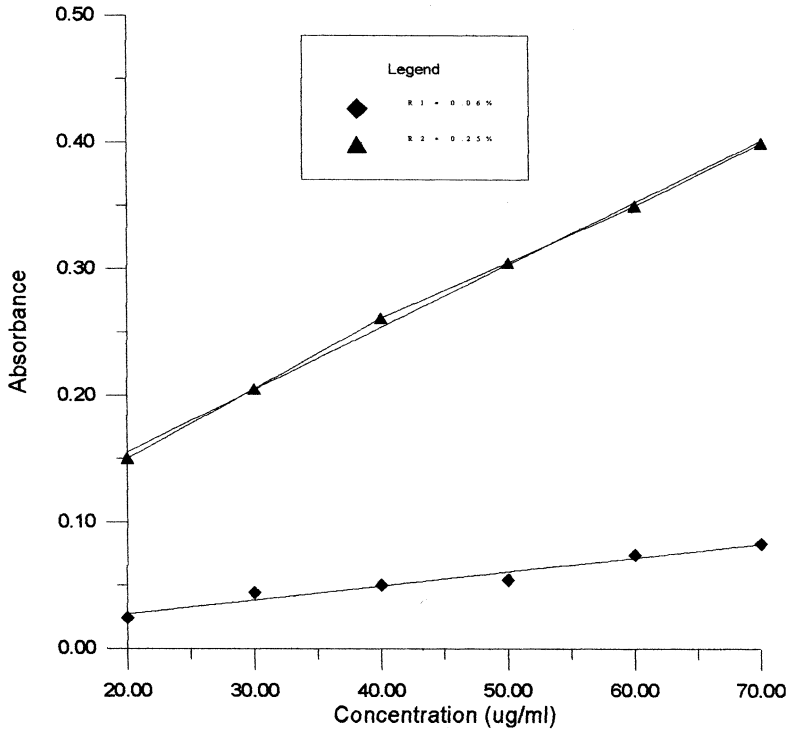

Fig. 4. Influence of reactive quantities for Mn(II).

2. Material and methods

1. Mn^{2+} stock solution, 0.1 mg ml^{-1}. $MnCl_2 \times 4H_2O$ (0.0360 g) is dissolved in 5 ml 36% HCl and water is added up to 100 ml. Etalon solutions with concentrations ranging between 10 and 50 μg ml^{-1} are prepared from this stock solution.
2. Solution reactive 0.25% (w/v) in absolute methanol.
3. Buffer, pH 6 (0.3920 g CH_3COOK are dissolved in 100 ml bidistilled water; pH is adjusted with CH_3COOH 0.04 M).
4. Electronic pH-meter Seibold-Wien.
5. Spectrophotometer ultraviolet–visible (UV–vis) Hewlett Packard 8453 E.

3. Reaction study between (I) and Mn^{2+} ions

1. Schiff bis base (**I**) forms with Mn^{2+} cations a brown complex, with maximum absorbance at 460 nm.
2. Because of pH influence upon complexation reaction, the absorbance variation as a concentration function was studied. Sodium acetate–acetic acid 0.2 M, and potassium acetate–acetic acid buffers was used, with pH ranging between 4.5 and 7.0. From Fig. 2, it can be seen that the optimum pH for Mn^{2+} complex formation is 6.0.
3. Combination rate was established by isomolar series method and it is illustrated in Fig. 3.
4. Stability apparent constant was established in concordance with relation [11]:

$$\beta_n = \left(\frac{\log C_{M^{x+}} C_L}{\log A - n \log V} \right)$$

where $C_{M^{x+}}$ is the cation concentration; C_L the ligand concentration; $\beta_n = 2.943 \times 10^{-5}$; A the absorbance; n the coordination number; and V is the solution volume (ml).

5. The reagent quantity influence upon complex with Mn^{2+} formation at pH 6 was studied.Thus, for a concentration of 30 μg ml^{-1} Mn^{2+}, adding 1 ml 0.025% R, the complexation reaction does not take place.Using a Mn^{2+} etalon solution with a concentration ranging between 20 and 70 μg, at pH 7 and adding 1 ml R 0.060%, raising absorbance values are obtained. For the same Mn^{2+} concentration, when adding 1 ml R 0.25%, absorbance values are much higher (Fig. 4). If 1 ml R 0.50% is added in the same conditions, precipitate results, that is not dissolving in methanol, when solution is completed to 5 ml.
6. To explain this complexation reaction of Mn^{2+} with Schiff bis base, the stability of this complex was also studied. From Fig. 5 is can be stated that after 10 min from reactive addition, the absorbance has a maximum peak, which is maintained at least 20 min, enough time for samples processing.
7. Absorbance is proportional with Mn^{2+} concentration for the range of 10–70 μg ml^{-1}. Lambert–Beer law is respected in this interval ($\bar{\varepsilon} = 9.8222 \times 10^4$); the linear coefficient being $r = 0.9989$.

   Slope $= 0.004989 \pm 8.28 \times 10^{-5}$;

   Intercept $= 0.05424 \pm 0.003714$;

   Lr $= 2$ μg; $D = 2 \times 10^{-6}$

8. In the same reaction conditions, there are others cations that form complexes, Ni^{2+} with maximum absorbtion at 440 nm ($\varepsilon = 1.76 \times 10^5$ mol l^{-1} cm^{-1}), Co^{2+} with $\lambda_{max} = 550$ nm ($\varepsilon = 5.28 \times 10^4$ mol l^{-1} cm^{-1}), Fe^{3+} with $\lambda_{max} = 490$ nm ($\varepsilon = 4.48 \times 10^5$ mol l^{-1} cm^{-1}) and Fe^{2+} with $\lambda_{max} = 495$ nm ($\varepsilon = 5.40 \times 10^5$ mol l^{-1} cm^{-1}). Complexation reaction is interfered by Fe^{2+} (if concentration exceeds 3

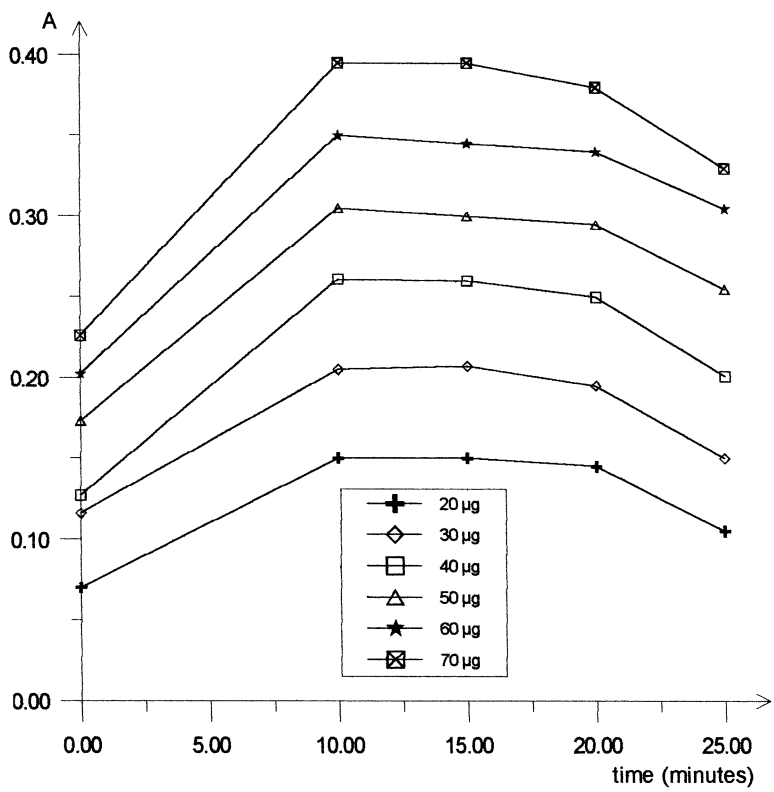

Fig. 5. Complex stability.

Table 1
Spectrophotometric determination of Mn(II) with Schiff bis base (**I**)

Product	Formula	The estimated value	Obtained value	Statistical data	
				Repetability	Reproducibility
Manganèse, cuivre, oligosol, labcatal-France	Manganese gluconat exprimed in Mn 3.64 mg, cooper gluconat exprimed in Cu 3.63 mg, glucose 5 mg, distillated water at 100 ml	3.64 mg Mn/100 ml solution	3.6141, 3.6341, 3.6541, 3.6341, 3.6541, 3.6341	$n = 6$, $M = 3.6374$, $S = 0.0129$, $S_{\bar{x}} = 0.005266$, $\alpha = 0.95$, $t_{\alpha} = 2.57$, $A = 3.6374 \pm 0.0135$, $CV_r = 0.3547\%$	$n = 18$, $t_{\alpha} = 2.11$, $\alpha = 0.95$, $M = 3.6258$, $S = 0.0253$, $A = 3.6258 \pm 0.0125$, $CV_r = 0.70\%$

μg ml^{-1}) and Ni^{2+} (if concentration exceeds 5 μg ml^{-1}). Fe^{3+} cations do not influence this complexation reaction of Mn^{2+}, (for Fe^{3+} complexation, the reactive concentration is 0.025%), thus Fe^{2+} cations are oxidised at Fe^{3+} [12].

4. Results and discussions

4.1. Mn^{2+} determination

Sample solution (1 ml), with a content of 10–70 μg ml^{-1} Mn^{2+} is treated with 1 ml buffer, pH 6, 1 ml reactive (**I**) 0.25% in methanol, and volume is adjusted at 5 ml with methanol. The absorbance at 460 nm, using a control prepared in the same conditions, is determined.

This results obtained in Mn^{2+} spectrophotometric determination using as reagent the studied Schiff base were applied with good results on pharmaceutical products Mn^{2+} containing (Table 1).

5. Conclusions

A new spectrophotometric method for Mn^{2+} determination from pharmaceutical forms is proposed, as a result of the study concerning the complexation reaction of Mn^{2+} with Schiff bis base 1-ethyl-salicylidene bis ethylene diamine, that has $\varepsilon = 9.8 \times 10^4$ at $\lambda_{max} = 460$ nm, while using as reactive (formaldoxime, tetrasodium hydroxy-calix[4]arene-*p*-sulfonate, antipyryl-*p*-methoxy-phenylmethane, diantipyryl(*p*-methoxy)phenyl-methane, rhodamine 6G etc.)

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