

Spectrophotometric & Potentiometric Studies of Some Multidentate Schiff Bases & Their Complexes

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Some multidentate schiff bases and their Fe(III), Co(II), Ni(II) and Cu(II) complexes have been studied spectrophotometrically and potentiometrically. The pK values of *o*-OH groups have been related to the flexibility of the ligands. The ligands form 1:1 complexes with different metal ions. The formation constants of the complexes have been evaluated using spectrophotometric and potentiometric methods. The pK_1 - pK_c relationship reveals that π -bonding is predominating in these complexes.

The schiff base compounds have been extensively studied in view of their biological and structural importance¹⁻⁵. In the present note, the acid-base and the coordinating properties of three schiff base compounds namely, N,N'-bis(salicylidene)ethylenediamine (Salen), N,N'-bis(salicylidene)propylenediamine (Salpr) and N,N'-bis(salicylidene)-*o*-phenylenediamine (Salph) are studied.

Materials and Methods

The multidentate schiff bases, N,N'-bis(salicylidene)-ethylenediamine (Salen), N,N'-bis(salicylidene)-propylenediamine (Salph), N,N'-bis(salicylidene)-*o*-phenylenediamine (Salph), were prepared according to the standard procedures given in literature⁶. The schiff bases were characterized on the basis of their m.p., elemental analyses and characteristic IR frequencies.

Stock solution ($10^{-3}M$) of each ligand was prepared by dissolving the required weight in 95% ethanol. Stock solutions ($10^{-3}M$) of Fe(III), Co(II), Ni(II) and Cu(II) were prepared by dissolving the required weight of the metal chloride in water. The exact concentration was determined by complexometric titration with $10^{-3}M$ EDTA solution as usual⁷.

The electronic spectra of the ligands were measured in the pH range 2-12 using a Unicam spectrophotometer, model SP 8000 in the wave length range 200-700 nm. The pH measurements were carried out using an ORION Digital pH-meter model 201. The instrument was calibrated with standard universal buffer solution, it had an accuracy of ± 0.05 pH unit⁸.

Methods of calculations

Spectrophotometric and potentiometric methods were used to evaluate the dissociation constants of the ligands and the stability constants of the complexes. The spectrophotometric methods used were: half-height (H-H⁹), limiting-absorbance (L-A)¹⁰, modified-limiting absorbance (M-L-A)¹¹ and Colleter¹² methods. The dissociation constants of the ligands were determined potentiometrically also by using the modified Irving and Rossotti equation¹³. The ligands were titrated potentiometrically against standard alkali. From the titration curves, the average number of protons associated with the reagent, \bar{n}_A was calculated. From \bar{n}_A -pH relationships, the values of pK_1 and pK_2 were evaluated at $\bar{n}_A=0.5$ and 1.5, respectively. Concordant results were obtained using the point-wise calculation method¹⁴.

The stability constants of the complexes were evaluated potentiometrically using the following methods:

(i) The formation curves were constructed by plotting \bar{n} -pL relationship, where \bar{n} stands for metal-ligand formation number and pL is the free ligand concentration¹⁵. All the data were corrected for the effect of the medium¹⁶. \bar{n} and pL were calculated using the following equations:

$$\bar{n} = \frac{(V_2 - V_1)}{V_0 C_M \bar{n}_A}$$

where V_2 and V_1 are the volumes of alkali required to neutralize the metal complex and the ligand solutions respectively at the same PH, C_M represents the initial concentration of the metal ion and V_0 is the initial volume of the complex solution.

pL can evaluated using the relation:

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$$pL = \log \frac{[H^+]/K_1 + [H^+]^2/K_1K_2}{C_L - nC_M} \frac{V_0 + V_2}{V_0}$$

All the terms have the usual meanings.

The data obtained for complex solutions on titrating a solution containing 5 ml $10^{-3} M$ metal ion + 25 ml $10^{-3} M$ ligand + 5 ml 2M HCl against $10^{-2} M$ KOH show that complexation takes place after deprotonation of the ligands.

(ii) From the formation curves, the values of $\log K$ were evaluated by point-wise calculation method¹³.

Results and Discussion

The electronic spectral behaviour of the ligands Salen, Salpr and Salph in universal buffer solutions is shown in Figs 1-3. The spectrum of $2 \times 10^{-5} M$ Salph solution (Fig. 1) in the pH range (3.45-11.95) shows five bands. The intensities of two bands located at 380 and 230 nm increase with pH in the range 4.65-11.95. The three bands at 325, 275 and 245 nm show irregular changes with pH. The spectrum shows five isosbestic points at 335, 292, 262, 241 and 217 nm. The existence of these points indicates that chemical equilibria exist

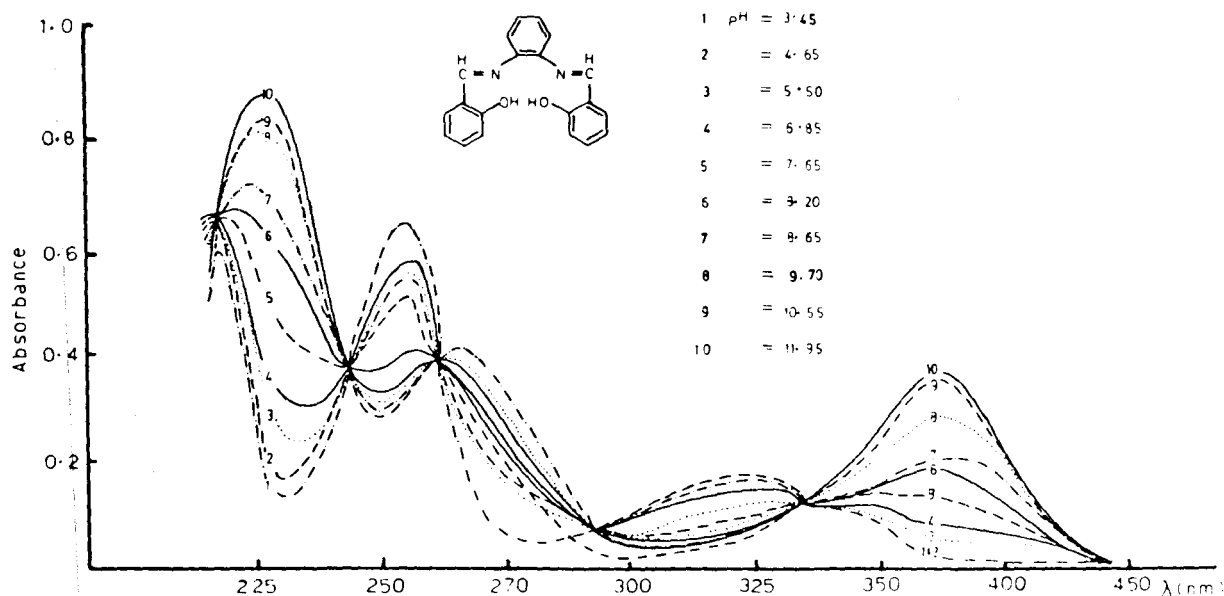


Fig. 1—Effect of pH on the electronic spectrum of $2 \times 10^{-5} M$ Salph.

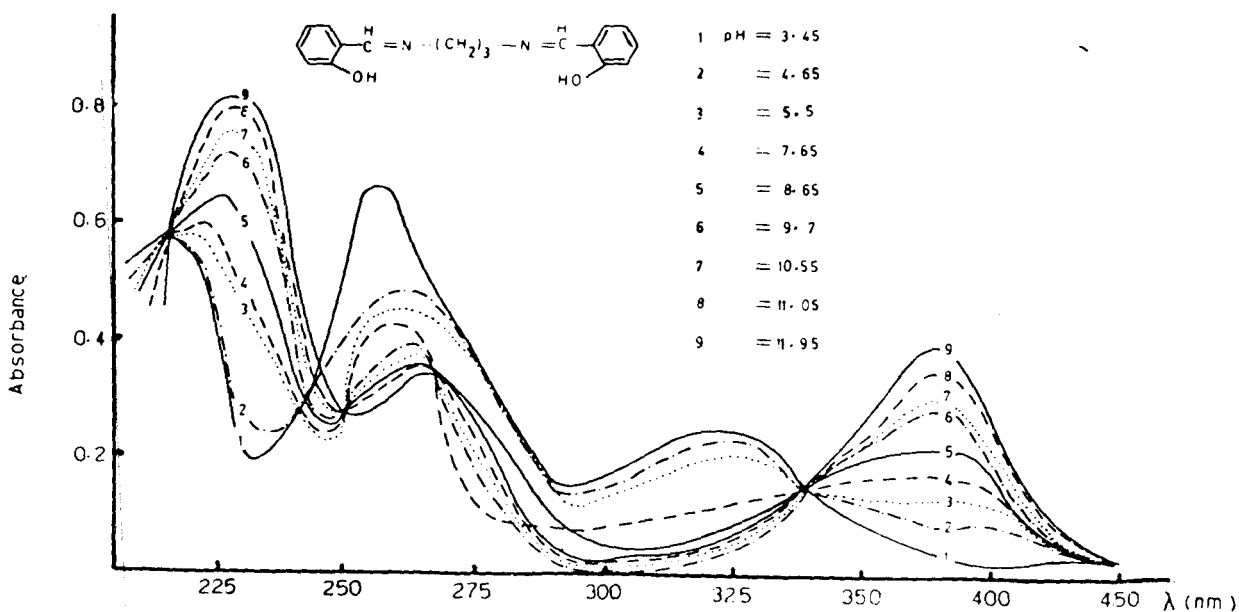


Fig. 2—Effect of pH on the electronic spectrum of $2 \times 10^{-5} M$ Salpr.

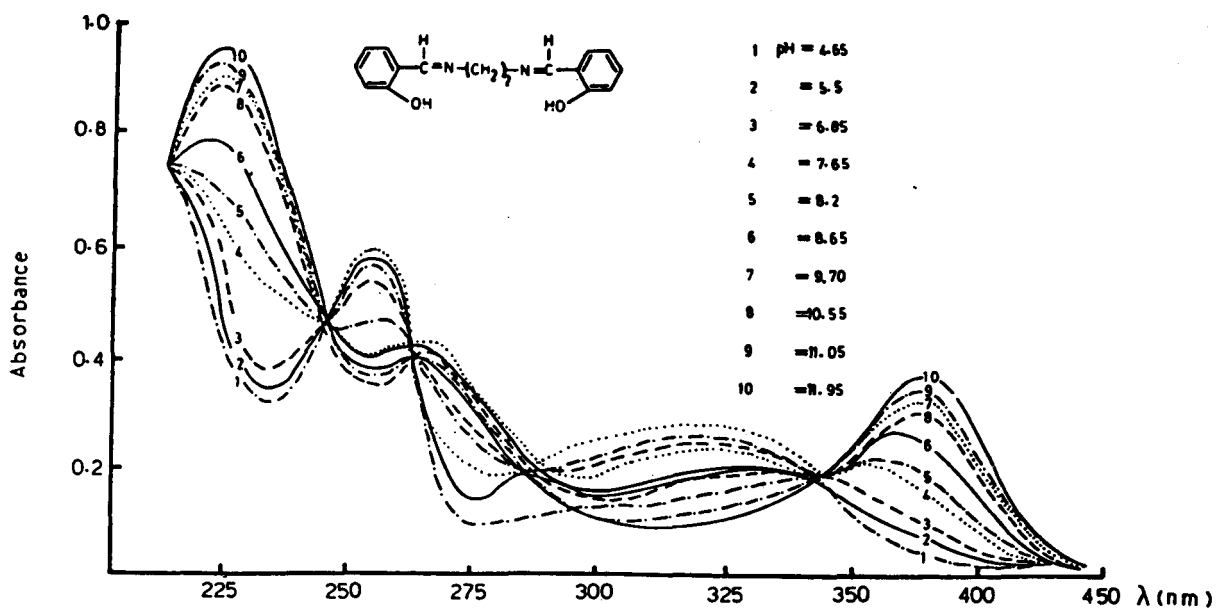


Fig. 3—Effect of pH on the electronic spectrum of $2 \times 10^{-5} M$ Salen.

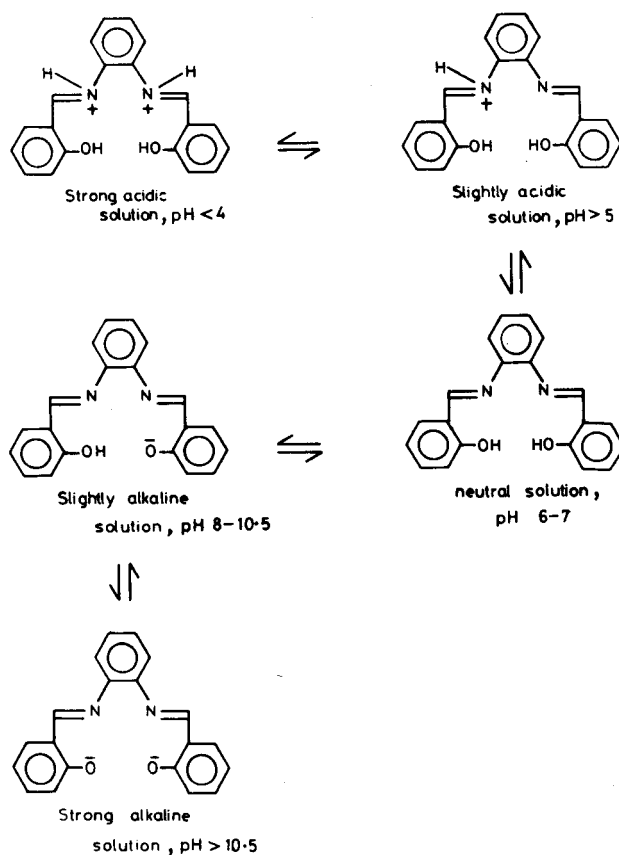
among different species. The possible species which may be formed at different pH values can be represented as shown in Scheme 1.

The spectra of Salpr and Salen solutions ($2 \times 10^{-5} M$) at different pH show similar isosbestic points (Figs 2, 3). In case of Salpr, less clear isosbestic points at 264 and 248 nm are observed, probably due to the overlap of the electronic spectral bands of different absorbing species.

The absorbance-pH relationships of these compounds are shown in Fig. 4, the pK values are compiled in Table 1. The $\log K$ values of the complexes are given in Table 2. N,N' -bis(salicylidene)propylenediamine gives three pK values ($pK_1 = 4.69$, $pK_2 = 8.48$, $pK_3 = 10.79$). pK_1 may be assigned to the deprotonation of azomethine $C=NH$ group, while pK_2 and pK_3 are assigned to the ionization of the phenolic o -OH groups. Such a mechanism would require the molecule to exhibit varied energy states owing to flexibility¹⁸. This means that one of the two o -OH groups is in a position that facilitates the formation of strong intramolecular hydrogen bond with the azomethine nitrogen. Again, protonation of the azomethine group is expected for that nitrogen which is not involved in an intramolecular hydrogen bond; hence, the n -electron would be available for protonation.

N,N' -bis(salicylidene)- o -phenylenediamine gives three pK values ($pK_1 = 4.95$, $pK_2 = 8.25$, $pK_3 = 8.72$). The latter two values are ascribed to the ionization of the two o -OH groups; the observation of two different pK values for the $-OH$ groups may be explained in the light of the phenomenon of rigidity¹⁹ which gives the ligand a certain planarity to allow simultaneous

ionization of the o -OH groups favoured by conjugation. Such a mechanism facilitates the ionization of one of the o -OH groups due to the presence of some steric factors; the ionization of the



Scheme 1

Table 1—The pK_a Values of Salicylidiamines Compounds

Compound	$\lambda_{(nm)}$	pK_a (Determined spectrophotometrically)				pK_a (Determined potentiometrically)	
		Half-height method	Limiting-absorbance method	Modified L.As. method	Colleter Method	Irving-Rossotti method	Point-wise calc. method
(Salph)	380	5.20	5.10	5.30	4.05	10.30	10.25
	230	8.80	8.30	8.75	8.92		
(Salpr)	230	5.05	4.70	5.10	4.75	8.90	9.05
		8.15	7.50	8.45	8.70		
	380	4.90	4.70	4.95	4.75		
		8.92	8.00	9.00	8.90		
(Salen)	230	9.01	7.00	9.00	8.80	9.65	9.70
		10.91	—	10.95	10.40		
	380	8.22	8.00	8.15	8.40		
		8.42	7.80	8.40	8.20		

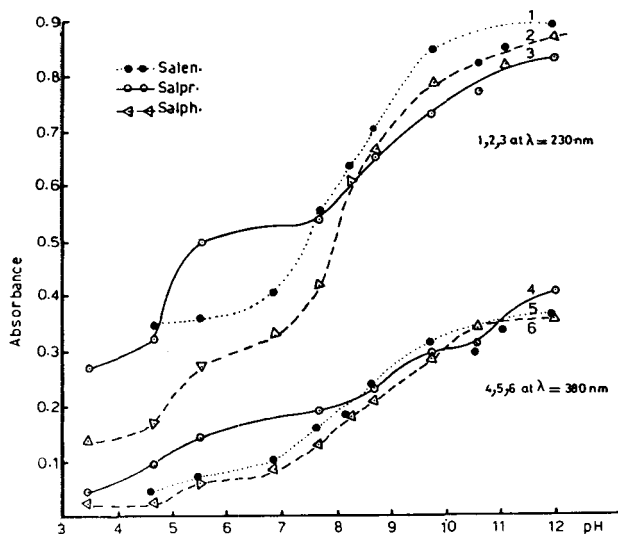


Fig. 4—Absorbance -pH relationships for Salen, Salpr and Salph.

second *o*-OH group is inhibited through intermolecular hydrogen bond.

The pK values of the ligands obtained by the pH metric method using modified Irving and Rossotti and point-wise calculation methods are listed in Table 1. The pK values follow the order: Salen < Salpr < Salph. The \bar{n} - pL relationship indicates the formation of 1:1 species. The formation constants, pK_c , are collected in Table 2.

The pK_c - pK_L relationships are linear for the present systems according to the relation: $pK_c = a.pK_L + b$, where a and b are constants.

Similar linear relations have been reported for a series of 1:1 complex ions with one metal and a set of similar ligands²⁰. The slope a of pK_c - pK_L plot would be unity if the bonding was similar in both the ligand and the complex.

 Table 2—log K Values for Transition Metal Complexes of N,N'-Bis(salicylidene) Compounds

	[Temp. = 25°C; $I=0.5$]			
	Fe(III)	Co(II)	Ni(II)	Cu(II)
Salen	3.69	3.03	3.04	3.36
Salpr	4.44	3.48	4.12	4.01
Salph	4.36	3.69	4.30	4.58

Deviations from unity result because of π -bonding in metal complexes^{21,22}. The observed values of slope a are: Fe(III) (3.32), Co(II) (0.34), Ni(II) (0.68) and Cu(II) (0.46).

The value of $a > 1$ in the iron(III) systems shows that bonding in such systems is of Fe-O type rather than of Fe-N type. The lower slopes in the remaining systems indicate that the metal-nitrogen bonding is more probable than the metal-oxygen bonding.

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