Inorganica Chimica Acta, *189* (1991) 195–206

Solution chemistry of *N,N'*-ethylenebis(salicylideneimine) and its copper(II), nickel(II) and iron(III) complexes

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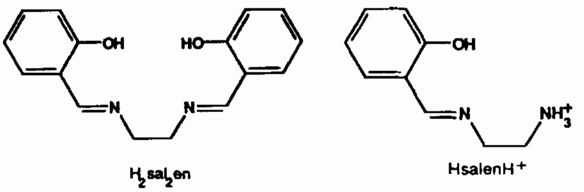
(Received April 23, 1991; revised July 9, 1991)

Abstract

Potentiometric determination of protonation–deprotonation equilibria of the *N,N'*-ethylenebis(salicylideneimine) (H_2sal_2en), the related *N*-(2-aminoethyl)salicylideneimine, (Hsalen), and their organic fragments, salicylaldehyde (Hsal) and ethylenediamine (en), has been used to study the equilibria involved in the formation of Schiff bases from Hsal, sal^- and en and in their complex formation with copper(II), nickel(II) and iron(III) ions in dimethyl sulfoxide (dmso)–water (80:20 wt./wt.) mixture (25 °C and 0.1 mol dm^{-3} $KClO_4$ ionic strength): $en + Hsal \Leftrightarrow Hsalen$; $en + 2Hsal \Leftrightarrow H_2sal_2en$; $en + sal^- \Leftrightarrow salen^-$; $en + 2sal^- \Leftrightarrow sal_2en^{2-}$; $sal^- + en + M^{N+} \Leftrightarrow [M(salen)]^{(n-1)+}$; $2sal^- + en + M^{n+} \Leftrightarrow [M(sal_2en)]^{(n-2)+}$. In these three cases, the ligand sal_2en^{2-} exhibits a planar configuration. However, it is forced to adopt the non-planar *cis-β* configuration (iron(III) complex) in the presence of a bidentate ligand such as catecholate (cat^{2-}) in order to accommodate the chelating bidentate ligand. This non-planar configuration is not observed in the sal_2en^{2-} containing copper(II) and nickel(II) complexes. All these features are analyzed and discussed.

Introduction

The metal complexes of tetradentate Schiff bases such as *N,N'*-ethylenebis(salicylideneimine), H_2sal_2en, are well known and they have played a key role in the field of coordination chemistry [1].



Scheme 1.

Research aspects concerning these complexes have been centered mainly on their synthesis, electronic properties and structural characterization. However, solution studies dealing with them are scarce [2–5]. The lack of thermodynamic data on the formation of this type of complex can be attributed to some of the following reasons: (i) the insolubility in water of the neutral Schiff bases and their metal complexes; (ii) the instability generally observed of the Schiff bases in aqueous solution because of their hydrolytic decomposition to yield the starting organic fragments (for instance the corresponding aldehyde and primary amine), and (iii) in the cases where hydrolytic decomposition does not occur, the highly acidic media which would be required to dissociate the very stable polydentate Schiff base–metal ion complexes. However, the knowledge of thermodynamic data on the formation of Schiff bases is of utmost importance in order to design and rationalize the synthesis of the very interesting asymmetric Schiff bases.

The potentiometric measurement of hydrogen ion concentration is by far the most widely employed technique to determine the stability of metal complexes. It is also one of the more accurate techniques owing to improved methods of data processing and the development of improved equipment for the measurement of hydrogen ion concentration [6]. In general, the potentiometric method using commercial glass electrodes requires the work to be carried out

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in aqueous solution and its accuracy is significantly lowered at low pH range (p[H] < 2).

Some years ago, we observed that the Schiff base H_2sal_2en as well as its iron(III) complex, $[Fe(sal_2en)Cl]$, were soluble and stable in a dimethyl sulfoxide (dmso)–water (80:20 wt./wt.) mixture [2, 3]. However, they undergo hydrolytic decomposition in acid media. This reaction is total at p[H] *c.* 3 and, consequently, it can be investigated by conventional potentiometry. Such a dmso–water mixture is very appropriate as solvent for potentiometric studies because of the nernstian response of a combined glass electrode. These features allowed us to study for the first time the hydrolytic equilibria

$$H_2sal_2en + 2H^+ \Leftrightarrow 2Hsal + H_2en^{2+}$$

$$[Fe(sal_2en)]^+ + 4H^+ \Leftrightarrow Fe^{3+} + 2Hsal + H_2en^{2+}$$

Some years ago, Leussing and co-workers investigated the kinetics of the formation equilibria of the mono(Schiff base), salen⁻, and its protonation reactions [4]. More recently, the system Hsal–en–Co(II) has been investigated by potentiometry in the dioxane–water (70:30 vol./vol.) solvent in order to determine the oxygenation constant of the cobalt(II) complex [5]. It should be noted that the theoretical treatment of these systems (at least four components) becomes very laborious. Many preliminary experiments are needed to get the equilibrium constants of the components before the stability constants of the complexes can be finally determined.

The contents of the present work is as follows. (i) Firstly, we report on the protonation–deprotonation equilibria of H_2sal_2en and its organic fragments; the determined constants allow us to calculate the formation constants of the bis- and mono(Schiff bases) H_2sal_2en and Hsalen (*N*-(2-aminoethyl)salicylideneimine), (see Scheme 1). (ii) Secondly, we have determined the stability constants of these Schiff bases with Cu^{2+}, Ni^{2+} and Fe^{3+}. (iii) Thirdly, a discussion on the interaction of these metal complexes with bidentate ligands such as catecholate (cat^{2-}) is carried out. The study of these multicomponent systems is illustrated by means of distribution diagrams.

Experimental

Reagents and solvent

The compounds H_2sal_2en [7], $[Cu(sal_2en)]$ [8], $[Ni(sal_2en)]$ [9] and $[Fe(sal_2en)Cl]_2$ [10] were synthesized and purified as reported in the literature. All other chemicals were Merck reagents. Dimethyl sulfoxide was purified as previously described [2]. From this solvent, the dmso–water mixture (80:20 wt./wt.) was easily prepared and used as solvent throughout this work. Carbonate-free potassium hydroxide (0.08 mol dm^{-3}) and perchloric acid (0.1 mol dm^{-3}) solutions were used in the potentiometric and spectrophotometric studies. Potassium perchlorate (0.1 mol dm^{-3}) was used as background electrolyte.

Synthesis of [HsalenH][PTS]

The protonated mono(salicylidene Schiff base) $HsalenH^+$ (see Scheme 1) was synthesized as a *p*-toluensulfonate salt, [HsalenH][PTS], by a careful dropwise addition of a diluted solution of *p*-toluenesulfonic acid (10 mmol) in diethyl ether (50 cm^3) to a solution of H_2sal_2en (12 mmol) in the same solvent (50 cm^3) with continuous stirring and at room temperature. Under these conditions $HsalenH^+$ is the first cationic species which is formed (see Fig. 1) and it precipitates as a *p*-toluenesulfonate salt. The yield was *c.* 70%. *Anal.* Calc. for $C_{16}H_{20}N_2O_4S$: C, 57.2; H, 5.9; N, 8.3. Found: C, 55.8; H, 5.9; N,

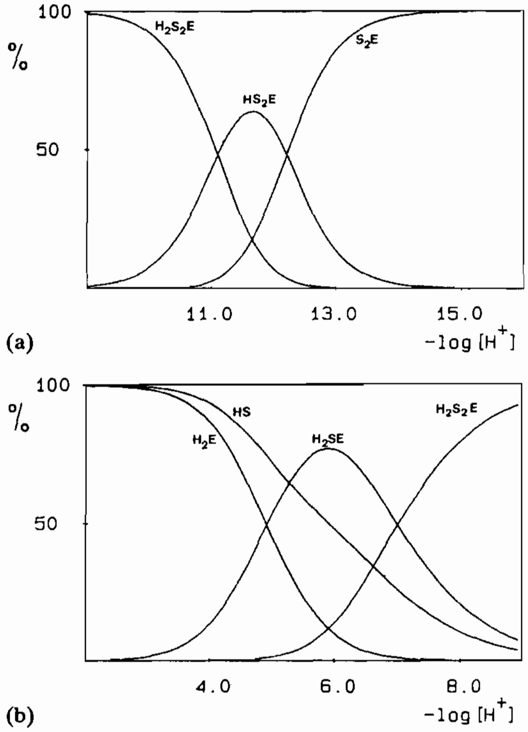

Fig. 1. Species distribution diagram for protonation–deprotonation equilibria of H_2sal_2en ($C_L = 10^{-3}$ mol dm^{-3}). (a) Species involved in the deprotonation of H_2sal_2en in basic medium at potentiometric times (metastable distribution involving only selected deprotonation constants, see text); (b) existing species in acid medium. $H_2E = H_2en^{2+}$, HS = Hsal, $H_2SE = HsalenH^+$, $H_2S_2E = H_2sal_2en$, $HS_2E = Hsal_2en^-$ and $S_2E = sal_2en^{2-}$. The % of all the ethylenediamine containing species have been defined with respect to the initial concentration of en.

8.0%. Although elemental analysis and IR data of this solid were consistent with the proposed formulation, small variable amounts of H_2en^{2+} or Hen^+ were detected by potentiometry (*vide infra*). All our attempts to improve the purity of this solid by recrystallization were unsuccessful.

Physical techniques

The potentiometric titrations were performed with an equipment (potentiometer, buret, stirrer, reaction vessel, microcomputer, electrode, etc.) that has been fully described [11]. The temperature of all solutions was held at 25 °C by circulating constant-temperature water through the water-jacketed titration cell. The electrode was dipped in dmso–water (80:20) for half an hour before use. Nernst's equation, $E=E^{\circ\prime}+0.0591\ \log[H^+]$ was strictly obeyed over the hydrogen ion concentration range that we have investigated. As a matter of convenience, p[H] instead of $-\log[H^+]$ will be used throughout the text. Solutions of 0.08 mol dm^{-3} potassium hydroxide were standardized with 0.1 mol dm^{-3} perchloric acid, Gran's plots [12] being used for end point determination. The logarithm of the ion product, K_w ($K_w=[H^+][OH^-]$), was found to be -18.34 ± 0.02 (25.0 °C, 0.1 mol dm^{-3} $KClO_4$). The computer programs SUPERQUAD [13] and BEST [6] were used to process data from each experiment and calculate the equilibrium constants concerning the protonation–deprotonation and complex formation reactions. In all the cases, both computer programs provided very close results in their refinement processes. The slight differences observed can be attributed to their different weighting schemes; the reported constants in the present work are the mean values.

Absorption spectra were recorded with a UV–Vis Pye Unicam SP 100-8 spectrophotometer using 0.1-cm length cuvettes.

The existence of Hsal in the acidified solutions of H_2sal_2en, $[Cu(sal_2en)]$, $[Ni(sal_2en)]$ and $[Fe(sal_2en)]^+$ was identified by silica-gel thin layer chromatography. The investigated solutions were extracted with diethyl ether. The ether extract was evaporated to dryness and the residue chromatographed with hexane–diethyl ether (1:9) as eluant. Exposure of the chromatograms to UV light ($\lambda=254$ nm) revealed a spot with the same R_f value (*c.* 0.8) as that of Hsal reference sample. On treating the plate with 2,4-dinitrophenylhydrazine, an orange spot of the corresponding 2,4-dinitrophenylhydrazone appeared. Hsal was found neither in non-acidified nor basic solutions.

Results

Acidity constants of $HsalenH^+$, Hsal and H_2en^{2+}

Solutions of [HsalenH][PTS] and Hsal of variable concentration, $C_L=10^{-2}$–10^{-3} mol dm^{-3} were potentiometrically titrated with KOH as indicated in 'Experimental' (see Table 1). Data processing by the SUPERQUAD and BEST programs of 100 (for $HsalenH^+$) and 60 (for Hsal) experimental points from different series for each system, allowed their deprotonation constants to be determined. In the case of $HsalenH^+$, the presence of variable amounts of protonated ethylenediamine was detected by potentiometry. We have titrated potentiometrically several samples of [HsalenH][PTS] from different syntheses. Experimental data were fitted taking into account the presence of H_2en^{2+} whose amount was a parameter to be refined in the calculation. In all these cases the calculated amount of $[H_2en][PTS]_2$ was lower than 10% from the initial sample weight. Acidity constants of H_2en^{2+} were determined previously in the same conditions [2]. The protonation constants of these species are given in Table 2 (eqns. (3)–(7)).

Deprotonation and hydrolysis equilibria of H_2sal_2en

The acid–base behavior of H_2sal_2en in a dmso–water (80:20 wt./wt.) mixture was studied in a previous work [2]. Let us summarize the most relevant features dealing with this study. When attempting to determine the possible protonation constants of the imine nitrogen atoms of this Schiff base by potentiometry, e.m.f. measurements were instable decreasing slowly with time. Spectrophotometric and chromatographic studies showed that a hydrolytic reaction occurred affording Hsal and H_2en^{2+} as products and that the required time to achieve the equilibrium was *c.* 20 days. In order to determine the existing species in this hydrolytic process and the values of its constants, samples containing different H_2sal_2en:$HClO_4$ ratios were prepared and their hydrogen ion concentrations were measured after 20 days. The potentiometric data showed that the following equilibria occurred

$$H_2sal_2en+H^+ \Leftrightarrow HsalenH^+ + Hsal \quad \log K=4.41 \qquad (i)$$

$$HsalenH^+ + H^+ \Leftrightarrow Hsal + H_2en^{2+} \quad \log K=2.79 \qquad (ii)$$

However, when potentiometric titrations of H_2sal_2en with KOH were carried out, no hydrolytic decomposition of H_2sal_2en was observed and this Schiff base behaved as a weak diprotic acid (eqns. (iii) and (iv)).

$$sal_2en^{2-} + H^+ \Leftrightarrow Hsal_2en^- \quad \log K=12.21 \qquad (iii)$$

$$Hsal_2en^- + H^+ \Leftrightarrow H_2sal_2en \quad \log K=11.10 \qquad (iv)$$

TABLE 1. Experimental details[a] of the e.m.f. measurements

Initial concentration (mM)						pH range		No. of data points
S	E	SE	S_2E	MS_2E	M	investigated	computed	
9.60						3.0–14.0	8.1–11.5	40
1.01						3.5–13.0	8.0–11.6	20
		8.05				7.5–16.0	8.0–13.5	40
		4.80				7.6–15.5	8.0–13.4	30
		1.75				7.7–16.1	8.1–13.2	18
		1.20				7.7–16.0	8.2–13.2	12
			7.95			2.0–8.9	2.8–8.9	30
			2.05			2.2–8.9	3.1–8.9	30
			6.90			8.9–16.1	9.1–13.9	40
			2.15			9.0–15.9	9.1–13.7	30
				7.35 (Fe)		2.0–5.9	2.5–5.2	30
				1.80 (Fe)		2.1–6.1	3.0–5.5	30
				8.05 (Cu)		1.9–7.5	2.2–5.5	30
				4.20 (Cu)		2.0–7.5	2.4–5.7	30
				1.80 (Cu)		2.2–7.4	2.5–6.0	30
				7.80 (Ni)		2.1–8.1	3.0–6.0	30
				3.75 (Ni)		2.1–8.0	3.5–6.7	30
				1.55 (Ni)		2.3–8.0	3.6–7.2	30
	8.50				4.05 (Cu)	2.1–9.0	3.2–6.1	35
	8.50				3.50 (Cu)	2.0–9.1	3.1–6.0	25
	8.50				2.80 (Cu)	2.0–10.5	3.1–5.9	25
	9.50				3.10 (Ni)	2.9–10.5	4.3–8.5	40
	9.50				2.50 (Ni)	2.8–11.0	4.3–8.1	30
	9.50				1.75 (Ni)	3.0–10.0	4.2–8.1	25

[a] S = Hsal, E = en, SE = $HsalH^+$, $S_2E = H_2sal_2en$, $MS_2E = [M(sal_2en)]^{(n-2)+}$, M = Cu^{2+}, Ni^{2+} or Fe^{3+}.

TABLE 2. Stepwise proton association constants of sal_2en^{2-} and its organic fragments in dmso–water (80:20 wt./wt.) (25 °C, 0.1 mol dm^{-3} $KClO_4$)

Reaction		log *K*
(1)	$sal_2en^{2-} + H^+ \Leftrightarrow Hsal_2en^-$	12.21(1)
(2)	$Hsal_2en^- + H^+ \Leftrightarrow H_2sal_2en$	11.10(1)
(3)	$sal^- + H^+ \Leftrightarrow Hsal$	9.75(1)
(4)	$en + H^+ \Leftrightarrow Hen^+$	10.00(1)
(5)	$Hen^+ + H^+ \Leftrightarrow H_2en^{2+}$	6.94(1)
(6)	$salen^- + H^+ \Leftrightarrow Hsalen$	11.5(1)
(7)	$Hsalen + H^+ \Leftrightarrow HsalenH^+$	9.7(1)

Such constants were computed by graphical methods [2] assuming that the equilibria (i)–(iv) were the only ones involved. In the present work, we have reinvestigated this system under the same conditions (see Table 1), and experimental data were processed by the powerful computer programs SUPERQUAD and BEST which allows to treat simultaneously many equilibria and determine their corresponding constants. The only species which were consistent with experimental data are the involved ones in equilibria (i)–(iv) and the evaluated equilibrium constants were identical to previously determined by graphical methods. Although species such as Hsalen, $H_2sal_2enH^+$ and $H_2sal_2enH_2^{2+}$ were introduced in the equilibrium scheme, they were ruled out by the programs in the refinement process suggesting that these species cannot be present in significant amounts under our experimental conditions

Stability constants of Cu(II) and Ni(II) with en

Solutions of Cu(II) and Ni(II) of variable concentration ($C_M = (1–5) \times 10^{-3}$ mol dm^{-3}) containing an excess of en ($C_L/C_M = 3–5$) were titrated with KOH (see Table 1). The values of the stability constants of the ethylenediamine–metal ion complexes were computed by means of the programs SUPERQUAD and BEST. They are listed in Table 3 (eqns. (11)–(13)). The distribution diagrams for Cu(II)–en and Ni(II)–en systems are shown in Fig. 2(a) and (b), respectively.

Solutions of [Cu(sal₂en)], [Ni(sal₂en)] and [Fe(sal₂en)]⁺ in acid medium: a spectrophotometric study

The complexes $[Fe(sal_2en)Cl]_2$, $[Cu(sal_2en)]$ and $[Ni(sal_2en)]$ were soluble in dmso–water (80:20 wt./wt.) yielding dark red, purple and orange coloured solutions, respectively. The UV–Vis spectra display absorption bands at 485 ($\epsilon = 3.74 \times 10^3$) and 316

TABLE 3. Species considered in calculation of complex formation for metal ion–salicylaldehyde–ethylenediamine system in dmso–water (80:20 wt./wt.) (25 °C, 0.1 mol dm^{-3} $KClO_4$)

Equation no.	sal^-	en	M^{n+}	H^+	log β		
(1)	1	0	0	1		9.75(1)	
(2)	0	1	0	1		10.00(1)	
(3)	0	1	0	2		16.94(1)	
(4)	1	1	0	0		2.7(1)	
(5)	2	1	0	0		5.93(1)	
(6)	1	1	0	1		14.2(1)	
(7)	1	1	0	2		23.91(2)	
(8)	2	1	0	1		18.14(2)	
(9)	2	1	0	2		29.24(2)	
(10)	0	0	0	−1		−18.34(2)	
					Cu(II)	Ni(II)	Fe(III)
(11)	0	1	1	0	11.02(1)	8.74(1)	
(12)	0	2	1	0	20.72(2)	16.69(1)	
(13)	0	3	1	0		23.17(2)	
(14)	1	1	1	0	23.44(2)	19.58(2)	21.69(2)
(15)	2	1	1	0	33.09(2)	28.53(2)	31.78(2)
(16)	4	2	2	−2			51.26(3)

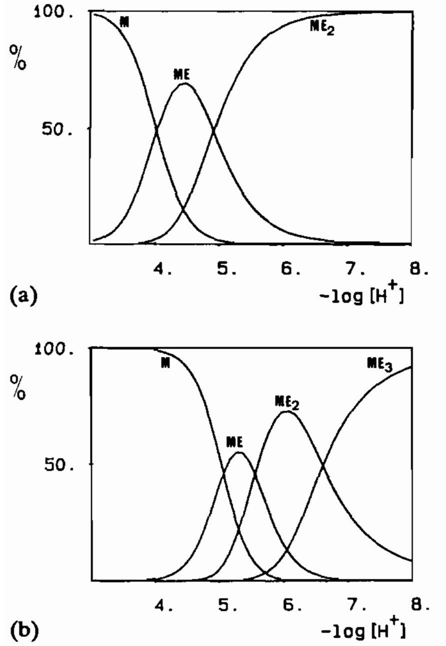

Fig. 2. Distribution diagrams for ethylenediamine complexes of (a) Cu^{2+} ($C_L/C_M=2$) and (b) Ni^{2+} ($C_L/C_M=3$). $M=M^{2+}$, ME = $[M(en)]^{2+}$, $ME_2=[M(en)_2]^{2+}$ and $ME_3=[M(en)_3]^{2+}$. The % of all these species have been defined with respect to the initial concentration of the metal ion.

($\epsilon=1.3\times10^4$) for $[Fe(sal_2en)]^+$, 359 (9.29×10^3) and 568 (298) for $[Cu(sal_2en)]$ and 403 nm (6.18×10^3 dm^3 mol^{-1} cm^{-1}) for $[Ni(sal_2en])$. These solutions are completely stable and no spectral changes with time are observed. Absorbance data at the above mentioned wavelengths strictly obey Beer–Lambert's law. Conductivity measurements of the $[Fe(sal_2en)Cl]$ solutions correspond to that of a strong 1:1 electrolyte supporting thus the existence of the $[Fe(sal_2en)]^+$ cationic species in solution.

A gradual decrease in the absorption at all the above mentioned wavelengths occurred when acidifying $[M(sal_2en)]^{(n-2)+}$ solutions ($M^{n+}=Fe^{3+}$, Cu^{2+}, Ni^{2+}). The solutions fully decolorize in the presence of an acid excess ($C_A:C_M\geqslant8$, $M=Fe^{3+}$; $C_A:C_M\geqslant8.5$, $M=Cu^{2+}$; $C_M:C_A\geqslant7.5$, $M=Ni^{2+}$). These reactions are very slow, thirty (Fe^{3+}) and sixty days (Cu^{2+} and Ni^{2+}) being necessary to reach equilibria. At this point, absorption measurements remain stable and are reproducible.

These processes are also completely reversible: a careful neutralization of such solution leads, also slowly, to a quantitative formation of $[M(sal_2en)]^{(n-2)+}$ complexes. The absorption spectra of colorless solutions are identical to those of Hsal-M^{n+} with concentrations $2C_M$ and C_M, respectively. No absorption of en is observed in the wavelength range investigated. Moreover, Hsal can be identified by thin-layer chromatography. Blue (for Cu^{2+}) and violet (for Ni^{2+}) coloured solutions were obtained after careful neutralization of acidified $[M(sal_2en)]^{(n-2)+}$ solutions which were previously extracted with diethyl ether. A precipitate of Fe_2O_3 formed in the case of Fe^{3+}. These features demonstrate that the only existing species in solution, after extraction of Hsal with diethyl ether, are H_2en^{2+} and M^{n+}. Therefore, a global hydrolytic decomposition of $[M(sal_2en)]^{(n-2)+}$ analogous to that of the free Schiff base takes place (eqn. (v)).

$$[M(sal_2en)]^{(n-2)+} + 4H^+ \Leftrightarrow M^{n+} + 2Hsal + H_2en^{2+} \quad (v)$$

Potentiometric determination of the stability constants of [Cu(sal₂en]), [Ni(sal₂en)] and [Fe(sal₂en)]⁺

A series of $[Cu(sal_2en)]$, $[Ni(sal_2en)]$ and $[Fe(sal_2en)]^+$ solutions of concentration $C_M = (1\text{–}5) \times 10^{-3}$ mol dm^{-3} were acidified with $HClO_4$ up to $8 \geqslant C_A{:}C_M \geqslant 0$ ratios (see Table 1). They were sealed and kept in the dark at 25 °C. Hydrogen ion concentration was measured after thirty (Fe^{3+}) and sixty days (Cu^{2+} and Ni^{2+}). The potentiometric data were treated with the programs SUPERQUAD and BEST showing that the only occurring equilibria involved in the hydrolytic decomposition of the metal complexes were (vi), (vii) and (ii).

$$[M(sal_2en)]^{(n-2)+} + H^+ \Leftrightarrow [M(salen)]^{(n-1)+} + Hsal \quad (vi)$$

$$[M(salen)]^{(n-1)+} + 2H^+ \Leftrightarrow HsalenH^+ + M^{n+} \quad (vii)$$

All the species involved in the calculation of complex formation (eqns. (14) and (15)) are given in Table 3.

Protonated species of M^{n+}–salen$^-$ and M^{n+}–sal$_2$en^{2-} as well as M^{n+}–sal$^-$ and M^{n+}–en complexes were considered in the equilibrium scheme but they were ruled out by the programs. So, these species cannot be present in significant amounts under our experimental conditions. Potentiometric titrations of $[M(sal_2en)]^{(n-2)+}$ solutions with KOH revealed that no hydroxo complex formation occurred for Cu(II) and Ni(II) complexes whereas in the case of the iron(III) species the following dimerization reaction takes place (eqn. (viii)) as reported elsewhere [3].

$$2[Fe(sal_2en)]^+ + H_2O \Leftrightarrow \{[Fe(sal_2en)]_2O\} + 2H^+ \quad \log K = -12.3 \quad (viii)$$

Discussion

On the dmso–water mixture as a solvent

The study of complex formation cannot be carried out in aqueous solution because of the nature of the compounds involved. The metal complexes as well as the ligands themselves are insoluble in water. The dmso–water (80:20 wt./wt.) mixture was the solvent chosen to make this study. In such a medium, the Schiff bases and their metal complexes are very soluble. The use of this mixed solvent has some advantages over the pure dmso for systems in which, as in ours, the exclusion of water is not necessary. Pure dmso is very hygroscopic and controlling its water content is difficult [14]. This fact would affect the reproducibility of experiments in dmso. However, dmso–water (80:20) mixture has only a small hygroscopic character. A further advantage is its compatibility with the standard glass electrode; so that, the required p[H] measurements may be carried out in a similar manner to that employed in purely aqueous systems. Furthermore, the acidity range of this mixture is larger ($pK_w = 18.38$) than in water or in the widely used dioxane–water (70:30 vol./vol.) mixture. So, it is possible to perform [H$^+$] measurements up to p[H] values as high as *c.* 16, whereas in water or dioxane:water (70:30 vol./vol.), the limit is at p[H] *c.* 12 and 14 [5], respectively. In principle, the dmso:water mixture is a better solvent to investigate deprotonation equilibria of neutral acids which could be hardly studied in water solution [2, 3, 11, 15].

On the formation of Schiff bases

The distribution diagram of the different species resulting from H_2sal_2en solutions in both basic and acid media (eqns. (i)–(iv)) are depicted in Figs. 1(a) and (b), respectively. This bis(Schiff base) behaves as a weak diprotic acid. The deprotonation of both phenolic groups is complete at $p[H] \geqslant 14.5$ whereas in the 9–14 p[H] range H_2sal_2en, $Hsal_2en^-$ and sal_2en^{2-} coexist (eqns. (iii)–(iv)). However, $Hsal_2en^-$ and sal_2en^{2-} are thermodynamically unstable species and will decompose very slowly to yield the corresponding organic fragments (*vide infra*). In other words, the rate of decomposition of these species is so low that H_2sal_2en behaves as a diprotic acid at potentiometric times. So, Fig. 1(a) is actually a distribution diagram involving metastable species.

In acid media H_2sal_2en is hydrolyzed to yield Hsal and H_2en^{2+} cation (Fig. 1(b)). This reaction is also very slow, but faster than the above mentioned one in basic medium. So, it was impossible to determine the possible protonation of the imine groups at potentiometric times (*vide supra*). This hydrolytic reaction is fully reversible and its extent depends on [H$^+$]. The reaction starts at p[H] *c.* 9.5 and is complete at $p[H] \leqslant 3.5$. This hydrolytic process occurs in two successive steps (eqns. (i)–(ii)). The $HsalenH^+$ species for which only one –CH=N–bond has been cleaved exists in solution as a stable species and it predominates at p[H] *c.* 6.5 (75%). The values of the acidity constants of the ethylenediammonium clearly show that within the p[H] range for which H_2sal_2en (and its metal complexes) decompose, ethylenediamine is fully protonated. There is no evidence about the existence in solution of species with a protonated imine-nitrogen atom such as $H_2sal_2enH_2^{2+}$ and $HsalenH_2^{2+}$. Leussing *et al.* [4] demonstrate spectrophotometrically that this last species, $HsalenH_2^{2+}$, is thermodynamically unstable with regard to its hydrolytic decomposition to yield H_2en^{2+} and Hsal in aqueous solution. By means of the stopped-flow technique, Leussing determined the protonation constant of $HsalenH^+$ ($\log K = 4.87$) from absorbance measurements within about 10 ms after solution mixture and before the hydrolytic decomposition occurred.

From the values of the constants of these hydrolytic processes and taking into account the acidity constants of Hsal, H_2en^{2+} and H_2sal_2en (eqns. (1)–(5) in Table 2) the formation constants of the neutral bis(Schiff base), H_2sal_2en, and its deprotonated form, sal_2en^{2-}, can be calculated (eqns. (ix) and (x)).

$$2Hsal + en \Leftrightarrow H_2sal_2en \quad \log \beta_2 = 9.74 \qquad (ix)$$

$$2sal^- + en \Leftrightarrow sal_2en^{2-} \quad \log \beta'_2 = 5.93 \qquad (x)$$

It is obvious that the neutral mono(Schiff base), Hsalen, is the essential intermediate in the formation of the bis(Schiff base), H_2sal_2en. However, the concentration of this species at equilibrium under the conditions used in this work is too low to be measured. Consequently its protonation–deprotonation constants could not be determined. In order to determine them, we isolated the salt [HsalenH][PTS] and titrated it potentiometrically. The values of the acidity constants of this protonated mono(Schiff base) are given in Table 2 (eqns. (6) and (7)). The low precision reported for these log *K* values must be ascribed to the low accuracy of the measurements, due to the scarce purity of the salt used (*vide supra*). The acidity of the phenolic group of the mono(Schiff base) (eqn. (6)) is similar to the corresponding one of the bis(Schiff base) (eqn. (2)) and the basicity of its amine group is very close to the one of en (eqn. (4)). These facts explain the absence of Hsalen in the p[H] range where the hydrolytic decomposition of H_2sal_2en takes place. By combining the acidity constants of $HsalenH^+$ with eqns. (ii) and (3)–(5) in Table 2, the formation constants of this mono(Schiff base) (neutral and anionic forms) from its components can be calculated (eqns. (xi) and (xii)).

$$Hsal + en \Leftrightarrow Hsalen \quad \log K_1 = 4.5 \qquad (xi)$$

$$sal^- + en \Leftrightarrow salen^- \quad \log K'_1 = 2.7 \qquad (xii)$$

It is interesting to compare the stepwise stability constants of the formation of these Schiff bases (eqns. (xi)–(xiv)).

$$Hsalen + Hsal \Leftrightarrow H_2sal_2en \quad \log K_2 = 5.3 \qquad (xiii)$$

$$salen^- + sal^- \Leftrightarrow sal_2en^{2-} \quad \log K'_2 = 3.2 \qquad (xiv)$$

As $K_1 < K_2$ ($K'_1 < K'_2$), the formation of the bis(Schiff base) is favoured with regards to the mono(Schiff base). The mono(Schiff base) disproportionates partially according to the equilibria

$$2Hsalen \Leftrightarrow H_2sal_2en + en \quad \log K = 0.8 \qquad (xv)$$

$$2salen^- \Leftrightarrow sal_2en^{2-} + en \quad \log K' = 0.5 \qquad (xvi)$$

These features can explain the difficulties found by us as well as by the other authors to synthesize the monobase, Hsalen, from its components (eqn. (xi)) to be used as a precursor of asymmetrical Schiff bases. Even from solutions containing an excess of amine with respect to the aldehyde, the extent of formation of the bis(Schiff base) is considerable and it separates easily probably due to its greater insolubility. The method of synthesis of this monobase that we propose is based on the distribution diagram depicted in Fig. 1. The protonated monobase, $HsalenH^+$, is the first species formed by careful acidification of solutions of the bis-base, H_2sal_2en. It is the only existing cationic species up to p[H] about 5.5 and with a high formation degree. The use of low polarity solvents which do not stabilize ionic species leads to the precipitation of the salt. The acid addition must be done carefully in order to avoid high local concentrations of acid which would lead to the precipitation of salts containing H_2en^{2+}.

On the kinetic and thermodynamic stabilities of these Schiff bases

The high value of β_2 (eqn. (ix)) indicates that H_2sal_2en is thermodynamically stable towards hydrolysis in dmso–water solvent in spite of the large water content of such a mixture. The favourable thermodynamics for the hydrolysis in acid medium is provided by the protonation of ethylenediamine. In this sense, the Schiff base *N,N'-o*-phenylenebis (salicylideneimine), $H_2saloph$, and its iron(III) complex $[Fe(saloph)]^+$ are completely stable in acid medium and do not undergo any decomposition due to the smaller basic character of the *o*-phenylenediamine which remains unprotonated in the media where the ethylenediamine is completely protonated [15]. The value of β'_2 (eqn. (x)) is four orders of magnitude smaller than β_2 revealing that it should be appreciably dissociated into its components sal^- and en. However, such a spontaneous decomposition must be kinetically inhibited because it is not observed. So, in spite of the stability of H_2sal_2en in dmso–water, its deprotonation leads to sal_2en^{2-} which would disproportionate. Nevertheless, H_2sal_2en behaves as a weak diprotic acid (eqns. (1) and (2) in Table 3) yielding $Hsal_2en^-$ and sal_2en^{2-} without further decomposition for a long time. The fact that sal_2en^{2-} is kinetically stable (but not thermodynamically), has allowed us to determine its protonation constants. Such a situation is also reproduced for $HsalenH^+$. This species is much more stable than Hsalen with regards to the disproportion to give H_2sal_2en and H_2en^{2+}. After neutralization it would disproportionate according to our data but the rate of this process must be so low at 25 °C that the potentiometric study of its deprotonation can be carried out before any significant decomposition occurs.

The constants of the equilibria involved in the solution chemistry of H_2sal_2en expressed as a function of its components are gathered in Table 3. The distribution diagrams of Fig. 3(a) (diluted solution) and (b) (concentrated solution) are the best way to illustrate the relative stabilities of the existing species and the resulting extent of formation of each one under a varying total concentration in this singular system. Figure 3(a) (at millimolar concentrations) shows that the formation degree of H_2sal_2en from Hsal and en at neutral conditions is very high being much lower in basic medium. However, the formation of the bis(Schiff base) is favoured at higher concentration as normally used in the synthesis (Fig. 3(b)) because of the stoichiometry of this reaction. It can be observed that H_2sal_2en and sal_2en^{2-} are the only existing species that would be formed both in neutral and basic media respectively, in agreement with the observed synthetic results.

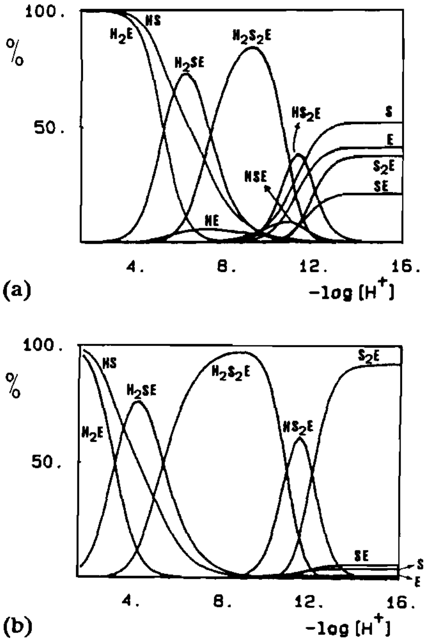

Fig. 3. Distribution diagrams of the Hsal–en system: (a) $[en]=10^{-3}$, $[Hsal]=2\times10^{-3}$ mol dm^{-3}; (b) $[en]=0.1$, $[Hsal]=0.2$ mol dm^{-3}. $H_2E=H_2en^{2+}$, $HE=Hen^+$, E = en, HS = Hsal, $S=sal^-$, $H_2SE=HsalenH^+$, HSE = Hsalen, $SE=salen^-$, $H_2S_2E=H_2sal_2en$, $HS_2E=Hsal_2en^-$ and $S_2E=sal_2en^{2-}$. The % of all the ethylenediamine containing species have been defined with respect to the initial concentration of en.

On the formation and stability of Schiff base–metal complexes

$[Cu(sal_2en)]$, $[Ni(sal_2en)]$ and $[Fe(sal_2en)]^+$ decompose in acid medium similarly to H_2sal_2en although not so easily. Greater hydrogen ion concentrations are required and the reaction is still slower. The hydrolytic decomposition of $[M(sal_2en)]^{(n-2)+}$ complexes occurs via $[M(salen)]^{(n-1)+}$ formation (eqns. (vi) and (vii)).

By combining the appropriate equilibria the following stability constants are calculated

$$salen^- + M^{n+} \Leftrightarrow [M(salen)]^{(n-1)+}$$

$$\log \beta = 20.7\ (Cu),\ 16.9\ (Ni),\ 19.0\ (Fe) \qquad (xvii)$$

$$sal_2en^{2-} + M^{n+} \Leftrightarrow [M(sal_2en)]^{(n-2)+}$$

$$\log \beta = 27.16\ (Cu),\ 22.60\ (Ni),\ 25.85\ (Fe) \qquad (xviii)$$

The formation constants of these metal complexes calculated from their components are listed in Table 3, and their corresponding distribution diagrams are shown in Fig. 4(a)–(c). The $[M(sal_2en)]^{(n-2)+}$ complex is the predominant species at $p[H]>6$ in all three cases. The formation of $[M(salen)]^{(n-1)+}$ occurs at lower p[H] values with a maximum extent of 30, 16 and 9% for Cu^{2+}, Ni^{2+} and Fe^{3+}, respectively. At p[H] values less than 2.5 (Cu^{2+}), 3.5 (Ni^{2+}) and 3 (Fe^{3+}), the decomposition of the metal complexes is total and M^{n+}, Hsal and H_2en^{2+} are the only existing species. Obviously, $[M(Hsalen)]^{n+}$ species must be an intermediate in the decomposition of $[M(salen)]^{(n-1)+}$ in acid medium. We have checked this species in the equilibrium scheme but its concentration must be too low to be measured. The monoprotonated mono(Schiff base), Hsalen, should be a bidentate ligand, the imine-nitrogen and phenolate-oxygen or amine-nitrogen being the donor atoms. The deprotonated mono- and bis(Schiff bases), $salen^-$ and sal_2en^{2-}, exhibit different donor groups: the former is a terdentate ligand with phenolate,

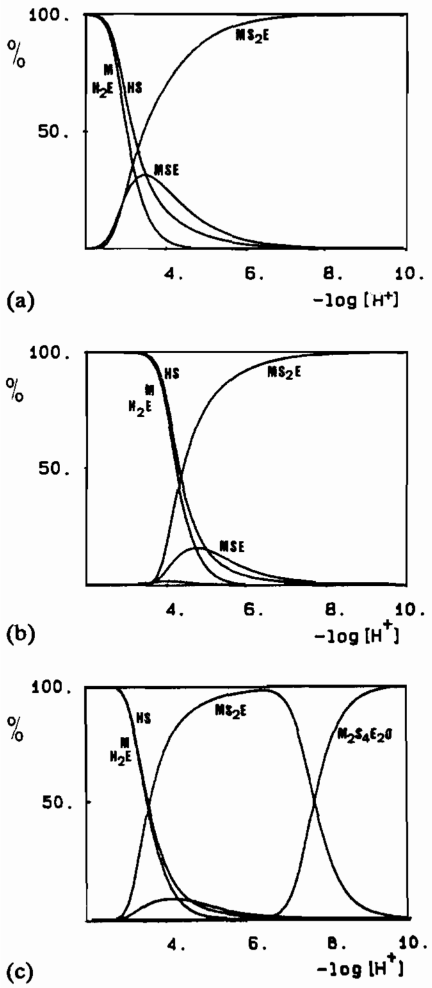

Fig. 4. Distribution diagram of the Hsal–en–M^{n+} system. [Hsal] = 2×10^{-3}, [en] = [M] = 10^{-3} mol dm^{-3}. (a) M = Cu^{2+}, (b) M = Ni^{2+} and (c) M = Fe^{3+}. M = M^{n+}, $H_2E = H_2en^{2+}$, HS = Hsal, MSE = $[M(salen)]^{(n-1)+}$, MS_2E = $[M(sal_2en)]^{(n-2)+}$ and $M_2S_4E_2O$ = {$[Fe(sal_2en)]_2O$}. The % of all the ethylenediamine containing species have been defined with respect to the initial concentration of en.

amine and imine groups whereas the latter is a tetradentate ligand with two phenolate and two imine groups. Consequently, the lower stability of $[M(Hsalen)]^{n+}$ with regards to the other species leads to a degree of formation so low that it is practically undetectable.

In the case of Fe^{3+}, $[Fe(sal_2en)]^+$ dimerizes in basic medium to yield $[Fe(sal_2en)]_2O$ (eqn. (viii)) which is the only existing species at high p[H] values. No hydroxo complex formation is observed for $[Cu(sal_2en)]$ and $[Ni(sal_2en)]$.

These metal complexes are very stable as indicated by the high values of their stability constants. Those with the tetradentate sal_2en^{2-} are more stable than the corresponding ones with the terdentate $salen^-$ ligand. In each series the Cu(II) complexes are more stable than the Ni(II) ones as expected. It is interesting to compare the stabilities of the $[Fe(sal_2en)]^+$ and $[Cu(sal_2en)]$ complexes with those of the corresponding 1:1 Fe^{3+}:cat^{2-} (log β = 23.9) [16] and Cu^{2+}:cat^{2-} (log β = 17.3) [17] species. It is observed that $[Fe(cat)]^+$ is almost as stable as $[Fe(sal_2en)]^+$. Therefore, the stability of $[Fe(sal_2en)]^+$ is mainly due to the coordination of phenolate groups, whereas in the case of $[Cu(sal_2en)]$, its stability is due to both imine and phenolate coordinated groups. The higher affinity of Fe(III) with respect to Cu(II) for phenolate-oxygen atoms and the lower affinity of Fe(III) with regard to Cu(II) for imine-nitrogen atoms explain the fact that $[Cu(sal_2en)]$ can be even slightly more stable than $[Fe(sal_2en)]^+$. These thermodynamic data are supported by known M–N(imine) (2.01 for Cu(II) [9, 18] and 2.10 Å for Fe(III) [19]) and M–O(phenolate) (1.97 for Cu(II) [9, 18] and 1.88 Å for Fe(III) [19]) bond lengths. Therefore, the loss of a phenolate group and the replacement of an imine group by an amine one when going from sal_2en^{2-} to $salen^-$ metal complexes are the factors that explain the low degree of formation of the $[Fe(salen)]^+$ complex (9%) with regard to $[Cu(salen)]^+$ (30%). This is reflected by the following reaction (eqn. (xix))

$$[M(salen)]^{(n-1)+} + sal^- \Leftrightarrow [M(sal_2en)]^{(n-2)+}$$

$$\log K = 10.1\ (Fe),\ 9.7\ (Cu),\ 8.9\ (Ni) \qquad (xix)$$

It is known that the nature of solvent used to recrystallize $[Cu(sal_2en)]$, $[Ni(sal_2en)]$ and $[Fe(sal_2en)Cl]$ determines the dimeric or monomeric structure exhibited by these compounds in the solid state [1]. It is also well known that $[Cu(sal_2en)]$ and $[Ni(sal_2en)]$ complexes can act as bidentate ligands yielding dinuclear and trinuclear species [20]. In a polar solvent such as dmso–water mixture, only the monomeric species are observed.

The sal_2en^{2-} ligand can adopt two kinds of configuration in its metal complexes: the planar and *cis*-β octahedral arrangements. This latter one occurs only in the presence of bidentate ligands when the octahedral environment is preferred by the metal ion. The square planar configuration is favoured for Ni^{2+} in the presence of strong fields ligands and the octahedral coordination for Cu^{2+} is precluded by the Jahn–Teller effect. So, $[Fe(sal_2en)]^+$ is the only complex from the three herein reported sal_2en^{2-} containing species that is able to adopt the *cis*-β-configuration in the presence of bidentate ligands [21, 22] because such a configuration provides two vacant *cis* positions around the metal ion. Therefore, it is interesting to note that if an excess of Hsal is used in the solution study of the Fe^{3+}–Hsal–en system, the neutral [Fe(sal$_2$en)(sal)] complex is formed and its synthesis is described in the literature [23]. Because sal$^-$ is not a good ligand, the μ-oxo complex (eqn. (viii)) competes strongly and becomes the predominant species at high p[H] values as we have observed. However, if very good ligands for Fe^{3+}, such as catecholate anion, cat^{2-}, are used, a very stable [Fe(sal$_2$en)(cat)]$^-$ complex is formed [3, 22] (eqn. (xx)) precluding the formation of the μ-oxo complex at high p[H] values as shown in Fig. 5. The great affinity of Fe^{3+} for cat^{2-} is the reason for the removal of sal$_2$en^{2-} from the coordination sphere of iron(III) (eqn. (xxi)) at higher p[H] values, leading to the formation of the tris(catecholato)-ferrate(III) complex, $[Fe(cat)_3]^{3-}$(log $\beta = 49.85$) [16]

$$\mathrm{Fe^{3+} + sal_2en^{2-} + cat^{2-} \Leftrightarrow [Fe(sal_2en)(cat)]^-} \qquad \log \beta = 40.53\ [3] \qquad \text{(xx)}$$

$$\mathrm{[Fe(sal_2en)(cat)]^- + 2cat^{2-} \Leftrightarrow [Fe(cat)_3]^{3-} + sal_2en^{2-}} \qquad \log K = 9.32 \qquad \text{(xxi)}$$

On the reported results in dioxane–water mixture

We have not determined the formation constants of M^{n+}–salicylaldehyde complexes. It was considered unnecessary because the stabilities of the salicylaldehydato complexes are low and these complexes are formed only at high p[H] values if other stronger ligands are not present. As ethylenediamine forms very stable complexes with Ni^{2+} and Cu^{2+} and its formation occurs in slightly acid media, we have determined them potentiometrically. These values, as well as the acidity constants of Hsal and H_2en^{2+} determined in dmso–water (80:20 wt./wt.) (Table 3) are very close to the ones found in dioxane–water [5, 24]. Therefore, the solvent effect on the apparent basicity and stability of the ligands and complexes, is similar. In pure water this effect is considerably different. Anionic ligands are less basic and the metal complexes are less stable in water than in the above mentioned mixed solvent [25].

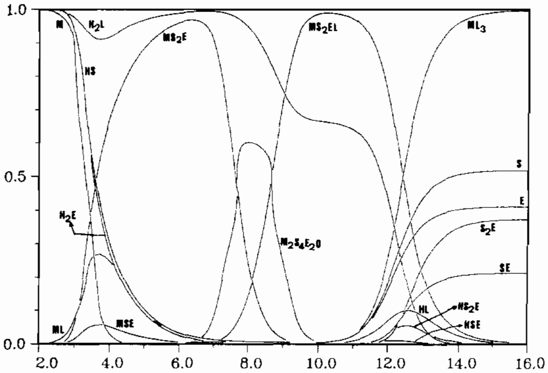

Fig. 5. Species distribution diagram of the Fe^{3+}–Hsal–en–H_2cat system: $[Fe^{3+}] = [en] = 10^{-3}$, $[Hsal] = 2\times10^{-3}$, $[H_2cat] = 3\times10^{-3}$ mol dm^{-3}. M = Fe^{3+}, $H_2L = H_2cat$, HL = Hcat$^-$, L = cat^{2-}, HS = Hsal, S = sal$^-$, $H_2E = H_2en^{2+}$, E = en, HSE = Hsalen, SE = salen$^-$, HS_2E = Hsal$_2$en$^-$, S_2E = sal$_2$en^{2-}, ML = [Fe(cat)]$^+$, $ML_3 = [Fe(cat)_3]^{3-}$, MSE = [Fe(salen)]$^{2+}$, MS_2E = [Fe(sal$_2$en)]$^+$, $M_2S_4E_2O$ = {[Fe(sal$_2$en)]$_2$O}, and MS_2EL = [Fe(sal$_2$en)(cat)]$^-$. The % of all the ethylenediamine containing species have been defined with respect to the initial concentration of en.

Recently, the Hsal–en system was reinvestigated by potentiometry in dioxane–water (70:30 vol./vol.) in order to determine the oxygenation constant of [Co(sal$_2$en)(MetPy)] (MetPy is 4-methylpyridine) [5b]. Such an investigation was carried out by continuous potentiometric titration of previously acidified solutions containing the different components (Co^{2+}, Hsal, en and MetPy) using a strong base as titrant. The treatment of this multicomponent system is extremely complicated because of the variety of species which are involved and the great number of constants to be computed simultaneously. In order to avoid this problematic situation and obtain unambiguous results, we have simplified it by using as starting solutions either the Schiff bases (H_2sal$_2$en, HsalenH$^+$) or their metal complexes ([M(sal$_2$en)]$^{(n-2)+}$), using $HClO_4$ and KOH as titrants in the corresponding potentiometric studies. The independent and different series of experiments that we have made are detailed in Table 1. No more than two constants are determined simultaneously in any of them, the only exception being the three constants involved in the system Ni(II)–en.

Although the scheme of formation of Schiff bases found in dioxane–water is qualitatively similar to that described herein in dmso–water, quantitatively there are remarkable differences both in the stability and acidity constants of these Schiff bases. They can be summarized as follows: (i) at millimolar concentrations and in neutral conditions in dmso–water, H_2sal$_2$en is a stable species and its formation is practically quantitative, whereas it decomposes partially in basic media. In dioxane–water the opposite situation is found: this bis(Schiff base) is much more stable in basic media than in neutral conditions where it decomposes to a high extent. From the stability constants given in ref. 5 it is easily inferred that the maximum degree of formation of H_2sal$_2$en is about 10% at p[H] *c.* 9. This result completely disagrees with our experimental observations. In fact, the synthesis of H_2sal$_2$en from Hsal and en in common organic solvents is practically quantitative even in dioxane–water mixtures. (ii) The logarithm of protonation constants of equilibria (1), (2), and (6) of Table 2 are 12.21, 11.10 and 11.5, respectively in dmso–water, whereas the corresponding values in dioxane–water [5b] are 9.55, 9.25 and 9.73. A comparison between these values and the corresponding ones to the free sal^- (9.75 in dmso–water and 10.18 in dioxane–water) shows that the phenolate group of sal^- is less basic than the one of Schiff bases in dmso–water, whereas in dioxane–water [5b] a similar basicity of the phenolate group is exhibited by all these species. The greater acidity of the phenolic group of the free Hsal with respect to the corresponding ones of the Schiff bases, can be understood taking into account that the hydrogen bond between the phenolic group and the imine-nitrogen is stronger than the corresponding one between the phenolic group and the carbonyl group. This phenomenon has been also observed in other Hsal-containing Schiff bases in a dioxane:water mixture [5a, 26]. We think that the origin of the differences between our results and the reported ones in ref. 5b lies in the low degree of formation ($\leqslant 10\%$) of $Hsal_2en^-$, H_2sal_2en, and Hsalen (eqns. (1), (2) and (6), respectively) under the presence of many others main species in dioxane–water [5b], which would lead to questionable values of such equilibrium constants. In the present work, the values of the constants concerning these equilibria have been determined through independent experiments (*vide supra*). (iii) The logarithm of the value of the stability constant (14.21) [5] for the reaction of complex formation between $salen^-$ and Co^{2+} in dioxane–water according to eqn. (xvii), compares well with the related ones for Cu^{2+} (20.7) and Ni^{2+} (16.9) herein reported. However, a too low value is reported in dioxane–water for the formation of $[Co(sal_2en)]$ species (14.56) [5b] when compared to the corresponding values for the related Cu^{2+} (26.16) and Ni^{2+} (22.60) ones in dmso–water. Of course, the higher stability of the sal_2en^{2-} complexes with respect to the $salen^-$ ones is due to the different chelating ability of these ligands (tetra- and terdentate, respectively). Surprisingly, stability constants of the same order of magnitude are obtained for the cobalt(II) complexes in dioxane–water.

Finally, since in ref. 5b the authors do not mention the slowness of the equilibria involved in Schiff bases formation, it is possible that the lack of equilibrium conditions were the origin of these discrepancies.

Conclusions

H_2sal_2en is thermodynamically stable in neutral media, its formation from Hsal and en being practically quantitative under such conditions. However, it is thermodynamically unstable with regards to the decomposition into its protonated or deprotonated components in acid or basic media. Therefore, the formation reaction of this bis(Schiff base) in basic medium from sal^- and en is precluded. Nevertheless, such a bis-base is kinetically stable due to its low rate of decomposition, so, its quantitative formation can be carried out by deprotonation of H_2sal_2en. Moreover, its formation is favored at high concentrations because of the stoichiometry of the corresponding formation reaction.

The neutral mono(Schiff base), Hsalen, as well as the anionic one, $salen^-$, are thermodynamically unstable with respect to the disproportionation reaction to yield the bis(Schiff base) and en. Therefore, their formation by reaction from their components is difficult. But again the low rate involved in this decomposition at room temperature allows their quantitative formation by deprotonation of $HsalenH^+$.

These Schiff bases are greatly stabilized by the presence of metal ions: sal_2en^{2-} and $salen^-$ are stable towards their disproportion when they are coordinated to metal ions. In this sense, the reaction of stoichiometric amounts of sal^- and en in the presence of M^{n+} (Cu^{2+} for instance) leads to the formation of the coordinated monobase to a high level. A slight excess of en favors its formation but a great excess precludes it, due to the formation of the corresponding ethylenediamine–metal complexes. $[Cu(sal_2en)]$ and $[Ni(sal_2en)]$ do not form hydroxo complexes, while $[Fe(sal_2en)]^+$ dimerizes to give a μ-oxo complex. In addition, $[Fe(sal_2en)]^+$ is able to coordinate bidentate ligands, L ($L=cat^{2-}$, sal^-, ox^{2-}). In these cases, the sal_2en^{2-} ligand adopts the *cis*-β octahedral configuration in order to accommodate the chelating ligand L. The demetallation of $[Fe(sal_2en)]^+$ is achieved in the presence of ligands such as catecholate which forms very stable complexes with Fe^{3+}.

Acknowledgements

Financial support by the Dirección General de Investigación Científica y Técnica (Project PB88-0490) is gratefully acknowledged. Thanks are also due to the Centro de Cálculo de la Universitat de València for computer facilities.

References

1 M. D. Hobday and T. D. Smith, *Coord. Chem. Rev., 9* (1972) 311.

2 F. Lloret, J. Moratal and J. Faus, *J. Chem. Soc., Dalton Trans.,* (1983) 1743.

3 F. Lloret, J. Moratal and J. Faus, *J. Chem. Soc., Dalton Trans.,* (1983) 1749.

4 R. S. McQuate and D. L. Leussing, *J. Am. Chem. Soc., 97* (1975) 5117; D. L. Leussing, *Met. Ions Biol. Syst., 5* (1976) 1.

5 (a) R. J. Motekaitis, A. E. Martell and D. A. Nelson, *Inorg. Chem., 23* (1984) 275; (b) R. J. Motekaitis and A. E. Martell, *Inorg. Chem., 27* (1988) 2718.

6 A. E. Martell and R. J. Motekaitis, *The Determination and Use of Stability Constants,* VCH, New York, 1988.

7 M. Gerloch, J. Lewis, F. E. Mabbs and A. Richards, *J. Chem. Soc. A,* (1968) 112.

8 J. Y. Dubsky and A. Sockol, *Collect. Czech. Chem. Commun., 3* (1931) 548.

9 D. Hall and T. N. Waters, *J. Chem. Soc. (London),* (1960) 2644.

10 R. Dingle, *Acta Chem. Scand., 20* (1966) 33.

11 E. García-España, M. J. Ballester, F. Lloret, J. Moratal and J. Faus, *J. Chem. Soc., Dalton Trans.,* (1988) 101.

12 G. Gran, *Analyst (London), 77* (1952) 661; F. J. C. Rossotti and H. Rossotti, *J. Chem. Educ., 42* (1965) 375.

13 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.,* (1985) 1195.

14 D. Martin and H. G. Hauthal, *Dimethyl Sulphoxide,* Van Nostrand Reinhold, Wokingham, Berks., UK, 1975.

15 F. Lloret, M. Mollar, J. Moratal and J. Faus, *Inorg. Chim. Acta, 124* (1986) 67.

16 F. Lloret, M. Julve, M. Mollar and J. Faus, unpublished work.

17 F. Lloret, J. Moratal and J. Faus, *An. Quim., 82B* (1986) 34.

18 K. Pachler and M. v. Stackelberg, *Z. Anorg. Chem., 305* (1960) 286.

19 M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A,* (1967) 1900.

20 E. Sinn, *Coord. Chem. Rev., 5* (1970) 313.

21 (a) F. Lloret, M. Julve, M. Mollar, I. Castro, J. Latorre, J. Faus, X. Solans and I. Morgenstern-Badarau, *J. Chem. Soc., Dalton Trans.,* (1989) 729; (b) F. Lloret, M. Julve, J. Faus, X. Solans, Y. Journaux and I. Morgenstern-Badarau, *Inorg. Chem., 29* (1990) 2232; (c) I. Malfant, I. Morgenstern-Badarau, M. Philoche-Levisalles and F. Lloret, *J. Chem. Soc., Chem. Commun.,* (1990) 1338.

22 R. B. Lauffer, R. H. Heinstand II and L. Que, Jr., *Inorg. Chem., 22* (1983) 50.

23 M. Nakamura, I. Itho, H. Okawa and S. Kida, *J. Inorg. Nucl. Chem., 43* (1981) 2281.

24 A. E. Martell and R. M. Smith, *Critical Stability Constants,* Vol. III, Plenum, New York, 1977.

25 M. Mollar, F. Lloret, J. Moratal and J. Faus, *Bull. Soc. Chim. Fr., 2* (1985) 170, and refs. therein.

26 R. W. Green and P. W. Alexander, *Aust. J. Chem., 18* (1965) 329.