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Complexation equilibria of N,N′-*o*-phenylenebis(salicylideneimine)

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Abstract—The ionization constants of the Schiff base ligand N,N′-*o*-phenylenebis(salicylideneimine) (sal-*o*-phn) and its stability constants with Fe^{III}, Ni^{II}, Co^{II}, Zn^{II}, Cd^{II}, Ca^{II} and Mg^{II} have been determined for the first time in DMSO–water 80 : 20 wt/wt ($T = 25°C$; $I = 0.5$ mol dm^{-3} in $NaClO_4$) by potentiometric methods. The monomer species [ML] and $[MHL]^+$ are found to be formed. In the case of Fe^{III}-sal-*o*-phn the hydroxocomplex species [FeOHL] was also detected. Fe^{3+} was observed to be hydrolyzed to a much lesser extent in DMSO–water 80 : 20 wt/wt than in aqueous solution. © 1997 Elsevier Science Ltd

Keywords: Schiff base complexes; stability constants; monomer complexes; iron(III).

Schiff bases derived from *o*-phenylenediamines and salicylaldehyde with a N_2O_2 donor set have been widely studied in solid state [1]. The conformation of these Schiff bases with the nitrogen atoms in *ortho* position on the aromatic ring permits their simultaneous coordination to the same metal to give mainly monomer complexes as has been established by the determination of the crystal structures of the complexes: N,N′-*o*-phenylenebis(salicylideneimine) (sal-*o*-phn) with Co^{II} [2] and Cu^{II} [3] and of N,N′-3-4-toluenebis(salicylideneimine) (sal-3,4-toluen) with Ni^{II} [4].

Thermodynamic data available for these type of Schiff base complexes are in general scarce, which can be attributed mainly to their insolubility in water which is the most common solvent for potentiometric determination. For this reason, the potentiometric study of these compounds requires the use of an organic or aquo–organic solvent where these complexes are soluble and which presents furthermore compatibility with the standard glass electrode. In this context, the DMSO–water 80 : 20 wt/wt [5–7] as well as dioxane–water mixtures [8] have been reported to be suitable solvents for the solution study of Schiff base complexes similar to those of the present paper.

In the literature, to our knowledge, the only thermodynamic studies of Schiff base complexes derived from *o*-phenylenediamines described so far are: the dimerization of the complex [6] Fe(sal-*o*-phn)Cl, the multicomponent system 3-fluorosalicylaldehyde-*o*-phenylenediamine-4-methylpyridine-Co^{II}-oxygen [8] and the study of sal-3,4-toluen with some divalent cations [4].

In this work we have determined for the first time by potentiometric methods the ionization constant of the ligand sal-*o*-phn and the stability of its complexes with Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, Ca^{II} and Mg^{II} in DMSO–water 80 : 20 wt/wt ($T = 25°C$; $I = 0.5$ mol dm^{-3} $NaClO_4$). The study of the hydrolysis of Fe^{III} in this mixed solvent was also carried out.

EXPERIMENTAL

Reagents

Ortho-phenylenediamine and salicylaldehyde were purchased from Merck and used without further purification. The Schiff base ligand sal-*o*-phn was synthesized by refluxing in ethanol the *o*-phenylenediamine with salicylaldehyde in the ratio 1 : 2 as previously described [9]. Dimethyl sulfoxide (DMSO) Merck p.a (max. 0.02% water) was purified by distillation under reduced pressure (*ca* 2 Torr) and stored in a dark bottle over 4 Å molecular sieves. The

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DMSO–water mixture (80 : 20 wt/wt) was prepared from this solvent. All solutions used in the potentiometric study were prepared from this mixed solvent. The Mg^{II}, Co^{II} and Ni^{II} stock solutions were prepared from commercial perchlorates (Aldrich). Zn^{II}, Cd^{II} and Ca^{II} perchlorates were prepared by reacting the corresponding metal carbonates with perchloric acid and further recrystallized. All these metal solutions were standardized complexiometrically. The iron(III) stock solution was prepared from $Fe(NO_3)_3 \cdot 9H_2O$ (Merck *a.g.*) and standardized according to the literature methods, by reduction to iron(II) with $SnCl_2$ and titrated with a standard solution of potassium dichromate [10]. A carbonate-free sodium hydroxide [prepared from ampoule 9959 Titrisol (Merck)] and perchloric acid (Merck) solutions were used as titrants in the potentiometric studies. $NaClO_4$ (Merck *a.g.*) was purified by recrystallization and then used as a background electrolyte.

Potentiometric measurements

Potentiometric titrations were carried out in DMSO–water (80 : 20 wt/wt) solution at ionic strength 0.5 mol dm^{-3} in $NaClO_4$ using a reaction vessel (capacity 70 cm^3) water-thermostatted at 25.0 ± 0.1°C. An argon presaturated with DMSO–water (80 : 20 wt/wt) was passed over the surface of the solution during the experiment to eliminate the atmospheric carbon dioxide. The titrant was delivered by a CRISON-microbur 2031. The potentiometric measurements were made using a Radiometer PHM-85 potentiometer and a Radiometer GK 2401 B combined electrode. The electrode was modified by replacing its aqueous KCl solution with a DMSO–water (80 : 20 wt/wt) solution of 0.5 mol dm^{-3} $NaClO_4$. A Basic program [11] was used to monitor the e.m.f. values and the volume of titrant added for each titration point. When the observed e.m.f. was constant, within user-defined limits, the next volume of titrant was added automatically and the cycle repeated until the predefined total volume of titrant had been added. The cell constants E° and the liquid junction potentials J were determined according to the method of Biedermann and Sillen [12], by means of a least-squares program. The liquid junction potential was found to be almost negligible within the ranges of $[H^+]$ studied. The autodissociation constant of the solvent was 18.25 in good agreement with the reported data [5–7]. This constant was determined at the beginning of each experiment to verify the correct working of the electrode and the reliability of the potential measurements.

Potentiometric measurements were carried out: (a) for the ligand alone at different concentrations: 2×10^{-3}, 3×10^{-3} and 4×10^{-3} mol dm^{-3} (titrations with NaOH and $HClO_4$); (b) for the ligand in the presence of the different metal cation at the ligand : metal ratios: 2 : 1, 1 : 1 and 1 : 2, using different metal concentrations $C_M = 1.0 \times 10^{-3}$, 2.0×10^{-3} and 3×10^{-3} mol dm^{-3}, (titrations with NaOH); (c) for the study of the hydrolysis of Fe^{3+}, solutions of ferric nitrate in DMSO–water 80 : 20 wt/wt of concentration $5\text{–}10 \times 10^{-3}$ mol dm^{-3} were titrated with $HClO_4$ 0.1 mol dm^{-3}. The SUPERQUAD program [13] was used to process all the experimental potentiometric data and calculate both the protonation and stability constants of sal-*o*-phn and its metal complexes.

UV–visible absorption spectra

The UV–vis spectra were performed on a SHIMADZU UV-2101 PC spectrophotometer.

RESULTS AND DISCUSSION

The study of complex formation of sal-*o*-phn cannot be carried out in aqueous solution because of the nature of the compounds involved. These metal complexes as well as the ligand itself are insoluble in water. This solvent have been most widely used for potentiometric determination of stability constants. The mixture DMSO–water 80 : 20 wt/wt was the chosen solvent for our study. In such a medium, both sal-*o*-phn and its metal complexes are soluble giving stable solutions. The use of this mixed solvent has some advantages over pure DMSO. Thus, pure DMSO is very hygroscopic and controlling its water content is difficult [14]. This fact would affect the reproducibility of our experiments. However, DMSO–water 80 : 20 wt/wt mixture has only a small hygroscopic character. A further advantage is its compatibility with the standard glass electrode, so that the pH measurements may be carried out in a similar way to that employed in a purely aqueous solution. In contrast, the glass electrode has a slow response and irreproducible behaviour in pure DMSO [15]. For these reasons, the use of pure DMSO is not recommended for potentiometry. Another advantage of the mixture DMSO–water 80 : 20 wt/wt is its large acidity range (pKw = 18.25) which allows the investigation of deprotonation equilibria of weak acids which could be hardly studied in water [4–5].

The sal-*o*-phn dissolves in DMSO–water 80 : 20 wt/wt to give a yellow solution which displays a band in the UV–vis spectrum at 337 nm ($\varepsilon = 1.34 \times 10^4$ dm^3 mol^{-1} cm^{-1}) corresponding to species H_2L (see species distribution diagram in Fig. 1). This solution is stable and the absorbance values do not change with time. The colour of this solution is intensified when adding NaOH, indicating the deprotonation of both phenolic groups. As a consequence, a shift in the absorption band to longer wavelength is observed: 385 nm ($\varepsilon = 1.28 \times 10^4$ dm^3 mol^{-1} cm^{-1}) related to species L^{2-} (Fig. 1). The reaction is reversible giving back the initial species when neutralizing the added NaOH.

When the yellow solution is acidified a decay in the intensity of the colour is observed due to protonation

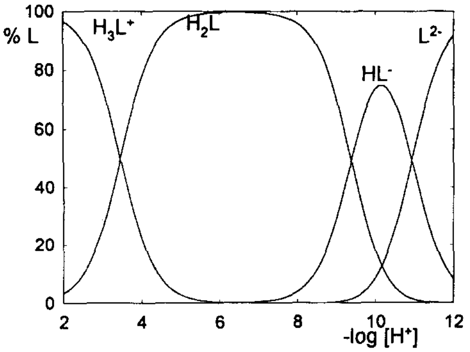

Fig. 1. Species distribution diagram as a function of $-\log[H]^+$ for N,N'-*o*-phenylenebis(salicylideneimine) (sal-*o*-phn).

of the aromatic nitrogen (species H_3L^+). Thus at pH 3, the spectrum shows a band centered at 330 nm ($\varepsilon = 6.50 \times 10^3$ dm^3 mol^{-1} cm^{-1}). When the solution is strongly acidified it becomes colourless.

The values of log β_{pr} (defined by equilibrium 1) and pK_i of the ligand, together with the value of the hydrolysis constant of Fe^{3+} are listed in Table 1. For comparative purposes, in Table 1 are also shown the pK_i values for the Schiff base ligands 3-fluoro-N,N'-*o*-phenylenebis(salicylideneimine) (3-F-sal-*o*-phn) [8] and sal-3,4-toluen [4].

$$pH^+ + rL^{2-} \rightleftarrows [H_pL_r]^{(p-2r)+} \quad \beta_{pr} \qquad (1)$$

The Schiff base sal-*o*-phn is tetradentate with two adjacent weak imine donors and two strongly basic phenolate groups, thus it behaves like a weak diprotic acid. Only one protonation constant has been obtained above pH 2.5, thus indicating the low basicity of the imine nitrogen. A second protonation step was not evidenced. The values obtained for the ionization constant of sal-*o*-phn (Table 1) are in good agreement with those reported for similar ligands such as 3-F-sal-*o*-phn [8] (despite the differences in the solvent, ionic strength and structural features of the ligands) and sal-3,4-toluen [4]. For the latter the pK_i values obtained in DMSO–water 80:20 wt/wt are slightly higher than those for sal-*o*-phn (Table 1) which is attributable to the electron-donor effect of the methyl substituent on the aromatic ring.

The Schiff base ligand N.N'-ethylenebis (salicylideneimine) (salen) and its metal complexes undergo hydrolytic decomposition in strongly acid DMSO–water 80:20 wt/wt solution induced by the highly basic character of the nitrogen atoms of the aliphatic ethylenediamine [5]. Contrarily, the Schiff base sal-*o*-phn and its complexes, due to the low basic character of the nitrogen atoms of the aromatic diamine are completely stable in DMSO–water 80:20 wt/wt solution above the pH range investigated (>2.5).

The species distribution diagram as a function of pH for the ligand sal-*o*-phn is displayed in Fig. 1. The diagram indicates that in the pH range 5–8, the only existing species is H_2L, whereas int he pH range 9–11, the species H_2L, HL^- and L^{2-} coexist. At pH> 12, only the fully deprotonated ligand (species L^{2-}) is present.

The hydrolysis of iron(III) has been widely studied in aqueous solution [16,17] and numerous models have been established including as major species Fe^{3+} (solv), $[Fe(OH)]^{2+}$, $[Fe(OH)_2]^+$ and $[Fe_2(OH)_2]^{4+}$. The great tendency to hydrolysis in aqueous solution of Fe^{3+} makes the study of its complexation equilibria difficult. However, the use of DMSO or DMSO–water 80:20 wt/wt mixtures as solvent presents the advantage of reducing considerably the hydrolysis of Fe^{3+}. In the conditions of concentrations and pH investigated (see Experimental), only the species Fe^{3+} and $Fe(OH)^{2+}$ were found to be formed. The hydrolysis constant (long $\beta_{-11} = -4.74(2)$) corresponding to equilibrium (2) is shown in Table 1. This value is in good agreement with the one reported in the literature [18] (Table 1) for the hydrolysis of Fe^{III} in this solvent $I = 0.1$ mol dm^{-3} $KClO_4$. There is no evidence for hydrolysis at pH less than 3 and at pH 3.5 the per-

Table 1. Hydrolysis of the Fe^{III} and ionization constants of sal-*o*-phn ligand in DMSO–water 80:20 wt/wt ($T = 25°C$; $I = 0.5$ mol dm^{-3} in $NaClO_4$)

(a) Hydrolysis of the Fe^{III}

pqr	Species	$-\log\beta_{pqr}$	
−110	$Fe(OH)^{2+}$	4.74(2)[a]	4.52(1)[b]

No. of titrations 2; no. of points 39; $-\log[H^+]$ range 2.3–3.5; $\sigma = 2.7$; $Chi^2 = 6.7$

(b) Ionization constants of the ligand (H_2L)

pr	log β_{pr}	Equilibria	pK_i	pK_i[c]	pK_i[d]
11	10.94(1)	L^{2-}/HL^-	10.94(1)	11.49(2)	11.23(2)
21	20.33(1)	HL^-/H_2L	9.39(1)	9.41(2)	8.41(5)
31	23.79(1)	H_2L/H_3L^+	3.46(1)	3.63(3)	3.17(2)

No. of titrations 5; no. of points 164; $-\log[H^+]$ range 3.1–10.3; $\sigma = 2.8$; $Chi^2 = 15.4$

[a] Values in parentheses are standard deviations.

[b] $I = 0.1$ mol dm^{-3} $KClO_4$ from ref. [18].

[c] sal-3,4-toluen ligand from ref. [4].

[d] 3-F-sal-*o*-phn from ref. [8].

centage of hydrolytic species $[Fe(OH)]^{2+}$ is only 5% at 10×10^{-3} mol dm^{-3}. We could not carry out the study of hydrolysis at higher pHs because the addition of NaOH leads to potentiometrically unstable solutions.

$$Fe^{3+}(solv.) \rightleftarrows Fe(OH)^{2+}(solv.) + H^{+}(solv.) \quad (2)$$

The $Fe(OH)^{2+}$ species was considered in the equilibrium scheme of the system Fe^{III}-sal-*o*-phn, however its influence was negligible in the values of the stability constants. This can be understood by the strong complexing ability of the ligand which leads to a very small $[Fe^{3+}]$ even at low pHs.

The model that best fits the experimental data for the metal–ligand systems investigated is that which corresponds to the complex species and log β_{pqr} values reported in Table 2. From the log β_{pqr} constants and taking into account the log β_{pr} of sal-*o*-phn, the stability constants (log K) of the complex species can be easily determined. β_{pqr} is defined by means of equilibrium (3).

$$pH^{+} + qM^{2+} + rL^{2-} \rightleftarrows [H_pM_qL_r]^{(p+2q-2r)+} \quad \beta_{pqr} \quad (3)$$

Only monomer species are observed. The species ML result from the coordination of the metal with the ligand fully deprotonated and in the species $[MHL]^{+}$ the metal is tricoordinated by the ligand, the other coordination positions being occupied by solvent molecules. The monoprotonated complex $[MHL]^{+}$ may be assumed to be protonated at the phenol oxygen on one salicylaldehyde moiety, as in the case of protonation of the free Schiff base.

For the system sal-*o*-phn-Fe^{III}, the hydroxocomplex [FeLOH] was also formed. The complex Fe(sal-*o*-phn)$^{+}$ hydrolyses in basic solution according to equilibrium (4) to give the μ-oxo-dimer $[Fe(sal\text{-}o\text{-}phn)_2]O$, this process being accompanied by a colour change from brownish-green to red

$$2Fe(sal\text{-}o\text{-}phn)^{+} + H_2O \rightleftarrows [Fe(sal\text{-}o\text{-}ph)]_2O + 2H^{+} \quad (4)$$

The μ-oxo-dimer $[FeL]_2O$ has been characterized in the solid state [19] and its crystal structure has been reported [20]. The dimerization constant in DMSO–water 80 : 20 wt/wt for equilibrium (4) was determined by Lloret *et al.* [6] by potentiometric and spectrophotometric titration of solutions of Fe(sal-*o*-phn)Cl with KOH but the stability constant of Fe(sal-*o*-phn)$^{+}$ was not determined. For this system, we could not determine the stability constant of the μ-oxo-dimer $[FeL]_2O$ because in the pH range where this species should be formed, the e.m.f. readings were unstable. No hydroxocomplex formation was observed for the remaining cations.

The Co(sal-*o*-phn) [2] and Ni(sal-3,4-toluen) [4] complexes in the solid state have a square planar arrangement of the N_2O_2 donors wrapped around the metal atom. The solutions of sal-*o*-phn in the presence of Co^{II} and Ni^{II} in DMSO–water 80 : 20 wt/wt are red as their solid complexes. So we may assume the retention of the square-planar geometry in solution. However, for this four-coordinate Co^{II} chelate a fifth coordination site can be occupied by a monodentate Lewis base such as pyridine to give an adduct which can bind reversibly molecular oxygen in a position *trans* to the axial base. In our case, the oxygenation of CoL does not occur since we have worked under inert conditions. Martell *et al.* [8] have studied the multicomponent system 3-fluorosalicylaldehyde-*o*-phenylenediamine-4-methylpyridine-Co^{II}-oxygen in dioxane : water 70 : 30 v/v in order to obtain the oxygenation constants of the Co^{II} complex. The values obtained for us for $[CoHL]^{+}$ and [CoL] are in good

Table 2. Stability constants of the complexes of sal-*o*-phn with Fe^{III}, Ni^{II}, Co^{II}, Zn^{II}, Cd^{II}, Mg^{II} and Ca^{II} in DMSO–water 80 : 20 wt/wt ($T = 25°C$; $I = 0.5$ mol dm^{-3} in $NaClO_4$)

				log β_{pqr}					
pqr	Fe^{III}		Ni^{II}	Co^{II}	Zn^{II}	Cd^{II}	Mg^{II}	Ca^{II}	
011	17.80(2)[a]		14.82(2)	14.64(6)	13.31(1)	7.24(1)	6.28(1)	4.28(1)	
111	21.52(2)		20.01(1)	20.75(2)	18.01(1)	15.77(1)	14.56(1)	13.49(1)	
−111	12.99(3)								
				log K					
Species		Species							Co^{II}[b]
$[FeHL]^{2+}$	10.58(2)	$[MHL]^{+}$	9.08(2)	9.81(6)	7.07(1)	4.83(1)	3.62(1)	2.55(1)	10.62(2)
$[FeL]^{+}$	17.80(2)	[ML]	14.82(1)	14.64(2)	13.31(1)	7.23(1)	6.28(1)	4.27(1)	14.91(2)
[FeL(OH)]	31.24(4)								
No. of titrations	3		4	4	4	3	3	4	
No. of points	151		50	88	93	48	68	83	
pH range	2.9–5.5		3.4–4.6	3.4–5.6	4.1–5.2	6.4–8.5	7.5–8.6	8.1–9.7	
σ/Chi^2	3.3/3.6		3.7/11.1	3.1/8.2	3.2/2.2	3.5/5.6	3.2/10.6	2.7/12.71	

[a] Values in parentheses are standard deviations.

[b] 3-F-sal-*o*-phn-Co^{II}, dioxane-water 70 : 30 *v/v* from ref. [8].

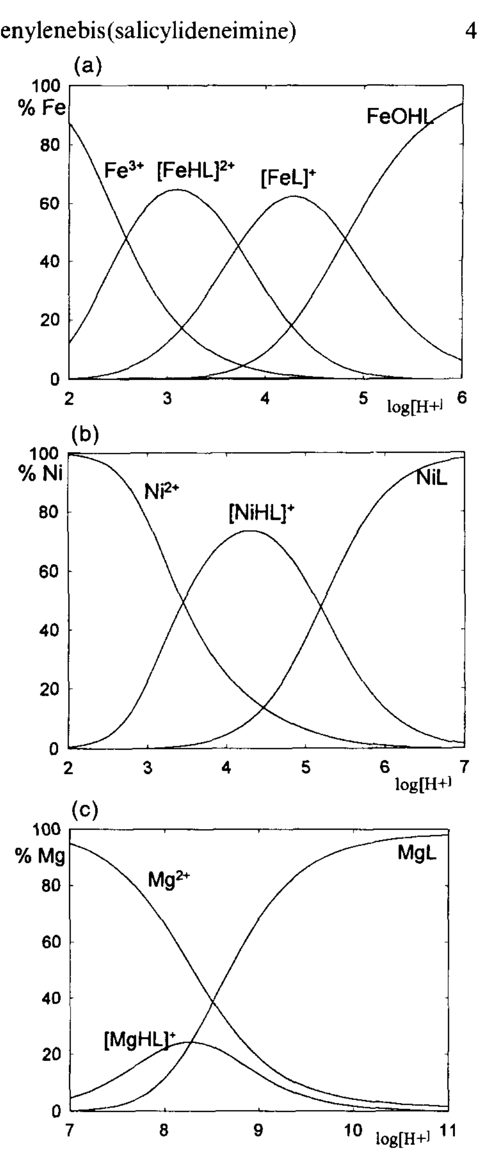

Fig. 2. Species distribution diagrams as a function of $-\log[H^+]$ at ligand : metal ratio 1 : 1 and $C_m = 3.0 \times 10^{-3}$ mol dm^{-3} for the systems : (a) sal-*o*-phn-Fe^{III} ; (b) sal-*o*-phn-Ni^{II} ; (c) sal–*o*-phn-Mg^{II}.

agreement with those reported by Martell *et al.* [8] for 3-F-sal-*o*-phn-Co^{II} (Table 2). The systems sal-3,4-toluen-M^{II} (M = Ni, Co, Zn, Cd, Ca and Mg) give complexes more stable than those of sal-*o*-phn due to the electron-donor effect of the methyl group of sal-3,4-toluen favourable to coordination [4].

As shown in Table 2, the complex species ML for M = Fe, Ni, Co and Zn are very stable as indicated by the high values of their stability constants, thus indicating coordination of both imino groups and the phenolate oxygens to metal. The stability constants for the Ni^{II} and Co^{II} species are similar and slightly higher than for Zn^{II}. This result agrees well with the crystallographic studies which indicate that the M—O and M—N bond distances in the solid complexes Co(sal-*o*-phn) [2] (1.84 and 1.87 Å average, respectively) and Ni(sal-3,4-toluen) · 1.5CHCl$_3$ [4] (1.84 and 1.86 Å average, respectively) are almost the same.

As expected, log K_{ML} for Ca^{II} and Mg^{II} are considerably smaller than those for the cations described above, the Mg^{II} complex species being more stable than the Ca^{II} ones. The Mg^{2+} (smaller in size than Ca^{2+}) can be better accommodated by the N_2O_2 compartment of the ligand than Ca^{2+} thus giving more stable species, regular sequence for Mg^{II} and Ca^{II} [21].

Studies in solid state [22] have shown the dimeric nature of [{Mg(sal-*o*-phn)}$_2$], [{Mg(salen)}$_2$] and [{Mg(acen)}$_2$] (acen = N,N′-ethylenebis(acetylacetoneimine)). For the latter the crystal structure has been determined [22]. The acen molecules are bridging the two metal atoms. The high tendency of Mg to achieve five coordination favours dimerization. However, this structure may differ from that in solution of oxygen-donor solvents, because of the equilibrium (5) (L = salen, sal-*o*-phn, acen ; solv = thf, acetone). The authors [22] have suggested that only one of the two forms is detectable in solution.

$$[\{Mg(L\text{-}L)\}_2] + 2solv \rightleftarrows 2(MgL)solv \qquad (5)$$

In DMSO–water 80 : 20 wt/wt we have only observed the monomer form in which probably magnesium binds a DMSO molecule to achieve five coordination.

The stability sequence observed for the species ML is: $Fe^{III} > Ni^{II} \approx Co^{II} > Zn^{II} > Cd^{II} > Mg^{II} > Ca^{II}$. Thus, the Irving–Williams order of complexation which is related to the ligand-field stabilization energies is fulfilled.

The species distribution diagrams are the best way to illustrate the relative stabilities of the existing species and the resulting extent of formation of each one. Furthermore, they permit us to select the best conditions of pH, concentration and ligand : metal ratio for the preparation of a complex in the solid state. The species distribution diagram as a function of pH for sal-*o*-phn-Fe^{III} [Fig. 2(a)] at $C_M = 3 \times 10^{-3}$ mol dm^{-3} and ligand : metal ratio 1 : 1 shows that in the pH range 3.8–4.8 [FeL]$^+$ is the major species which reaches at pH 4.5 a percentage of 60%. This species has been isolated in the solid state as the chloro complex [23] Fe(sal-*o*-phn)Cl and its crystal structure has been reported [24]. In the pH range 3.5–5.5 there is a coexistence of the species [FeHL]$^{2+}$, [FeL]$^+$ and [FeLOH]. Lloret *et al.* [6] have observed that the dimer [FeL]$_2$O begins to be formed at pH > 6.5. In our case, we could not get the complete titration curve because of the instability observed in the solutions of sal-*o*-phn-Fe^{III} at pH higher than 5.

For sal-*o*-phn-Ni^{II}, the species distribution diagram [Fig. 2(b)] indicates that the monoprotonated complex [NiHL]$^+$ is the major species in the pH range 3.5–5.0. This species deprotonates to give the species NiL, which is the only existing species at pH > 7. Analogous diagrams are obtained for Co^{II} and Zn^{II}. From these diagrams, we can conclude that a concentrated solution of ligand : metal ratio 1 : 1 at pH > 7 is the most suitable for the preparation of the ML complex (M = Ni, Co, Zn) in the solid state.

For sal-*o*-phn-Mg^{II}, the species distribution diagram [Fig. 2(c)] shows that the monoprotonated complex $[MgHL]^+$ exists in the wide pH range 6.5–10. The major species[MgL] begins to be formed at pH > 7.5, becoming the only existing species at pH > 10.5. An analogous diagram was obtained for Ca^{II}.

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