Solution Chemistry of *NN'*-Ethylenebis(salicylideneiminato)iron(III). Part 1. Deprotonation Equilibria and Reversible Decomposition in Acid Medium of *NN'*-Ethylenebis(salicylideneimine). Stability Constant of *NN'*-Ethylenebis(salicylideneiminato)iron(III)

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NN'-Ethylenebis(salicylideneimine), H_2salen, behaves as a weak diprotic acid in dimethyl sulphoxide (dmso)–H_2O (80:20 w/w) solution. The values of the overall association constants are $\beta_{j1} = (1.63 \pm 0.05) \times 10^{12}$ dm^3 mol^{-1} and $\beta_{j2} = (2.04 \pm 0.02) \times 10^{23}$ dm^6 mol^{-2}. H_2salen undergoes slow hydrolytic decomposition in acid medium [equations (i) and (ii)] (Hsal = salicylaldehyde, en = ethylenediamine);

$$H_2\text{salen} + H^+ \xrightleftharpoons{\beta_{h1}} \text{Hsal} + HOC_6H_4CH{=}N(CH_2)_2NH_3^+ \quad \text{(i)}$$

$$H_2\text{salen} + 2\,H^+ \xrightleftharpoons{\beta_{h2}} 2\,\text{Hsal} + H_2\text{en}^{2+} \quad \text{(ii)}$$

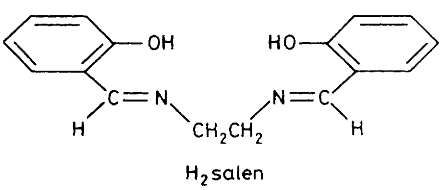
$\beta_{h1} = (2.60 \pm 0.05) \times 10^4$ and $\beta_{h2} = (1.60 \pm 0.02) \times 10^7$. The favourable thermodynamics for the hydrolysis are provided by the protonation of en. In neutral or basic media the hydrolysis is not spontaneous in spite of the large water content of the solvent. Solutions of [{Fe(salen)Cl}$_2$] in dmso–H_2O contain the cation [Fe(salen)]$^+$. The chloride is completely displaced from the co-ordination sphere of Fe^{III} by a solvent molecule, and [Fe(salen)]$^+$ decomposes, in acid medium, very slowly [equation (iii)].

$$[\text{Fe(salen)}]^+ + 4\,H^+ \rightleftharpoons Fe^{3+} + 2\,\text{Hsal} + H_2\text{en}^{2+} \quad \text{(iii)}$$

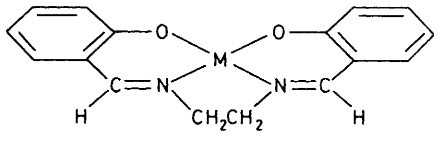
The study of this equilibrium allows the stability constant of the complex, $Fe^{3+} + \text{salen}^{2-} \rightleftharpoons [\text{Fe(salen)}]^+$, $\beta = (7.1 \pm 0.1) \times 10^{25}$ dm^3 mol^{-1} to be obtained. This is the first reported stability constant of a metal complex of H_2salen. All equilibrium constants were determined at 25 °C and 0.1 mol dm^{-3} $KClO_4$ in dmso–H_2O (80:20 w/w).

The iron(III) complexes of *NN'*-ethylenebis(salicylideneimine) (H_2salen) have aroused great interest since the first synthesis of [{Fe(salen)Cl}$_2$] was reported.[1] This compound can exist, in the solid state, either in dimeric or monomeric form depending on the nature of the solvent used in its recrystallization.[2] A dimeric oxo-complex [{Fe(salen)}$_2$O] [1,3] is also known. By the end of the 1960's the magnetic properties [3,4] and molecular structure [2,5,6] of these complexes were widely investigated. More recently, Hendrickson and co-workers [7,8] have studied the redox reactions between [Fe^{II}(salen)] and several quinones, isolating a variety of Fe^{III}(salen) complexes with diphenolate or semiquinone ligands. Que and co-workers [9-11] have obtained Fe^{III}(salen) complexes with catecholate ligands and Okawa and co-workers [12] have isolated a series of Fe^{III}(salen) complexes with bidentate ligands such as acetylacetone, salicylaldehyde, *etc.*

All the research concerning these complexes has been based on their syntheses and structural characterization, however their solution behaviour has not yet been studied. In addition, neither the formation equilibrium of [Fe(salen)]$^+$ nor its interaction with other ligands have yet been investigated. In fact, up to now, the stability constant of any metal complex of H_2salen has not been established and the available data about the stability of other Schiff-base complexes are very scarce.[13,14]



H_2salen



[M^{III}(salen)]$^+$

Experimental

Reagents and Solvent.—The compounds H_2salen and [{Fe(salen)Cl}$_2$] were synthesized and purified as reported in the literature.[4] All the other chemicals were Merck reagents. Dimethyl sulphoxide (dmso) was purified by distillation under reduced pressure (~2 Torr) and stored in a dark bottle over 4A molecular sieves. From this solvent the dmso–H_2O mixture (80 : 20 w/w) was obtained. All the solutions used in this work were prepared with this mixed solvent. Carbonate-free potassium hydroxide (0.1 mol dm^{-3}) and perchloric acid (0.1 mol dm^{-3}) solutions were used in the potentiometric and spectrophotometric studies.

Physical Techniques.—Potential measurements were performed with a Radiometer 84 pH-meter using a GK2401C combined glass electrode. The electrode was dipped in dmso–H_2O (80 : 20) for 30 min before use. The response of the electrode was instantaneous and potential readings were reproducible within the instrument uncertainty (±0.1 mV). Nernst's equation, $E = E_A^{0'} + 0.0591 \log [H^+]$, was strictly obeyed by the electrode in this medium. Accurate concentration of the basic titrant as well as the $E_A^{0'}$ value were determined with a perchloric acid solution before each titration series. Measurements were carried out at 25.0 ± 0.1 °C in an N_2 atmosphere and in 0.1 mol dm^{-3} $KClO_4$.

Absorption spectra were recorded with a u.v.-visible Pye Unicam SP 100-8 spectrophotometer using 0.1-cm length cuvettes. Conductivity measurements were performed with a Radiometer CDM3 conductimeter.

Autodissociation Constant of the Solvent.—We determined K_w, the autodissociation constant of the solvent, by potentiometry, titrating $HClO_4$ solutions of accurately known concentration with KOH. From the acid side of the potentiometric curve the $E_A^{0'}$ value is obtained from $E = E_A^{0'} + 0.0591 \log [H^+]$, whereas $E_B^{0'}$ is obtained from the basic side using $E = E_B^{0'} - 0.0591 \log [OH^-]$. pK_w is given by $(E_B^{0'} - E_A^{0'})/0.0591$ ($E_A^{0'}$ and $E_B^{0'}$ are the specific cell constants for the acidic and basic regions respectively). From a large number of experiments we obtained $pK_w = 18.34 \pm 0.02$ (25 °C, 0.1 mol dm^{-3} $KClO_4$). The constant K_w was determined at the beginning of this work and then many times during its realization in order to verify the correct working of the electrode and the reliability of the potential measurements.

Chromatographic Identification of Salicylaldehyde.—The existence of salicylaldehyde (Hsal) in the acidified solutions of H_2salen and $[Fe(salen)]^+$ 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 chromatogram to u.v. light (λ = 254 nm) revealed a spot with the same R_f value (~0.8) as that of a Hsal reference sample. On treating the plate with 2,4-dinitrophenylhydrazine, a specific reagent for aldehydes and ketones, an orange spot of the corresponding 2,4-dinitrophenylhydrazone appears. We did not find Hsal in non-acidified or basic solutions.

Results

Solutions of H_2salen *and* $[\{Fe(salen)Cl\}_2]$: *A Spectrophotometric Study.*—The Schiff-base H_2salen dissolves readily in dmso–H_2O (80 : 20) to give yellow solutions which display three absorption bands at 400 (ε *ca.* 10^3 dm^3 mol^{-1} cm^{-1}), 316 (*ca.* 7×10^3), and 255 nm (*ca.* 2×10^4). These solutions are stable and the absorption values do not change with time (Figure 1). When adding KOH to these solutions a remarkable spectral change takes place (Figure 1). The reaction, which is complete when adding two moles of OH^- for each mole of H_2salen, is reversible giving back the initial species when neutralizing the added base. These changes indicate the deprotonation of the H_2salen phenolic groups [equation (1)].

When the yellow H_2salen solutions are acidified, a slow drop in the intensity of the colour is observed. When enough acid

$$H_2\text{salen} + 2\,OH^- \rightleftharpoons \text{salen}^{2-} + 2\,H_2O \qquad (1)$$

is added the decolouration becomes complete. We recorded the u.v.-visible absorption spectra of a series of solutions in which the H_2salen concentration was kept constant, c_L = *ca.* 5×10^{-3} mol dm^{-3}, and the acid concentration, c_A, was varied. All the spectra showed gradual modifications with time, requiring about 15 d to reach equilibrium, after which the absorption values were stable and reproducible. The spectra of solutions with ratios $c_A : c_L < 2$, still yellow, revealed that the band at 255 nm remained almost unchanged; the intensity of the band at 400 nm decreased as the $c_A : c_L$ ratio increased whereas the band at 316 nm shifted towards longer wavelength. Solutions with $c_A : c_L \geqslant 2$ were completely colourless and only displayed two absorption bands at 255 and 328 nm (Figure 1).

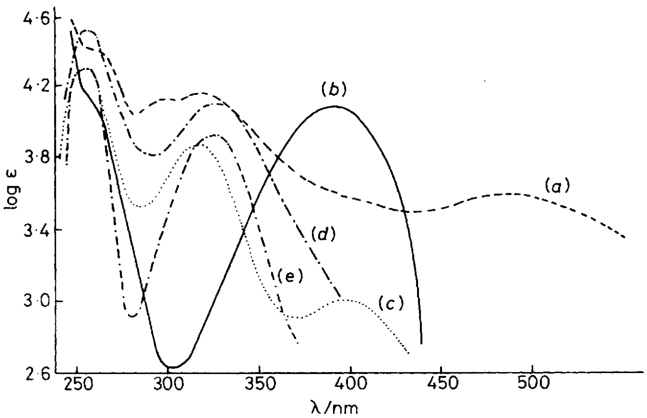


Figure 1. U.v.–visible absorption spectra, in dmso–H_2O (80 : 20) solution, of (*a*) $[Fe(salen)]^+$; (*b*) salen^{2-}; (*c*) H_2salen; (*d*) $[Fe(salen)]^+$ with an excess of $HClO_4$; and (*e*) H_2salen with an excess of $HClO_4$. Spectra (*d*) and (*e*) were recorded after 30 and 15 d, respectively, following the preparation of the solutions; for further details see text

This process was completely reversible. A careful neutralization of the solutions reversed, also slowly, the spectral changes mentioned above and the initial solutions were quantitatively obtained. Although at first sight we considered a protonation–deprotonation equilibrium, similar to that which takes place in basic medium, additional experimental data revealed that a hydrolytic decomposition was taking place [equation (2)], were Hsal is salicylaldehyde and H_2en^{2+} the

$$H_2\text{salen} + 2\,H^+ \rightleftharpoons 2\,\text{Hsal} + H_2en^{2+} \qquad (2)$$

ethylenediammonium cation. Thus, the spectra of the colourless acidified solutions were identical to that of a salicylaldehyde solution of concentration $2c_L$ (H_2en^{2+} is transparent in the studied spectral range). Furthermore, we identified free salicylaldehyde in these solutions by thin-layer chromatography (see Experimental section).

The complex $[\{Fe(salen)Cl\}_2]$ was soluble in dmso–H_2O (80 : 20) giving dark red solutions. The u.v.–visible spectrum displays absorption bands at 485 ($\varepsilon = 3.74 \times 10^3$ dm^3 mol^{-1} cm^{-1}) and 316 nm (1.3×10^4) (Figure 1). These solutions are completely stable and no spectral changes with time are observed. Measurements at 485 nm strictly obey the Beer–Lambert law and conductivity measurements corresponded to those of a strong 1 : 1 electrolyte. These facts evidence that the Cl^- is not co-ordinated to Fe^{III}, so, the existing species in solution must be the complex cation $[Fe(salen)]^+$.

When acidifying $[Fe(salen)]^+$ solutions of concentration c_M = *ca.* 3×10^{-3} mol dm^{-3}, a gradual decrease in the absorption at 485 nm occurred. With an acid excess ($c_A : c_M \geqslant 8$) the solution fully decolourizes. The reaction is very slow, almost thirty days are required to reach equilibrium. From then the absorption measurements remain stable and reproducible. This process is also completely reversible, a careful neutralization of the solution yields, also slowly, a quantitative formation of the $[Fe(salen)]^+$ complex. The absorption spectra of colourless solutions are identical to that of Hsal plus Fe^{3+} solutions of concentrations $2c_M$ and c_M respectively. Moreover, salicylaldehyde can be identified by thin-layer chromatography.

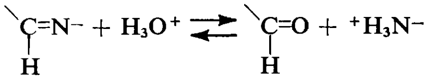
Therefore, a hydrolytic decomposition of $[Fe(salen)]^+$ similar to that of the free Schiff base is taking place [equation (3)].

$$[Fe(salen)]^+ + 4\ H^+ \rightleftharpoons Fe^{3+} + 2\ Hsal + H_2en^{2+} \quad (3)$$

Along the pH * range in which the reaction occurs, the metal ion is not co-ordinated with salicylaldehyde and the ethylenediamine is completely protonated (see later).

Acidity Constants of H_2salen.—We titrated potentiometrically H_2salen solutions with KOH. The deprotonation reaction is slow and hourly intervals between each base addition were required for reliable potential measurements. We carried out back-titrations, obtaining identical results. The potentiometric curves show that 2 moles of OH^- are required for each mole of H_2salen, which is in agreement with the spectrophotometric data. The potentiometric data give the protonation curve $\bar{j}$ *versus* $-\log [H^+]$ ($\bar{j}$ is the average number of protons bound to the ligand in the solution; see Figure 2). By plotting $\bar{j}/(1 - \bar{j})[H^+]$ *versus* $(\bar{j} - 2)[H^+]/(\bar{j} - 1)$ a straight line is obtained. The overall proton association constants β_{j1} and β_{j2} are given by the intercept and slope respectively. In the calculus we used 70 experimental points from three different experiments to give the values $\beta_{j1} = (1.63 \pm 0.05) \times 10^{12}$ dm^3 mol^{-1} and β_{j2} $(2.04 \pm 0.02) \times 10^{23}$ dm^6 mol^{-2} (25 °C, 0.1 mol dm^{-3}, $KClO_4$). The errors indicated for the values of the stability constants were estimated for a 99% confidence level and 68 degrees of freedom. The theoretical protonation curve calculated from these constants fits very well the experimental data.

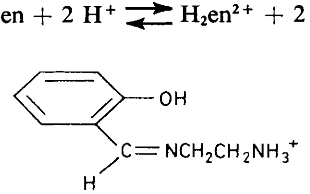
Hydrolysis Formation Equilibria of H_2salen *in Acid Medium.*—As indicated above, H_2salen is hydrolysed in acidic dmso–H_2O (80 : 20) solution giving salicylaldehyde and ethylenediammonium [equation (2)]. The extent to which the reaction proceeds is controlled by the $[H^+]$ of the medium. Since the reaction involves the cleavage of both $>C=N$ bonds [equation (4)] we may consider that the reaction takes place in two consecutive steps [equations (5) and (6); see structure below]. These reactions are not conventional protonation reactions, since the initial species, although reversible, decomposes. However, it is useful to consider them as 'effective protonation' reactions. Thus, it is possible to determine the (hydrolysis) equilibrium constants β_{h1} and β_{h2} by using, although with slight modifications, the usual methods for determining acidity constants.



$$\underset{H}{\overset{\diagdown}{C}}{=}N- + H_3O^+ \rightleftharpoons \underset{H}{\overset{\diagdown}{C}}{=}O + {}^+H_3N- \quad (4)$$

$$H_2salen + H^+ \xrightleftharpoons{\beta_{h1}} HOC_6H_4CH{=}N(CH_2)_2NH_3^+ + Hsal \quad (5)$$

$$H_2salen + 2\ H^+ \xrightleftharpoons{\beta_{h2}} H_2en^{2+} + 2\ Hsal \quad (6)$$



Let us define $\bar{j}_{\text{eff.}}$, the 'effective protonation degree,' as the average number of bonded protons (to the H_2salen hydrolysis products) for each initial H_2salen [equation (7)];

$$\bar{j}_{\text{eff.}} = ([HOC_6H_4CH{=}N(CH_2)_2NH_3^+] + 2[H_2en^{2+}])/c_L \quad (7)$$

$\bar{j}_{\text{eff.}}$ can be easily related to the hydrolysis constants β_{h1} and β_{h2} by equation (8). This equation is analogous to that which

$$\bar{j}_{\text{eff.}} = \frac{\beta_{h1}([H^+]/[Hsal]) + 2\beta_{h2}([H^+]^2/[Hsal]^2)}{1 + \beta_{h1}([H^+]/[Hsal]) + \beta_{h2}([H^+]^2/[Hsal]^2)} \quad (8)$$

relates the protonation degree $\bar{j}$ with the overall association constants β_j in a simple protonation reaction except that $[H^+]$ is substituted by $[H^+]/[Hsal]$.

On the other hand, having to account for the mass balances of the system and $\bar{j}_{\text{eff.}}$, it can be easily inferred that $[Hsal] = \bar{j}_{\text{eff.}} c_L$. By measuring the hydrogen-ion concentration of a series of solutions of known c_A and c_L we can immediately determine values of the $\bar{j}_{\text{eff.}}$ and [Hsal] since equation (9) holds.

$$\bar{j}_{\text{eff.}} = (c_A - [H^+] + [H^+]/K_w)/c_L \quad (9)$$

Plotting $\bar{j}_{\text{eff.}}/(1 - \bar{j}_{\text{eff.}})([H^+]/[Hsal])$ *versus* $\{(\bar{j}_{\text{eff.}} - 2)([H^+]/[Hsal])\}/(\bar{j}_{\text{eff.}} - 1)$ gives a straight line with the slope and intercept being β_{h2} and β_{h1} respectively.

We have prepared a series of solutions in which the initial H_2salen concentration, c_L, was kept constant and the ratio $c_A : c_L$ varied. The samples were sealed and kept in the dark at 25 ± 1 °C, measuring their $[H^+]$ after 20 d. In this case a titrimetric technique could not be used, because of the slowness to reach equilibrium. From the potentiometric data we have obtained the effective protonation curve (Figure 2) and calculated the equilibrium constants as indicated above. In the calculus we used 50 experimental points from three different experiments to give $\beta_{h1} = (2.60 \pm 0.05) \times 10^4$ and $\beta_{h2} = (1.60 \pm 0.02) \times 10^7$ (25 °C, 0.1 mol dm^{-3} $KClO_4$). The theoretical curve calculated from these constants fits very well the experimental points.

If we formally consider that salen^{2-} behaves as a tetraprotic base it will be possible to consider the behaviour of H_2salen in acid or basic solution as a whole. Its proton association equilibria can be represented by equations (10)—(13),

$$salen^{2-} + H^+ \xrightleftharpoons{\beta_{j1}} Hsalen^- \quad (10)$$

$$salen^{2-} + 2\ H^+ \xrightleftharpoons{\beta_{j2}} H_2salen \quad (11)$$

$$salen^{2-} + 3\ H^+ \xrightleftharpoons{\beta_{j3}} Hsal + HOC_6H_4CH{=}N(CH_2)_2NH_3^+ \quad (12)$$

$$salen^{2-} + 4\ H^+ \xrightleftharpoons{\beta_{j4}} 2\ Hsal + H_2en^{2+} \quad (13)$$

where $\beta_{j3} = \beta_{j2}\beta_{h1}$ and $\beta_{j4} = \beta_{j2}\beta_{h2}$. Figure 3 shows the distribution diagram of the species in solution.

Stability Constant of $[Fe(salen)]^+$.—The quantitative study of the hydrolysis of $[Fe(salen)]^+$ in acid medium and the β_j values of the salen^{2-} ligand previously obtained allow the

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* The electrode was always calibrated as a hydrogen-ion concentration probe but, as a matter of convenience, pH instead of $-\log [H^+]$ is used through the text.

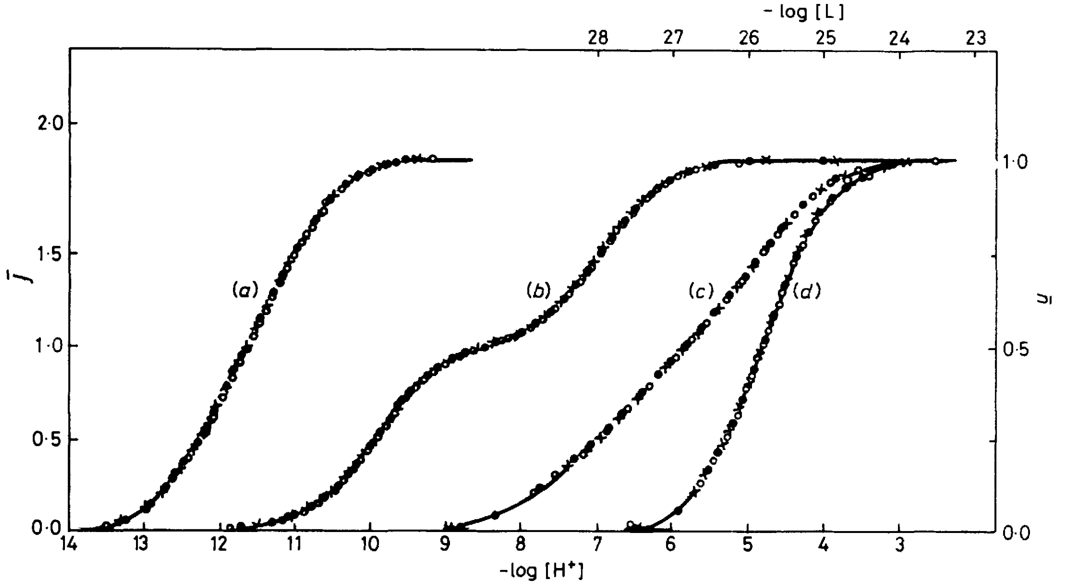

Figure 2. (*a*) Protonation curve of salen^{2-}: (●) 1.22 × 10^{-3}, (○) 2.71 × 10^{-3}, (x) 5.65 × 10^{-3} mol dm^{-3}. (*b*) Protonation curve of ethylenediamine: (●) 3.77 × 10^{-3}, (○) 7.05 × 10^{-3}, (x) 1.43 × 10^{-2} mol dm^{-3}. (*c*) Protonation 'effective' curve of H_2salen: (●) 1.10 × 10^{-3}, (○) 2.83 × 10^{-3}, (x) 5.44 × 10^{-3} mol dm^{-3}. (*d*) Formation curve of [Fe(salen)]$^+$: (●) 1.09 × 10^{-3}, (○) 3.01 × 10^{-3}, (x) 6.32 × 10^{-3} mol dm^{-3}. The symbols (●), (○), and (x) represent experimental points. The curves are calculated for the computed constants

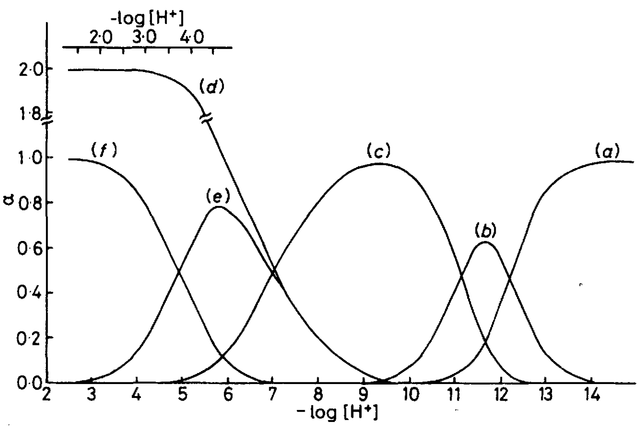

Figure 3. Distribution diagram for the existing species in a solution of H_2salen in dmso–H_2O (80 : 20) as a function of pH. α is the ratio between the concentration of each species and the initial concentration of H_2salen. (*a*) salen^{2-}, (*b*) Hsalen$^-$, (*c*) H_2salen, (*d*) Hsal, (*e*) $HOC_6H_4CH{=}N(CH_2)_2NH_3^+$, and (*f*) H_2en^{2+}. Top scale is for upper part of curve (*d*)

determination of the stability constant of the complex [equation (14)]. We prepared a series of [Fe(salen)]$^+$ solutions of

$$Fe^{3+} + salen^{2-} \overset{\beta}{\rightleftharpoons} [Fe(salen)]^+ \qquad (14)$$

concentration c_M, adding variable amounts of $HClO_4$ so that $0 \leqslant c_A : c_M \leqslant 6$. The solutions, hermetically sealed, were kept in the dark for 30 days. Then, the absorption at 485 nm, D_{485}, and [H$^+$] were measured.

The D_{485} value gives the equilibrium concentration of the complex, since it is the only absorbing species at this wavelength, $[Fe(salen)^+] = D_{485}/\varepsilon_{485}l$ (l = pathlength in cm), and, therefore, the formation degree of the system $\bar{n} = [Fe(salen)^+]/c_M$. On the other hand, the [H$^+$] measurements allow the calculation of the free-ligand concentration, [salen^{2-}] [equation (15)].

$$[salen^{2-}] = [(1-\bar{n})c_M]/\{1 + \beta_{j1}[H^+] + \beta_{j2}[H^+]^2 + \beta_{j3}([H^+]^3/[Hsal]) + \beta_{j4}([H^+]^4/[Hsal]^2)\} \qquad (15)$$

Although, at first instance, [Hsal] is not known, it can be related to the experimental values of [H$^+$] and [Fe(salen)$^+$] using equation (16). Therefore, each one of the prepared solutions allows the determination of a point on the formation

$$[Hsal] = c_A - 2c_M - [H^+] + 2[Fe(salen)^+] \qquad (16)$$

curve of the system (Figure 2). From this curve we computed the stability constant of [Fe(salen)]$^+$ by the usual methods. The calculus has been performed with 45 experimental points from three different experiments giving β = (7.1 ± 0.1) × 10^{25} dm^3 mol^{-1} (25 °C, 0.1 mol dm^{-3} $KClO_4$).

Acidity Constants of H_2en^{2+}.—We titrated ethylenediamine solutions with 0.1 mol dm^{-3} $HClO_4$. In this case protonation was instantaneous. The potentiometric data treatment, as indicated above for H_2salen, leads to the following values: $\beta_{j1} = (9.5 \pm 0.1) \times 10^9$ dm^3 mol^{-1} and $\beta_{j2} = (8.8 \pm 0.1) \times 10^{16}$ dm^6 mol^{-2} (25 °C, 0.1 mol dm^{-3} $KClO_4$). In Figure 3 the protonation curve is shown. In the calculus we used 120 experimental points from three different experiments.

Discussion

The mixture dmso–H_2O (80 : 20 w/w) was the chosen solvent for our study. In this medium, both H_2salen and [{Fe(salen)Cl}$_2$] are very soluble giving stable solutions. The utilization of this mixed solvent has advantages over the pure dmso for systems in which, as ours, the exclusion of water is not necessary.[15] We have carried out reliable potentiometric measurements by using a commercial glass electrode (with Ag–AgCl as reference electrode). Georgieva *et al.*[15] used a 10^{-2} mol dm^{-3} KCl solution in dmso–H_2O (50 : 50) as a reference cell solution, but we found it satisfactory to use a saturated aqueous solution. We determined the autoproto-

Table. Acidity constants in dmso–H_2O (80 : 20) at 25 °C and 0.1 mol dm^{-3} $KClO_4$

Compound	K_{a1}	K_{a2}	Ref.
H_2salen	8.0×10^{-12}	6.3×10^{-13}	This work
Catechol	1.6×10^{-13}	2.7×10^{-16}	*a*
p-Nitrophenol	4.2×10^{-9}		*b*
Ethylenediammonium	1.1×10^{-7}	1.0×10^{-10}	This work

[a] F. LLoret, J. Moratal, and J. Faus, following paper. [b] F. LLoret, J. Moratal, and J. Faus, unpublished work.

lysis constant for this solvent, $pK_w = 18.34 \pm 0.02$ (25 °C, 0.1 mol dm^{-3} $KClO_4$). This value agrees with that reported in the literature,[15] $pK_w = 18.38$ (25 °C, 0.1 mol dm^{-3} NEt_4Br). Although in this solvent the acidity range is shorter than in pure dmso ($pK_w \simeq 33$),[16] it is possible to perform [H^+] measurements up to very low values (pH $\simeq$ 16) whereas in dmso with a very low water content the working of the glass electrode limits the measurements up to pH *ca.* 8 in practice.[17]

The Schiff base H_2salen behaves as a weak diprotic acid (see Table). The deprotonation of both OH groups is complete at pH > 14.5, whereas at pH = 10.5—12.5 the three species coexist (Figure 3).

Although salen^{2-} is, generally, the ligand in the many metal complexes of H_2salen known,[18] the deprotonation equilibria of this Schiff base have not previously been studied. The salen^{2-} anion seems to be stable in dmso–H_2O (80 : 20).

In acid medium, H_2salen is hydrolyzed to give salicylaldehyde and the ethylenediammonium ion [equation (2)]. The reaction, although very slow, proceeds quantitatively. The susceptibility to hydrolysis of Schiff bases is well known [13,18] but there are few available equilibrium studies about these reactions. Cordes and Jenks [19] observed that the protonation of the imine nitrogen in *N-p*-chlorobenzylideneaniline causes slow decomposition and they made an estimation of its equilibrium constant. There is no previous study of the H_2salen hydrolysis. In dmso–H_2O (80 : 20) hydrolytic decomposition of H_2salen is fully reversible. The extent of the reaction depends on [H^+]. The reaction begins at pH *ca.* 9.5 and is almost complete at pH $\leqslant$ 3.5 (Figure 3). The hydrolysis takes place in two successive steps [equations (5) and (6)]. The $HOC_6H_4CH{=}N(CH_2)_2NH_3^+$ species, in which only one $H\underset{|}{C}{=}N{-}$ bond has been cleaved exists in solution as a stable species and is predominant at pH ~ 6 ($\alpha = 0.78$). However we have not attempted its isolation. There is no evidence about the existence in solution of non-hydrolyzed protonated forms at equilibrium.

The ethylenediammonium acidity constants (Table) clearly show that at the pH range in which H_2salen and [Fe(salen)]$^+$ decompose, it is completely protonated. This fact justifies the omission of en and Hen$^+$ species in the study of these decomposition equilibria. On the other hand the study of ethylenediamine protonation is also relevant because it enabled us to calculate the equilibrium constant of the H_2salen hydrolysis ' without protonation ' [equation (17)] [$K = \beta_{h2}/\beta_{j2}(\mathrm{en}) =$

$$H_2\mathrm{salen} \overset{K}{\rightleftarrows} 2\,\mathrm{Hsal} + \mathrm{en} \qquad (17)$$

1.84×10^{-10} mol^2 dm^{-6}]. This value shows that H_2salen is stable towards hydrolysis in dmso–H_2O (80 : 20) despite the large water content of the solvent. The favourable thermodynamics for the hydrolysis in acid medium are provided by the protonation of ethylenediamine. Moreover, hydrogen ions can act as catalysts in the reaction. The complex [{Fe(salen)Cl}$_2$] is very soluble in dmso–H_2O (80 : 20) whereas it is practically insoluble in water or methanol.[4] When dissolving, the Cl^- ligand dissociates and the cationic complex [Fe(salen)]$^+$ is formed. Presumably, a solvent molecule replaces the halide in the co-ordination sphere of metal ion. In unco-ordinating solvents such as nitromethane or chloroform the Cl^- remains co-ordinated to the metal ion.[4] This behaviour is analogous to that reported for the manganese complexes [Mn(salen)Cl] and [Mn(salen)Cl_2] which are non-electrolytes in acetonitrile but strong electrolytes in methanol.[20]

Similarly to H_2salen, [Fe(salen)]$^+$ decomposes in acid medium although with more difficulty. Greater hydrogen-ion concentrations are required and the reaction is still slower than for H_2salen. Under these conditions, the only ligand decomposition products are Hsal and H_2en^{2+} and they are not co-ordinated to Fe^{3+}. Therefore, equation (3) correctly describes the occurring process. The equilibrium constant $K = \beta_{j4}/\beta = 4.5 \times 10^4$ dm^3 mol^{-1} indicates that an acid excess is required for full decomposition.

The stabilization of H_2salen towards hydrolysis by co-ordination to Fe^{III} agrees with the reported behaviour of other Schiff bases.[21] The complex Cu^{II}–salicylideneglycine is stable in dioxane-water acid solutions whereas the free ligand undergoes hydrolysis in this medium.[22] However *NN'*-ethylenediaminebis(thiophenol) is hydrolyzed in ethanol-water medium more easily if Cu^{II} is present;[23] this is possibly due to the co-ordination of the metal ion to en formed in the Schiff-base hydrolysis.

The cation [Fe(salen]$^+$ is formed in dmso–H_2O (80 : 20) by direct reaction between Fe^{3+} and H_2salen, but partial hydrolysis occurs if the liberated protons are not neutralized. Although the hydrolytical instability of [Fe(salen)]$^+$, at first instance, might seem troublesome for the study of the formation reaction, it is advantageous for the results of the hydrolysis reaction. In other cases, very acid media would be required to dissociate the complex and the determination of the stability constant is more difficult.

[Fe(salen)]$^+$, as indicated by its stability constant of 7.1×10^{25} dm^3 mol^{-1}, is very stable. This value is very high for a 1 : 1 complex. However, it is interesting to compare this value with the stability constant of [Fe(cat)]$^+$ (7.9×10^{23}) (H_2cat = catechol) recently obtained under the same conditions.[24] It is apparent that Fe^{III} has a much greater affinity for the phenolate oxygen atoms than for the amine nitrogen atoms since the bidentate ligand catecholate forms a complex almost as stable as the tetradentate salen^{2-}. This fact is also reflected in structural data such as bond lengths,[2] for example, in [Fe(salen)Cl] *d*(Fe–N) = 2.09 and *d*(Fe–O) = 1.88 Å.

Acknowledgements

We thank the Comisión Asesora de Investigación Científica y Técnica de la Presidencia del Gobierno (Spain) for financial support.

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Received 8th November 1982; *Paper* 2/1874