SPECTROPHOTOMETRIC STUDY OF THE FORMATION OF IRON(III) COMPLEXES WITH SOME SALICYLIC ACID DERIVATIVES

Terezia M. SURANYI, Evgenija A. DJURENDIC and Gyongyi Gy. VASTAG

Institute of Chemistry,
Faculty of Novi Sad, Trg D. Obradovica 3, 21000 Novi Sad, Yugoslavia

The stoichiometric ratio and stability constants of iron(III) complexes with 1,n-di-O-salicyloylalkane-1,n-diols ($n = 2 - 8$) and N,N'-disalicyloyl-1,n-alkanediamines ($n = 2 - 4$) were determined spectrophotometrically. In 61.10% aqueous ethanol, the iron-to-ligand ratio is $1 : 1$ (FeL$^+$). The stability constants of the complexes were measured at 298 K and $\mu = 0.5$ mol dm^{-3} (LiCl). Since the determination was performed in a glycinate buffer, the constants were corrected for the side reaction of iron(III) with glycine.

Since the salicylic acid derivatives investigated in this work (see below) were either diamides or diesters possessing free phenolic OH groups, it is useful to give a brief account of iron(III) complexes with some ligands of a similar kind. With phenol, iron(III) forms in acidic medium only the 1 : 1 complex[1–4], whereas the complexes with salicylic acid, involving both phenolic and carboxylic groups, may contain either one, two, or three dianion ligand species[5–7]. With salicylamide, iron(III) forms both the 1 : 1 and 1 : 2 complexes[8], while only the 1 : 1 complex is formed[9] with methyl salicylate.

Esters of salicylic acid and dienols and amides of salicylic acid and diamines have been prepared in our laboratory[10,11] (compounds **1 – 10**). Both groups of compounds contain two free phenolic OH groups and two COO or CONH groups.

In the present work, the formation of iron(III) complexes with these salicylic acid derivatives was investigated spectrophotometrically using the continuous variations method[12]. Because of low solubilities of the salicylic acid derivatives, the composition and stability constants of the iron(III) complexes were determined in 61.10% aqueous ethanol at a constant ionic strength of $\mu = 0.5$ mol dm^{-3} and pH 1.82.

EXPERIMENTAL

All chemicals were of analytical reagent grade or better. All stock solutions were prepared in 61.10 wt.% aqueous ethanol at a constant ionic strength of $\mu = 0.5$ (LiCl); this electrolyte solution was also used for their dilution. The pure synthesized compounds were kept protected from light and were dried in a vacuum before preparing their solutions. Solutions for the determination of the composi-

tion and stability of the iron(III) complexes were obtained by diluting the stock solutions with a gly-cinate buffer. The $FeCl_3$ solution (0.01 mol dm^{-3}) was standardized by titration of iron(II) with permanganate. Buffer solutions of suitable pH were prepared by adding appropriate volumes of glycine (HA) at a concentration of 0.1027 mol dm^{-3} to a 9.396 . 10^{-2} mol dm^{-3} solution of LiOH. The pH values for various [HA]/[A^-] ratios, calculated from the measured potentials and the E^0 value for the glass electrode in the same solution, were taken from our previous work[13]. The concentration of the solution containing 0.1 mol dm^{-3} HCl and 0.4 mol dm^{-3} LiCl in 61.10% aqueous ethanol was determined by potentiometric titration with standardized 0.2 mol dm^{-3} NaOH (0.3 mol dm^{-3} LiCl, 61.10% ethanol) using the Gran plot[14]. The carbonate-free lithium hydroxide and sodium hydroxide were standardized against potassium biphthalate recrystallized from water in the presence of potassium carbonate, followed by an additional recrystallization from water and drying at 398 K. The concentration of the 0.1 mol dm^{-3} glycine solution was checked by potentiometric titration.

The spectrophotometric measurements were performed on a Specord UV/VIS spectrophotometer (Zeiss, Jena) at 298 ± 1 K, using 1 cm quartz cells. A 0.5 mol dm^{-3} LiCl solution containing the same amount of buffer as the solution of the reactants served as the reference system.

Potentiometric measurements were performed on Beckman 4500 digital pH meter with an accuracy of ±0.1 mV, using a Beckman 40498 glass electrode and an Ag/AgCl electrode prepared after Brown[15]. The glass electrode was connected to the reference electrode via a Wilhelm bridge[16]. The solutions were stirred on a magnetic stirrer and purged with nitrogen. During measurement, the titration vessel and the Wilhelm bridge were inserted in a paraffin oil thermostat at 298 ± 0.1 K, while room temperature was held at 298 ± K.

$n = 2 - 8$

1 – 7

$n = 2 - 4$

8 – 10
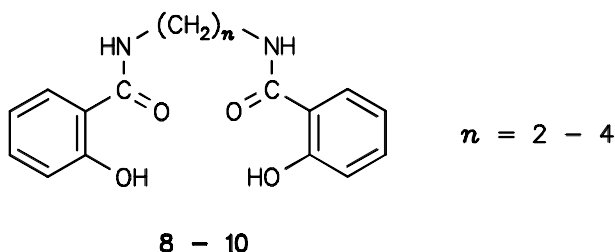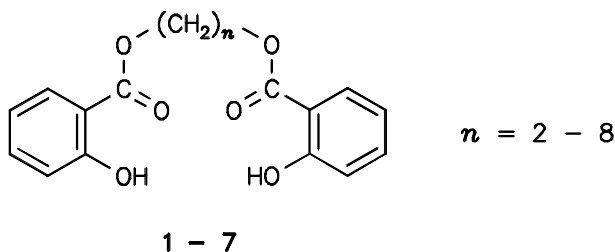
RESULTS AND DISCUSSION

Acid solutions of iron(III) complexes with the ligands examined are dark-red or violet. To prevent hydrolysis Fe^{3+} at low concentrations, the spectrophotometric measurements in the UV region were carried out at pH 1.82. By way of example, the formation of the iron(III) complexes with ligand **8** is shown in Fig. 1.

Composition of the complexes was determined by the molar ratio method[17]. The ligand concentrations were increased until the absorbance of the $FeCl_3$ solution did not change any more. Figure 2 demonstrates that the iron(III)/ligand mole ratio is 1 : 1. The same data served to determine the composition of the complexes, using the method of Beltrán-Porter and coworkers[18]. Tests were carried out for complexes with the
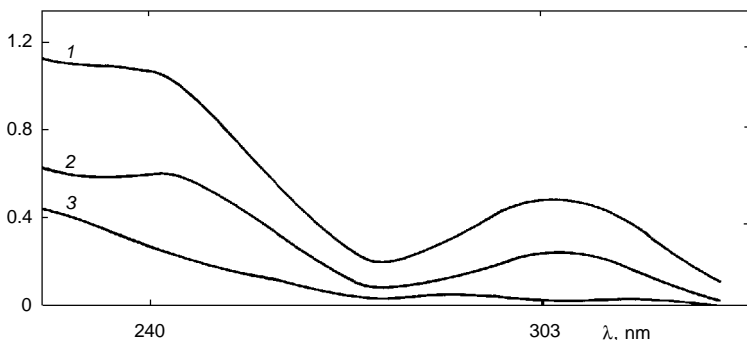

FIG. 1

Absorption spectra of: *1* Fe^{3+}–H_2L complex, *2* H_2L (**8**) and *3* $FeCl_3$ at a concentration of $2 \cdot 10^{-5}$ mol dm^{-3}
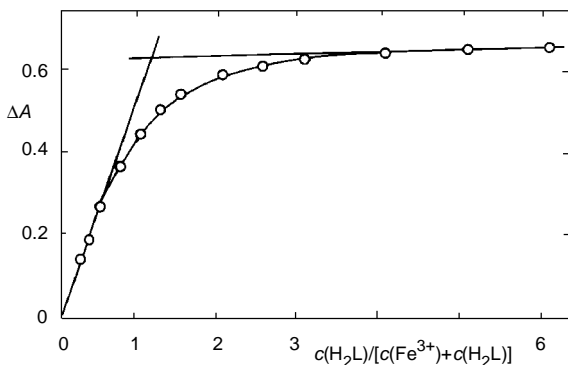

FIG. 2

Dependence of absorbances on the $c(H_2L)/c(Fe^{3+})$ ratio at a constant concentration of $FeCl_3$; $c(Fe^{3+})$ = $1 \cdot 10^{-4}$ mol dm^{-3}, H_2L is **8**, λ = 541 nm, pH 1.82

iron(III)/ligand ratios 1 : 1, 1 : 2, 2 : 1, 2 : 2, and 3 : 3. From the fact that a constant K^* value was only obtained for the 1 : 1 complex we inferred that the monomeric FeL^+ complex was formed (Fig. 3).

The stability constants of the complexes were determined by the method of continuous variations[12]. The values of the apparent stability constants were calculated from the relation

$$\beta' = \frac{A/A_{ex}}{c_x(1 - A/A_{ex})^2} \qquad (1)$$

based on the Job curves. In Eq. (*1*) *A* is the absorbance of the mixture of solutions of $FeCl_3$ and H_2L at $c(Fe^{3+}) = c(H_2L) = c_x$ mol dm^{-3}, whereas A_{ex} is its extrapolated value under the same conditions, i.e. absorbance of the solution that would be obtained if all Fe^{3+} ions (ligand molecules) were bound in the complex (Fig. 4).

The absorbances for obtaining the Job curves were measured on a series of solutions such that $c(Fe^{3+}) + c(H_2L) = c^0 = 4 \cdot 10^{-5}$ or $6 \cdot 10^{-5}$ mol dm^{-3} while the ligand to cation concentration ratios were varied over the range of $0 - 1$. In addition, two series of individual solutions of $FeCl_3$ and the ligand at the same concentrations as in the mixtures were prepared. The absorbances of the three series of solutions were employed to construct the Job curve $\Delta A = f\{c(H_2L)/[c(FeCl_3) + c(H_2L)]\}$ where ΔA is the absorbance due to the complex, i.e. absorbance of the mixed solution of $FeCl_3$ and the ligand corrected for the absorbance of the excess $FeCl_3$ (at $x < 0.5$) or ligand (at $x > 0.5$).
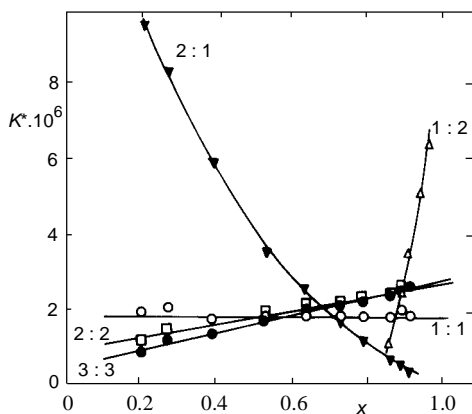

FIG. 3

K^* vs x for different stoichiometric ratios; $c(FeCl_3) = 1 \cdot 10^{-4}$ mol dm^{-3}, H_2L is **8**, $\lambda = 541$ nm, pH 1.82

FIG. 4

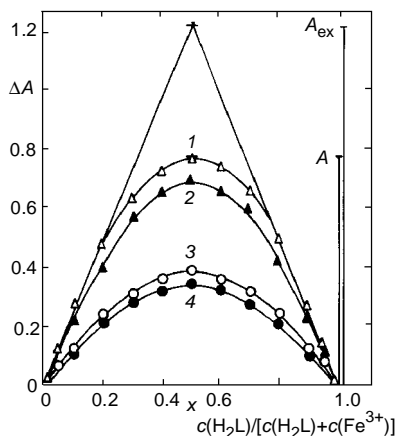Job curves for Fe^{3+}–H_2L (**8**): *1*, *2* $c^0 = 6 \cdot 10^{-5}$ mol dm^{-3}, *3*, *4*, $c^0 = 4 \cdot 10^{-5}$ mol dm^{-3}; *1*, *3* $\lambda = 556$ nm, *2*, *4* $\lambda = 588$ nm; pH 1.82

The calculated values of the apparent stability constants

$$\beta' = \frac{[FeL^+]}{[(Fe^{3+})'] \, [L']}$$, (2)

where $[(Fe^{3+})'] = [Fe^{3+}] + [FeA^{2+}]$ and $[L'] = [H_2L] + [HL^-] + [L^{2-}]$,
hold only at pH 1.82 in the presence of a defined amount of glycinate buffer.

The values of the stability constants

$$\beta = \frac{[FeL^+]}{[Fe^{3+}] \, [L^{2-}]}$$ (3)

were calculated from the relation

$$\beta = \beta' \alpha(Fe(A)) \, \alpha(L(H))$$, (4)

where $\alpha(Fe(A))$ is the α-coefficient for the side reaction of iron(III) with glycine, calculated as

$$\alpha(Fe(A)) = 1 + \gamma_1[A^-]$$. (5)

In this equation, γ_1 is the stability constant of the glycinatoferrate(III) complex, FeA^{2+}, and the equilibrium concentration of glycinate ion, $[A^-]$, is calculated based on the pH of the solution and the total concentration of glycine in the solution, $c(HA)$:

$$[A^-] = \frac{c(HA)}{1 + \dfrac{[H_3O^+]}{K_{a2}(HA)} + \dfrac{[H_3O^+]^2}{K_{a1}(HA) \, K_{a2}(HA)}}$$. (6)

$K_{a1}(HA)$ and $K_{a2}(HA)$ are the acidity constants of glycine.

The α-coefficient for protonation of the H_2L ligand is expressed in terms of the acidity constants of the ligand, K_{a1} and K_{a2}, as

$$\alpha(L(H)) = 1 + \frac{[H_3O^+]}{K_{a2}} + \frac{[H_3O^+]^2}{K_{a1} \, K_{a2}}$$. (7)

The acidity constants of the ligands **1** – **10** have been determined previously in our laboratory under identical conditions[11] ($\mu = 0.5$ mol dm^{-3}, 61.10% ethanol, 298 K).

To calculate $\alpha(Fe(A))$, we determined the acidity constants of glycine as well as the composition and stability constants of the glycinato complexes formed under the same conditions.

Potentiometric titration of the mixtures of HCl and glycine with NaOH solution gave the following acidity constants for glycine:

$$pK_{a1}(HA) = \log \frac{[NH_3^+CH_2COOH]}{[NH_3^+CH_2COO^-][H_3O^+]} = 2.966 \pm 0.004 \tag{8}$$

and

$$pK_{a2}(HA) = \log \frac{[NH_3^+CH_2COO^-]}{[NH_2CH_2COO^-][H_3O^+]} = 9.008 \pm 0.001 \quad . \tag{9}$$

Also, potentiometric titrations of the mixtures containing HCl, glycine and $FeCl_3$ with NaOH solution showed that in acidic medium the FeA^{2+} complex is formed, whose stability constant γ_1 is:

$$\log \gamma_1 = \log \frac{[Fe(NH_2CH_2COO)^{2+}]}{[Fe^{3+}][NH_2CH_2COO^-]} = 9.66 \pm 0.02 \quad . \tag{10}$$

At the given concentrations of Fe^{3+} and glycine and pH $\geq$ 1.7 the solution became turbid because of the formation of a sparingly soluble hydroxo-glycinate complex of iron(III). It has also been found[10] that in an aqueous acidic medium a 1 : 1 glycinato complex of iron(III) is formed with log β = 8.57, and that precipitation occurs even in acetic medium.
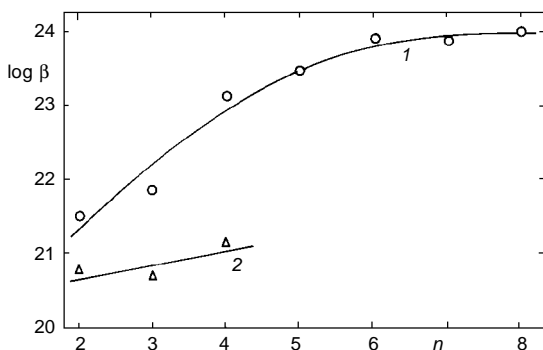

FIG. 5

Dependence of the stability constants of the iron(III) complexes with compounds **1** – **7** (*1*) and **8** – **10** (*2*) on the number of methylene groups in the ligand molecule (*n*)

The stability constants of the iron(III) complexes with compounds **1 – 10**, calculated by using Eqs (*1*) and (*4*), are given in Table I, and their dependences on the number of methylene groups in the ligand molecule are shown in Fig. 5.

It is evident from Fig. 5 that the stability constants exhibit a marked increase with increasing number of methylene groups in the ligand molecule. The increase in the number of methylene groups from 2 to 8, corresponding to an increase in the number of the members in the methylene ring from 9 to 15 (see structures *I* and *II*) contributes to a better flexibility of the ligand molecule, as can be demonstrated on the ligand model. As a consequence, the oxygen donor atoms can better approach the central ion and thus form a more stable complex.

Table I demonstrates that the ligands with odd numbers of methylene groups form somewhat less stable complexes.

Ligands of the diester type (**1 – 7**) form more stable complexes with iron(III) than those of the diamide type (**8 – 10**). This can be explained by the fact that the former are weaker acids, so that their complexing capacity is more pronounced.

The lower stability of the iron(III) complexes with the amide type ligands can also be explained by the presence of intramolecular hydrogen bonds in the ligands. In fact, the amide compounds form two kinds of hydrogen bond, viz. O−H...O=C and N−H...O−H

TABLE I
Stability constants of iron(III) complexes with compounds **1 – 10** in 61.10% aqueous ethanol, at $\mu = 0.5$ mol dm^{-3} and 298 K

Ligand H$_2$L	n	Wavelength, nm	log β′	log β
		Diesters		
1	2	240, 308	5.74 ± 0.02	21.54
2	3	238, 308	5.78 ± 0.08[a]	21.91
3	4	240, 308	6.27 ± 0.02	23.17
4	5	238, 308	6.88 ± 0.08[a]	23.52
5	6	238, 308	6.92 ± 0.01[a]	23.98
6	7	238, 308	6.93 ± 0.02	23.92
7	8	238, 308	6.94 ± 0.04	24.07
		Diamides		
8	2	240, 303	6.58 ± 0.01	20.80
9	3	241, 303	6.61 ± 0.01	20.77
10	4	241, 303	6.63 ± 0.01	21.19

[a] Ref.[20].

(structures *III* and *IV*), while the ester-type ligands form only the O–H...O=C bonds. Hence, in the former case there occurs a competition between Fe^{3+} and H^+ for the oxygen atoms, i.e. between the process of complexation (structure *I*) and intramolecular hydrogen bond formation (structures *III* and *IV*), resulting in the formation of less stable complexes.
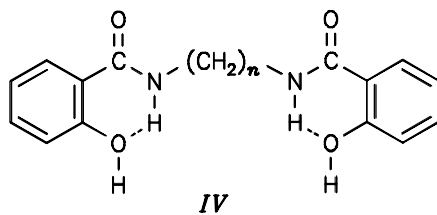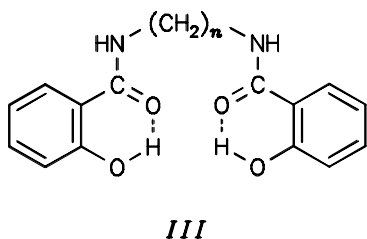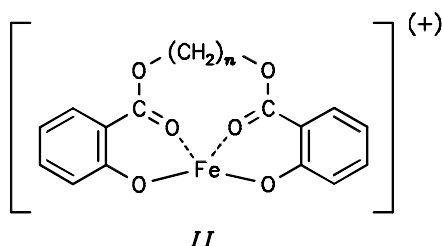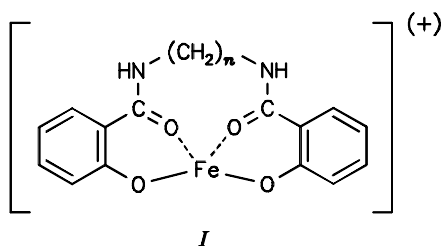
I

II

III

IV

REFERENCES

1. Bartusek M., Ruzickova J.: Collect. Czech. Chem. Commun. *31*, 207 (1966).
2. Limb G. R., Robinson R. J.: Anal. Chim. Acta *47*, 451 (1969).
3. Desai A. G., Milburn M. L.: J. Am. Chem. Soc. *91*, 1958 (1969).
4. Veselinovic D., Malesev J.: J. Serb. Chem. Soc. *43*, 545 (1978).
5. Ogawa K., Tobe N.: Bull. Chem. Soc. Jpn. *39*, 227 (1966).
6. Zolotukhin V. K.: Zh. Neorg. Khim. *13*, 702 (1969).
7. Ramamoorthy S., Manning P. G.: J. Inorg. Nucl. Chem. *35*, 1571 (1973).
8. Agrin A.: Svensk Kem. Tidsks. *68*, 189 (1956).
9. Perrin D. D.: Nature *182*, 741 (1958).
10. Miljkovic D. A., Djurendic E. A., Suranyi T. M.: Rev. Res. Fac. Sci., Univ. Novi Sad *13*, 5 (1983).
11. Djurendic E. A., Suranyi T. M., Miljkovic D. A.: Collect. Czech. Chem. Commun. *55*, 1763 (1990); *56*, 1446 (1991).
12. Job P.: C. R. Acad. Sci. *180*, 928 (1925); Ann. Chim. Phys. (Paris) *9*, 113 (1928).

13. Suranyi T., Djurendic E., Miljkovic D.: *10th Yugoslav Symposium on Electrochemistry, Becici 1987*, Book of the Papers, p. 266. Chemical Society of Montenegro, Titograd 1987.
14. Gran G.: Analyst *77*, 661 (1952).
15. Brown A. S.: J. Am. Chem. Soc. *56*, 646 (1934).
16. Forschling W., Hietanen S., Sillen L. G.: Acta Chem. Scand. *6*, 901 (1952).
17. Yoe J. H., Jones A. L.: Ind. Eng. Chem., Anal. Ed. *16*, 111 (1944); Harvey A. E., Manning D. L.: J. Am. Chem. Soc. *72*, 4488 (1950).
18. Beltran-Porter A., Beltran-Porter D., Cervilla A.: Talanta *30*, 124 (1983).
19. Djurdjevic P.: Transition Met. Chem. *15*, 845 (1990).
20. Djurendic E., Suranyi T., Miljkovic D.: Glasnik Hem. Tehn. Makedonija *8*, 129 (1990).