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Formation of Iron(II) Complexes with some Aromatic Anions in DMSO

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Abstract

The complexes formed between iron(II) and some aromatic anions (benzoate and 4-aminoderivate, salicylate and 4-aminoderivate, thiosalicylate) have been investigated in dimethylsulphoxide (DMSO). The complexation ratios and the stability constants of the species have been determined at 25 °C and compared, when possible, with the data obtained in ethanol. The results allow us to discuss the effect of the solvent properties and of the substituent position on the aromatic ring.

Introduction

When studying complexes equilibria in solution the attention given to the solvation of the ligand is normally minimal with respect to that of the coordinating cation, even if this effect is not negligible and may become quite strong for ligands capable of forming hydrogen bonds in protic solvents. In fact, complexes with such ligands should be more stable in aprotic solvents, where no hydrogen bond occurs, than in water or other protic solvents, assuming that metal ions are not solvated much better in aprotic solvents.

In order to investigate the influence of the solvent on the stability of the complex species, formation equilibria of some complexes were studied in ethanol (EtOH) and dimethylsulphoxide (DMSO) which are characterized by different donor numbers (*DN*), acceptor numbers (*AN*), dielectric constants (*DEC*) and a different capacity to form hydrogen bonds (y_w).

In this paper the systems of iron(II) with different ligands: sodium salicylate (sal), sodium thiosalicylate (thiosal), sodium 4-NH_2-salicylate (4-NH_2-sal), sodium 4-NH_2-benzoate (4-NH_2-benz) and sodium benzoate (benz) were examined. So it is also possible to evaluate the role of ligand properties in governing the complexation ratio in a series of complexes of a given metal ion.

Experimental

Apparatus

Optical density measurements were made on a Perkin-Elmer 559 spectrophotometer. Thermogravimetric studies were carried out on a Perkin-Elmer model TGS-2.

Infrared spectra were recorded in the range 4000–400 cm^{-1} using a Perkin-Elmer 983 spectrophotometer in KBr discs.

All reagents were of pure grade of Merck. The iron(II) ion was in the form of perchlorate hexahydrate with different concentrations in the 0.2–2 $\times 10^{-3}$ M range.

The ionic strength was maintained at 0.05 M with tetrabutylammonium perchlorate. Solvents were dehydrated and purified in the usual way [1]. The water content of the products was found to be less than 0.05% in all cases. Solutions were prepared in a dry box under a dry nitrogen atmosphere.

Results

From some preliminary tests it was shown that the absorbance of the solutions containing both iron(II) and the studied ligands increased with time. Constant values are reached in different times depending on the ligands: 75 min for salicylate, 60 min for 4-NH_2-salicylate, 30 min for thiosalicylate and 3–4 min for benzoate and the 4-NH_2-derivate.

The spectra of the complexes examined, except for the thiosalicylate system, consist of two well-defined bands, the first in the UV and the second one, of much lower intensity, in the visible region. In the latter region, the optical densities of all the solutions are considerably greater than the corresponding solution of iron(II) perchlorate. Thus, in this region, the absorption bands must be ascribed to transitions of electrons which participate in complex formation. Moreover, as seen from Table I, the position of the peaks of these characteristic bands depends on the nature of the substituents and on the complexation ratios.

The concentrations quotients at equilibrium of iron(II) with sal and 4-NH_2-sal and thiosal were estimated by the method of 'corresponding solutions' [2] and their formation curves are reported in Fig. 1, while the systems of iron(II) with benz and 4-NH_2-benz were studied by the method of the 'straight line' [3]. With regard to the last two systems, the curves A *versus* C_L/C_M at different metal concentrations over-

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TABLE I. Complexation Ratios and Maxima Wavelengths for the Systems Examined in Solution at 25 °C

Systems	EtOH		DMSO	
	Complexation ratios (M/L)	λ_{max} (nm)	Complexation ratios (M/L)	λ_{max} (nm)
Iron(II)–salicylate	1/1 1/2 1/3	520 500 480	1/1 1/2 1/3	540 510 490
Iron(II)–4-NH_2-salicylate			1/1 1/2 1/3	500 480 440
Iron(II)–thiosalicylate			1/1	500 and 680
Iron(II)–benzoate	1/2	460	1/2	540
Iron(II)–4-NH_2-benzoate			1/3	420

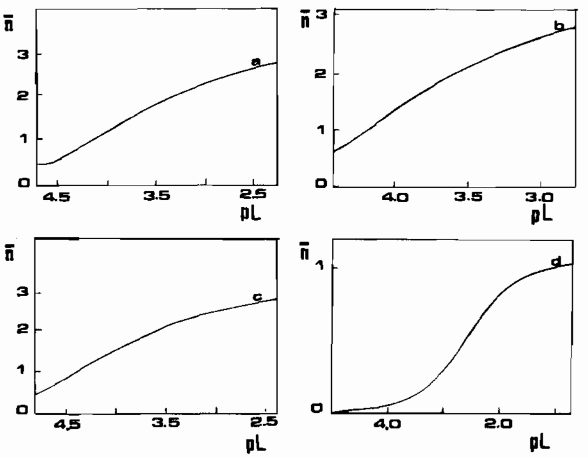

Fig. 1. Variation of the formation function $\bar{n} = (C_L - [L])/C_M$ depending on the free ligand concentration (pL) for the systems: (a) iron(II)–salicylate in DMSO, (b) iron(II)–4-NH_2-salicylate in DMSO, (c) iron(II)–salicylate in EtOH, (d) iron(II)–thiosalicylate in DMSO.

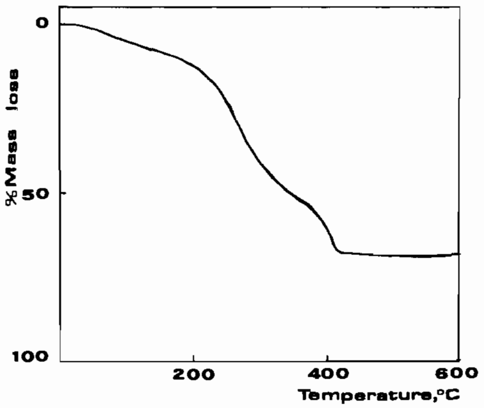

Fig. 2. Thermogravimetric curve of the iron(II)–4-NH_2-salicylate complex in air (10 °C min^{-1}).

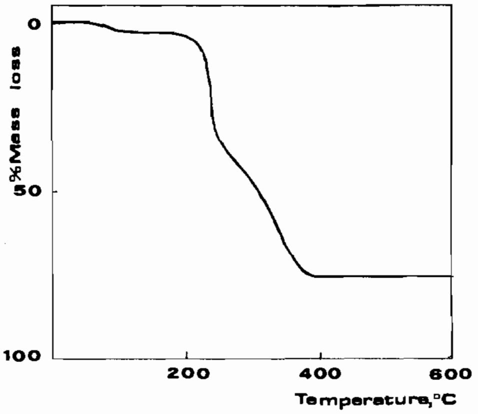

Fig. 3. Thermogravimetric curve of the iron(II)–(4-NH_2-benzoate)$_2$ complex in air (10 °C min^{-1}).

lapped so that the first computing method was not applicable.

Table II reports the values of concentration quotients at equilibrium (K_i) and molar absorptivity (ϵ_i) of the evidenced species.

The data of the system Fe^{2+}/thiosal in EtOH are not reported because the complexes are not detectable by spectrophotometry and probably are not formed. Those of Fe^{2+}/4-NH_2-sal and Fe^{2+}/4-NH_2-benz systems in EtOH are not reported because the complexes are not soluble in this solvent. In order to have more information about the solid compounds, we have examined them by TGA and IR. The behaviour of the thermogravimetric analyses, given in Figs. 2 and 3, show that the 4-NH_2-sal/metal ratio is 1/1 and that the 4-NH_2-benz/metal ratio is 2/1. The first complex (Fig. 2) decomposes gradually with a mass-loss of about 14%, losing two moles of water of crystallization per mole of complex. The successive decomposition process starts at 180 °C and through unresolved steps it leads to an intermediate compound at 370 °C, that, by chemical analyses, appeared

TABLE II. Concentration Quotients at Equilibrium log K_i and Molar Absorptivities ϵ_i (mol^{-1} l cm^{-1}) for the Systems Examined in Solution at 25 °C and Complexation Ratios for the Solid Complexes Obtained

Systems	EtOH[a] (*DN* = 24.0, *AN* = 37.9 *DEC* = 24.3, y_w = 38)		DMSO[a] (*DN* = 29.8, *AN* = 19.3 *DEC* = 45.0, y_w = 79)
	Solution[b]	Solid state	Solution[b]
Iron(II)–salicylate	log K_1 = 4.60 ± 0.04 ϵ_1 = 1190 (λ = 520 nm)		log K_1 = 4.40 ± 0.05 ϵ_1 = 1120 (λ = 540 nm)
	log K_2 = 4.29 ± 0.07 ϵ_2 = 1730 (λ = 520 nm)		log K_2 = 3.89 ± 0.03 ϵ_2 = 2300 (λ = 490 nm)
	log K_3 = 3.08 ± 0.09 ϵ_3 = 3000 (λ = 480 nm)		log K_3 = 2.93 ± 0.02 ϵ_3 = 3500 (λ = 490 nm)
Iron(II)–4-NH_2-salicylate		Fe(4-NH_2-sal)·$2H_2O$↓	log K_1 = 4.62 ± 0.03 ϵ_1 = 1250 (λ = 500 nm)
			log K_2 = 4.27 ± 0.06 ϵ_2 = 1900 (λ = 500 nm)
			log K_3 = 3.20 ± 0.07 ϵ_3 = 3420 (λ = 440 nm)
Iron(II)–thiosalicylate			log K_1 = 2.58 ± 0.03 ϵ_1 = 850 (λ = 680 nm)
Iron(II)–benzoate	log β_2 = 3.56 ± 0.04 ϵ_2 = 100 (λ = 460 nm)		log β_2 = 4.19 ± 0.08 ϵ_2 = 140 (λ = 540 nm)
Iron(II)–4-NH_2-benzoate		Fe(4-NH_2-benz)$_2$↓	log β_3 = 8.67 ± 0.03 ϵ_3 = 315 (λ = 420 nm)

[a] For solvent parameters see refs. 7–9. [b] The reported values are the average of at least four measurements, the error is expressed by the mean deviation.

to be $FeCO_3$. The successive decomposition step leads to a red–brown residue of Fe_2O_3 (calc.: 32.7%, found: 30.9%).

For the second complex (Fig. 3) that is anhydrous, the decomposition process starts at 200 °C and proceeds in two steps unresolved, leading to a residue of Fe_2O_3 (calc.: 24%, found: 24.5%). The analyses of the evolved gases in the first step shows the presence of ammonia obtained by decomposition of the amino group so it is possible to suppose that these groups are not involved in the metal ion coordination. The IR spectrum of the iron(II)–(4-NH_2-benz)$_2$ confirms this hypothesis evidencing the presence of bonded carboxylate groups. In fact, infrared-active ν(COO) absorptions are observed as a very intense doublet band at 1630 and 1600 cm^{-1} and a band at 1390 cm^{-1} for the complex species (1600 and 1550 and 1400 cm^{-1} for the free benzoate) which characterize covalently bonded –COO groups [4].

Discussion

The obtained data, summarized in Table II, allows us to formulate some hypotheses about the influence of some substituents on benzoate and about the influence of the solvent on the complexation equilibria in the systems examined.

Comparing the results of the salicylate and benzoate systems it appeared that the presence of the ortho hydroxyl group to the carboxylate in the former ligand causes, as expected, a higher stability of the complex species because of chelation.

It appears, moreover, that where the substituent possesses a +R mesomeric effect as does the aminic group in 4-NH_2-sal and 4-NH_2-benz, the π-electron density in the ring is increased with a corresponding increase in the values of formation constants.

An other effect of the aminic group is the decrease of the solubility of the complex in ethanol so much that these species are not soluble in this solvent.

With regard to the difference between salicylate and thiosalicylate the stability constant of the complex species obtained in DMSO with the first ligand is higher than that obtained with the second one. This fact can be explained if we consider the different basicity of carboxylate groups present in both ligands. Indeed, thiosal is less basic than sal, as shown by their p*K* values in DMSO, which are 5.4 for the former [5] and 6.6 for the latter [6]. The thio group is also involved in the coordination of the metal ion as shown, for the Fe(II) thiosal system, by the presence of two bands in the visible region with two λ_{max} at 550 and 680 nm.

The nature of the solvent seems very important in the thiosal–iron(II) system. In fact, in this case, colored complexes are formed only in dipolar aprotic solvents such as dimethylacetamide, dimethylsulfoxide and dimethylformamide contrary to what occurs in ethanol and other tested solvents (methanol, propanol). It is evident that the different hydrogen bonding ability of the solvent plays a favourable role in the formation of the complex species. In particular, in DMSO, that is a good acceptor of hydrogen bonding, the intermolecular bonds are favoured, while in protic solvents the favoured intramolecular bond determines a decrease in the basicity of the atoms involved in the chelating ring.

The values of concentration quotients at equilibrium of the salicylate systems examined, are slightly higher in EtOH with respect to DMSO for the salicylate systems examined. This result suggests some hypotheses based on solvent properties: in fact, the higher DEC (that increases ligand ionization) and the smaller *AN* (that decreases the solvation of the ligand) exhibited by DMSO with respect to EtOH, favour the stabilization of complex species in DMSO balancing, with a higher ligand concentration, the complex destabilization expected, taking into account the higher *DN* of DMSO.

In the case of the benzoate system the β_2 value in EtOH is smaller than DMSO. This result is due to the effects mentioned above and in addition to an interaction between the carboxylate group and EtOH by hydrogen bonding that increases the solvation of this ligand. It is noteworthy that this interaction is not seen in the salicylate ligand because probably intramolecular hydrogen bonding is prevailing.

Acknowledgement

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