Full Paper

Potentiometric Study of Azide Complexes of Iron(III) in Water/THF Medium

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Abstract: The stepwise formation of iron(III)-azide complexes in water/THF medium has been investigated at 20.0 ($\pm$ 0.1) °C and 1.00 mol L^{-1} ionic strength (NaClO$_4$). By the indirect potentiometric method employed, using a glass electrode and under the conditions studied, three mononuclear complexes were successively detected for each water/THF ratio. No evidence of polynuclear species was found. The final analyses of the data for aqueous-tetrahydrofurane (20.0-40.0%, v/v) medium, by solution of adjusted simultaneous equations with Fronaeus function values, led to the overall stability constants varying from $\beta_1 = 7.11 \times 10^3$ L mol^{-1} to $\beta_3 = 4.12 \times 10^{12}$ L^3 mol^{-3}. The results showed that the organic solvent proportion is an important parameter for formation of these complexes. Iron complexes with higher stability were produced in the presence of 40.0% (v/v) tetrahydrofuran. Comparison with literature values suggests that the organic solvent has high influence on the coordination of the metallic ion.

Keywords: complexes; stability constants; water/THF medium

1. INTRODUCTION

Studies involving metallic complexes play an important role in science because these compounds take part in several industrial processes in the chemical industry, besides being extensively employed in almost all scientific areas. In medicine, for instance, undesirable metallic species are removed by complexation with suitable ligands. A typical example is the removal of Ca^{2+} ions with EDTA in order to prevent formation of kidney stones and cataract disease. In electrochemistry, metallic complexes are employed for the electrodeposition and formation of more homogeneous films, since they provide a slower, more gradual release of metallic species [1].

In this context, studying the stability constant of metallic species is crucial for the determination and prevention of interation of a specific ligand in a medium containing several metals. Moreover, equilibrium studies are also at the heart of the discussion about coordination compounds in solution, the obtainment of different kinds of stability series, the characterization of species present in a solution, and the development of analytical methodologies.

This research group has investigated equilibrium reactions involving complexes formed between halides, pseudo-halides and carboxylate ligands and several transition metal ions [2-9]. Furthermore, we have employed some organic solvents, such as THF and dimethyl ketone, with a view to increasing the analytical sensitivity of these systems, in the case of the quantitative spectrophotometric determination of metals in pharmaceutical formulations [10] and rock samples [11], for example.

In the last 30 years, complexes formed by azide (N$_3^-$) and several transition metallic species have been investigated aiming at obtaining information about their coordination nature [2, 7, 12, 13], and developing new analytical methodologies [10, 14-18], such as

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calculation of other parameters of interest [19], determination of the equilibrium constant of successive complexes [20, 21], and establishment of thermodynamic parameters [13, 22].

The study of complex formation and the determination of their stability constants have also been carried out indirectly, by using other groups, like a metallic ion, a second ligand, or H⁺, which interact with one of the species in the main system and whose concentration can be accurately determined [23].

Several methods can be used for the determination of stability constants [24-31]. Among them, the most important are: spectroscopic methods (spectrophotometry, infrared, Raman, nuclear magnetic resonance, spin resonance, Mössbauer, refractometry, spectropolarimetry, light scattering and ultrasonic absorption), distribution methods (solvent extraction, Solubility, ion exchange, gas chromatography, liquid chromatography and thin layer chromatography), electrochemical methods (potentiometry, polarography, anodic redissolution voltammetry, conductivity and dielectric constant) and calorimetric methods (direct calorimetry and thermometric titration calorimetry).

The use of H⁺ as a substituting group, for example, can be achieved by means of a buffer system formed by a weak acid (HX) and its corresponding salt, whose anion or conjugated basis (X⁻) is the ligand itself. In this case, a competition between H⁺ and other cations for the ligand is observed, being the stability constants indirectly obtained by pH measurements. In this case, the glass electrode can accompany the pH changes that occur upon complexation throughout titrations.

The formation of iron (III)/azide complexes has been studied in aqueous medium and five global constants (β_1 to β_5) [4] have been obtained. However, studies carried out in mixed medium [4, 10] have indicated that the presence of tetrahydrofuran (THF) in the iron (II)/azide system leads to the appearance of a more sensitive band in the absorption spectrum of these complexes, similar to the one observed for the iron(III)/azide system [15]. So, immediate oxidation of the metallic species (Fe-II) under these conditions, with subsequent and very rapid complexation, could increase the analytical applications for iron. However, no study elucidating this behavior has been already reported. In this sense, the aim of this work is to investigate iron(III)/azide complexes and determine their formation constants in water/THF, as well as compare the obtained constants with those previously

determined in aqueous medium [4]. An additional objective is to investigate the influence of the organic solvent on the proposed system.

2. MATERIAL AND METHODS

Reagents and Chemicals

All chemical reagents used in this work were analytical purity grade: a 3.49 mol L⁻¹ HClO₄ (Merck) solution was standardized with 1.00 mol L⁻¹ NaOH (Merck) solution by potentiometric titration; a 3.74 mol L⁻¹ NaN₃ (Merck) solution was adjusted with a 1.00 mol L⁻¹ AgNO₃ (Synth) solution also by potentiometric titration; a 0.48 mol L⁻¹ Fe(ClO₄)₃ (Aldrich) solution was appropriately reduced and normalized by UV-Vis spectrophotometry, using 1,10-phenantroline (Acros) as the complexing agent; a 7.58 mol L⁻¹ NaClO₄ (Merck) solution, standardized by direct gravimetry and tetrahydrofuran (Merck) without any previous treatment. The water used to prepare all solutions had been purified in a milli-Q system.

Apparatus

A potentiometer from Micronal, model B-374, containing a combined glass electrode from Metrohm, model EA-121, was employed for potentiometric measurements. The thermostatic bath was provided by a Tecnal, model TE-184 equipment, adjusted to 20.0 °C.

A titration cell of 20.0 mL with a thermostatic jacket was employed.

Procedure

Due to the presence of perchlorate ions in the system, the internal solution of the combined glass electrode (KCl) was substituted by NaCl = 3.00 mol L⁻¹ solution, in order to prevent KClO₄ precipitation in the electrode membrane.

For each different percentage of THF and ionic strength, the glass electrode was kept immersed for at least 24 h in a solution with pH 2.00, in the same ionic strength and percentage of THF as the studied system.

The angular coefficient (slope) of the glass electrode response was determined in the same conditions of the work (ionic strength and THF percentage), being aliquots of 20.0 mL of 0.10 mol L⁻¹ HClO₄ titrated with a 0.50 mol L⁻¹ NaOH standard

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solution. The ionic strength of both solutions ($HClO_4$ and NaOH) was adjusted with a $NaClO_4$ solution.

The free acidity of the solution containing Fe^{3+} was also studied by potentiometric titration. The method of Gran I [23] was employed in the presence of oxalate excess.

The formation constants for the Fe^{3+}/N_3^- complexes were determined in media containing 20.0, 30.0 and 40.0% (v/v) THF under a 1.00 mol L^{-1} ionic strength. The potentiometric measurements of all the studied systems were carried out in buffered conditions (HN_3/NaN_3) in promptly adjusted ionic strength and solvent percentage. Into the thermostatized cell containing 20.0 mL of each buffered solution, we added successive aliquots of $Fe(ClO_4)_3$ solution, in order to provide pH variations in the range of 0.10.

3. RESULTS AND DISCUSSION

After monitoring the variation of pH produced by successive additions of Fe^{3+} solution to the proposed system, it was possible to calculate the values of the average number of ligands and free ligand concentration for each equilibrium, using mathematical treatment [8]. As an example, the results which were adjusted to the formation curve for Fe^{3+}/N_3^- system in 20.0% THF are shown in Figure 1. An analogous procedure was carried out for the other proposed conditions.
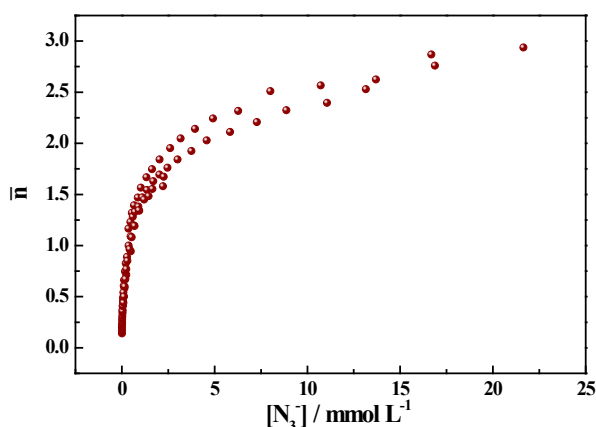

Figure 1. Formation curve for complex species $[Fe(N_3)_n]^{3-n}$, in 20.0% (v/v) THF solution at an ionic strength of 1.0 mol L^{-1} (T = 20.0 ± 0.1 °C).

Analysis of Figure 1 indicates the possible coexistence of at least three complex mononuclear species in equilibrium ($[Fe(N_3)]^{2+}$, $[Fe(N_3)_2]^+$ and $[Fe(N_3)_3]$), because the maximum average number of

ligands tends to be stabilized in this order in the studied concentration range.

After that, the experimental values of $\bar{n}$ and the complex stability constants were established according to the Fronaeus function [33], $F_0(L)$:

$$F_0(L) = 1 + \beta_1[L] + \beta_2[L]^2 + ... + \beta_n[L]^n$$

The values of $F_1(L)$ and $F_2(L)$ can also be calculated by means of $F_0(L)$:

$$F_1(L) = \frac{F_0(L) - 1}{[L]} = \beta_1 + \beta_2[L] + ... + \beta_n[L]^{n-1}$$

$$F_2(L) = \frac{F_1(L) - \beta_1}{[L]} = \beta_2 + \beta_3[L] + ... + \beta_n[L]^{n-2}$$

After the graphic treatment of Leden [34], the β_1 and β_2 values can also be calculated. In this case, if $F_2(L)$ is linear, the value of β_3 can also be obtained. Figures 2 and 3 depict the results of these functions for the Fe^{3+}/N_3^- system in 20.0% THF.
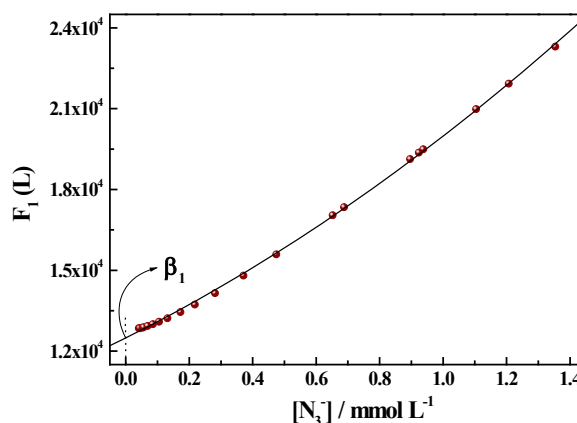

Figure 2. Graphic extrapolation of $F_1(L)$ *vs.* $[N_3^-]$ (mmol L^{-1}) curve for determination of β_1 in the Fe (III)/N_3^- system, in a 20.0% (v/v) THF solution and ionic strength of 1.0 mol L^{-1} (T = 20.0 ± 0.1 °C). Adjusted points for second grade equation (f(x) = a + bx + cx^2).

The values for the respective global formation constants using the method of Leden were:

$$\beta_1 \approx 1.25 \times 10^4 \ (mol \ L^{-1})^{-1} \ for \ [Fe(N_3)]^{2+}$$

$$\beta_2 \approx 6.67 \times 10^6 \ (mol \ L^{-1})^{-2} \ for \ [Fe(N_3)_2]^+$$

$$\beta_3 \approx 9.01 \times 10^8 \ (mol \ L^{-1})^{-3} \ for \ [Fe(N_3)_3]$$

The method of Milcken [35] updated by Tavares [36] was also employed. These methods employ the function of Fronaeus, whose corrected values represent a group of simultaneous equations, that can be solved by the matrix method of minimum

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squares. Therefore, the final values of complex stability constants obtained by computational method (matrix 3x3) for the ionic strength of 1.00 mol L^{-1} in 20.0% THF (v/v) were:

$$\beta_1 = 1.24 \times 10^4 \ (mol \ L^{-1})^{-1}$$

$$\beta_2 = 6.66 \times 10^6 \ (mol \ L^{-1})^{-2}$$

$$\beta_3 = 9.11 \times 10^8 \ (mol \ L^{-1})^{-3}$$
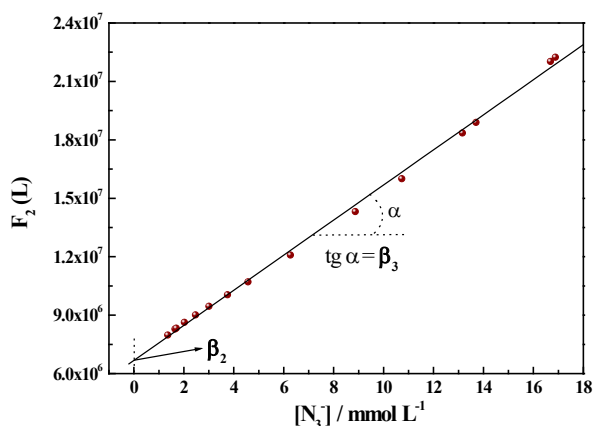

Figure 3. Graphic extrapolation of $F_2(L)$ *vs.* $[N_3^-]$ (mmol L^{-1}) curve for determination of β_2 and β_3 in a 20.0% (v/v) THF solution and ionic strength of 1.00 mol L^{-1} (T = 20.0 ± 0.1 °C). Adjusted points for first grade equation (f(x) = a + bx).

This laborious treatment of the experimental values was employed in the above mentioned conditions in order to determine the respective formation constants. Table 1 presents the final values of these constants for all the media containing THF investigated in this work.

Table 1. Conditional formation constants [β_n / (mol L^{-1})$^{-n}$] for different media containing THF, carried out at an ionic strength of 1.0 mol L^{-1} (T = 20.0 ± 0.1 °C).

THF Percentage (v/v)	20.0	30.0	40.0
β_1 (mol L^{-1})$^{-1}$	1.24×10^4	7.11×10^3	7.94×10^5
β_2 (mol L^{-1})$^{-2}$	6.66×10^6	3.33×10^6	3.69×10^9
β_3 (mol L^{-1})$^{-3}$	9.11×10^8	2.50×10^9	4.12×10^{12}

According to this Table, it is possible to observe that the highest β values were obtained in media containing 40.0% THF. Another important verification is that the three complex species coexist in all the investigated experimental conditions. In fact, $[Fe(N_3)]^{2+}$, $[Fe(N_3)_2]^+$ and $[Fe(N_3)_3]$ are stable, since they present high values of conditional formation constants.

Furthermore, once the values of β_1, β_2 and β_3 have been calculated, it is possible to determine the fractions of each species in solution, α. When plotted in a graphic, these values give a general view of the system, as shown in Figure 4.
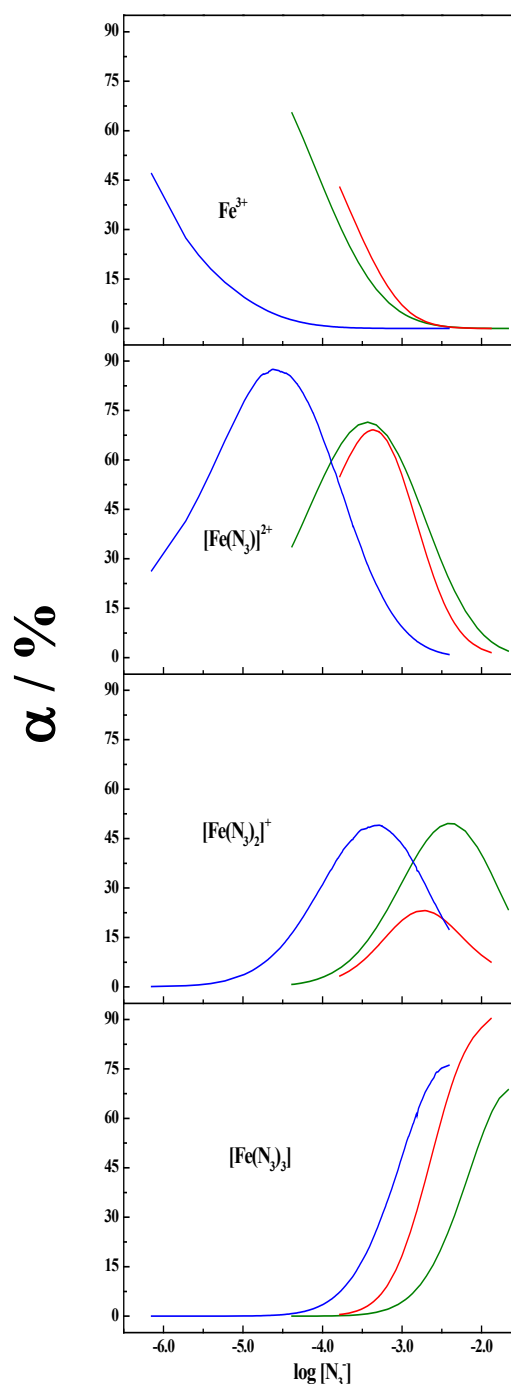

Figure 4. Diagram for the equilibrium distribution of species in the Fe (III)/N$_3^-$ system in media containing: (—) 20.0, (- - -) 30.0 and (·····) 40.0% (v/v) THF at an ionic strength of 1.00 mol L^{-1} (T = 20.0 ± 0.1 °C).

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According to distribution diagrams (Figure 4), the two first formed complexes (until $\bar{n} = 2$) are predominant in all investigated conditions, calling for only small amounts of ligand. Furthermore, smaller amounts of Fe^{3+} ions are found in media with higher percentage of organic solvent, and this behavior was observed in all the studied concentration range. These results agree with the higher formation constant values calculated for these media.

To check the influence of the organic solvent in the formation of the complex species, the results obtained in this work were compared with those reported by Neves [4] and Avşar [22], in aqueous media, where the coexistence of up to five complex species was observed. In this way, it is possible to verify that THF also acts as a ligand in our system, competing with the azo ligand for the coordination sphere of the metallic ion and leading to the preferential formation of neutral complexes.

4. CONCLUSION

While aqueous systems give evidence of formation of up to five complex species between Fe(III) and N_3^-, the THF-containing system gives only three complex species due to the solvation effect, which hinders the formation of anionic species. The percentage of organic solvent in the medium also affects the stability constant values, indicating a competition between the organic solvent and the ligand for the coordination sphere of the metallic ion.

5. ACKNOWLEDGMENTS

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