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Poonma Malik[a]; Ana Paula Paiva[a]; Nuno R. Neng[b]; José M. Florêncio Nogueira[b]
[a] Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa (DQB-FCUL), Centro de Química e Bioquímica, Lisboa, Portugal [b] Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa (DQB-FCUL), Centro de Ciências Moleculares e Materiais, Lisboa, Portugal

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The Mutual Effect of Iron(III) and Silver(I) Species in Concentrated Chloride Medium

Poonma Malik and Ana Paula Paiva
Centro de Química e Bioquímica, Departamento de Química e
Bioquímica, Faculdade de Ciências da Universidade de Lisboa
(DQB-FCUL), Lisboa, Portugal

Nuno R. Neng and José M. Florêncio Nogueira
Centro de Ciências Moleculares e Materiais, Departamento de Química e
Bioquímica, Faculdade de Ciências da Universidade de Lisboa
(DQB-FCUL), Lisboa, Portugal

Abstract: Earlier studies carried out to evaluate the selectivity of solvating extractants towards silver(I) in concentrated chloride media revealed that an intriguing situation occurs if a given excess of iron(III) concentration is present in the aqueous solution: the extraction of silver(I) becomes almost quantitative and independent of the initial chloride content. On the assumption that this effect may be due to a phenomenon occurring in the aqueous phase, a systematic study involving solutions containing different Ag(I), Fe(III), and HCl concentrations was carried out by solvent extraction and capillary electrophoresis. Capillary electrophoresis suggests that the $AgCl_3^{2-}$ amount in solution decreases in the presence of Fe(III), whereas $FeCl_3$ seems to be partially converted onto $FeCl_4^-$. From the experiments performed, it can be concluded that the presence of Fe(III) seems to facilitate the formation of less anionic Ag(I) species, which are in turn more easily extracted by solvating extractants. Furthermore, the presence of $FeCl_4^-$ has been detected in the organic phase of triisobutylphosphine sulfide (TIBPS) by UV-Vis spectrophotometry, after equilibration with HCl solutions containing both Ag(I) and Fe(III), which was not identified during similar experiments carried out in the absence of

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Address correspondence to Ana Paula Paiva, Centro de Química e Bioquímica, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa (DQB-FCUL), Rua Ernesto de Vasconcelos, Ed. C8, 1749-016 Lisboa, Portugal. Fax: +351 217500088; E-mail: appaiva@fc.ul.pt

Ag(I). Speciation of silver(I) and iron(III) in concentrated chloride medium has also been worked out by a numerical methodology.

Keywords: Capillary electrophoresis, iron chlorocomplexes, silver chlorocomplexes, triisobutylphosphine sulfide (TIBPS)

INTRODUCTION

It is well known that chloride media has the capability to easily complex metal ions, for which iron(III) and silver(I) are not being an exception. In fact, it is generally accepted that, for increasing chloride concentrations in the aqueous solutions, iron(III) can progressively form $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$, and $FeCl_4^-$ (1), whereas silver(I) species are $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$ (2). Although there are some contradictions in literature regarding which species predominate for a given chloride concentration in solution, the major tendency points out to the predominance of $FeCl_3$ and $AgCl_3^{2-}$ for chloride contents within 3 and 12 M (1, 2).

Paiva et al. (3–7) have been investigating the solvent extraction of silver(I) from chloride solutions for some time and, during selectivity studies carried out with solvating extractants, a curious effect was noticed: when present in the aqueous chloride phases together with silver(I), iron(III) "helped" on the extraction of the precious metal. For instance, triisobutylphosphine sulfide (TIBPS) extracted 77% Ag(I) from a 5 M chloride solution for a given set of experimental conditions, whereas the extraction of Ag(I) increased to 99% when Fe(III) coexisted in the aqueous solution in a 65-molar fold excess (3, 4). This beneficial effect of iron(III) on Ag(I) extraction by TIBPS has been confirmed for different chloride concentrated solutions (8) and it is as more pronounced as higher Fe(III) concentrations are involved (9). Another important feature is that the opposite is also true, that is, the extraction efficiency of iron(III) by TIBPS also increases when Ag(I) is present (iron(III) is almost not extracted by TIBPS when it is the only metal ion in the chloride aqueous phase) (3, 8).

Apart from TIBPS, this iron(III) and silver(I) mutual effect has also been observed with diethylthiuram disulfide (*disulfiram*) (5) and tri-*n*-butyl- and tri-*n*-octylphosphine sulfides (TBPS and TOPS, respectively) (6). Under a similar set of experimental conditions, the coexistence of a 65-molar fold excess of iron(III) in a 5 M chloride aqueous solution caused Ag(I) to be extracted by *disulfiram* from 21% [Ag(I) alone] to 92% (5), whereas with TBPS it increased from 82% to 99% and with TOPS from 73% to 99% (6).

Explanations of this iron(III) and silver(I) mutual effect have been attempted but are not straightforward. There is much evidence in literature that solvating organic ligands act over Ag(I) anionic chlorocomplexes in aqueous solutions by displacement of chloride anions from the coordination sphere of the metal ion and leading to the formation of $AgCl \cdot nL$ species (L being the organic ligand) in the organic phase (4, 6, 10). An interpretation of the phenomenon based on that fact would be to suppose that Fe(III) can in some way affect the metallic chlorocomplex species in solution and somehow favour the formation of less anionic Ag(I) species (4). Such an assumption is in accordance with some research carried out on silver leaching using either Fe(III) or Cu(II) chloride solutions (11, 12), which showed that the contribution of free chloride ions by a given concentration of Cu(II) chloride always exceeds that of a similar concentration of Fe(III) chloride, considering for both cases a constant total chloride concentration. However, how can such supposition be confirmed?

In the present work, Ag(I) solvent extraction by TIBPS is again revisited in order to analyze the involved aqueous and organic phases by UV-Vis spectrophotometry, the influence of parameters such as hydrochloric acid and Fe(III) concentration in the aqueous phases being evaluated. The information obtained was subsequently used to apply capillary electrophoresis (CE) for the analysis of concentrated hydrochloric acid solutions containing fixed proportions of Fe(III) and Ag(I). The development of different mathematical derivations and computer simulations to establish Ag(I) and Fe(III) speciation has also been carried out. The theoretical treatment is based on the equilibrium constants of silver chloride and related anionic silver species (2) and on iron chloride species found in literature (13–15), and also on the model proposed by Pitzer (16) and Bromley (14) to estimate activity coefficients of the involved entities.

EXPERIMENTAL

Reagents

All reagents and solvents used during experimentation were of analytical grade and used without purification. Cyanex 471X (whose active ingredient is triisobutylphosphine sulfide, TIBPS, 95% purity) was gently supplied by Cytec (Canada). Deionized water from a Milli-Q water purification system (Molsheim, France) was used for preparation of the solutions.

Procedure

Silver(I) solutions of known concentration were prepared by dissolving silver nitrate in a minimum amount of deionized water and diluting up to a known volume by hydrochloric acid solutions (≥ 3.0 M). Iron(III) solutions were prepared by dissolving iron(III) chloride hexahydrate in a known volume of hydrochloric acid solutions. TIBPS organic solutions were prepared in toluene. A di-sodium hydrogen phosphate buffer of 50 mM and pH 9.07

was prepared by dissolution of the respective salt in deionized water. The pH was checked periodically using a Ino-Lab (Level 1) pH Meter (Weilheim, Germany).

Extraction experiments were carried out by shaking equal volumes of aqueous and organic phases for 30 minutes at a constant stirring speed of 1000 r.p.m. and at a temperature of $25 \pm 0.1°C$. Analysis of metal contents was carried out by Flame Atomic Absorption Spectroscopy, using a Pye Unicam model (SP9). Metal ion concentrations in the organic solutions were calculated by mass balance. For each sample, three aliquots were considered and the results were critically evaluated and accepted only if a reasonable standard deviation was achieved.

The absorption spectra of the aqueous and organic phases were recorded on a Shimatzu (model 1603) spectrophotometer using 1.0×1.0 cm quartz cells. The necessary blank corrections were carried out for every analysis.

Capillary Electrophoresis

Capillary electrophoretic separations were performed on a ^{3D}CE system equipped with a UV-Vis diode array detector (DAD) (Agilent Technologies, Waldbronn, Germany). A ^{3D}CE ChemStation software (Rev.A.08.03, G1601) was used for instrument control and data collection. Uncoated fused-silica capillaries of 75 μm internal diameter (id) and extended light path (Agilent Technologies) were used throughout the work. The positive mode of polarity (detection window on negative terminal) was chosen. The temperature of the capillary was maintained at 25°C and the procedure of direct detection for DAD at 224 nm was always used.

A particular experimental working session with the capillary electrophoresis instrument began with the preconditioning of the capillary (20 min) using 1.0 M NaOH. The preconditioned capillary was subsequently rinsed with deionized water for 10 min and with the background electrolyte (BGE) for 20 min. The capillary, treated by the above method, was filled with the working solution and the electropherogram recorded. After the completion of the experiment, the capillary was purged with the BGE for 3 min and reused for recording further electropherograms. At the end of the experimental session, the capillary was flushed with deionized water (15 min) and air (10 min).

All the samples and standards were first degassed in an ultrasonic bath and filtered through a 0.45 μm filter (Supelco, Bellefonte, PA, USA), being then introduced in the capillary through a hydrodynamic injection (50 mbar, 1 s). The velocity of the electro osmotic flow (EOF) was determined by the migration time of acetone. The BGE vials were replenished after every analysis. The blank corrections, with respect to the BGE and the acid, were incorporated during the recording of the electropherograms. All the determinations were repeated for three times to verify the reproducibility of the results.

Mathematical Modeling Calculations

For mathematical calculations, the iterative program “solver” add-in (Microsoft Excel 2003) was used.

RESULTS AND DISCUSSION

Speciation of Silver(I) and Iron(III) in Concentrated Hydrochloric Acid Media by Numerical Methodology

Mathematical modeling is often a useful tool to compute the concentration of ionic species in aqueous solutions. Several advancements have been observed in this area of research over the past decades. Some models, like those proposed by Bromley (14) and Pitzer (16), are quite well recognized for the speciation of ionic species in a concentrated aqueous medium.

Silver(I) speciation has been carried out by considering the practical composition of the aqueous phase as containing Ag(I) = 1.4 mM, HCl = 3.0 – 8.0 M, and via proposing the following equations:

$$\mathrm{Ag^+ + Cl^- \Leftrightarrow AgCl} \quad {}^{0}\beta_1 = {}^{\mathrm{I}}\beta_1 \times \frac{\gamma_{\mathrm{AgCl}}}{\gamma_{\mathrm{Ag^+}}\gamma_{\mathrm{Cl^-}}} \tag{1}$$

$$\mathrm{Ag^+ + 2Cl^- \Leftrightarrow AgCl_2^-} \quad {}^{0}\beta_2 = {}^{\mathrm{I}}\beta_2 \times \frac{\gamma_{\mathrm{AgCl_2^-}}}{\gamma_{\mathrm{Ag^+}}\gamma^2_{\mathrm{Cl^-}}} \tag{2}$$

$$\mathrm{Ag^+ + 3Cl^- \Leftrightarrow AgCl_3^{2-}} \quad {}^{0}\beta_3 = {}^{\mathrm{I}}\beta_3 \times \frac{\gamma_{\mathrm{AgCl_3^{2-}}}}{\gamma_{\mathrm{Ag^+}}\gamma^3_{\mathrm{Cl^-}}} \tag{3}$$

$$\mathrm{Ag^+ + 4Cl^- \Leftrightarrow AgCl_4^{3-}} \quad {}^{0}\beta_4 = {}^{\mathrm{I}}\beta_4 \times \frac{\gamma_{\mathrm{AgCl_4^{3-}}}}{\gamma_{\mathrm{Ag^+}}\gamma^4_{\mathrm{Cl^-}}} \tag{4}$$

Here, ${}^{0}\beta_{\mathrm{i}}$ and ${}^{\mathrm{I}}\beta_{\mathrm{i}}$ (i = 1, 2, 3, 4) denote the thermodynamic and apparent equilibrium constants, respectively, and γ_{x} are the correspondent activity coefficients.

The determination of ${}^{\mathrm{I}}\beta_{\mathrm{i}}$ and thus the concentration of the different possible Ag(I) species in solution requires the knowledge of the respective ${}^{0}\beta_{\mathrm{i}}$ and γ_{x}. As cited in the literature (2), the values of ${}^{0}\beta_{\mathrm{i}}$ were taken to be ${}^{0}\beta_{\mathrm{AgCl}} = 1.7 \times 10^3$, ${}^{0}\beta_{\mathrm{AgCl_2^-}} = 1.4 \times 10^5$, ${}^{0}\beta_{\mathrm{AgCl_3}^{2-}} = 1.1 \times 10^5$ and ${}^{0}\beta_{\mathrm{AgCl_4}^{3-}} = 4.4 \times 10^3$. Depending upon the availability of the required parameters, the Pitzer model (16) has been applied to determine the activity coefficients of $\mathrm{Ag^+}$, $\mathrm{Cl^-}$, AgCl, $\mathrm{AgCl_2^-}$, $\mathrm{AgCl_3^{2-}}$, and $\mathrm{AgCl_4^{3-}}$.

In the simple form, the Pitzer model describes the following equations to estimate the activity coefficients of the cation "M" and anion "X",

$$\begin{aligned}\ln \gamma_{\mathrm{M}} = {} & \mathrm{Z}_{\mathrm{M}}^{2}\,\mathrm{f}^{\gamma} + 2\sum_{\mathrm{a}} \mathrm{m_a}(\mathrm{B_{Ma}} + \mathrm{EC_{Ma}}) + \mathrm{Z}_{\mathrm{M}}^{2}\sum_{\mathrm{c}}\sum_{\mathrm{a}} \mathrm{m_c m_a B'_{ca}} \\ & + \mathrm{Z_M}\sum_{\mathrm{c}}\sum_{\mathrm{a}} \mathrm{m_c m_a C_{ca}} + \sum_{\mathrm{c}} \mathrm{m_c}(2\Theta_{\mathrm{Mc}} + \sum_{\mathrm{a}} \mathrm{m_a}\Psi_{\mathrm{Mca}}) \\ & + \sum_{\mathrm{a}}\sum_{\mathrm{a'}} \mathrm{m_a m_{a'_{\Psi_{aa'M}}}} \end{aligned} \tag{5}$$

$$\begin{aligned}\ln \gamma_{\mathrm{X}} = {} & \mathrm{Z}_{\mathrm{X}}^{2}\,\mathrm{f}^{\gamma} + 2\sum_{\mathrm{c}} \mathrm{m_c}(\mathrm{B_{cX}} + \mathrm{EC_{cX}}) + \mathrm{Z}_{\mathrm{X}}^{2}\sum_{\mathrm{c}}\sum_{\mathrm{a}} \mathrm{m_c m_a B'_{ca}} \\ & + \mathrm{Z_X}\sum_{\mathrm{c}}\sum_{\mathrm{a}} \mathrm{m_c m_a C_{ca}} + \sum_{\mathrm{a}} \mathrm{m_a}(2\Theta_{\mathrm{Xa}} + \sum_{\mathrm{c}} \mathrm{m_c}\Psi_{\mathrm{Mca}}) \\ & + \sum_{\mathrm{c}}\sum_{\mathrm{c'}} \mathrm{m_c m_{c'_{\Psi_{cc'X}}}} \end{aligned} \tag{6}$$

where "c" and "a" stand for the cations and anions including "M" and "X" (if not shown independently) having charge $\mathrm{z_i}$. The different terms are described in the proceeding text. The molality $\mathrm{m_i}$ is defined as:

$$\mathrm{m_i} = \frac{\text{molarity}}{\text{(density of solution)} - (0.001 \times \text{molarity} \times \text{molecular weight of electrolyte})}$$

It might be important to point out that, under the present conditions, the molarities of all the involved ions have been changed to molalities. The equivalent molality E is equal to $1/2\sum m_i z_i$ and f^{γ}, the Debye- Hückel limiting law slope, is given by equation (7).

$$\mathrm{f}^{\gamma} = -\mathrm{A}_{\phi}\left(\frac{I^{1/2}}{(1 + \mathrm{bI}^{1/2})} + \frac{2}{b}\ln(1 + \mathrm{bI}^{1/2})\right)$$

At 298 K, "A_{φ}" has a value of 0.392 $(\mathrm{mol\ kg^{-1}})^{1/2}$ and "b" has a constant value of 1.2. The ionic strength "I" was calculated as:

$$\mathrm{I} = \frac{1}{2}\sum \mathrm{m_i z_i^2} \tag{8}$$

In the Pitzer equation, the parameters Θ and ψ interpret the binary interaction of the similarly charged ions and the ternary interaction of the two similarly charged ions with an ion of opposite charge, respectively. The values of Θ and ψ are either negligible or so small that their omission in practical calculations is acceptable for most of the cases (17). The terms $\mathrm{B_{Ma}}$, $\mathrm{B'_{Ma}}$, $\mathrm{B_{cX}}$, and $\mathrm{B'_{cX}}$ represent the short-range binary interactions of the involved ions and their values are computed as:

$$B_{ij} = \beta^0_{ij} + \beta^1_{ij}\, f(2I^{1/2}) \tag{9}$$

$$B'_{ij} = \frac{\beta^1_{ij} f'(2I^{1/2})}{I} \tag{10}$$

where ij = Ma or cX. β^0 and β^1 are the solute specific parameters and their required values for (H^+, Cl^-), (Ag^+, Cl^-), (H^+, $AgCl_2^-$), (H^+, $AgCl_3^{2-}$), (H^+, $AgCl_4^{3-}$) interactions have been taken from the literature (2, 18). The mathematical functions $f(2I^{1/2})$ and $f'(2I^{1/2})$ are solved as in equations (11) and (12).

$$f(x) = \frac{2(1-(1+x)e^{-x})}{x^2} \tag{11}$$

$$f'(x) = \frac{-2(1-(1+x+0.5x^2)e^{-x})}{x^2} \tag{12}$$

Here function (x) = $2I^{1/2}$.

C_{Ma} and C_{cX}, the ternary interaction parameters in equations (5) and (6), are calculated by using the following expression:

$$C_{ij} = \frac{C^{\Phi}_{ij}}{2|z_M z_X|^{1/2}} \tag{13}$$

where C^{Φ} is a numerical constant, specific to the solute, and their required values were taken from the early reports (2, 18). The activity coefficient of the "AgCl" pair has been calculated by using the following expression given in literature (2).

$$\ln \gamma_{AgCl} = AI; \quad A = 0.156 \text{ for HCl solutions} \tag{14}$$

The speciation of the various aqueous phase solutions was finally assessed by solving equations (1–4), considering the mass balance as stated in equations (15,16) and the charge balance as in equation (17).

$$m_{Ag(Total)} = m_{Ag^+} + m_{AgCl} + m_{AgCl_2^-} + m_{AgCl_3^{2-}} + m_{AgCl_4^{3-}} \tag{15}$$

$$m_{Cl^-(Total)} = m_{AgCl} + 2m_{AgCl_2^-} + 3m_{AgCl_3^{2-}} + 4m_{AgCl_4^{3-}} + m_{freeCl^-} \tag{16}$$

$$m_{H^+} + m_{Ag^+} = m_{AgCl_2^-} + 2m_{AgCl_3^{2-}} + 3m_{AgCl_4^{3-}} \tag{17}$$

The data presented in Fig. 1 highlight the highest proportion of $AgCl_3^{2-}$ species from 3.0 to 8.0 M HCl; however, the percent contribution of $AgCl_4^{3-}$ species increases with increasing acidity and it becomes almost 42% at 8.0 M HCl. It can be admitted from the speciation diagram that the percent contribution of $AgCl_4^{3-}$ would increase with acidity and, at some point, its contribution could surpass $AgCl_3^{2-}$ concentration in HCl solutions higher than 8.0 M.

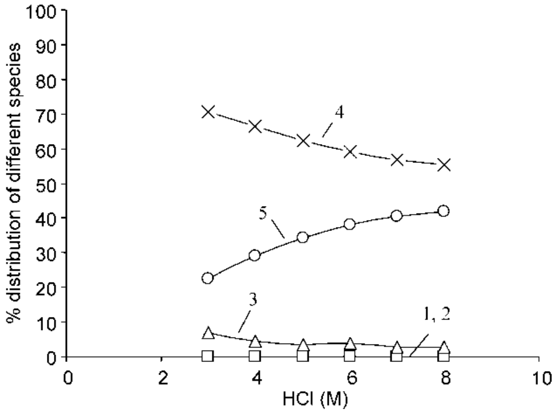

Figure 1. Effect of hydrochloric acid concentration on the speciation of silver(I). Conditions: [Ag(I)] = 1.4 mM; (1) Ag^+, (2) AgCl, (3) $AgCl_2^-$, (4) $AgCl_3^{2-}$, (5) $AgCl_4^{3-}$.

Iron(III) speciation in concentrated chloride media has been carried out by the Bromley model based approach (14). Different species of iron(III) can be expected to form [equations (18) to (21)] in concentrated hydrochloric acid media (3–8 M),

$$Fe^{3+} + Cl^- \Longleftrightarrow FeCl^{2+} \quad {}^0\beta_1 = {}^I\beta_1 \times \frac{\gamma_{FeCl^{2+}}}{\gamma_{Fe^{3+}}\gamma_{Cl^-}} \tag{18}$$

$$Fe^{3+} + 2Cl^- \Longleftrightarrow FeCl_2^+ \quad {}^0\beta_2 = {}^I\beta_2 \times \frac{\gamma_{FeCl_2^+}}{\gamma_{Fe^{3+}}\gamma_{Cl^-}^2} \tag{19}$$

$$Fe^{3+} + 3Cl^- \Longleftrightarrow FeCl_3 \quad {}^0\beta_3 = {}^I\beta_3 \times \frac{\gamma_{FeCl_3}}{\gamma_{Fe^{3+}}\gamma_{Cl^-}^3} \tag{20}$$

$$Fe^{3+} + 4Cl^- \Longleftrightarrow FeCl_4^- \quad {}^0\beta_4 = {}^I\beta_4 \times \frac{\gamma_{FeCl_4^-}}{\gamma_{Fe^{3+}}\gamma_{Cl^-}^4} \tag{21}$$

where ${}^0\beta_i$, ${}^I\beta_i$ (i = 1, 2, 3, 4) and γ_x denote the thermodynamic equilibrium constants, the concentration based equilibrium constants, and the activity coefficients, respectively. The determination of ${}^I\beta_i$, and thus the concentration of the above said different possible Fe(III) species in solution, requires the knowledge of ${}^0\beta_i$ and γ_x. The needed values of ${}^0\beta_i$ for the different species were taken from a standard handbook (13). Bromley model (14) has been applied to estimate the individual activity coefficients γ_x. The required Bromley parameters (B_{Fe^{3+},Cl^-}, B_{FeCl^{2+},Cl^-}, $B_{FeCl_2^+,Cl^-}$, $S_{FeCl_3,HCl}$, $B_{FeCl_4^-,H^+}$) (B_{H^+,Cl^-}) for Fe-Cl or H-Cl interactions have been reported elsewhere (14, 15).

After calculating the ${}^I\beta_i$ values, the concentrations of the species were computed by solving equations (18) to (21) along with the equations of mass balance (22, 23) and charge balance, equation (24).

$$
\begin{aligned}
m_{\mathrm{Fe(Total)}} &= m_{\mathrm{Fe^{3+}}} + m_{\mathrm{FeCl^{2+}}} + m_{\mathrm{FeCl_2^+}} \\
&\quad + m_{\mathrm{FeCl_3}} + m_{\mathrm{FeCl_4^-}} \qquad (22)
\end{aligned}
$$

$$
\begin{aligned}
m_{\mathrm{Cl^-(Total)}} &= m_{\mathrm{freeCl^-}} + m_{\mathrm{FeCl^{2+}}} + 2m_{\mathrm{FeCl_2^+}} \\
&\quad + 3m_{\mathrm{FeCl_3}} + 4m_{\mathrm{FeCl_4^-}} \qquad (23)
\end{aligned}
$$

$$
m_{\mathrm{H^+}} + 3m_{\mathrm{Fe^{3+}}} + 2m_{\mathrm{FeCl^{2+}}} + m_{\mathrm{FeCl_2^+}} = m_{\mathrm{FeCl_4^-}} + m_{\mathrm{Cl^-}} \qquad (24)
$$

(m_i represents the molality).

The results of the modeling studies—Fig. 2—reveal that $FeCl_3$ is the predominant species in the hydrochloric acid concentration range of 3–8 M. A noticeable formation of $FeCl_4^-$ species starts at 8 M HCl.

Liquid-Liquid Extraction Experiments

In order to get details on speciation in between silver(I) and iron(III), some experiments were conducted by the use of the solvent extraction technique. The aqueous and organic phases were also analyzed spectrophotometrically, in order to find out probable changes in their UV-Vis spectra before and after extraction. The extractant chosen for these studies was Cyanex 471X (triisobutylphosphine sulfide, TIBPS). This extractant is specifically selective for silver(I), and an enhancement in silver(I) extraction in the presence of iron(III) in chloride solutions has already been observed for this system (3, 4, 8).

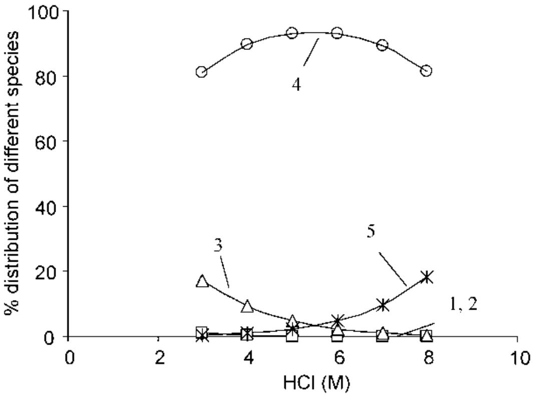

Figure 2. Effect of hydrochloric acid concentration on the speciation of iron(III). Conditions: [Fe(III)] = 0.5 M, (1) Fe^{3+}, (2) $FeCl^{2+}$, (3) $FeCl_2^+$, (4) $FeCl_3$, (5) $FeCl_4^-$.

Effect of Hydrochloric Acid Concentration on Silver(I) Extraction

The experiment was carried out by varying the hydrochloric acid concentration from 2.0 to 7.0 M and keeping constant the silver(I) concentration at 0.3 mM and Cyanex 471X (TIBPS) at 0.1 M. As the hydrochloric acid concentration increases, the percent extraction of silver(I) decreases uniformly—Fig. 3. A change in the λ_{max} value is observed in the UV-Vis spectra of the aqueous phases before and after extraction, i.e. the λ_{max} value for the aqueous solution obtained after contact with the organic phase (219 nm), is lower than the one found for the initial aqueous phase (224 nm). This displacement to lower wavelengths is less noticeable as the hydrochloric acid concentration increases and percent extraction of silver(I) decreases.

Effect of Iron(III) Concentration on Silver(I) Extraction

This particular effect was studied at 5.0 M HCl with 0.1 M TIBPS, keeping silver(I) concentration constant at 1.4×10^{-3} M and varying iron(III) concentration in between 1.4×10^{-3} to 0.5 M. It is relevant to the matter that, under the present experimental conditions, the extraction of silver(I) in the absence of iron(III) is around 55% and vice-versa, for iron(III), is around 4%. As the iron(III) concentration increases, the percent extraction of silver(I) increases and it becomes quantitative at around 0.5 M Fe(III) concentration—Fig. 4. The percent extraction of iron(III) under these conditions also increases and it becomes around 10% at 0.5 M Fe(III).

In the UV-Vis spectra of the aqueous phases it was observed that, as the iron(III) content increases, the spectrum of silver(I) is overlapped by the

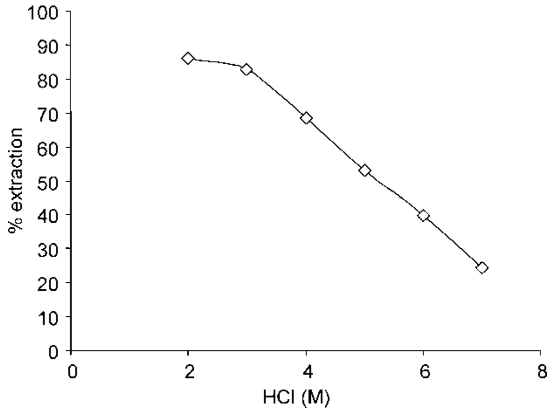

Figure 3. Effect of hydrochloric acid concentration on the extraction of silver(I) by TIBPS. Conditions: [Ag(I)] = 0.3 mM; [TIBPS] = 0.1 M.

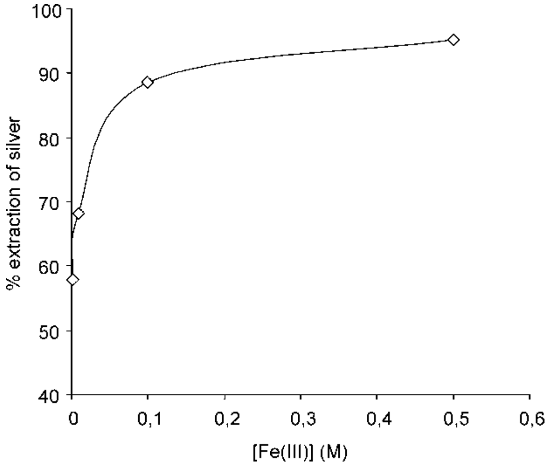

Figure 4. Effect of iron(III) concentration on silver(I) extraction by TIBPS at 5.0 M HCl. Conditions: [Ag(I)] = 1.4 mM; [Fe(III)] = 1.4 mM – 0.5 M; [TIBPS] = 0.1 M.

spectrum due to iron(III). The UV-Vis spectra obtained from the loaded organic phases after contact with the silver(I) and iron(III) mixture are different from the ones coming from iron(III) alone—Fig. 5. The UV-Vis spectra of organic phases loaded with silver(I) alone do not show anything new in comparison to the organic phase without silver(I). However, as it is evident from Fig. 5, the organic phase after contact with the solution containing iron(III) alone in 5.0 M HCl shows absorption maxima at around 340 nm (Fig. 5, spectrum 1), which should be due to the transfer of $FeCl_3$ species into the organic phase. The spectra obtained from the TIBPS organic solution after equilibration with the mixture of iron(III) and silver(I) at the same HCl concentration exhibit two maxima at around 322 and 364 nm (Fig. 5, spectrum 2). The presence of the 364 nm band in the organic phase indicates that, in the presence of silver(I), iron(III) goes into the organic phase as $FeCl_4^-$ species (19).

Effect of Hydrochloric Acid Concentration on the Extraction of Silver(I) in the Presence of a Constant Proportion of Iron(III)

To observe the effect of a fixed proportion of iron(III) on silver(I) extraction, a simple experiment was designed and the effect of HCl (3.0–8.0 M) on the extraction of silver(I) (1.4 mM) was studied again in the presence of a constant molar proportion of iron(III) (0.5 M). It was observed that, in the presence of a large excess of iron(III), the percent extraction of silver(I) by TIBPS is not getting influenced by the HCl concentration and it remained more than 90% from 3.0 M HCl onwards.

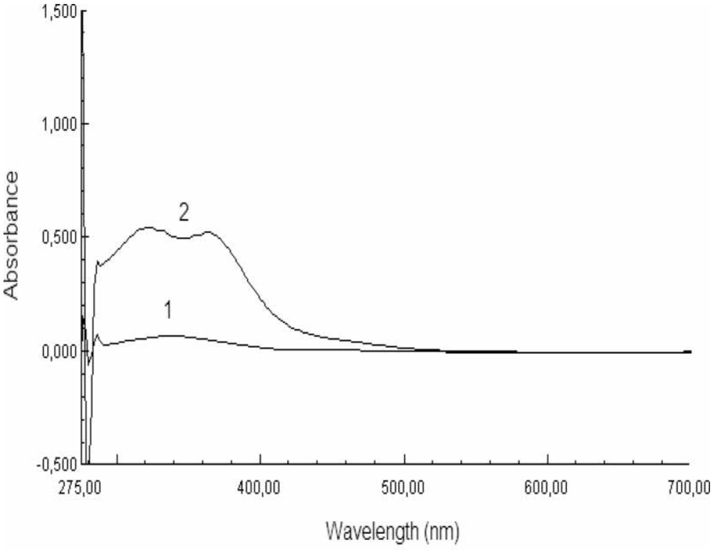

Figure 5. UV-Vis spectra of organic phases after contact with iron(III) and a mixture of silver(I) and iron(III) at 5.0 M HCl. Conditions: [Ag(I)] = 1.4 mM; [Fe(III)] = 0.5 M; [TIBPS] = 0.1 M; (1) loaded organic phase contacted with 0.5 M Fe(III), $\lambda_{max} = 340$ nm; (2) loaded organic phase contacted with a mixture of 1.4 mM Ag(I) and 0.5 M Fe(III), $\lambda_{max} = 322$ and 364 nm; all the organic phases were diluted 25 times with toluene.

It can be summarized from these solvent extraction studies that the presence of iron(III) in the chloride aqueous phases seems to change the speciation trend of silver(I) species originally present in chloride medium and, due to this modification, the extraction pattern of silver(I) in HCl medium, by TIBPS, changes. As a matter of fact, silver(I) in concentrated chloride medium exists mainly in the form of $AgCl_3^{2-}$. The contribution of $AgCl_4^{3-}$ species increases with increasing hydrochloric acid concentrations. Concerning Fe(III) in concentrated chloride medium, there is always the predominant presence of $FeCl_3$ species, although the $FeCl_4^-$ content increases with chloride concentrations. When iron(III) is mixed with silver(I) in a chloride medium, $FeCl_3$ species seem to interact with the anionic species of silver(I) and change them to less anionic species, iron(III) itself changing into $FeCl_4^-$ species. The presence of $FeCl_4^-$ species in the loaded organic phases after contact with Ag(I) and Fe(III) solutions confirms this interpretation. It is already known that the extraction of less anionic species of silver(I) by TIBPS is more favorable than that of higher chlorocomplex species present in concentrated chloride medium (4–7, 10). For this particular silver(I) – iron(III) interaction, a large amount of iron(III) is invariably required to observe this effect on a practical level.

In order to further confirm this interpretation, some more experiments were carried out by CE on a mixture of iron(III) and silver(I) in concentrated chloride medium.

Capillary Electrophoresis Experiments

During the CE studies, a di-sodium hydrogen phosphate buffer of 50 mM (pH 9.07) was used as BGE and the experiments were carried out first in pure

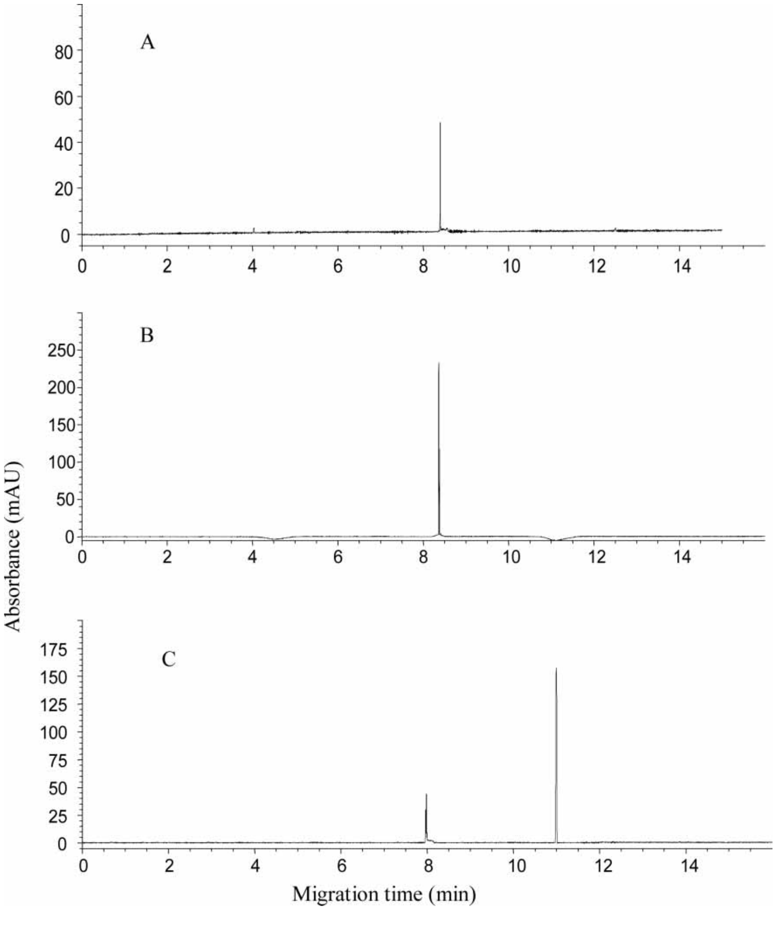

Figure 6. Electropherograms of silver(I) and iron(III) in 5.0 M HCl. Conditions: (A) 1.4 mM Ag(I); (B) 50 mM Fe(III); (C) mixture having 1.4 mM Ag(I) and 50 mM Fe(III). CE conditions: fused silica capillary, 75 μm id × 61 cm; BGE, 50 mM di-sodium hydrogen phosphate buffer (pH 9.07), hydrodynamic injection, 50 mbar, 1 s; voltage, 20 kV; temperature, 25°C; direct UV detection at 224 nm.

solutions (with one metal ion only) and then in solutions with a mixture of iron(III) and silver(I). The effect was studied at 5.0 and 11.0 M HCl, keeping silver(I) concentration to 1.4 mM and iron(III) concentration to 50 mM.

As a representative case, electropherograms obtained at 5.0 M HCl solutions can be seen in Fig. 6. For the solutions containing either silver(I) or iron(III) only, a single peak is observed in their corresponding electropherograms—Fig. 6 (A and B). For a mixture of silver(I) and iron(III), two different peaks are observed—Fig. 6 (C). In terms of speciation, it is likely that silver(I) alone exhibits the predominant peak $AgCl_3^{2-}$ (8.4 min) in the electropherogram—Fig. 6 (A)—whereas for the iron(III) solution—Fig. 6 (B)—the peak detected can possibly be ascribed to the neutral species, $FeCl_3$ (8.35 min), due to its similarity with the EOF marker. For the solution containing the mixture of silver(I) and iron(III)—Fig. 6 (C)—, the peak at around 8.00 min should be due to the neutral species of $FeCl_3$ and possibly to the AgCl species, whereas the peak at 11.00 min should reveal the presence of the anionic $FeCl_4^-$, complexed or not with hydroxyl ions present in vicinity.

In terms of comparison in between cases A, B, and C—Fig. 6—it is apparent that, for a mixture of silver(I) and iron(III), the peak due to the anionic chlorocomplex species of silver(I) has totally disappeared. The concentration of iron(III) as neutral species also decreased and the appearance of a new anionic species in the mixture of silver(I) and iron(III) system, absent earlier on the non-mixed Ag(I) and Fe(III) solutions, is observed without any doubt.

CONCLUSIONS

The speciation of silver(I) and/or iron(III) in chloride media has been investigated through the use of solvent extraction and capillary electrophoresis. A numerical methodology was also considered to compute the speciation of silver(I) and iron(III) separately.

The overall studies described in this work suggest that in aqueous solutions of silver(I) and iron(III) in concentrated chloride medium, iron(III) in neutral form is interacting with silver(I) species and is getting converted into its respective anionic species. In this transformation, silver(I) species are converted from higher anionic species to less anionic, or even to the neutral one. The phenomena can probably be expressed by the following equations:

$$FeCl_3 + AgCl_4^{3-} \Leftrightarrow FeCl_4^- + AgCl_3^{2-} \tag{25}$$

$$FeCl_3 + AgCl_3^{2-} \Leftrightarrow FeCl_4^- + AgCl_2^- \tag{26}$$

$$FeCl_3 + AgCl_2^- \Leftrightarrow FeCl_4^- + AgCl \tag{27}$$

However, it is important to find out the feasibility of these proposed equations by a further thermodynamic treatment. It is equally necessary to continue research on this subject, particularly to find out other suitable approaches to establish metal ion speciation in concentrated media. The present work aims to be a step towards that direction.

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