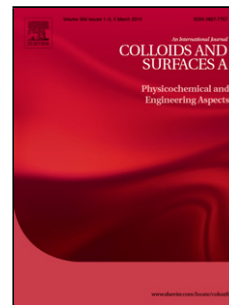# Accepted Manuscript

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Author: Sabriye Aydinoglu Tarita Biver Fernando Secco
Marcella Venturini

Please cite this article as: Sabriye Aydinoglu, Tarita Biver, Fernando Secco, Marcella
Venturini, The mechanism of the reaction between Au(III) and PADA in Sodium
dodecylsulphate, Colloids and Surfaces A: Physicochemical and Engineering Aspects
http://dx.doi.org/10.1016/j.colsurfa.2016.03.036

The mechanism of the reaction between Au(III) and PADA in Sodium dodecylsulphate

Sabriye Aydinoglu,[a] Tarita Biver, [b] Fernando Secco,[*,b] Marcella Venturini[b]

[a] Department of Analytical Chemistry, Faculty of Pharmacy, Cukurova University, 01330 Adana, Turkey
[b] Dipartimento di Chimica e Chimica Industriale, Università di Pisa – Via G. Moruzzi, 13 – 56124 - Pisa (Italy)

E-mails: saydinoglu@cu.edu.tr (S. Aydinoglu); tarita.biver@unipi.it (T. Biver); fernando.secco@unipi.it (F. Secco); marcella.venturini@dcci.unipi.it (M. Venturini)

Corresponding Author: Fernando Secco, Dipartimento di Chimica e Chimica Industriale, Università di Pisa – Via Moruzzi, 13 – 56124 - Pisa (Italy), fernando.secco@unipi.it, +390502219259
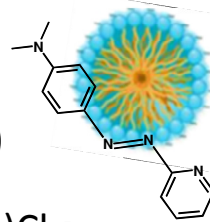
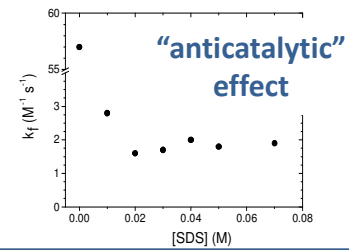**Graphical abstract**

Gold Reacts with PADA on the SDS micelle surface

$k_f^{SDS@cmc} << k_f^{water}$

pH

High: $Au(OH)_3(H_2O)$

Low: $AuCl_4^-$, $Au(OH)Cl_3^-$

"anticatalytic" effect

k_f (M^{-1} s^{-1})

[SDS] (M)

HIGHLIGHTS

- Au(III) reacts with PADA on SDS surface; the Au-PADA complex is fully retained.

- The reaction rate is modulated by suitable changes of pH and NaCl concentration.

- The reaction at high pH is much faster owing to the high reactivity of the $Au(OH)_3(H_2O)$ species

- LM-MEUF of the Au(III)-PADA system in SDS provides high extraction yields.

Abstract

The PADA/SDS system provides an excellent tool to selectively extract metal ions using the ligand-modified micellar-enhanced ultrafitration (LM-MEUF) technique. Application of this method to the extraction of Au(III) has required a detailed knowledge of the conditions under which the interaction of the metal ion with the extractor are optimal. For this purpose the kinetics and the equilibria of the reaction between tetrachloro-aurate ion and PADA have been investigated in water/SDS medium, exploring wide ranges of pH values and NaCl concentrations. Addition of PADA to the water/SDS medium results in the full adsorption of the ligand on the micelle and, in the presence of Au(III), the resulting Au-PADA complex is fully retained on the SDS surface. The binding process is, in fact, a ligand displacement reaction where PADA interacts with different Au(III) chloro-aquo complexes, displacing Cl^- or OH^- or H_2O molecules, depending on pH. The reaction is biphasic and its mechanism is discussed. Experiments at different SDS concentrations show that the reaction of complex formation is retarded on going from pure water to a water/SDS mixture with [SDS] just above the cmc, while for further increases of the SDS content the reaction rate tends to stay constant. The obtained results enabled to establish that the reaction occurs on the SDS surface while the aquo-species, $Au(Cl)_3(H_2O)$ and $Au(OH)_3(H_2O)$, which are not involved in the binding process in pure water, play an important kinetic role in the H_2O/SDS medium.

1. Introduction

The recovery of gold (and other precious metals) from secondary grade sources such as electronic scraps, spent catalysts and other waste constituting materials is now a tool of crucial importance. Recent research on metal extraction based on metal entrapping systems has led to the development of clean and safe methods that could be favorably used to remove metal ions from waste streams. In this context, the Micellar Enhanced Ultrafiltration (MEUF) provides a surfactant based method to extract metal ions with high yields [1]. Metal ions are attracted on the surface of an oppositely charged micelle by the electrostatic force and the resulting complex is removed from the aqueous phase by ultrafiltration. However, MEUF is not a selective method since ions of same-sign charges are removed with similar yields [2]. In order to impart selectivity to MEUF, the ligand-modified micellar-enhanced ultrafitration (LM-MEUF) technique was developed by Scamehorn and coworkers [3]. This method is based on the addition of a suitable complexing agent (the extractor) and a surfactant (in concentration higher than the critical micellar concentration, cmc) to the solution containing the target metal.

The commercially available ligand PADA (Figure 1) is totally adsorbed on a variety of surfactants, including SDS [4] and has proven to be an excellent metal extractor, being able to transfer metal ions from water to micellar phases with yields approaching 100% [5-7] Moreover, we have found that PADA is able to complex Au(III) with great affinity even if the coordination shell of the metal is occupied, as in $AuCl_4^-$ [8, 9]. In this case, a molecule of PADA replaces two chloride ions forming a strong chelate. As a consequence of this ligand replacement process, the resulting Au-PADA complex will display a positive charge and therefore will be bound to a negatively charged micelle by the double action of hydrophobic adsorption and electrostatic attraction. Since the optimization of the extraction process can be achieved through the knowledge of the physicochemical parameters that rule the process itself, we have found it interesting and useful to investigate the mechanism of the binding of $AuCl_4^-$ to PADA in the presence of SDS micelles under the conditions employed to extract gold with LM-MEUF. Different from most of the studies of this kind, the metal containing species is negatively charged; hence, simple MEUF could not be applied.

2. Experimental

Materials. All the chemicals not expressly cited are of analytical grade and were employed without further purification. Chloroauric acid, $HAuCl_4 \cdot 3H_2O$, the complexing ligand, pyridine-2-azo-p-dimethylaniline (PADA), and the surfactants, sodium dodecylsulphate (SDS) and dodecyltrimethylammonium chloride (DTAC), were obtained from Sigma-Aldrich. The stock solutions of these reactants were prepared by dissolving appropriate amounts of the relevant solid material in water. The gold content was determined by direct UV absorption spectrometry

exploiting the absorption band of $AuCl_4^-$ ion centred at 233 nm whose maximum absorption is proportional to the gold concentration [8, 9]. Water, purified by pumping deionized water through a Milli-Q apparatus, was used to prepare the solutions and also as the reaction medium.

Methods. The pH measurements were made using a Metrohm 713 pH-meter equipped with a combined glass microelectrode.

The spectra of PADA and of its complex with Au(III) were recorded using a Shimadzu 2450 double-beam spectrophotometer in quartz cells (1 cm path length) thermostatted to within ± 0.1°C. The kinetic experiments were all done under pseudo first-order conditions, keeping the analytical concentration of metal ion, C_{Au}, at least ten times higher than that of the ligand, C_L ($C_{Au} \geq 10C_L$). In these experiments both solutions where brought to the same acidity, ionic strength and surfactant concentration before mixing. The reaction between Au(III) and PADA displays both slow and fast kinetic effects. The fast process was investigated using the stopped-flow method. The apparatus, assembled in our laboratory, uses a Hi-Tech SHU-61SX2 stopped-flow sample handling unit with a mixing time of about 1 ms. The reactant solutions were mixed and the absorbance change associated to the reaction course was monitored spectrophotometrically. Most of the experiments have been carried out at 633 nm using as a light source a red laser diode, which provides a signal to noise ratio much more favourable than that provided by conventional tungsten lamps [10]. Each experiment was repeated at least five times,. The kinetic traces were stored in a Tektronix 2210 digital oscilloscope and then transferred to a personal computer for the mathematical analysis. The slow effect was investigated using the above cited Shimadzu 2450 double-beam spectrophotometer. The reaction was started by adding a calibrated excess of $HAuCl_4$ to a known amount of PADA already contained in the spectrophotometric cell at prefixed values of acidity and ionic strength. The kinetic curves of both effects were processed according to single or double exponential functions using a non-linear least square program of the Jandel Scientific package (AISN software, Richmond, CA). The reported data values are the average of at least four repeated runs. A further, very slow, kinetic effect was detected, which was ascribed to a redox process; however, this process has been disregarded because it was much slower than the substitution reaction.

3. Results and Discussion

3.1 The partitioning of PADA, Au(III) and Au-PADA complex between SDS and water.

The partitioning of PADA between SDS and water has been determined using a combination of spectrophotometric and ultrafiltration methods. A solution of SDS was added to an aqueous solution of PADA in such a proportion that the resulting mixture contains 1×10^{-5} M PADA and 0.04 M SDS. The absorbance spectrum of the mixture was recorded. Then, the mixture was subjected to ultrafiltration under pressure using a filter with a cut-off capability of 3000 Dalton.

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Doing so, the micellar pseudo-phase has been separated from the aqueous pseudo-phase. Afterwards, the absorbance spectrum of the filtrate was recorded. The amount of PADA retained on the SDS micelles has been calculated as the difference between the absorbance values of initial and filtered solutions. Fig. 2 shows that the ligand is totally retained by the micelles (black stars). The figure shows as well that Au(III), if complexed by PADA, is almost totally retained on the micelle surface (open circles), whereas, in the absence of PADA (black triangles), all the gold remains in the aqueous pseudo-phase (as expected). The extent of retention is independent of the solution pH.

3.2 Spectral observations

Fig. 3 shows the spectra of $AuCl_4^-$ ions recorded at pH 5.0 in water, in 0.04 M SDS, and in 0.04 M DTAC. The comparison reveals that the spectrum in DTAC, where the Au(III) species are adsorbed [8], is totally different from the spectrum in water. In contrast, the shape of the spectrum in SDS does not differ from that of the spectrum recorded in water. One can conclude that the Au(III) ions do not interact with SDS and stay essentially in the aqueous pseudo phase.

Fig. 4 shows the spectra recorded during titration of PADA with $AuCl_4^-$ in water (Fig. 4A) and in SDS 0.02M (Fig. 4B). The two families of spectra are totally different, thus revealing that, in the presence of SDS, the binding reaction does not occur in the aqueous pseudo-phase; it occurs, instead, on the micellar pseudo-phase, where the free ligand *and* the complex are both adsorbed on the surfactant surface. The free ligand spectrum exhibits a maximum at 460 nm, but during the titration in the presence of SDS, the maximum is shifted to 530 nm corresponding to the absorption band of the Au(III)/PADA complex. The well-defined isosbestic point reveals the occurrence of a single overall binding process under the investigated conditions. Further additions of Au(III) result in the disruption of the isosbestic point. This effect is ascribed to a slow fading effect, already observed in water and in DTAC [8], that could interfere with the binding process. So, the static method, as a tool to study the binding equilibria, has been discarded, although the interference starts to appear after more than one hour after the mixing of the reactants.

3.3 Kinetic measurements

The kinetic method, allowing monitoring the temporal course of the reaction, enables to separate the complex formation process from the (much slower) fading process.

The reaction under study is a ligand exchange process which, in its simplest form, can be represented by reaction (1)

ML' + L ⇆ ML + L'   (1)

Under conditions of constant pH and chloride ion (L') excess (with respect to the PADA concentrations, L) reaction (1) is reduced to the apparent reaction (2) which constitutes a useful basis for the analysis of the kinetic behaviour.

M + L ⇆ ML   (2)

The apparent reaction (2) exhibits two kinetic effects which manifest themselves within different pH ranges and display different reaction velocities. It has been found that, under pseudo first-order conditions ($C_{Au} \geq 10\ C_{PADA}$), the time constant, $1/\tau$, of both effects depends linearly on C_{Au} according to Eq. (3)

$$\frac{1}{\tau} = k_f C_{Au} + k_d$$ (3)

3.3.1 Kinetics of the slow effect

The slow effect was observed between pH 4.0 and 6.0 and displays mono-exponential kinetic curves. A typical trace is shown as an inset in Fig. 5. The values of the time constant of the slow effect, $1/\tau_s$, depend linearly on the analytical Au(III) concentration, C_{Au}, according to eq. (3), as shown in Fig. 5. The slope of the plot gives the value of the apparent forward rate constant, k_f, of reaction 2, while the intercept gives the value of the reverse rate constant, k_d.

Rate dependence on pH. Table 1 and Table 2 report the values of k_f and k_d respectively for different pH values and different concentrations of SDS. Inspection of the tables shows that, in the presence of SDS, both rate constants do increase on rising the pH values except that at pH 6.0 where the rate constants suddenly display values definitely lower than expected on the basis of the trend. The graphical representation given in Fig. 6A and B provides a clearer description of the behaviour observed, which suggests that a change of reactive Au(III) species has occurred at pH 6.0. The behaviour in water ([SDS]=0M in Tables 1 and 2) is opposite to that displayed in the presence of SDS

Rate dependence on Cl⁻. The rate of the reaction depends on the concentration of added chloride ions, as shown in Table 3 where the values of $1/\tau_s$ measured at the different [Cl⁻] and pH values are reported.

Fig. 7 shows that, on increasing [Cl⁻], the time constant values display a flat minimum, mainly at the lower pH values. This behaviour suggests opposite dependence of k_f and k_d on [Cl⁻]. Moreover, the level of the curves displays a general increase with pH up to pH 5.5 but, at pH 6, the plotted data (black stars) fall to values definitely lower than expected. Such an abrupt change suggests again, that, at the highest pH level, a change of reacting species has occurred. The observed trends will be rationalized on the basis of the reaction scheme shown below.

The mechanism of the slow phase. Since the Au(III) species are neither attracted nor adsorbed on the micelle surface, their distribution in water/SDS should be the same as in water. The distribution diagram of Au(III) (Fig. 2S) shows that, between pH 4 and 6 (where the slow phase has been investigated) and at the chloride ion concentrations employed, the prevailing complexes are $AuCl_4^-$ and $AuCl_3(OH)^-$ in equilibrium. Therefore, the reaction mechanism of the slow phase should involve most conceivably these species. The results agree with the reaction scheme (4)-(5) where the vertical steps are assumed to be fast because they do not include the chelating process which could cause rate reduction. In contrast, chelation is present in the horizontal steps (here PADA chelator is written as L-L to explicit the presence of the two binding sites).

$$
\begin{array}{c}
{}^{+}\text{HL L} \\[2pt]
+\text{H}^+ \updownarrow K_{A2} \\[4pt]
AuCl_4^- + \text{L L} \xrightleftharpoons[k_{-1}]{k_1} AuCl_2^+ \big(\text{L, L}\big) + 2Cl^- \qquad (4) \\[8pt]
-OH^-, +Cl^- \updownarrow K \qquad\qquad -OH^-, +Cl^- \updownarrow K' \\[6pt]
Au(OH)Cl_3^- + \text{L L} \xrightleftharpoons[k_{-2}]{k_2} AuCl(OH)^+ \big(\text{L, L}\big) + 2Cl^- \qquad (5)
\end{array}
$$

Being $K[Cl^-] \gg [OH^-]$, the expression for $1/\tau_s$ is given, according to the above reaction scheme, by the relationship (Supplementary Material):

7

$$\frac{1}{\tau_s} = \left(k_1 + \frac{k_2[OH^-]}{K[Cl^-]}\right)\left(\frac{K_{A2}}{K_{A2} + [H^+]}\right)C_{Au} + \left(k_{-1} + \frac{k_{-2}[OH^-]}{K'[Cl^-]}\right)[Cl^-]^2 \tag{6}$$

A non-linear least square analysis of the results according to equation (6), where K_{A2} is derived from Figure 4D of ref.[4] and has been introduced as a known parameter, provides the values of the rate parameters $k_1 = 1.0 \pm 0.5$ $M^{-1}s^{-1}$, $k_2/K = (4.1\pm0.6)\times10^7$ $M^{-1}s^{-1}$, $k_{-1} = 0.21\pm0.06$ $M^{-2}s^{-1}$ and $k_{-2}/K' = (1.0 \pm 0.1)\times10^7$ $M^{-2}s^{-1}$. A check of the goodness of the proposed mechanism is provided by the combination of the equilibrium constants of the cyclic scheme (4)-(5) according to which it results that $k_1/k_{-1} = K'k_2/Kk_{-2}$. Using the above reported data one obtains $k_1/k_{-1} = 4.8$ and $K'k_2/Kk_{-2} = 4.1$. Considering the errors of the rate parameters, the test should be considered valid. Using the Baes and Mesmer value of K (1.7×10^{-8}) one obtains $k_2 = 0.70$ $M^{-1}s^{-1}$. The similarity of the values of k_1 and k_2 reveals that the hydroxide ion present in $AuCl_3(OH)^-$ does not affect the energetics of the ligand substitution process, thus confirming that only Cl^- ions are replaced in the reaction step (5).

The vertical steps of the reaction scheme could induce the reader to think that the displacement of Cl^- ions could be operated by the direct attack of OH^- ions. However, it should be noted that, in the investigated range of pH ($4.0 < pH < 6$) the concentration of OH^- ion is so low that it results improbable that OH^- ions could succeed in displacing directly the Cl^- ion from the metal coordination shell at measurable rates. The most probable process should be the one represented by the sequence (7)-(9) whose combination yields the vertical step with equilibrium constant K. In the first step of the sequence a H_2O molecule operates a nucleophilic attack at the metal centre; in the second (diffusion controlled) step, the coordinated water molecule loses a proton which eventually is neutralized according to step 9.
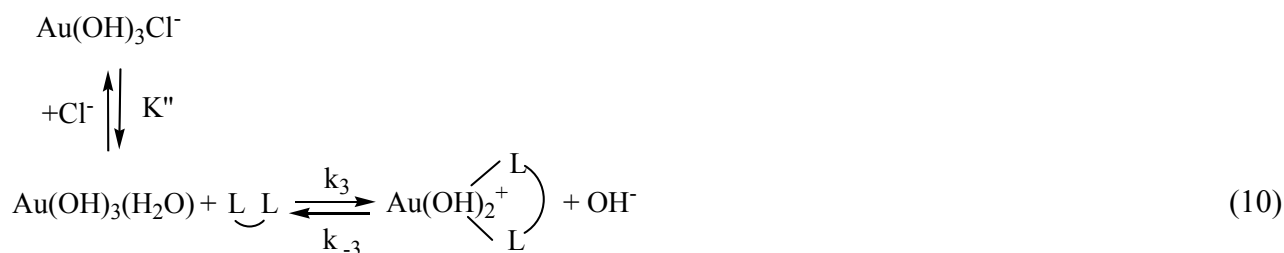
$$AuCl_4^- + H_2O \rightleftarrows Au(H_2O)Cl_3 + Cl^- \tag{7}$$

$$Au(H_2O)Cl_3 \rightleftarrows Au(OH)Cl_3^- + H^+ \tag{8}$$

$$H^+ + OH^- \rightleftarrows H_2O \tag{9}$$

It should be noted that the aquo-chloro species $Au(H_2O)Cl_3$ has been detected or postulated in speciation studies of gold(III); however, this species seems to behave as a strong acid [11-13] and therefore, under the conditions of the experiments here described, it acts only as a transient intermediate.

3.3.2 Kinetics of the fast effect

The fast kinetic effect has been investigated between pH 8 and 9. A typical monoexponential curve is shown as an inset in Fig. 8A. Moreover, the figure shows that the fast effect is first-order with respect to Au(III), as revealed by the plot of the relevant time constant, $1/\tau_f$, against the gold concentration, in agreement with Eq. (3). The positive value of the intercept reveals that, under the employed conditions, the binding process is not quantitative. Fig. 8B shows, instead, the dependence of the reaction rate on the concentration of NaCl. It is found that the value of $1/\tau_f$ decreases on increasing $[Cl^-]$. According to Reaction (1) the rate of the reverse step, corresponding to k_d in Eq. (3), should increase on increasing [L'], i.e. $[Cl^-]$, but this is not the case. The decreasing trend observed indicates that the ligand substitution reaction is coupled to another reaction through the chloride ion as a common component. Fig. 8C shows that a plot of $1/\tau_f$ vs $[OH^-]$ is linear, thus indicating the existence of a reaction step first-order with respect to the hydroxide ion.

The mechanism of the fast phase. The fast phase has been observed in a range of pH values between 8.0 and 9.0 where the main species present in solution is the $Au(OH)_3Cl^-$ ion. The analysis of the results allows Scheme (10), where non-coordinated water molecules are omitted for simplicity, to represent in the best way the kinetic features of this phase.
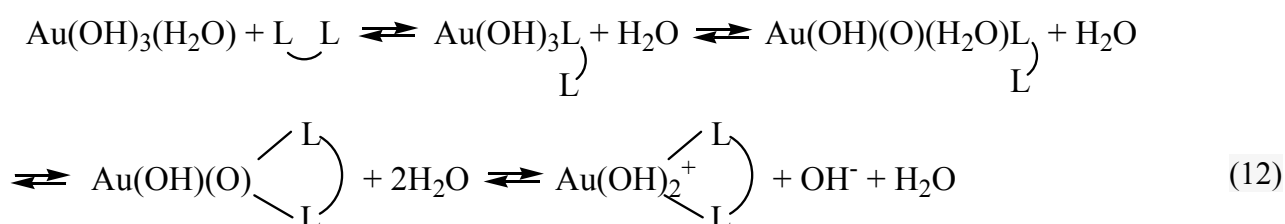
$Au(OH)_3Cl^-$

$+Cl^- \updownarrow K''$

$$Au(OH)_3(H_2O) + \underbrace{L\ L} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Au(OH)_2^+\left(\begin{smallmatrix} L \\ L \end{smallmatrix}\right) + OH^- \tag{10}$$

The existence of the vertical equilibrium (K'') was postulated in a study of the hydrolysis products of tetrachloroaurate ion [11]. No evidence could be found for a reaction of $Au(OH)_3Cl^-$ ion with L-L. Owing to the high lability of the coordinated water, one con reasonably assume that $Au(OH)_3Cl^-$ reacts with L-L at a much lower rate than $Au(OH)_3(H_2O)$, so the entire complex formation process undergoes through the horizontal path (10). In deriving the rate law, it has been assumed, as for the slow phase, that the vertical reaction is faster than the horizontal reaction. The expression for $1/\tau_f$ is expressed by Eq. (11) (Supplementary Material).

$$1/\tau_f = (k_3/K^{''})C_{Au} /[Cl^-] + k_{-3}[OH^-] \tag{11}$$

A non-linear least square analysis of the results according to equation (11) provides the values of the rate parameters $k_3/K^{''} = (55\pm14)$ s^{-1}, $k_{-3} = (4.7\pm2.3) \times10^5$ $M^{-1}s^{-1}$. Being $K^{''}= 7.9 \times10^5 M^{-1}$ [11] it turns out that $k_3 = 4.3\times10^7$ $M^{-1}s^{-1}$.

Although this paper is focused mainly on the investigation of the effect of the SDS micelles on the kinetics, we find interesting to make a short discussion on the role of OH^- in the fast phase. Even if the concentration of hydroxide ions is more than 10^3 times higher than in the slow phase, it is still too low to make feasible a reaction path where OH^- ion acts as a nucleophililic reagent. Rather, the fact that measurable changes of $1/\tau_f$ are observed at the very low levels of $[OH^-]$ employed, suggests for this anion a mode of activation different from the SN_2 mechanism generally assumed for ligand substitution at square-planar complexes. We propose for reaction (10) the sequence (12) where the role of the hydroxide ion is that of extracting a proton from the final complex in the reverse of reaction (10), generating the neutral oxo species Au(O)OHL-L as a reaction intermediate.

$$Au(OH)_3(H_2O) + L\,\smile\,L \rightleftharpoons Au(OH)_3L\overset{L}{)} + H_2O \rightleftharpoons Au(OH)(O)(H_2O)L\overset{L}{)} + H_2O$$

$$\rightleftharpoons Au(OH)(O)\overset{L}{\underset{L}{\big\langle}}) + 2H_2O \rightleftharpoons Au(OH)_2^+\overset{L}{\underset{L}{\big\langle}}) + OH^- + H_2O \tag{12}$$

It could be argued that ring closure with direct elimination of OH^-, as in the scheme (13),

$$Au(OH)_3L\overset{L}{)} \rightleftharpoons Au(OH)_2^+\overset{L}{\underset{L}{\big\langle}}) + OH^- \tag{13}$$
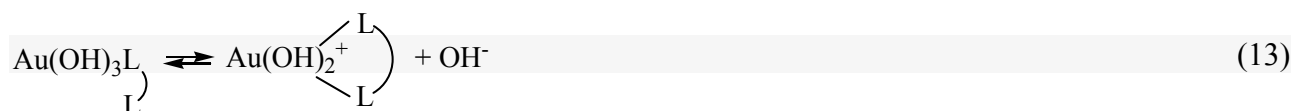
would render the reaction mechanism much simpler. Nevertheless we reject this mechanism since it implies the direct attack of the OH^- to the metal in the reverse path. Analogous considerations were made in order to explain the mechanism of the base hydrolysis of $Co(NH_3)_5Cl^{2+}$ ion [14]. Here the function of OH^- is that of extracting a proton from one of the five ammonia atoms yielding the intermediate $Co(NH_3)_4(NH_2)Cl^+$ which plays the same role of $Au(OH)(O)\overset{L}{\underset{L}{}}$) in the present system.

10

The effect of the SDS concentration. Fig. 9A shows the dependence of the forward rate constant of the slow step on the SDS concentration. The negatively charged SDS micelles exert a retarding effect on the binding reaction. Actually, the rate in 0.01 M SDS (just above the cmc [7]) is lower than in water (experiment at [SDS] = 0.0 M), contrary to the behaviour observed in DTAC where a remarkable increase of rate was obtained under similar conditions [8].

The rate reduction, improperly defined as "anticatalytic effect" [15-17] can be explained on the basis of fact that the gold aquo-chlorocomplexes are all in the aqueous pseudo-phase, while the ligand is totally absorbed on the negatively charged micelle surface. Under these circumstances, the two reaction partners are kept apart, due to the electrostatic repulsion and, as a consequence, the reaction rate is reduced compared to the value in pure water. On raising the SDS level, the rates remain almost constant unless one wants to accept the occurrence of a very slight rate increase which could be ascribed to a small reduction of the micelle electrostatic potential induced by the rise of [SDS] [18]. The fact that the kinetic behaviour in SDS differs from that in water enables us to rule out a mechanism where the reaction occurs in the aqueous phase and the reaction product is transferred to SDS by diffusion. If this were the case, the kinetic results obtained in water would be coincident with the results in SDS, contrary to the experimental evidence. Actually, Table 1 shows that in water, i.e. for [SDS] = 0 M, the values of k_f decrease monotonically as pH values do increase, while for [SDS] > 0 M the values of k_f increase with pH and only at pH 6 a decrease of rate occurs, which could suggest that the contribution to the overall reaction rate from a less reactive Au(III) species begins to make itself felt.

Finally, it seems useful to make a brief discussion about the protonation sites of PADA which, in Fig. 1, is protonated in the pyridine nitrogen and in the $-N(CH_3)_2$ group. Since dimethyl azo benzene behaves as a diprotic acid, being able to be protonated at the $-N(CH_3)_2$ group and at the $-N=N-$ group, one can conceivably suppose that PADA as well could bear an additional proton at the $-N=N-$ residue. Actually, the spectra of PADA reported in a paper by Klotz and Ming [19] display an expressed bathochromic shift, which could be ascribed to the protonation of the azo group, although the authors did not consider this point. Hence, the hypothesis that PADA could be a triprotic acid, could not be excluded, in principle. However, our previous experiments [4] aimed to measure the proton dissociation constants of PADA in the pH range between 0.5 and 6, are perfectly fitted by *two* dissociation steps both in pure water and in micellar solution, and the relevant dissociation constants were found to be rather different. Moreover, it should be noted that protonation at the $-N=N-$ group (where chelation occur) would entail a direct dependence on [H$^+$]

in the kinetics of the complex dissociation step, which is not the case for the Au-PADA system here investigated.

Acknowledgements

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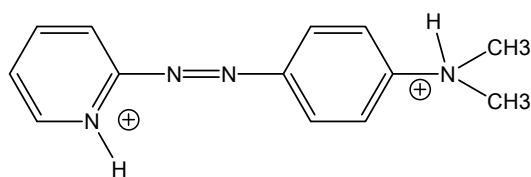
Fig. 1 Molecular structure of pyridine-2-azo-p-dimethylaniline (PADA) in the di-protonated form (HL-LH^{2+}).
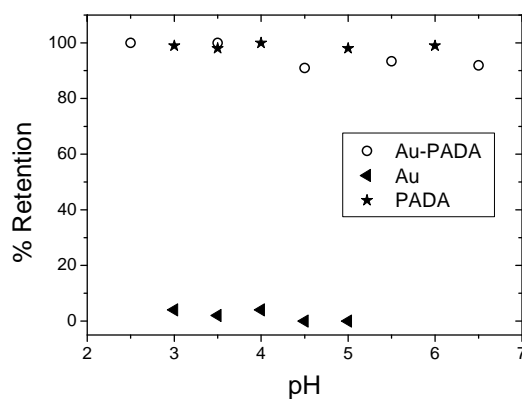
Fig. 2 Retention percentage of species composing the Au(III)/PADA system at different pH values; SDS 0.04 M, ◄Au, ○ AuPADA, ★ PADA.
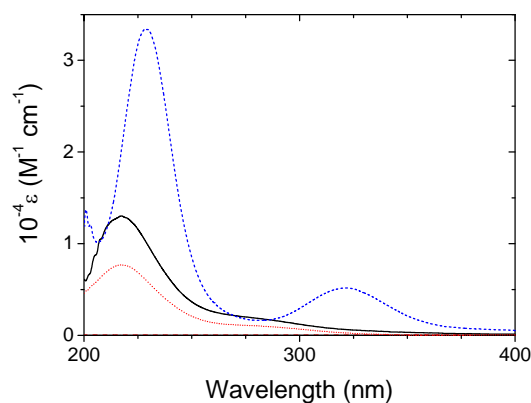
Fig. 3 Spectra of AuCl$_4^-$ at pH 5.0, [NaCl]= 0.0 M, T= 25°C: (•••) water, (─) SDS 0.04 M, (--) DTAC 0.04M.
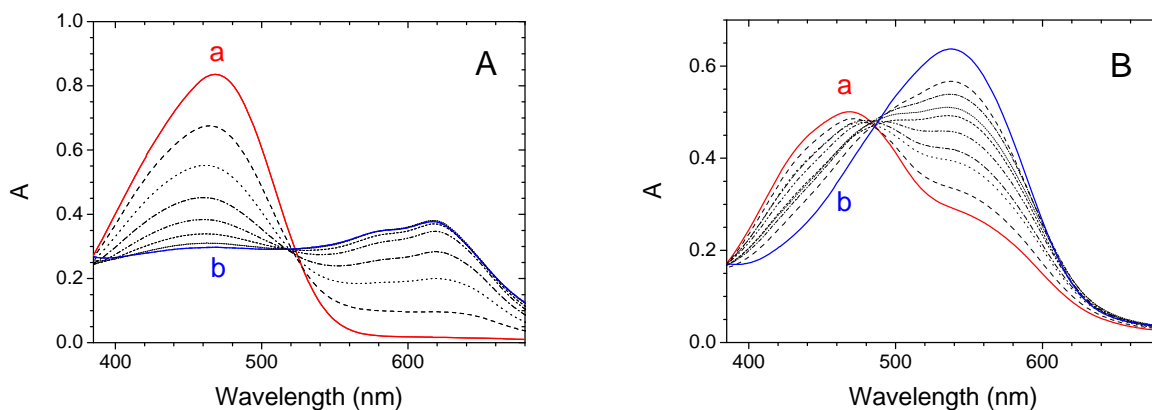
Fig. 4 Spectral changes recorded during titration of PADA with Au(III); C_{Au} from 0 M (**a**) to 1.0×10^{-3} M (**b**), $C_{PADA} = 3.0 \times 10^{-5}$ M, [NaCl] = 0.03 M, T = 25° C. (A) water pH 7.9 (0.03 M phosphate buffer), (B) SDS 0.02 M, pH 7.9.
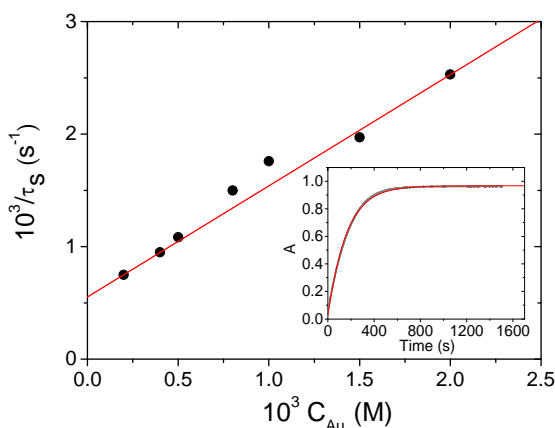
Fig. 5. Slow effect: dependence of the time constant ($1/\tau_s$) on the Au(III) concentration for the reaction between Au(III) and PADA in 0.02 M SDS; [NaCl] = 0.02 M, pH = 4.5, T = 25°C. Inset: kinetic curve recorded for $C_{PADA} = 2.0 \times 10^{-5}$ M, $C_{Au} = 2.0 \times 10^{-3}$ M, $\lambda = 633$ nm; the continuous line represents the fit according to a monoexponential function which provides the value of the time constant, $1/\tau_s$.
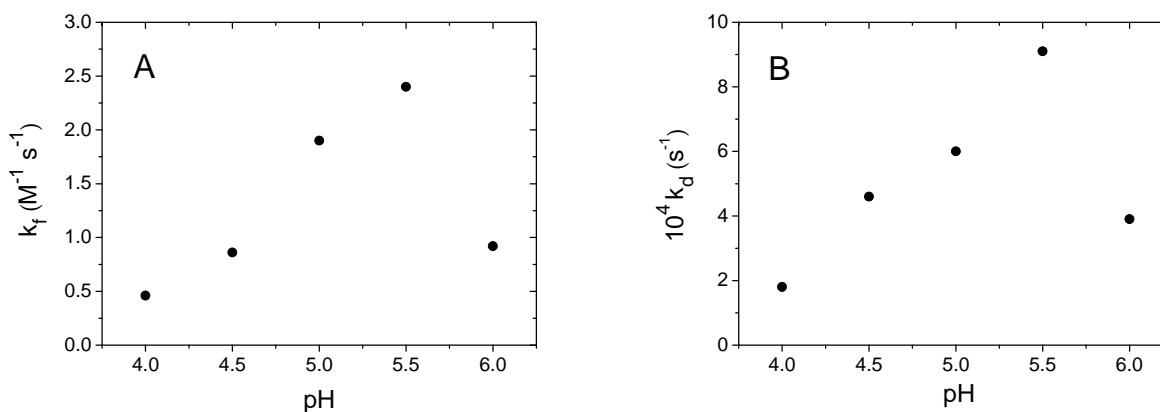

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Fig. 6. Slow effect: plots of rate constants k_f (A) and k_d (B) vs. pH for the Au(III)/PADA system in 0.07 M SDS; [NaCl] = 0.04 M, T = 25 °C.
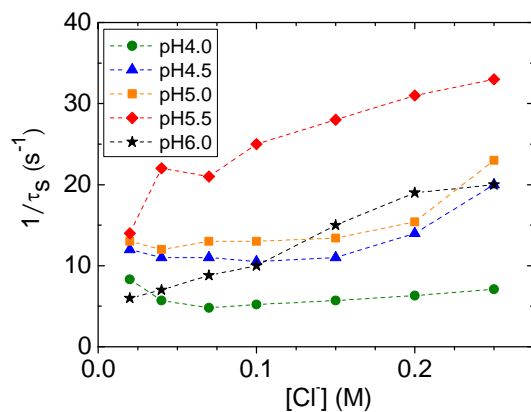

Fig. 7 Slow effect: reciprocal time constants of the Au(III)/PADA system, $1/\tau_s$, measured at different chloride ion concentrations and at different pH values in 0.02 M SDS. $C_{Au} = 5 \times 10^{-4}$ M, $C_{PADA} = 2 \times 10^{-5}$ M, T = 25°C.
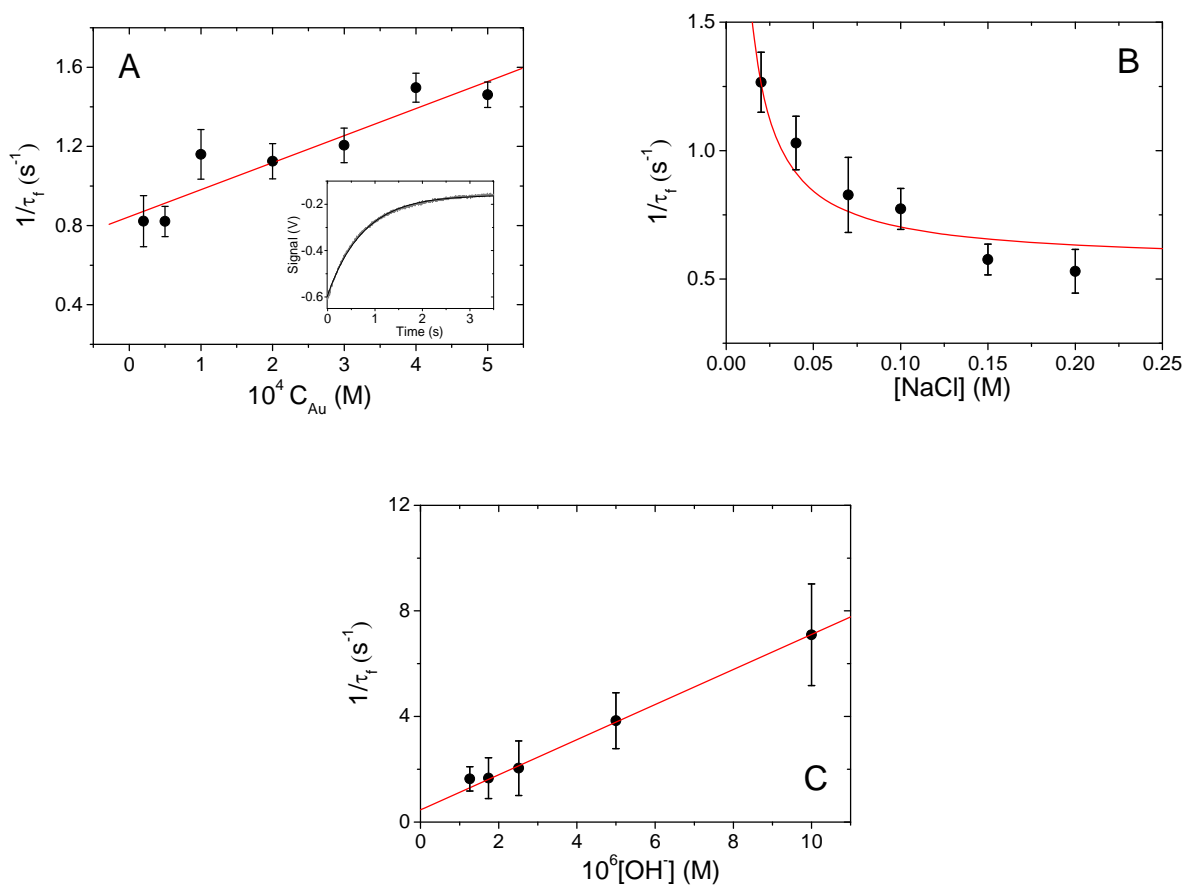
Fig. 8 Fast effect: (A) Dependence of the fast time constant, $1/\tau_f$, on C_{Au} for the reaction between Au(III) and PADA in 0.02 M SDS, [NaCl] = 0.03 M, pH = 8.2, T = 25° C.; inset: monoexponential stopped-flow curve obtained for C_{PADA}= 1.0×10^{-5} M and C_{Au} = 3.0×10^{-4} M. (B) Dependence of $1/\tau_f$ on [NaCl] at [SDS] = 0.02 M, C_{Au} = 2.0×10^{-4} M, pH = 8.2. (C) Dependence of $1/\tau_f$ on [OH⁻] at [SDS] = 0.02 M, C_{Au} = 2.0×10^{-4} M, [NaCl] = 0.03 M. The continuous lines represent the fits according to Eq. (11);

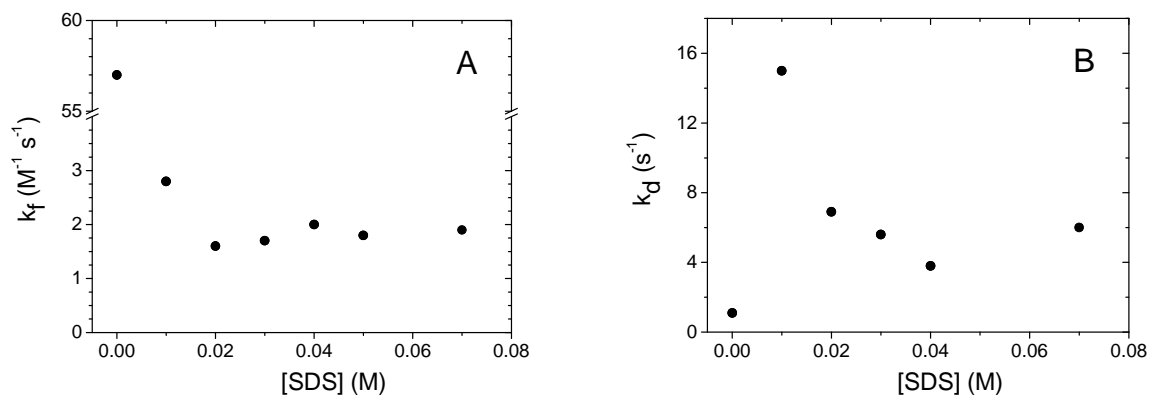**Fig. 9.** Rate dependence on the SDS concentration for the Au(III)/PADA system: slow effect at pH = 5.0, [NaCl] = 0.03 M, T=25°C. (A) Plot of k_f vs [SDS], (B) plot of k_d vs [SDS].

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Table 1 Forward rate constant for the slow effect relevant to the interaction of Au(III) with PADA measured at different pH values and SDS concentrations. [NaCl] = 0.04 M, T = 25 °C.

[SDS] (M)	k_f (M^{-1} s^{-1}) pH = 4.0	k_f (M^{-1} s^{-1}) pH = 4.5	k_f (M^{-1} s^{-1}) pH = 5.0	k_f (M^{-1} s^{-1}) pH = 5.5	k_f (M^{-1} s^{-1}) pH = 6.0
0	72	70	57	22	7.3
0.01	0.95	1.38	2.8	3.6	3.1
0.02	0.32	0.86	1.6	2.8	2.2
0.03	0.45	0.73	1.7	2.3	1.4
0.04	-	-	2.0	-	-
0.05	0.42	0.76	1.8	2.2	1.1
0.07	0.46	0.86	1.9	2.4	0.92

Table 2 Slow effect: reverse rate constant, k_d, for the interaction of Au(III) with PADA measured at different pH values and SDS concentrations. [NaCl] = 0.04 M, T = 25 °C.

[SDS] (M)	$10^4 k_d$ (s^{-1}) pH = 4.0	$10^4 k_d$ (s^{-1}) pH = 4.5	$10^4 k_d$ (s^{-1}) pH = 5.0	$10^4 k_d$ (s^{-1}) pH = 5.5	$10^4 k_d$ (s^{-1}) pH = 6.0
0	5.4	5.6	1.1	1.8	0.19
0.01	4.6	8.6	15	19	2.8
0.02	2.4	5.5	6.9	6.4	3.6
0.03	4.3	5.5	5.6	14	4.2
0.04	-	-	3.8	-	-
0.05	2.0	4.3	6.2	9.5	5.9
0.07	1.8	4.6	6.0	9.1	3.9

Table 3 Values of the reciprocal time constant of the slow process, $1/\tau_s$, for the gold(III)-PADA system in 0.02 M SDS at different [Cl$^-$] and pH values. $C_{Au} = 5.0 \times 10^{-4}$ M, $C_{PADA} = 2.0 \times 10^{-5}$ M, T = 25 °C.

[Cl]	$10^4 1/\tau_{s\ pH=4.0}$	$10^4 1/\tau_{s\ pH=4.5}$	$10^4 1/\tau_{s\ pH=5.0}$	$10^4 1/\tau_{s\ pH=5.5}$	$10^4 1/\tau_{s\ pH=6.0}$
0.02	8.3	12.0	13.0	14.0	6.0
0.04	5.7	11.0	12.0	22.0	7.0
0.07	4.8	11.0	13.0	21.0	8.8
0.10	5.2	10.5	13.0	25.0	10.0
0.15	5.7	11.0	13.4	28.0	15.0
0.20	6.3	14.0	15.4	31.0	19.0
0.25	7.1	20.0	23.0	33.0	20.0