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# Use of $Cr(phen)_3^{3+}$ as luminescence probe to study the binding constants of phenols to micelles of SDS

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## Abstract

Steady-state and time resolved luminescence quenching measurements of $(^2T/^2E)Cr(phen)_3^{3+}$ were used to investigate the association of phenols to sodium dodecyl sulfate (SDS) micelles. Steady-state results show the quenching process occurs in the micellar pseudo phase. Scatchard plots indicate that the process is a partition between aqueous and micelles. The $k_+$ and $k_-$ rate constant have been evaluated from time resolved data and the binding constants were obtained. The trend found in the $K$'s were 4-H-Ph < 2,6-diMe-Ph < 4-Br-Ph. We concluded that it is possible to use $^*Cr(phen)_3^{3+}$ as a luminescent probe to determine association parameters for quenchers to micelles of SDS.

*Keywords:* Chromium polypyridyl complexes; Luminescence properties; SDS micelles; Binding constants

## 1. Introduction

The photochemistry and photophysics of α-diimine-metal complexes have been extensively studied in homogenous systems whereas there are fewer works in microheterogeneous systems [1–4]. In our laboratory there is a continuous interest in the study of electron transfer reactions involving excited states of ruthenium(II) and chromium(III) complexes with phenolic derivatives and their characterization in aqueous as well as in micellar media. Previous papers have dealt with the photophysics and mechanistic aspects of polypyridyl chromium complexes with phenols [5–8]. We also studied the binding of the polypyridyl chromium complexes to sodium dodecyl sulfate (SDS) micelles, i.e. we found that the tris-1,10-phenantroline chromium(III) ($Cr(phen)_3^{3+}$) binds tightly to SDS micelles [9]. Besides, the phenols are one of the main contaminants of industrial waste so the kinetic processes involved in the photo-oxidation of phenolic compounds are of interest owing to their relevance in the photochemical treatment of industrial effluents in addition to the probability of their use in photo-cleaning processes.

It is known that the solubility of a hydrophobic compound in water can be dramatically enhanced by the addition of a surfactant to the aqueous solution. This change is produced by the formation of micelles by the surfactant. This effect in phenolic compounds was observed in inverted and direct micelles [4].

There are some previous studies that deal with the interaction between phenolic compounds and ionic or neutral surfactants using tris(2,2′-bipyridine)ruthenium(II) as luminescent probe [10–13]. A more recent study has used the uranyl ion as luminescence probe through the study of the quenching processes between the $^*UO_2^{2+}$ and phenols in SDS micelles [14]. Nevertheless, the use of the $Cr(phen)_3^{3+}$ as luminescent probe has not been reported to the best of our knowledge. This complex shows interesting photophysical properties to be considered as probe. The addition of surfactant changes its lifetime as well as its luminescent properties. This complex binds tightly to SDS micelles and its excited state shows good oxidant properties and it can undergo a bimolecular reaction with a number of organic compounds [7].

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In the present work, we describe the interaction of phenol (4-H-Ph), 4-Br-phenol (4-Br-Ph) and 2,6-dimethyl-phenol (2,6-diMe-Ph) in their neutral forms, with sodium dodecyl sulfate employing the luminescent quenching of $Cr(phen)_3^{3+}$ by phenolic compounds as a method to determine the binding parameters.

## 2. Experimental

Tris-phenantroline chrommiun(III) perchlorate ($Cr(phen)_3(ClO_4)_3$) was obtained from previous studies [7]. Phenol (4-H-Ph), 4-Br-phenol (4-Br-Ph) and 2,6-dimethylphenol (2,6-diMe-Ph) (Aldrich) compounds were purified by vacuum sublimation. Sodium chloride (Merck) and sodium dodecyl sulfate (Sigma, purity >99%) were used without further purification. Deionized water used for the preparation of the solutions was obtained with a Milli-Q System Millipore.

The quenching measurements with phenols were carried out by steady-state as well as time resolved methods using a PTI-QM2 spectrometer. The excitation wavelength was 330 nm. Cut-off filter (620 nm) was placed between the sample and the entrance slit of the emission monochromator to prevent scattered light from reaching the photomultiplier of detection. The luminescent spectra were recorded in the range of 690–750 nm and the decay was monitored at 730 nm. The estimated experimental errors are within 10%.

The samples were typically $(1.0\text{–}2.0) \times 10^{-5}$ M in $Cr(phen)_3^{3+}$, in NaCl 0.1 M and 0.01 M HCl. The experiments were carried out at $31.0 \pm 0.2\,°C$ and the SDS concentrations were in the range of 0.0015–0.10 M. The occupancy number $\tilde{n}$, ($\tilde{n} = \frac{[Cr(phen)_3{}^{3+}]}{[M]}$, where $[M]$ is the micelle concentration) was held less than 0.1 to assure that only one molecule of fluorosphore were inside the micelle according to Poisson statistics [4].

In a typical experiment, 2.0 mL of aqueous solution of $Cr(phen)_3^{3+}$ with or without SDS was added to the fluorescence cell, and successive aliquots of concentrated phenol stock solution were added using a Hamilton microliter syringe.

## 3. Results and discussion

### 3.1. Luminescent quenching method

In water, linear Stern–Volmer are obtained from steady-state and time resolved experiments. Very close values of the quenching rate constants are obtained, indicating that only dynamic quenching by phenols is taking place [7].

In the presence of SDS micelles Stern–Volmer plots either by steady-state or lifetime measurements were always linear in the range of quencher concetrations used. However, slightly higher slopes were obtained from steady-state data at the same SDS concentration; this should indicate that a static quenching is present. In fact, the quenching process in a micelle containing an $^*Cr(phen)_3^{3+}$ and a quencher molecule is faster than the luminescence decay so that, luminiscence is observed only from micelles retaining $^*Cr(phen)_3^{3+}$ and devoid of quenchers, and therefore, its luminiscence lifetime is reduced by the dynamic diffusional quenching by water solubilized quencher molecules [4]. This kind of behavior was found before [13,15–17] and clearly indicates that the quencher associates with SDS micelles. The $k_q$ values obtained by both techniques are collected in Table 1.

From Table 1, it is evident that the luminescent quenching efficiency by phenolic compounds decreases with the increase of SDS concentration, as was previously found in other systems already studied [13,14].

### 3.2. Stationary results

The Stern–Volmer plots obtained by steady-state measurements can be used as diagnosis of the site accesibles by the quencher [18] if we use the following rearrenged Stern–Volmer equation:

$$\log\left(\frac{I_0 - I}{I}\right) = \log K_{SV} + \log[Q] \qquad (1)$$

where $I_0$ and $I$ are the luminescent intensity in absence and in presence of quencher, respectively.

A quenching that occurs in only one site of the micelle should give a linear plot of $\log((I_0 - I)/I)$ versus $\log[Q]$ with

Table 1
Quenching rate constants ($k_q$) for the reaction between $^*Cr(phen)_3^{3+}$ and phenols (SDS concentrations higher than icmc = 1.0 mM, pH 2 and 100 mM NaCl)

| [SDS] (M) | 4-H-Ph, $k_q$ ($M^{-1}s^{-1} \times 10^{-8}$) | | 4-Br-Ph, $k_q$ ($M^{-1}s^{-1} \times 10^{-8}$) | | 2,6-diMePh, $k_q$ ($M^{-1}s^{-1} \times 10^{-9}$) | |
|---|---|---|---|---|---|---|
| | $\tau_0/\tau$ | $I_0/I$ | $\tau_0/\tau$ | $I_0/I$ | $\tau_0/\tau$ | $I_0/I$ |
| 0.0159 | | | | | 3.75 | 4.76 |
| 0.02 | 3.48 | 3.41 | 10.5 | 11.2 | | |
| 0.03 | 3.035 | 2.97 | 7.25 | 8.37 | | |
| 0.0384 | | | | | 2.62 | 2.93 |
| 0.04 | 3.00 | 2.88 | 6.25 | 6.59 | 2.54 | 2.54 |
| 0.06 | 2.69 | 2.69 | 4.80 | 5.40 | | |
| 0.0698 | | | | | 1.68 | 1.94 |
| 0.0799 | 2.39 | 2.57 | 3.51 | 4.04 | 1.81 | 2.14 |
| 0.0999 | 2.41 | 2.25 | 2.89 | 2.41 | 1.76 | 2.01 |

Steady-state ($I_0/I$) and time resolved ($\tau_0/\tau$) experiments.

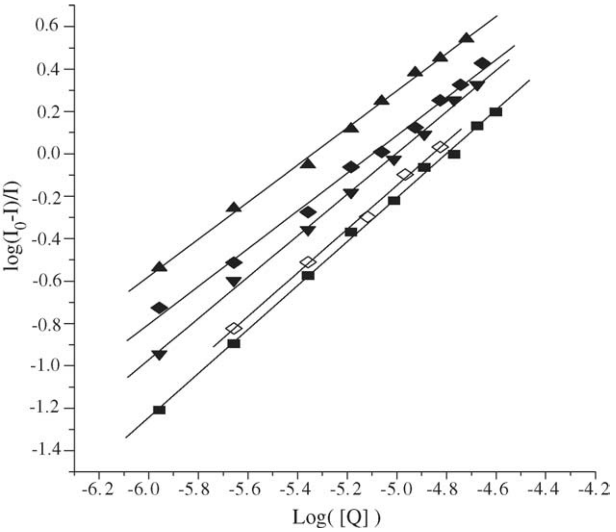


Fig. 1. Logarithmic Stern–Volmer plots for the steady-state quenching of $*Cr(phen)_3^{3+}$ by 2,6-diMe-Ph at different SDS concentrations: the slope for 0.10 (■), 0.06 (▼), 0.04 (♦), 0.02 (▲) M SDS and pure water (◇) are 1.04, 0.89, 0.86, 0.97 and 1.03, respectively.

a slope equal to 1. If the slope is higher than 1, a steady-state quenching could be present. Otherwise, if it were lesser than 1 it could be understood as the presence of two kinds of fluorophores, one of each would be inaccessible by the quencher.

Fig. 1 shows a representative plot of $\log((I_0 - I)/I)$ versus $\log [Q]$ for 2,6-diMe-Ph at different concentrations of surfactant. The slopes of the plots are close to the unity within the experimental error. Similar behavior was found for 4-H-Ph and 4-Br-Ph, and as we stated before, $Cr(phen)_3^{3+}$ binds tightly to SDS micelles, the present results indicate that the quenching process occur in the micellar phase.

On the other hand, when the probe is completely incorporated into the micelle, the quenching process occurs only in the micellar pseudo phase and the $I_0/I$ ratio depends on the average concentration of the quencher in the micelle. In these cases, the steady-state measurements could be used to differentiate between partition and binding processes of distribution of the probe in the micelles [17,19]. If we define the average number of quenchers per micelles as $\langle Q \rangle = [Q_m]/[M]$ as an independent variable, the total quencher concentration $[Q_T] = [Q_m] + [Q_w]$could be expressed as:

$$[Q_T] = \langle Q \rangle [M] + [Q_w] \qquad (2)$$

If the distribution is only a partition process between both phases, a Scatchard [20] type plot $\langle Q \rangle/[Q_w]$ versus $\langle Q \rangle$ should be lineal with slope equal to zero. Conversely, if only the binding process is present, a straight line with negative slope should be found and if both processes are present at the same time, negative curved plots should be obtained [17].

Fig. 2 shows plots of $[Q_T]$ versus micelle concentration at the same quenching efficiency and the results were evaluated on the basis of Encinas and Lissi [16] method. The chosen efficiency values were $I_0/I = 1.5$, 2.0, 2.5, 3.0 and 3.5. Then $\langle Q \rangle$ and $[Q_w]$ were evaluated from the slopes and abscissa intercept, respectively. With these values, Scatchard plots were made (Fig. 3). As it can be seem from the plots, phenols show constant Scatchard plots indicating that the process is a partition between the aqueous and the SDS micellar pseudo phase micellar. Senz and Gsponer found a similar behavior in the quenching of $Ru(bpy)_3^{2+}$ by nitro-phenols in presence of SDS [13]. In that study the steady-state Stern–Volmer plots showed an upward deviating curvature at every SDS concentration used for all the phenols studied and there was proposed a partition process for the distribution of nitro-phenol derivatives.

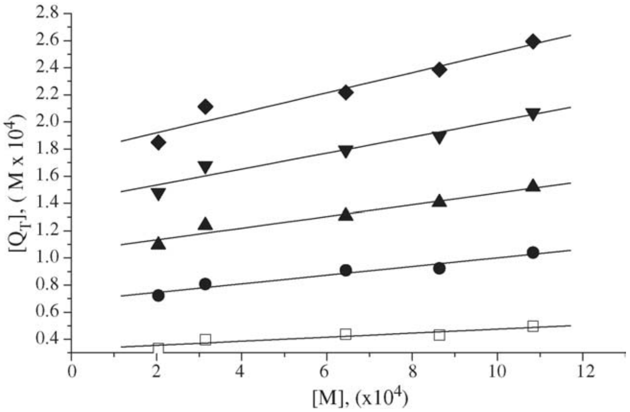


Fig. 2. Representation of $[Q_T]$ as a function of $[M]$ for quenching efficiencies $I_0/I = 1.5$ (□), 2.0 (●), 2.5 (▲), 3.0 (▼) and 3.5 (♦) from experiments were $Q$ = 4-H-Phenol at pH 2 in 0.1 M NaCl.

In view of the results we already have, it is possible to evaluate the association constants of phenols to micelles $\left(K = \frac{[Q_m]}{[Q_w][M]} = \frac{\langle Q \rangle}{[Q_w]}\right)$ introducing this expression into Eq.

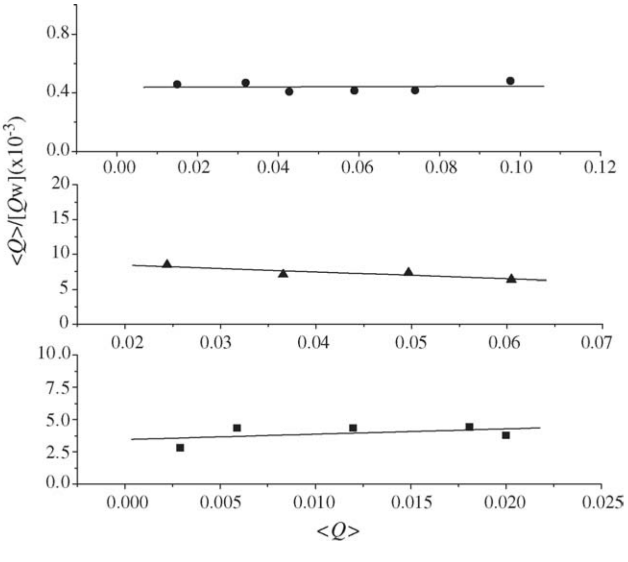


Fig. 3. Scatchard plots for the interaction of phenols with SDS micelles. (●) 4-H-Ph, (▲) 4-Br-Ph and (■) 2,6-diMe-Ph in 0.1 M NaCl.

Table 2
Association parameters[a] for phenols in SDS micelles obtained by the use of $Cr(phen)_3{}^{3+}$ as luminescent probe

| Phenol | Steady-state | Time resolved | | |
|---|---|---|---|---|
| | $K \times 10^{-3}$ ($M^{-1}$) | $K \times 10^{-3}$ ($M^{-1}$) | $k_+$ ($\times 10^{-9}$ $s^{-1}$ $M^{-1}$) | $k_-$ ($\times 10^{-5}$ $s^{-1}$) |
| 4-H-Ph | 0.44 | 0.66 | 3.84 | 5.85 |
| 2,6-di-Me-Ph | 3.9 | 2.6 | 5.32 | 20.8 |
| 4-Br-Ph | 7.3 | 6.0 | 2.22 | 3.72 |

[a] Estimated experimental errors were ±10%.

(2) as follow:

$$[Q_\mathrm{T}] = \langle Q \rangle [M] + \frac{\langle Q \rangle}{K} \tag{3}$$

From plots of $[Q_\mathrm{T}]$ versus $[M]$, $K$ values were evaluated and are shown in Table 2 second column.

### 3.3. Time resolved results

It is known that $Cr(phen)_3{}^{3+}$ binds tightly to SDS micelles [9] and the residence time is long enough to permit a quenching process proceed in the micelle [21,22]. If we assume that one intramicellar quenching event occurs during the residence time of the quencher inside the micelle with a quenching probability of 1, the mechanism for the quenching of $Cr(phen)_3{}^{3+}$ by phenols could be described as in Scheme 1.

In the Scheme 1, A is the sensor, Q is the quencher and the subscript m and w mean that the sensor or the quencher is in the micellar or aqueous pseudo phase, respectively. The $k_+$ and $k_-$ are the rate constants for the entrance and the exit of the quencher from the micelle, respectively; $k_\mathrm{AM}$ is the decay rate constant of the probe in the micelle and $k_\mathrm{q}$ is the quenching rate constant.

According to the mechanism and the assumptions made the observed rate constant would be controlled by the quencher concentration in the aqueous phase, $Q_\mathrm{w}$, and by the entrance rate constant of the quencher to the micelle, then the observed rate constant ($k_\mathrm{obs}$) is:

$$k_\mathrm{obs} = k_\mathrm{AM} + k_+[Q_\mathrm{w}] \tag{4}$$

The total quencher concetration, $Q_\mathrm{T}$, is $[Q_\mathrm{T}] = [Q_\mathrm{m}] + [Q_\mathrm{w}]$, and combining this expresion with $K = \frac{[Q_\mathrm{m}]}{[Q_\mathrm{w}][M]}$ and Eq. (4), we obtain:

$$k_\mathrm{obs} = k_\mathrm{AM} + \left(\frac{k_+[Q_\mathrm{T}]}{1 + K[M]}\right) = k_\mathrm{AM} + k_\mathrm{m}[Q_\mathrm{T}] \tag{5}$$

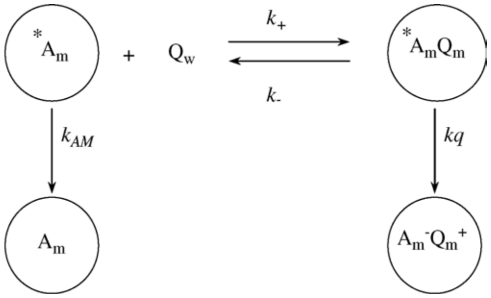
where

$$k_\mathrm{m} = \frac{k_+}{1 + K[M]} \tag{6}$$

From these equations, a plot of $k_\mathrm{obs}$ versus $[Q_\mathrm{T}]$ should be linear with $k_\mathrm{m}$ as slope, and the reciprocal of the slopes should depend linearly on $[M]$,

$$\frac{1}{k_\mathrm{m}} = \frac{1}{k_+} + \frac{K}{k_+}[M] \quad \text{or} \quad \frac{1}{k_\mathrm{m}} = \frac{1}{k_+} + \frac{1}{k_-}[M] \tag{7}$$

taking account that $K = \frac{k_+}{k_-}$. Fig. 4 shows the variation of $1/k_\mathrm{m}$ with the micelle concentration for the three phenols used. $k_\mathrm{m}$ values were obtained from the slope of plots of $k_\mathrm{obs}$ versus quencher concentration for the different SDS concentrations. The inset of Fig. 4 shows a representative plot of the variation of $k_\mathrm{obs}$ with the quencher concentration for different SDS concentrations and for 2,6-diMe-Ph. The $k_+$ and $k_-$ values were obtained from the intersection and the slope of these plots in Fig. 4 and are collected in Table 2.



Scheme 1.

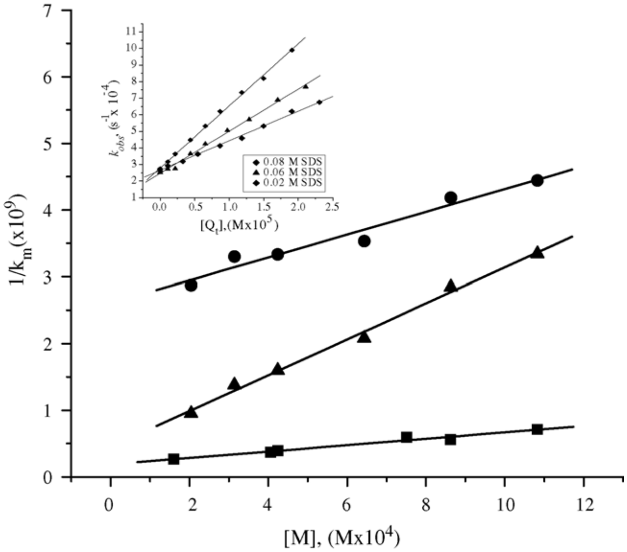


Fig. 4. Plot of the reciprocal of $k_\mathrm{m}$ vs. $[M]$ according to Eq. (7) of the data for phenols at pH 2 in 0.1 M NaCl ((●) 4-H-Ph, (▲) 4-Br-Ph and (■) 2,6-diMe-Ph). Inset: Variation of $k_\mathrm{obs}$ as a function of the 2,6-diMe-Ph concentration at different surfactant concentrations (◆, 0.02 M; ●, 0.06 M; ▲, 0.08 M).

There is some discrepancy in the equilibrium constants found by steady-state and time resolved experiments. From an estimation of the errors in the graphic evaluation of the intensities data we found that the error associated to the values of the *K* calculated from the steady-state data is around 20–30%, and we could concluded that the *K*'s values obtained from steady-state or lifetime measurements are comparable. The trend for the equilibrium constants found for both set of data remains the same as it could be seen in Table 2. In general, *K* follows the trend: 4-H-Ph < 2,6-diMe-Ph < 4-Br-Ph. Because the equilibrium constants are representative of the solubility of the phenols in a non-polar medium and according to the fact that the experience were done at pH 2, that is the protonated form of phenols, we should expect a trend with hydrophobicity. From table, we can see that this is the case for 4-H-Ph < 2,6-diMe-Ph. However, the observed association constant for 4-Br-Ph was greater than expected. Same trend with the equilibrium constants were found by Shah et al. [23] in the study of solubilization of phenols in anionic surfactant micelles by differential spectroscopy. Moreover, some tendency with dipolar moment of the phenols also would be expected. This tendency was not observed, indicating that other factors should be affecting the solubility of these compounds in the micellar environment.

It can be noticed from Table 2 that $k_+$ values are in the range of $(\sim 2–5) \times 10^9\ s^{-1}\ M^{-1}$ and $k_-$ values between $(\sim 3–21) \times 10^5\ s^{-1}$. These values are consistent with the constant values found for nitro-phenols [13], benzene and toluene [24]. Massad et al. [14] found an average value of $2.2 \times 10^9\ s^{-1}\ M^{-1}$ for the entrance rate constant of different phenols using uranyl ion ($UO_2^{2+}$) as luminescent probe, that value is close to the ones we obtained. The values found for $k_+$ and $k_-$ confirm the proposed mechanism (Scheme 1). We had assumed that the intramicellar quenching was faster than the residence time ($\tau_R$) of the luminescent probe in the micelles and this $\tau_R$ has a value estimated larger than 40 μs [21]. On the other hand, the residence time of the quencher inside the micelle should be longer than the intramicellar process; we found that this time ($1/k_-$) is in the order of 0.05–1 μs. If we take the value found by Thomas [24] for the intramicellar quenching rate constant of an organic system as reference ($k_q = 7.5 \times 10^7\ s^{-1}$ that is $\tau \sim 13$ ns), we can state that the intramicellar quenching would be occurring in the nanosecond scale. Then, the intramicellar quenching is faster than the exit rate constant of the fluorophore and the quencher and we can conclude that the initial condition of quenching efficiency equal to 1 mentioned above fulfils in all the cases studied here.

From the above results it is proposed that $^*Cr(phen)_3^{3+}$ as a luminescent probe can be used for the determination of association parameters to micelles of SDS.

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