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Interaction of α-diimine–chromium(III) complexes with non-ionic surfactant Triton X-100

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ABSTRACT

Using either luminescence intensity or lifetime measurements, we have studied the binding interactions of $Cr(NN)_3^{3+}$ (NN = α-diimine ligands) with non-ionic solutions of surfactant *p*-(1,1,3,3-tetramethylbutyl)phenoxypoly(ethylene glycol), Triton X-100 (TX-100). The titration curves consisted of two curved regions with different slopes. This biphasic behavior of lifetime-TX-100 concentration data revealed the presence of premicellar aggregates at low TX-100 concentration and the formation of normal micelles at high surfactant concentration. The results were analyzed with a model that includes binding of $Cr(NN)_3^{3+}$ (probe) to small premicellar aggregates and to micelles. There is a good correlation between the hydrophobicity of the ligands of Cr(III) complex and the strength of the binding of the complexes to the micelles. A comparison with the binding of $Cr(NN)_3^{3+}$ to sodium dodecylsulfate (SDS) is discussed.

1. Introduction

The importance of micellar solubilization is that it can be used in a wide range of applications, from cleaning technologies, environmental remediation, and micellar catalysis to more recent uses including advanced drug delivery systems [1–3], due to the properties that present the substrate–surfactant mixture.

It is well known that aqueous surfactant solutions allow highly localized concentration of a hydrophobic substrate dissolved in the micelles, while its analytical concentration remains low in the bulk. This fact becomes important in terms of reactivity and selectivity of bimolecular processes in which excited species can participate [4], with potential applications in photocleaning processes. The study of such systems has been a continuous interest area. In the literature, there are many works that report the interaction of α-diimine–ruthenium(II) ($Ru(NN)_3^{2+}$) complexes to different micellar media [5–11] as well as the influence of these interactions on the reactions with various compounds [12,13]. Moreover, the photochemistry and photophysics of α-diimine–chromium(III) ($Cr(NN)_3^{3+}$) complexes have been extensively studied in homogeneous systems [14,18], whereas there are, to the best of our knowledge, only a few works in micellar systems. One of them investigated the interaction of $Cr(NN)_3^{3+}$ complexes to SDS micelles and gave an important foundation for further studies which have shown that the $Cr(NN)_3^{3+}$ can be used as luminescent probes for determination of the association parameters of phenols to anionic micelles [19,20]. Furthermore, non-ionic surfactants ensure that the location of the probes within the micelles is not affected by electrostatic attractions. The interaction of $Cr(NN)_3^{3+}$ complexes with non-ionic surfactants has not been reported in the literature so far, then, such study would allow the examination of hydrophobic and hydrophilic interactions isolated from electrostatic effects.

In our laboratory, there is a continuous interest in the study of systems using $Cr(NN)_3^{3+}$ complexes as probes in various microheterogeneous environments for the further study of bimolecular processes in which these complexes are involved. Hence, it is important to characterize the binding of these complexes in different micellar media. Ionic $Cr(NN)_3^{3+}$ complexes can be designed, and in fact, we have synthesized several complexes with different hydrophobic ligands that we would expect that they will have a significant effect on the association of this complexes to interface regions in microheterogeneous systems.

It is also known that the addition of a surfactant to an aqueous solution changes the luminescent intensity and lifetime of many $Ru(NN)_3^{2+}$ and $Cr(NN)_3^{3+}$ complexes [19,10,21]. For the $Ru(NN)_3^{2+}$ surfactant complex system, Snyder et al. [10] developed a model that describes interactions with cationic, anionic, and non-ionic surfactants and was successfully employed with $Cr(NN)_3^{3+}$ complexes in anionic micelles [19]. It was observed that, in general, both electrostatic and hydrophobic interactions are present in the binding of the probe to the anionic micelles due to the charge of the complex and

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the hydrophobicity of the ligands, respectively. However, the binding follows the expected trend based on interactions, that is, the higher the electrostatic attraction the higher the binding and the lower the repulsion, even more, the complex ion $Ru(bpy)_3^{2+}$ showed no binding to cationic cetyltrimethylammonium chloride (CTAC) micelles [22]. On the other hand, an increase in the hydrophobicity of the ligand favors the association. Both, Ru(II) and Cr(III) complexes bind tightly to SDS micelles with a binding constant of 10^4 and $10^5\ M^{-1}$, respectively, the latter being higher for Cr(III) complexes due to its higher charge.

One of the most fundamental and important structural parameters of micellar aggregates is the aggregation number (N), which is the number of surfactant monomers that form a micelle. The value of N provides information on the micellar size and shape, which may be significant in determining the stability and practical applications of the systems under study [23]. The value of N is affected by various factors including temperature, type, and concentration of added electrolyte and/or organic additives [24]. The measurement of N is therefore of great significance. To determine the value of N, various methods can be used (NMR, thermodynamic, and scattering methods); however, a method to assess the aggregation number of a surfactant easily performed under a variety of experimental conditions like the one to be described in the present work should be of particular interest.

We report here a study which extends our knowledge of the interactions of transition–metal complexes with non-ionic surfactants. In particular, we have undertaken a systematic characterization of the interaction of $Cr(NN)_3^{3+}$ complexes with non-ionic surfactant of TX-100 micelles in air-saturated and N_2-purged micellar solutions. The quantitative description of the interaction was obtained using fluorescence techniques including time-resolved as well as steady-state measurements, through titration curves and applying the method of Snyder et al. [10] for the treatment of the data. We discussed here the results obtained previously for the interaction of $Cr(NN)_3^{3+}$ complexes with SDS micelles in terms of the importance of hydrophobic as well as electrostatic interactions present in the binding process. The methodology used in the present work also allows an estimation of N under the experimental conditions employed.

2. Experimental

The $Cr(NN)_3^{3+}$ (NN represents the following: 2,2′-bipyridine (bpy); 1,10-phenanthroline (phen); 5-chlorophenanthroline (5Clphen); 3,4,7,8-tetramethylphenanthroline (Me_4phen); 4,7-dimethylphenanthroline (Me_2phen); 4,7-diphenylphenanthroline (Ph_2phen) were obtained from previous works and synthesized according to the literature [19,25–27]. Fig. 1 shows the molecular structures of the probes employed. Sodium chloride (Merk), hydrochloric acid (Cicarelli, PA), and Triton TX-100 (Sigma, purity >99%) were used without further purification. Deionized water used to prepare the solutions was obtained with a Milli-Q System Millipore Co.

Steady-state measurements were carried out using a PTI-QM2 spectrometer from Photon Technology International adapted to obtain phosphorescence lifetime. The excitation wavelength was set at 430 nm. Cut-off filter (500 nm) was placed between the sample and the entrance slit of the emission monochromator to prevent scattered light reaching the photomultiplier detector. Lifetime experiments were carried out either on a N_2 laser system described previously [28] or by using a PTI-QM2 spectrometer. The excitation was set at the 337 nm laser line or at 330 nm, respectively, and the luminescent spectra were recorded in the range of 650–800 nm; the decay was monitored at the maximum of emission of each complex (725–745) nm. Decays were recorded on a Tektronix TDS 3032B and analyzed with non-linear least-square software on a personal computer. The lifetime traces consist of at least the average of eight consecutive decays. In each experiment, fresh solutions were used. The pH of the solutions was measured with a Hanna Instrument pH meter.

The binding constants for the interaction of chromium(III) complexes with TX-100 micelles were determined by titration in air-saturated and N_2-purged solutions. Typical experiments were carried out in aqueous solution in 0.1 M NaCl at pH = 2 (HCl) at 25 ± 0.5 °C. The binding constants for the interaction of $Cr(NN)_3^{3+}$ complexes with TX-100 surfactant were determined by titration curves. The concentration of TX-100 was varied from 1.0×10^{-4} M to 0.3 M, while the ionic strength of 0.1 M was kept with the addition of NaCl. The titration was carried out by adding aliquots of $(1.2–2.5) \times 10^{-5}$ M stock $Cr(NN)_3^{3+}$ complexes free of TX-100 to a 0.3 M solution in TX-100 with an identical initial concentration of $Cr(NN)_3^{3+}$ complex to reach dilution up to 1.0×10^{-4} M in TX-100. The intensity and lifetime were measured after mixing and allowing thermal equilibrium.

The data were fitted according to the model discussed below using a non-linear least-squares method through Microcal Origin™ software, Version 7.0.

3. Results and discussion

3.1. Luminescence spectra

The photophysical and photochemical properties of α-diimine–chromium(III) complexes have been the subject of extensive investigation [14–18]. Luminescence from the lowest-energy excited states consists of two bands from the thermally equilibrated states $^2E/^2T_1$, with a maximum assigned to $^2E \rightarrow {}^4A_2$ transition and a shoulder assigned to the transition $^2T_1 \rightarrow {}^4A_2$, both transitions are metal-centered ligand-field (d–d) character [29]. Values for decay lifetimes (τ) for $(^2E/^2T_1)$ $[Cr(NN)_3]^{3+}$ result from contribution of different modes of decay, $1/\tau = k_{rad} + k_{nr} + k_{rx} + k_g[^4A_2] + k_q[Q]$ (k_{rad}, rate constant for luminescence decay; k_{nr}, rate constant for non-radiative decay; k_{rx}, rate constant for reactive decay, such as photoaquation; k_g, rate constant for ground-state quenching; k_q, rate constant for other quenching modes) [29]. Infinite diluted solutions in the absence of quenchers display an intrinsic lifetime of $^2T_1/^2E$, τ_o, given by $1/(^2k_{nr} + {}^2k_{rx})$ [29]. Lifetime measurements and absorption decays showed that the excited-state lifetimes have a strong dependence on the nature of the ligands, the pH of the solution, and the presence of added salts [30,31].

Moreover, α-diimine–chromium(III) complexes display low activity toward photoaquation (photoinduced ligand substitution by water molecules or hydroxyl ions) upon excitation with light (λ_{exc} = 313–464 nm) [32,29]. Quantum yields for photoaquation decrease at lower temperature, lower pH, and with the increase in ionic strength.

On the other hand, Triton X-100 is a non-ionic surfactant with a critical micellar concentration (*cmc*) in pure water between 0.2 and 0.31 mM [33–35]. Song et al. [36] reported a *cmc* value of 0.21 mM for TX-100 in presence of NaCl 0.2 M, value very close to the values reported for TX-100 in pure water. Also, a very recent study [37] showed that there is no change in the viscosity of TX-100 solution ≈ 0.1 M as a function of pH (ranges 2–10, at 30 °C), and no change in micelle size was reported. Then, we use pH = 2 and an ionic strength 0.1 M of NaCl as experimental conditions in order to achieve the highest photostability of the Cr(III) complexes.

Fig. 2 shows the luminescence spectrum of $Cr(phen)_3^{3+}$ in the absence and presence of TX-100; in the latter case, the spectrum has the same appearance as that found in water, but with less intensity and no maximum shift. This behavior was observed for all the Cr(III) complexes studied and was also observed previously

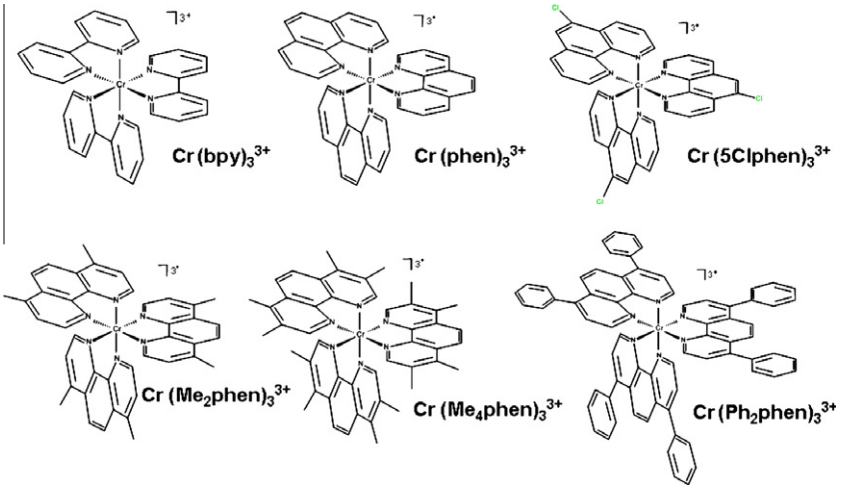

Fig. 1. Molecular structures of the α-diimine–chromium(III) complexes.

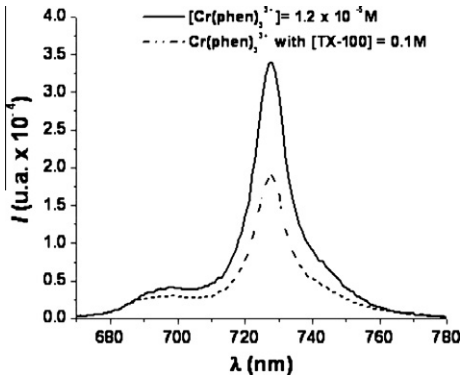

Fig. 2. Luminescence spectrum of $Cr(phen)_3^{3+}$ in 0.1 M NaCl at pH = 2 (HCl) at 25 ± 0.5 °C in the presence and absence of TX-100.

for the interaction of the $Cr(NN)_3^{3+}$ complexes with SDS [19]. Gsponer et al. studied the interaction of $Ru(bpy)_3^{2+}$ in SDS micelles under the same experimental conditions as in the present work. They found that the emission intensity in SDS was higher than that in water, and the maximum of the spectrum shifted to red. These changes were attributed to a stabilization of the metal-to-ligand charge-transfer (MLCT) luminescent state in a medium of less dielectric constant [38].

At variance with the excited state $Ru(NN)_3^{2+}$, a MLTC state, the excited state $Cr(NN)_3^{3+}$ is metal-centered (MMCT) and shows little ligand character [39]. This implies that only small changes in intensity and lifetime would be produced via deactivation by the interaction with the surfactant or solvent molecules in the second coordination sphere. Thus, the spectral changes observed in the present work can be explained in terms of a quenching process (see below).

3.2. Luminescence lifetime vs. TX-100 concentration titration curves

In general, when the surfactant concentration range is close to the *cmc*, some physical properties of the system undergo an abrupt change which can be used to determine *cmc* [40]. The presence of ionic compounds, such as sodium chloride and $Cr(NN)_3^{3+}$ complexes, should induce the formation of micelles. Then, *icmc* (induced critical micellar concentration), instead of *cmc*, should be employed.

The luminescence decays of the $Cr(NN)_3^{3+}$ complexes observed in aqueous solutions were in all cases a single-exponential, as expected. Furthermore, in the presence of TX-100, the decays were also single-exponential for all the chromium(III) complex–surfactant systems studied (Fig. 3). Single-exponential decays of chromium(III) complexes have been observed in SDS micelles [19]. We carried out a series of titration curves by following lifetime vs. TX-100 concentration in the range of (0–0.3) M for all the $Cr(NN)_3^{3+}$ complexes (Fig. 4).

The lifetime titration curves for all the complexes show a biphasic behavior with negative slope before and after a breakpoint. Before this point, the slope had always been more pronounced than that after the breakpoint (at larger TX-100 concentrations). Then, *icmc* in the presence of $Cr(NN)_3^{3+}$ complexes can be estimated from the concentration of TX-100 at which the breakpoint occurs. The changes in the lifetime and emission intensity with the addition of TX-100 reflect the binding of the chromium(III) complexes to the TX-100 surfactant. The biphasic behavior found was similar to that observed previously for the interaction of $Cr(NN)_3^{3+}$ with micelles of SDS.

We have used a model developed by Demas et al. [6], which was extensively developed by Snyder et al. [10] to interpret our results. This model takes into account the interaction between the chromium complex (*A*) and both surfactant monomer (*S*) and micelle (*M*), described by the following equations:

$$A \xrightarrow{h\nu} {}^{*}A \rightarrow A + h\nu_p \quad \tau_A \tag{1}$$

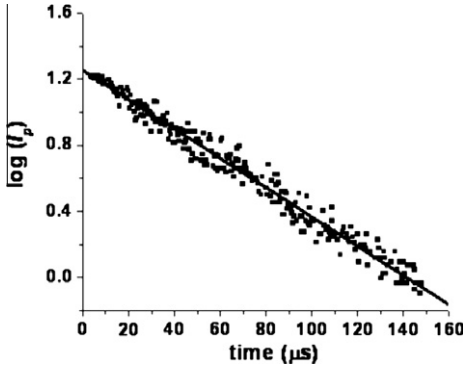

Fig. 3. Luminescence decay of 1.2×10^{-5} M $Cr(phen)_3^{3+}$ in 0.1 M NaCl at pH = 2 (HCl) at 25 ± 0.5 °C in the presence of air-saturated solution 0.1 M of TX-100 ($\log I_p$ shows single-exponential decay, τ = 13 μs).

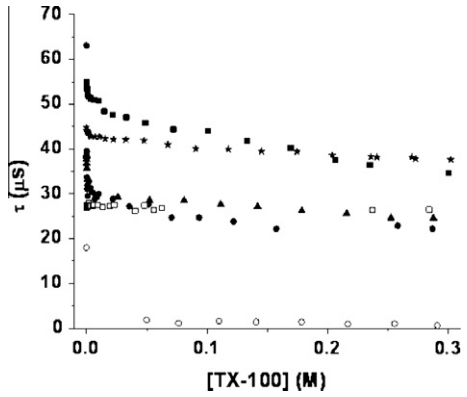

Fig. 4. Titration curves from lifetime vs. [TX-100] for all $Cr(NN)_3^{3+}$ complexes in 0.1 M NaCl at pH = 2 (HCl) at 25 ± 0.5 °C ■ $(Cr(5Clphen)_3^{3+})$; ▲ $\left(Cr(bpy)_3^{3+}\right)$; ● $(Cr(phen)_3^{3+})$; ○ $\left(Cr(Ph_2phen)_3^{3+}\right)$; □ $(Cr(Me_4phen)_3^{3+})$ and ∗ $\left(Cr(Me_2phen)_3^{3+}\right)$.

$$AS_n \xrightarrow{h\nu} {}^*AS_n \rightarrow AS_n + h\nu_p \quad \tau_{ASn} \tag{2}$$

$$AM \xrightarrow{h\nu} {}^*AM \rightarrow AM + h\nu_p \quad \tau_{AM} \tag{3}$$

$$A + ns \rightleftarrows AS_n \qquad K_{ASn} \tag{4}$$

$$A + M \rightleftarrows AM \quad K_{AM} = \frac{k_A}{k_{-A}} \tag{5}$$

Our measurements follow the excited-state species ${}^*A$. If the excited-state equilibrium is rapid enough compared with the excited-state lifetimes in the aqueous phase (τ_A) and/or micellar pseudo phase (τ_{AM}), then the equilibrium constant ${}^*{}_{KAM}$ is monitored. On the other hand, if the equilibrium is too slow, K_{AM} is obtained. We have assumed that the interchange between ${}^*A$ and ${}^*AM$ in our system is faster than that of the lifetimes τ_A and τ_{AM}, and consequently, we have evaluated ${}^*K_{AM}$. Nevertheless, we would expect ${}^*{}_{KAM}$ to be similar to K_{AM}.

At low concentration of surfactant, A interacts with S to form premicellar aggregates of n molecules of surfactant and one molecule of the metallic complex, AS_n. From Eq. (4), the premicellar binding constant, K_{ASn}, is provided by:

$$K_{AS_n} = \frac{[AS_n]}{[A][S]^n} \tag{6}$$

At high concentration of surfactant, A interacts with M to form $Cr(NN)_3^{3+}$–micelle association complex (AM) as represented by Eq. (5), where the micellar binding constant, K_{AM}, is given by:

$$K_{AM} = \frac{[AM]}{[A][M]} \tag{7}$$

and $[M]$ is the micelle concentration in the solution defined as:

$$[M] = \frac{[S] - icmc}{N} \tag{8}$$

where N is the aggregation number of TX-100 micelles in the present aqueous media.

As we stated above, the luminescence decays observed were in all cases single-exponentials; therefore, the rate constant found, k_{obs} (τ_{obs}^{-1}), obtained from the semilogarithmic plots of intensity vs time, can be expressed as follows:

$$k_{obs} = \tau_{obs}^{-1} = f_A\tau_A^{-1} + f_{AS_n}\tau_{AS_n}^{-1} + f_{AM}\tau_{AM}^{-1} \tag{9}$$

where f_A, f_{AS_n}, and f_{AM} are the fractions of the A, AS_n, and AM present in equilibrium, respectively. The τ values indicate the lifetime that would be measured for the different species in the absence of exchange [19].

Following Snyder et al. (Eqs. (1)–(7)), we introduced the expressions for the different f fractions extracted from Eqs. (6) and (7). Eq. (9) can be rewritten as follows:

$$\tau_{obs}^{-1} = \frac{\tau_A^{-1} + K_{AS_n}[S]^n\tau_{AS_n}^{-1} + K_{AM}[M](1 + K_{AS_n}[S]^n)\tau_{AM}^{-1}}{1 + K_{AS_n}[S]^n + K_{AM}[M](1 + K_{AS_n}[S]^n)} \tag{10}$$

This equation is a general form used to fit the experimental data and in which only the aggregates of size "n" are considered, as the model does not take into account a distribution of size aggregates. However, "n" is not only one of the fitting parameters, but it also represents the mean number of surfactants associated with each $Cr(NN)_3^{3+}$ complex in the premicellar region. The validity of this model to obtain all the parameters and binding constants from the titration curve fitting has been demonstrated previously [19].

Titration curves were also carried out by measuring the changes in the luminescence intensity vs. TX-100 concentration. Data from steady-state experiments can be treated equally, considering the total luminescence intensity as the sum of the individual contribution of the species in equilibrium. An expression similar to Eq. (10) can be obtained by replacing τ^{-1} by I.

To start the fitting process, a set of initial parameters was chosen; τ_A or I_A was experimentally known and τ_{AM} or I_{AM} was taken as the average in the plateau at high TX-100 concentration; n was fixed at integer values equal to 1, 2, 3, 4, and 5. As a convergence criterion, it was established that the change in χ^2 between two successive iterations was $<10^{-5}$. The success of the fit was judged by the magnitude of χ^2 and the appearance of residual plots. Then, by fixing n for different values, we released the program to fit the whole titration curve until convergence was reached. We varied n and examined the quality of the fitting curve, the better χ^2 was obtained for $n = 2$ (Table 1), for $n > 5$, χ^2 starts to increase, rendering values too large to be considered as a good fit.

Firstly, N was fixed at 76. This value was obtained following a slightly modified fluorescence steady-state quenching method presented by Turro and Yekta [41], in aqueous solution at pH = 2 (HCl) at 25 ± 0.5 °C and 0.1 M of NaCl using pyrene as probe and cetylpyridinium bromide as quencher. We found that N remains constant at a value of 76 for TX-100 concentrations from 0.01 to 0.3 M.

Fig. 5 exhibits the titration curves from lifetime as well as the intensity data for $Cr(5Clphen)_3^{3+}$ complex and the corresponding residual plot. Both plots show a similar behavior indicating that, by intensity or lifetime measurement, good concordance was achieved, it being representative of all the complexes studied. Table 1 displays the parameters obtained for this complex with a fixed cmc = 0.32 mM [42,34].

As shown in Table 1, the best fitting was achieved for $n = 2$; with this value, all the parameters were obtained using unweighted fitting process, including an estimation of the values of N.[1]

Three different models have been described by Demas et al. [6] in order to interpret the experimental data. We initially used the Model II, which assumes no interaction between the chromium complex and the free surfactant monomer and, the cmc was fixed at 0.32 mM [34]. Nevertheless, attempts to fit the data failed systematically. Then, we changed to Model III where the cmc was varied to achieve the best fit. In this model, the cmc is affected by the presence of the probe; we referred it as an $icmc$. In the fitting process we used an initial set of input parameters with which the program yielded $icmc$ values ranging from 0 to 0.5 mM for all the Cr(III) complexes. Nevertheless, the output values for KAM did not show any reasonable

[1] We looked for differences between weighed and unweighted fitting, taking the weighting factor as $1/\sigma^2$, where σ is the standard for each τ_{obs} or I_{obs} and no large differences were found.

Table 1
Parameters obtained for the binding of $Cr(5Clphen)_3^{3+}$ complex to TX-100 of the titration curves of both lifetime and intensity measurements.

$Cr(5Clphen)_3^{3+}$	I, τ_A (μs)	I, τ_{ASn} (μs)	I, τ_{AM} (μs)	K_{ASn} ($M^{-n} \times 10^{-7}$)	K_{AM} ($M^{-1} \times 10^1$)	*cmc* (mM)	*n*	χ^{2a}
Intensity (I)	2310	2080	270	0.89	15.2	0.32	2	275
Lifetime (τ)	54.7	50.8	22.9	12	14.4	0.32	2	0.59

[a] For $n = 3$, 4 and 5; $\chi^2_{(Intensity)} = 530,\ 586$ and 633 and $\chi^2_{(Lifetime)} = 0.62,\ 0.68$ and 0.72 respectively.

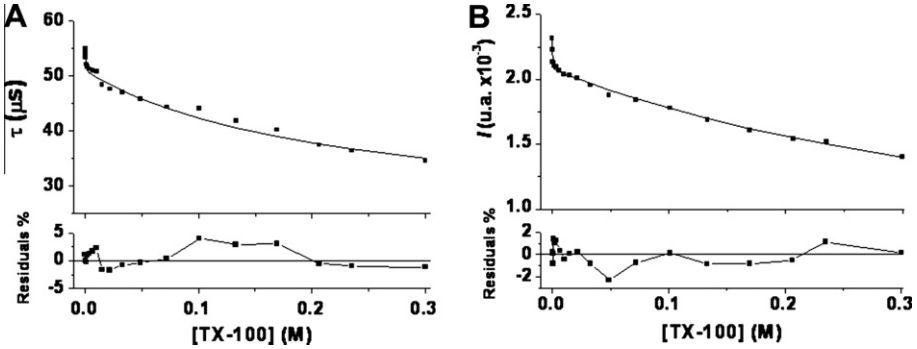

Fig. 5. Titration curves from (A) lifetime as well as (B) intensity vs. TX-100 concentration for $Cr(5Clphen)_3^{3+}$ complex in 0.1 M NaCl at pH = 2 (HCl) at 25 ± 0.5 °C. Solid lines show the best fit of the experimental data.

physical meaning and, in some cases, convergence could not be reached; then, we had to discard the use of Model II. Therefore, we applied the Model I which takes into account the interaction between the Cr(III) complexes and both surfactant monomer (premicellar aggregates) and micelles. In this model, the *cmc* is not affected by the presence of the complexes, so this model with a fixed *cmc* fits all of the experimental data and yields a physically realistic set of parameters for the different complexes, showing that the $Cr(NN)_3^{3+}$–TX-100 premicellar aggregates should be present and also that the presence of $Cr(NN)_3^{3+}$ complexes does not induce the TX-100 micelles formation. This fact contrasts with what was found for the $Ru(NN)_3^{2+}$ complexes [10] where the *icmc* values were lower than in water. This different effect on the micelle formation could be explained if we consider that the reduction in formal charge from 3^+ in the Cr(III) complexes to 2^+ in the Ru(II) complexes reduce the tendency for the salvation of the complexes by water while permitting the hydrophobic interactions with the micelle to predominate. A similar behavior was observed by Demas et al. for ruthenium and osmium complexes in TX-100 micelles [8]. The increase in this interaction is reflected in the high value of the association constants found for $Ru(NN)_3^{2+}$–TX-100 systems, which are generally ~2–3 orders of magnitude higher than those found in the present work for the same α-diimine ligand, and by decreased *icmc*'s. This example provides an illustration of the role of charge in the competitive solvation leading to probe micellization.

Once K_{AM} values were obtained, we let the program to find the best value of N (initially fixed, $N = 76$). The values found did not differ significantly from the starting value.

Table 2 summarizes all the parameters from lifetime measurement for the binding of $Cr(NN)_3^{3+}$ complexes to TX-100, showing the best unweighted fit for all the experimental data. For comparison purposes, the results for the $Cr(NN)_3^{3+}$–SDS systems obtained earlier [19] are also provided.

Demas et al. [6,9] studied the interaction of $Ru(NN)_3^{2+}$ complexes with micelles of TX-100. In all cases, they found that τ_{obs} (I_{obs}) ($\tau_A(I_A)$ and τ_{ASn} (I_{ASn}) according to Model II) remained constant at concentration below *icmc* and, above *icmc*, it started increasing once a plateau was reached. The authors postulate that there is only interaction between $Ru(NN)_3^{2+}$ complexes and the micelles at concentrations of TX-100 above *icmc* since their experimental data did not provide conclusive evidence for formation of premicellar aggregates. This behavior differs from our results. In all the $Cr(NN)_3^{3+}$–TX-100 systems, $\tau_{ASn}(I_{ASn})$ are smaller than $\tau_A(I_A)$, in agreement with what was found earlier for SDS micelles [19]. These changes suggest the formation of small aggregates at TX-100 concentrations below *cmc*. Thus, our results lead us to conclude that for $Cr(NN)_3^{3+}$–TX-100 systems, we cannot exclude the formation of premicellar aggregates, with an average number of two surfactant monomers for each metal complex.

Table 2
Parameters obtained for the binding of $Cr(NN)_3^{3+}$ complexes to TX-100. A comparison with the binding of the $Cr(NN)_3^{3+}$ to SDS.

Ligand	Purged gas	τ_A (μs)	τ_{ASn} (μs)	τ_{AM} (μs)	K_{ASn} ($M^{-n} \times 10^{-6}$)	K_{AM} (τ) ($M^{-1} \times 10^1$)	K_{AM} (I) ($M^{-1} \times 10^1$)	[b] K_{AM} (τ) ($M^{-1} \times 10^{-5}$) SDS
bpy	Air	38.9	30.0	8.0	6.8	2.3 (0.3)	3.0 (0.4)	7.6 (8.3)
bpy	N_2	43.4	31.4	10.0	1.1	3.8 (0.5)	–	–
phen	Air	63.0	30.0	13.0	32.2	12.9 (1.7)	12.9 (1.7)	2.3 (2.5)
phen	N_2	265.0	45.0	18.0	14.4	13.7 (1.8)	–	–
5Clphen	Air	54.7	50.8	22.9	1.2	14.4 (1.9)	15.2 (2.0)	27.4 (30.1)
5Clphen	N_2	292.4	186.0	49.0	3.3	15.2 (2.0)	–	–
Me_2phen	Air	44.9	43.4	31.2	127.0	18.2 (2.4)	16.7 (2.2)	–
Me_2phen	N_2	440.5	380.0	123.0	11.1	17.5 (2.3)	–	–
Me_4phen	Air	28.0	27.3	25.2	0.1	22.8 (3.0)	25.1 (3.3)	5.8 (6.4)
Me_4phen	N_2	549.3	570.0	180.1	59.3	25.7 (3.4)	–	–
Ph_2phen	Air	18.0	2.0	0.7	1.0	27.4 (3.6)	30.4 (4.0)	4.2 (4.6)

Note: In all cases, the best fit was obtained for $n = 2$, *cmc* = 0.32 mM and $N = 76$, parentheses K_{AM}/N (M^{-1}).
[b] Binding constants of $Cr(NN)_3^{3+}$ complexes to SDS, $N = 91$, parentheses K_{AM}/N ($M^{-1} \times 10^{-3}$).

Furthermore, other notable difference that have be noticed in the interaction between $Cr(NN)_3^{3+}$ and $Ru(NN)_3^{2+}$ complexes with TX-100 micelles implies that, while this interaction increases τ_{obs} and I_{obs} for $Ru(NN)_3^{2+}$ complexes, both τ_{obs} and I_{obs} of $Cr(NN)_3^{3+}$ complexes decrease abruptly with the TX-100 concentration, reaching a constant value at high surfactant concentrations. A similar behavior was observed earlier by Cañete et al. [43] for the interaction of $Cr(Ph_2phen)_3^{3+}$ complex with anionic polyelectrolytes. The authors found that the luminescence of this complex decreases in presence of aromatic hydrophobic microdomains formed by cyclohexyl, phenyl, or naphthyl as side chain groups. Consequently, the luminescent behavior of the $Cr(NN)_3^{3+}$ complexes in presence of TX-100 possibly undergoes a quenching reaction (probably related to a charge transfer process) by phenyl group of the TX-100 as a quencher.

In the $Ru(NN)_3^{2+}$–TX-100 systems, τ_{AM} was found to be larger than τ_A, and this difference was attributed to the interaction of the micelle with the ligand which produces a stabilization of MLCT energy in complexes. In our system, this type of stabilization would not occur in $Cr(NN)_3^{3+}$ complexes as the charge transfer is focused on the metal, then these changes would be explained in terms of a quenching process (see above).

The following tendency in the lifetimes $\tau_A > \tau_{ASn} > \tau_{AM}$ was observed for all $Cr(NN)_3^{3+}$ complexes (Table 2). TX-100 forms neutral micelles; hence, the association complex-micelle is likely to be attributed to hydrophobic interactions. The same complexes in the presence of SDS, an anionic surfactant, behaved, in general, according to $\tau_A > \tau_{AM} > \tau_{ASn}$. In addition, K_{AM} was markedly lower in TX-100 than in SDS, ranging from 0.2 to $3.1 \times 10^2\ M^{-1}$ for TX-100, which were four orders of magnitude smaller than in the presence of SDS, ranging from 0.7 to $3.0 \times 10^6\ M^{-1}$. This result emphasizes the relative importance of the electrostatic contribution with respect to the hydrophobic contribution in these systems, evidenced not only in the formation of premicellar aggregates but also in the difference seen in the magnitude of K_{AM}. Then, we could conclude that the association of $Cr(NN)_3^{3+}$ complexes with TX-100 is determined mainly by hydrophobic interactions, thus, expecting that, by increasing the hydrophobicity of the ligands, the hydrophobic interaction between the ligands and the hydrocarbon region of the micelles should increase. This effect should be reflected in the values of K_{AM}.

To eliminate the possible influence of variation of N with the surfactant in the comparison of the binding constant of $Cr(NN)_3^{3+}$ to TX-100 and SDS, we report in Table 2 (K_{AM}/N), the binding constant per monomer unit, which is insensitive to variations in N. Therefore, a direct comparison of the relative strength of the interactions between each surfactant and the $Cr(NN)_3^{3+}$ complexes is performed.

Examination of Table 2 shows that the value of K_{AM} (τ) for $Cr(bpy)_3^{3+}$ is lower than that for $Cr(phen)_3^{3+}$, namely, $2.3 \times 10^1\ M^{-1}$ and $12.9 \times 10^1\ M^{-1}$, respectively, a difference which agrees with the higher hydrophobicity of phen compared with the bpy ligand. This is opposite to the K_{AM} values observed for SDS where the order expected was not found. According to the discussion in a previous work [19], K_{AM} for $Cr(bpy)_3^{3+}$ complex is higher than that for $Cr(phen)_3^{3+}$ since the charge–size relation is higher for $Cr(bpy)_3^{3+}$ complex, resulting in a higher affinity constant to the micelle. The reversal of K_{AM} values for an anionic micelle confirms the importance of coulombic interactions in charged systems in relation to neutral ones. As expected, by increasing the hydrophobicity in the phen ligand from $Cr(phen)_3^{3+}$ to $Cr(Ph_2phen)_3^{3+}$ complexes by different substitutions, an increase in the respective K_{AM} constants was observed. Table 2 shows that K_{AM} values obtained for lifetime (τ) as well as for luminescence (I) are similar, and that the model can be applied to our system, regardless of the method of experimental data acquisition.

As stated above, we allow the program to find the best value of N for our system; in all the cases studied, the values of N were from 86 to 90. Streletzky and Phillies [44] found a value of N of 97 for TX-100 concentrations up to 0.32 M at 25 °C. Charlton and Doherty [45] found a value of 89 for TX-100 concentrations up to 0.2 M at this temperature. The values of N reported in these studies and in the present one agree, within the experimental error.

In addition, our results show no dependence on N with the surfactant concentration because, as stated above, the value found for N remains constant for all the range of TX-100 concentrations studied. Brown et al. [46] determined the value of N with fluorescence quenching experiments. It should be noted that they report a high dependence of N on the concentration of TX-100, but only at temperature above 25 °C, especially at concentrations much larger than those used in this analysis.

We will now consider the assumption of a rapid interchange between $^*A$ and $^*AM$. For an excited-state equilibrium to be established, the rate of escape of $^*A$ (k_{-A}) from the micelles must be at least five times faster than that of the τ_A and τ_{AM} lifetimes. Using this approach, we can estimate the forward bimolecular rate constant (k_A) using Eq. (5), and the values for K_{AM} from Table 2. For the different complexes, the k_A values range from 1.5 to $6 \times 10^7\ M^{-1}\ s^{-1}$, at least two orders of magnitude higher than those of the excited-state decay. Thus, contrary to what Demas et al. [6] proposed for ruthenium(II) complexes, a fast exchange equilibrium of the probe in the excited state cannot be ruled out.

On the other hand, it has been seen that the microviscosity of surfactants increases when the micelles increase in size and become elongated at high concentrations of surfactant [47]. Several studies have shown that the micellar growth can be due to an increase in the N and/or an increase in the micellar hydration [48,44]. It is well-known that the hydrated polyoxyethylene mantle of the TX-100 micelles is quite sensitive to the nature and concentration of electrolytes in the medium and the increasing temperature [49,44]. Zana [47] has shown that the microviscosity of ionic and non-ionic surfactants varies slightly with increasing concentration of surfactant. This behavior is expected if the probe is fully incorporated into the micelle and if the micelle does not change its size or shape. Assuming that micelles in an established range of the detergent concentration share the same shape and size, the N for various TX-100 concentrations should be the same. Our results suggest that there were no changes in the size and shape of the micelles because the value of N does not change in the range of TX-100 concentrations studied. On the other hand, in as much as in the present work, both the temperature and the concentration of electrolytes have remained constants, and no changes are expected in the hydration of oxyethylene units of the surfactant and in the microviscosity at the site of the probe under the experimental conditions employed.

There was initial concern that the use of concentrated aerated TX-100 surfactant in the determination of K_{AM} for $Cr(NN)_3^{3+}$ might produce erroneous binding constant. The viscosity of the TX-100 solutions increases markedly with the surfactant concentration, and this behavior might have led to changes in the oxygen solubility and/or mobility in the system and consequently affect the excited state quenching of $Cr(NN)_3^{3+}$ by oxygen since the latter is a diffusion controlled process. We could thus discard this hypothesis; in fact, we took the lifetime data of $Cr(Me_4phen)_3^{3+}$ complex in the presence of air-saturated solutions of TX-100 at concentrations from 0.02 to 0.3 M. For this complex, $K_{AM} = 22.8 \times 10^1\ M^{-1}$ and small changes were expected in the lifetime of the complex for TX-100 concentrations >0.02 M in the absence of an oxygen effect. The values of τ were kept constant within the experimental error (26.9 ± 0.9) μs for air-saturated TX-100 solutions from 0.02 to 0.3 M concentrations (a similar behavior was found for all $Cr(NN)_3^{3+}$ complexes). The absence of lifetime effect at high TX-

100 concentrations indicates that the microviscosity in the TX-100 micelle as sampled by the probe remains constant. Such behavior is not uncommon and has been reported previously [9]. Consequently, the oxygen solubility and mobility within the micelle are unchanged with the increase in TX-100 concentration. Indeed, the behavior shown in Fig. 4 derives from the association of the probes to micelles.

The oxygen concentration in air-saturated aqueous solutions is 2.5×10^{-4} M [50]. The oxygen solubility in the micelles of TX-100 has been reported in 1.5×10^{-3} M (for TX-100 concentrations from 0.08 to 0.24 M), in line with the value of oxygen solubility found in hydrocarbons ($\approx 2 \times 10^{-3}$ M) [51]. On the other hand, the partition coefficient for oxygen (K_P) in TX-100 was estimated in a value of $K_P = 6$ according to bibliographic data found for SDS and CTAB micellar systems [4] and consistent with the generally greater solubility of oxygen in organic solvents compared with that in water. When the concentration of oxygen is higher than that in water in the micellar phase, the decay of phosphorescence of the probe should be non-exponential with an initial fast decay arising from the rapid quenching of the probe in micelles which contains the oxygen (quencher) and a long time decay characterized by unquenched probe. In our case, we observed a single exponential decay in the presence of oxygen even at concentration of micelles up to 0.1 M. When the probe goes into a micelle containing one more quencher molecules, the quenching process is extremely rapid compared with the decay of the probe (as in static quenching), and then, the contribution from quenched probe molecule emission will be negligible and in essence a single exponential decay is observed [4].

Finally, in order to verify the influence of oxygen on phosphorescence lifetime of $Cr(NN)_3^{3+}$ complexes in the micelles, we performed experiments in N_2-purged micellar solutions. Table 2 shows the lifetime values and binding constant obtained. As stated above, if we assume, as an upper limit, that the oxygen concentration in the micelles is equal to its solubility, then, from the values of τ_A for $Cr(phen)_3^{3+}$ in N_2-purged ($\tau_{A(N_2)} = 265.0\ \mu s$) and in air-saturated ($\tau_{A(O_2)} = 63.0\ \mu s$) aqueous solutions and the value of τ_{AM} in N_2-purged ($\tau_{AM(N_2)} = 158.0\ \mu s$) and in air-saturated ($\tau_{AM(O_2)} = 13.0\ \mu s$) micellar solutions (Table 2), the quenching rate constant (k_q) of the excited state of this complex by oxygen in aqueous solutions and in inside the micelles can be estimated ($\tau_{A(N_2)}/\tau_{A(O_2)} = 1 + k_q^{aq}\,\tau_{A(N_2)}\,[O_2^{aq}]$ and $\tau_{AM(N_2)}/\tau_{AM(O_2)} = 1 + k_q^{M}\,\tau_{AM(N_2)}\,[O_2^{M}]$ respectively). We found a value of $k_q^{aq} = 4.8 \times 10^7\ M^{-1}\ s^{-1}$ for aqueous and $k_q^{M} = 4.7 \times 10^7\ M^{-1}\ s^{-1}$ for micellar solutions. These values agree quite well with those provided in the literature [50] and indicate that there is not a dependence of the oxygen concentration with increasing concentration of TX-100. The binding constants in air-saturated and N_2-purged micellar solution indicate a similar strength binding for the complexes to micelles, confirming the validity of the model used.

4. Conclusions

This work has studied the binding interactions of $Cr(NN)_3^{3+}$ complexes with non-ionic surfactant of TX-100. The results indicate that this interaction indeed causes important changes on the luminescence intensity and lifetime of the complexes. These changes suggest the hydrophobic interaction between the ligands and the hydrocarbon region of the micelles. The titration curves (either luminescence intensity or lifetime vs. TX-100 concentration) evidence, in all cases, the presence of premicellar aggregates, in contrast to what was found for $Ru(NN)_3^{2+}$ complexes [6,9]. All the parameters for the binding of $Cr(NN)_3^{3+}$ complexes to TX-100 were obtained by fitting titration curves, including a reliable estimation of the values of N under the present experimental conditions. In order to validate the magnitude of this theoretical value obtained, we measured experimentally the value of N using fluorescence steady-state quenching methods [41], which agree, within the experimental error, with the one we have found by fitting titration curves and those reported by other authors [44,45]. This facts show that the methodology used in this work can be a valuable tool for these purposes.

The micellar binding constants obtained for $Cr(NN)_3^{3+}$ complexes to TX-100 micelles were lower than those obtained previously for $Cr(NN)_3^{3+}$ complexes to SDS micelles [19], indicating that in the former, the interactions between complexes and micelles are mainly of a hydrophobic nature, whereas the latter shows the importance of the electrostatic interaction in the binding of charged complexes to anionic micelles. In agreement with data reported by other authors in TX-100 micelles [6,9,10], we found that there is a good correlation between the strength of the binding and the hydrophobic nature of the α-diimine ligands on the metal complex. This effect is reflected in the K_{AM} values obtained which, as expected, increases with the increase in the hydrophobicity of the ligand. The present study combined with our earlier results in SDS micelles provides a clearer picture of the relative importance of these interactions in the binding process. In addition, the K_{AM} values obtained in air-saturated and N_2-purged micellar solutions indicate a similar strength binding of the $Cr(NN)_3^{3+}$ complexes to TX-100 micelles, confirming the validity of the model used.

Our overall results provide an important foundation for further studies such as the use of $Cr(NN)_3^{3+}$ complexes as luminescence probes to study the distribution of different solutes to micellar systems. Among other applications mentioned in this paper, results of this study can be used in the design of luminescent probes for specific microheterogeneous environments. In a recent work [43], the authors suggest that the affinity of the chromium(III) complexes containing α-diimine ligands allow the detection of hydrophobic microdomains arising from the host–guest interaction in membranes, micelles, and amphipathic polyelectrolytes. Hence, it is hoped that our findings will stimulate further research in these areas.

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