LUMINESCENCE INTENSITY AS A PROBE OF THE INTERACTION OF TRANSITION METAL PHOTOSENSITIZERS WITH MICELLES

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Summary

Binding interactions of ruthenium(II) photosensitizers with non-ionic surfactants were studied using an emission intensity method. A quantitative model that permits evaluation of binding constants and critical micelle concentrations is given for the binding. Binding constants obtained by the intensity method agree within experimental error with results obtained by an analogous lifetime method. The intensity method uses more readily available instrumentation, is more rapid and lends itself better to weak binding systems than the lifetime method.

1. Introduction

The interactions of transition metal complexes with surfactants continue to attract attention because of their applications in various catalytic [1 - 4] and solar energy storage schemes [5 - 10]. We have studied the interactions of polypyridyl ruthenium(II) and osmium(II) complexes with various micellar systems [11 - 14] by exploiting their long-lived metal-to-ligand charge transfer (MLCT) emissions. Significant changes in the lifetime, as well as in the shape and intensity of the emission spectra, occur in the presence of surfactants. These changes reflect variations in the environment of the MLCT state owing to its interaction with the surfactant and provide a means of estimating the binding strengths.

We have recently described the interactions of a number of polypyridyl ruthenium(II) complexes with surfactants including Triton X-100 (TX-100) (octylphenoxypolyethoxyethanol ($C_8H_{17}C_6H_4(OCH_2CH_2)_xOH$, $x = 9$, 10)) [11 - 14]. Our model utilized the changes in the lifetimes of the MLCT states that occurred on binding to the micelles. A quantitative description of the binding was obtained by monitoring the emission lifetime as a function of surfactant concentration. The binding strength varied over a wide range and

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correlated well with the charge of the complexes and the nature of the ligands.

The use of lifetime measurements, however, has shortcomings. Not every laboratory is equipped for rapid measurements of the large number of short lifetimes required for a complete titration curve. Further, if the widely available pulsed UV nitrogen lasers are used, the strong surfactant fluorescence (*e.g.* that of Tritons) can interfere with data acquisition. This problem is particularly severe if the binding is weak and high surfactant concentrations must be used.

We report here the development of a method for studying binding interactions that uses emission intensity rather than lifetime measurements. We verify the technique using a number of polypyridyl ruthenium(II) complexes with the non-ionic surfactant TX-100. The ruthenium(II) complex–TX-100 system [13] was chosen for study to allow a comparison between the lifetime and intensity methods to be made. As we shall show, the intensity method provides a simple way of measuring even weak binding constants and can supply the same quantitative binding information as the τ method.

2. Experimental section

The ligands 1,10-phenanthroline (phen), 5-chloro-1,10-phenanthroline (Clphen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2phen) and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen) were used as received from G. Frederick Smith. The preparation of the ruthenium(II) complexes has been described previously [15, 16]. The complexes studied are summarized in Table 1. TX-100 was used as received from the Sigma Chemical Company.

The emission instrumentation and laser lifetime apparatus [18 - 20] have been described elsewhere. Absorption spectra were obtained using a Cary 14 spectrophotometer. All emission measurements were recorded at 25.0 ± 0.5 °C.

Binding constants (*i.e.* K_{DM}) for the interaction of the ruthenium(II) complexes with the TX-100 micelles were determined by titration in aerated solutions. We have previously shown that there are no differences between the K_{DM} values for aerated or deoxygenated solutions [17]. In a typical experiment a known volume (4 - 6 ml) of a dilute surfactant-free solution of the ruthenium(II) complex (less than 10 μM) was placed in a glass cuvette [21] in the spectrofluorometer. After thermal equilibration, the emission intensity at the uncorrected emission maximum for the micelle-bound complex was recorded. The excitation wavelength was 425 nm for $Ru(Me_4phen)_3Cl_2$ and 450 nm for the remaining complexes. This wavelength was far enough removed from the absorptions of the TX-100 and its impurities to eliminate the fluorescence background completely even at 0.5 M TX-100.

TABLE 1

Binding constants of polypyridine ruthenium(II) complexes to Triton X-100 micelles

Complex[a]	K_{DM}[b] (l mol^{-1}) (ICMC[c] (mmol l^{-1})) *from the following methods*	
	Lifetime method[d]	*Intensity method*
$Ru(Me_4phen)_3Cl_2$	102000[e] (0.83)	114600 (0.05)
$Ru(5,6\text{-}Me_2phen)_3Cl_2$	57000[e] (0.25)	53000 (0.00)
$(Me_4phen)_2Ru(phen)(ClO_4)_2$	26400 (0.00)	27900 (0.00)
$Ru(Clphen)_3(ClO_4)_2$	6400 (1.49)	5800[f] (1.90)
$Ru(phen)_3Cl_2$	—[g]	210 (0.00)

[a] All complexes were Cl^- or ClO_4^- salts. These anions do not affect the magnitude of the observed K_{DM} values [17]. The emission intensity measurements were made at the uncorrected emission maximum for the bound sensitizers. The wavelengths of maximum emission intensity were 608 nm, 612 nm, 628 nm, 610 nm and 605 nm for the complexes $Ru(Me_4phen)_3Cl_2$, $Ru(5,6\text{-}Me_2phen)_3Cl_2$, $(Me_4phen)_2Ru(phen)(ClO_4)_2$, $Ru(Clphen)_3(ClO_4)_2$ and $Ru(phen)_3Cl_2$ respectively.

[b] Equilibrium binding constant. The uncertainty is ±15%. The measurements were made in aerated H_2O solutions unless noted.

[c] Value of the critical micelle concentration of the TX-100 surfactant in the presence of the sensitizers.

[d] As described in ref. 13.

[e] Nitrogen-degassed solution (data from ref. 13).

[f] Measured in aerated D_2O solution.

[g] Insufficient change between the lifetimes of the bound and free sensitizers precludes determination of K_{DM}.

The titration was carried out by adding aliquots of a stock TX-100 solution to the surfactant-free solution; both had identical concentrations of the ruthenium(II) complex. After thorough mixing and re-equilibration the emission intensity was measured.

Data for the titrations of the various complexes consisted of emission intensity–[TX-100] data pairs. The data were fitted to the model (see below) using a non-linear least-squares simplex method [13, 22, 23]. The parameters which were fitted are described below.

3. Results and discussion

Typical intensity titrations are shown in Fig. 1 for $(Me_4phen)_2Ru(phen)^{2+}$ and $Ru(phen)_3^{2+}$ in TX-100. The emission intensity increases monotonically with [TX-100] and approaches a limiting value at high [TX-100]. This behavior is consistent with that reported earlier for similar species using the lifetime technique [13].

The changes in the emission intensity with added TX-100 shown in Fig. 1 reflect the binding of the sensitizer to the TX-100 surfactant. For our

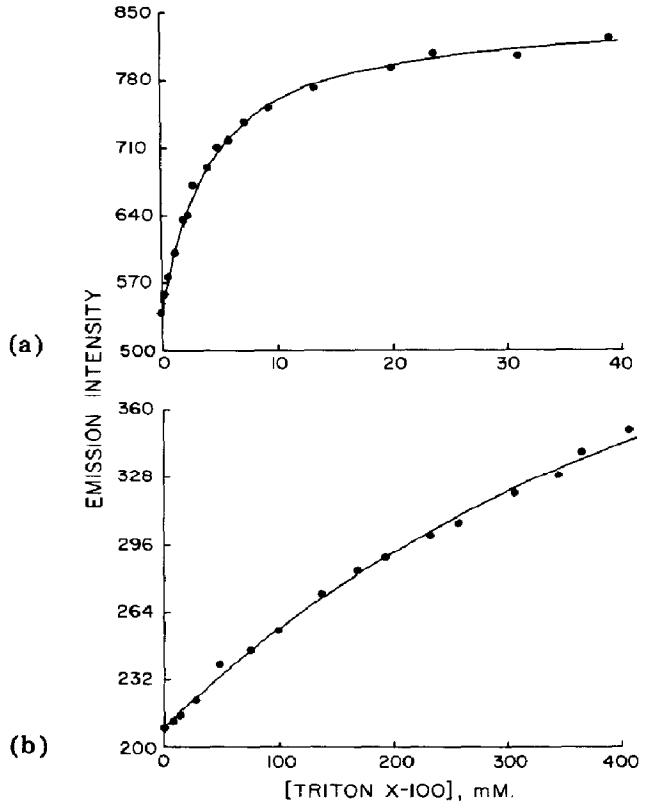
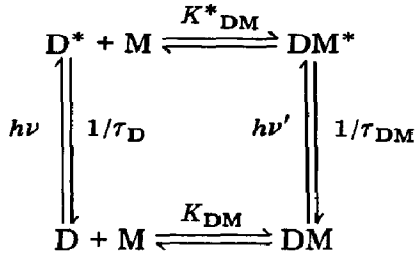


Fig. 1. Intensity titration curves in TX-100 for (a) $(Me_4phen)_2Ru(phen)(ClO_4)_2$ (I_{DM} = 857; K_{DM} = 27 900 M^{-1}; ICMC = 0.0 mM) and (b) $Ru(phen)_3(ClO_4)_2$ (I_{DM} = 574; K_{DM} = 210 M^{-1}; ICMC = 0.0 M): ——, best fit using the model of eqn. (6) (see text).

sensitizers binding to the surfactant can be described by the following simple model [13]:



D and D* are the ground state and the excited state respectively of the sensitizer and M represents the TX-100 micelle. τ_D and τ_{DM} are respectively the excited state lifetimes of the unbound and bound photosensitizer. The scheme is applicable under the following conditions and assumptions.

(i) Interactions between individual surfactant molecules and the sensitizer can be neglected.

(ii) Our methods monitor only the excited state species D* and DM*. If the establishment of the excited state equilibrium is rapid compared with the excited state lifetimes, then the measurements monitor K^*_{DM}. If the equilibrium is established too slowly then K_{DM} is obtained. The interconversion between D* and DM* in our current systems is slow compared with τ_D and τ_{DM}. Therefore we measure predominantly K_{DM}. In general, we would expect K_{DM} to be similar to K^*_{DM}, and the distinction between the two cases would vanish.

(iii) A rapid exchange of the sensitizer between the bound and unbound forms is not necessary to give our data. The model makes no distinction as to the rate of this exchange. The only requirement is that τ_D and τ_{DM} differ by less than about a factor of 2 [13]. The systems studied here all meet this requirement.

Using the model in the scheme, we define K_{DM} by

$$K_{DM} = \frac{[DM]}{[D][M]} \tag{1}$$

where [D] is the concentration of the unbound sensitizer, [DM] is the concentration of the micelle-bound sensitizer and [M] is the micelle concentration in the solution.

In describing the sensitizer–micelle interactions using the emission intensity, we proceed in a manner analogous to that for the lifetime approach:

$$I = f_D I_D + f_{DM} I_{DM} \tag{2}$$

where the f coefficients represent the fraction of each species in the solution (see below) and I is the emission intensity of the solution at a fixed monitoring wavelength. I_D and I_{DM} are the emission intensities corresponding to the free and totally micelle-bound sensitizers respectively.

In eqns. (1) and (2), f_D and f_{DM} are defined by

$$f_D = \frac{[D]}{[D] + [DM]} = \frac{1}{1 + K_{DM}[M]} \tag{3}$$

$$f_{DM} = 1 - f_D = \frac{K_{DM}[M]}{1 + K_{DM}[M]} \tag{4}$$

where eqn. (1) has been used. [M] is given by

$$[M] = \frac{[S] - \mathrm{ICMC}}{N} \tag{5}$$

where [S] is the total surfactant concentration, ICMC is the critical micelle concentration in the presence of D and N is the aggregation number. The ICMC is an induced critical micelle concentration and reflects the premature formation of micelles induced by surfactant interactions with the sensitizers. In the absence of information regarding the variation in N in the presence of sensitizer, we used the sensitizer-free value of 140 [24]. For surfactant concentrations above the ICMC, eqn. (2) taken with eqns. (3) - (5) yields

$$I = \frac{NI_D + K_{DM}GI_{DM}}{N + K_{DM}G} \tag{6a}$$

$$G = [S] - \text{ICMC} \tag{6b}$$

The I, N, [S] and I_D are known, and the K_{DM}, ICMC and I_{DM} are parameters which are fitted. Below the ICMC, I is a constant and can be equated with I_D.

It should be noted that this is a "two-site" model. The sensitizer can exist only as a free sensitizer or as a micelle-bound sensitizer. The equilibrium constant K_{DM} provides a measure of the relative amounts of these two species in the solution.

Although the scheme quantitatively fits the titration data (see below), the system is in fact more complicated. A two-component system should exhibit isosbestic points in the emission curves during the titrations, but we observe no isoemissive points. The emission spectra shift smoothly with increasing surfactant concentration suggesting a near continuum of possible structures as surfactant molecules add in a stepwise fashion to the sensitizer. Further, we cannot extract individual binding constants but must be content with an average quantity fitted over the entire titration curve.

The results of the application of eqn. (6) to the titration data for five different ruthenium(II) complexes are shown in Table 1. Values of K_{DM} and the ICMC obtained by both the lifetime and intensity methods are given for the complexes. The K_{DM} values derived from the lifetime and intensity methods agree within experimental error. Typical fits to experimental data using eqn. (6) are shown in Fig. 1. The K_{DM} values are the same in both aerated and deoxygenated solutions and are invariant to solvent deuteration. These observations are expected and are consistent with the scheme.

There are some large differences in the ICMC values determined by each method, but these are not troublesome. The ICMC parameter is determined primarily by the data in the region of low [TX-100] (less than about 1 mM). The number of data points in this region is often small (see Fig. 1). Consequently, small errors in τ or I and the [TX-100] will greatly alter the ICMC values. Without extensive data in this region, an accurate determination of the ICMC is not possible. We chose to take data at higher surfactant concentrations to maximize the accuracy of the K_{DM} values.

$Ru(phen)_3^{2+}$ demonstrates the utility of the intensity method. Using the intensity method, we find $K_{DM} = 210\ M^{-1}$ and ICMC = 0 mM. The low K_{DM} requires a large [TX-100] for appreciable binding. TX-100 fluoresces in the presence of UV light ($\lambda < 350$ nm). At high [TX-100] this fluorescence tails into the red and obscures the emission ($\lambda \approx 600$ nm) from the $Ru(phen)_3^{2+}$ complex. For this reason we were unable to determine the K_{DM} and ICMC for $Ru(phen)_3^{2+}$ using our nitrogen laser lifetime apparatus ($\lambda_{ex} = 337$ nm) [13]. The intensity method circumvents this problem by allowing visible excitation.

There was initial concern that the use of concentrated aerated TX-100 surfactant in the determination of K_{DM} for $Ru(phen)_3^{2+}$ might produce

erroneous binding constants. The viscosity of the TX-100 solutions increases markedly with [TX-100]. This behavior might have led to a decreased solubility or mobility of oxygen in the system as [TX-100] was increased. The possibility then existed that the behavior shown in Fig. 1 for $Ru(phen)_3^{2+}$ was not due to the binding of the sensitizer to the micelle but was the result of decreased oxygen quenching of the excited state emission in the presence of the TX-100.

We were able to discount this hypothesis. Measurements of the lifetime of the $Ru(5,6\text{-}Me_2phen)_3^{2+}$ complex were made in the presence of aerated TX-100 solutions of concentrations 50, 100 and 500 mM. For this complex $K_{DM} = 57\,000\ M^{-1}$ and little change is expected in the lifetime of the complex for [TX-100] > 50 mM in the absence of an oxygen effect. The values of τ are 2.85 μs, 2.93 μs and 2.89 μs for aerated TX-100 solutions at the 50 mM, 100 mM and 500 mM concentrations respectively. The absence of a lifetime effect at high [TX-100] indicates that, although the macroscopic viscosity of the solution may change, the microscopic viscosity in the TX-100 micelle as sampled by the sensitizer remains constant. Such behavior is not uncommon and has been reported previously in the study of polymer solutions [25]. Consequently, the oxygen solubility and mobility within the micelle is unchanged for [TX-100] = 0 - 500 mM and the behavior shown in Fig. 1 is indeed due to binding.

In conclusion, we have presented a method for determining the equilibrium constants for the interaction of the TX-100 surfactant with several polypyridyl ruthenium(II) complexes using the emission intensity of the solution. The binding constants obtained are in good agreement with those determined earlier [13] using a method based on a more cumbersome lifetime technique. A comparison of the two methods indicates that the intensity method offers advantages over the lifetime method with respect to cost and availability of the necessary instrumentation as well as the range of binding constants which can be investigated.

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