

Dynamics of the Quenching of Pyrene Fluorescence by the Thiosulfate Ion in Cationic Micelles

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Utilizaram-se medidas de decaimento de fluorescência de pireno para estudar a dinâmica de supressão intramicelar e de saída do contraíon tiosulfato ($S_2O_3^{2-}$) de micelas de cloreto de hexadeciltrimetilamônio (CTACl) sobre uma ampla faixa de concentração de CTACl e sal (NaCl). Obteve-se um valor de $k_q = 9 (\pm 2) 10^6 s^{-1}$ para a constante de velocidade de supressão intramolecular do estado singlete excitado do pireno numa micela contendo um único íon $S_2O_3^{2-}$ supressor, independente de [CTACl] ou [NaCl]. A constante de velocidade k_e para a saída do contraíon $S_2O_3^{2-}$ da micela depende do potencial elétrico da micela de CTACl, sendo que a barreira energética para a saída é da ordem da metade do trabalho eletrostático para transferência completa de um íon tiosulfato da superfície da micela até a fase aquosa.

Time resolved fluorescence decay measurements with pyrene as probe have been employed to study the dynamics of intramicellar quenching and exit of the thiosulfate counterion ($S_2O_3^{2-}$) from micelles of hexadecyltrimethylammonium chloride (CTACl) over a wide range of concentration of CTACl and added common counterion salt (NaCl). The rate constant k_q for intramicellar quenching of an excited pyrene in a micelle containing a single $S_2O_3^{2-}$ quencher counterion is $9 (\pm 2) 10^6 s^{-1}$, independent of either [CTACl] or [NaCl]. The rate constant k_e for micellar exit of $S_2O_3^{2-}$ is governed by the micellar surface potential, the effective free energy barrier for escape of $S_2O_3^{2-}$ from the CTACl micelle being equivalent to about half of the overall electrostatic work for complete transfer of the thiosulfate ion from the micelle surface to the aqueous phase.

Keywords: micelle, fluorescence, counterion exchange, quenching

Introduction

Much of the basis for our current qualitative and quantitative understanding of the origin of micellar effects on the rates of bimolecular reactions has come from studies of counterion binding and exchange at the surface of ionic micelles¹. Photophysical techniques^{2,3} have played a prominent role in many of these studies of counterion binding. Thus, steady-state fluorescence measurements of the quenching of micelle-solubilized aromatic hydrocarbons by counterions can be used to determine selectivity coefficients for monovalent-monovalent, monovalent-divalent and divalent-divalent counterion exchange⁴⁻⁷. In previous work⁵, a selectivity coefficient of 1.3 ± 0.3 was determined for thiosulfate/chloride counterion exchange from the quenching of pyrene fluorescence by the thiosulfate ion ($S_2O_3^{2-}$) in micellar hexadecyltrimethylammonium

chloride (CTACl). In the present work, we have employed time resolved fluorescence decay measurements to examine the dynamics of intramicellar quenching and exit of $S_2O_3^{2-}$ from CTACl micelles over a wide range of concentration of CTACl and added common counterion salt (NaCl). The rate constants for micellar exit of $S_2O_3^{2-}$ are governed by the micellar surface potential.

Materials and Methods

Materials

Pyrene (Aldrich) was purified by the method of Geiger and Turro⁸. CTACl was prepared from the corresponding bromide (CTAB, Aldrich) by the xanthate counterion exchange technique of Sepúlveda⁹ and purified by recrystallization from acetone. Sodium thiosulfate (Merck, p.a.) was used as received. All solutions were prepared in ultrapure (Millipore Milli-Q) water.

Methods

All experiments were performed at 30 °C. Pyrene ($5\text{--}8 \times 10^{-6}$ M) was added to air-equilibrated aqueous micellar solutions of CTACl (0.010–0.080 M) containing NaCl (0–0.080 M) and sodium thiosulfate (0.1–2 mM, depending on [NaCl] and [CTACl]). Fluorescence decay curves of pyrene (Fig. 1) in these solutions were collected by the single photon counting technique^{10,11} using an Edinburgh Instruments Model FL-900 Lifetime Spectrometer (H₂ lamp, 337 nm excitation; 390 nm emission) at an appropriate total added quencher concentration, [S₂O₃²⁻]_T. Fluorescence decay curves of pyrene in the absence of quencher were analyzed utilizing the standard single exponential decay routines of the FL-900 operating software. The corresponding decay curves in the presence of quencher were fit using the micelle quenching module of Edinburgh Analytical Instruments Level2 analysis software (Version 1.60).

An average micellar aggregation number of $N = 100$ and an apparent degree of micellar dissociation of $\alpha = 0.25$ were assumed^{12,13} in all calculations; critical micelle concentrations (cmc) of CTACl were estimated from the transcendental equation^{5,12}: $\log \text{cmc} = -5.00 - 0.75 \log (\text{cmc} + [\text{NaCl}])$.

Results

Analysis of the fluorescence decay of a completely micelle-solubilized probe such as pyrene in the presence of a suitable mobile quencher provides information on the dynamics of the intramicellar quenching process and of the micellar entry and exit of the quencher^{2,3,13,14}. Pyrene fluorescence decay curves in micellar CTACl in the presence of added S₂O₃²⁻ (Fig. 1) were analysed in terms of the Infelta-Tachiya Eq.^{2,3,13,14}:

$$F(t) = A_1 \exp[-A_2 t - A_3 \{1 - \exp(-A_4 t)\}]$$

where the parameters A_1 – A_4 represent the quantities:

$$A_1 = F(0)$$

$$A_2 = 1/\tau^0 + k \cdot \langle n \rangle k_q / (k_q + k)$$

$$A_3 = \langle n \rangle [k_q / (k_q + k)]$$

$$A_4 = k_q + k$$

In these equations, $F(0)$ is the initial pyrene fluorescence intensity, τ^0 is the pyrene fluorescence lifetime in the absence of S₂O₃²⁻ (170 ns in air-equilibrated CTACl, independent of detergent concentration or added NaCl), k is the unimolecular rate constant for exit of S₂O₃²⁻ from the CTACl micelle, k_q is the pseudo-unimolecular rate constant for intramicellar quenching of excited pyrene by a single S₂O₃²⁻ ion and $\langle n \rangle$ is the average number of bound

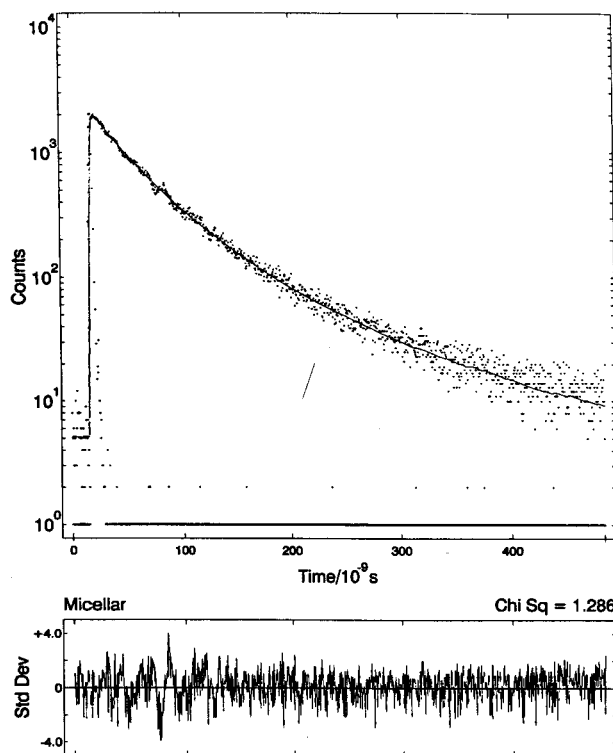


Figure 1. Typical experimental fluorescence decay curve of pyrene in micellar CTACl in the presence of added NaCl and Na₂S₂O₃ and the corresponding fit the Infelta-Tachiya equation.

S₂O₃²⁻ per micelle. The values of A_2 – A_4 and τ^0 were then employed in the set of equations:

$$k_q = A_3(A_4)^2 / [A_2 - 1/\tau^0 + A_3 A_4]$$

$$k = A_4 - k_q$$

$$\langle n \rangle = A_3(A_4)^2 / k_q^2$$

to obtain the rate constants k_q and k , and the corresponding value of $\langle n \rangle$ (Table 1).

One can in principle⁶ calculate the bimolecular rate constant k_+ for entry of S₂O₃²⁻ into the CTACl micelle from the equation:

$$k_+ = k \cdot \langle n \rangle / ([S_2O_3^{2-}]_T - \langle n \rangle [M])$$

where $[M] = C_D/N$ is the concentration of micelles, equal to the concentration of micellized detergent ($C_D = [\text{CTACl}]_T - \text{cmc}$) divided by the micellar aggregation number N . The k_+ values are in the range of 10^{10} – 10^{11} M⁻¹ s⁻¹, but precise values could not be obtained from the data since $\langle n \rangle \cdot [M]$ and $[S_2O_3^{2-}]_T$ are similar in magnitude.

Discussion

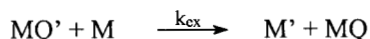
The rate constant k_q for intramicellar quenching of an excited pyrene in a micelle containing a single S₂O₃²⁻ quencher counterion is $9 (\pm 2) \times 10^6$ s⁻¹, independent of

Table 1. Fluorescence decay parameters and derived rate constants for the quenching of pyrene fluorescence by the thiosulfate ion in micellar solutions of CTACl.

[CTACl] M x 10 ³	[NaCl] M x 10 ³	[S ₂ O ₃ ²⁻] M x 10 ⁴	1/A ₂ ns	A ₃	1/A ₄ ns	k _q s ⁻¹ x 10 ⁻⁶	k ₋ s ⁻¹ x 10 ⁻⁶	<n>
10	0	2.0	152.6	1.939	104.8	9.2	0.3	2.08
40	0	5.0	143.7	0.798	90.4	9.9	1.2	1.00
40	0	10.0	127.8	1.747	101.5	8.9	1.0	2.16
40	0	14.9	113.9	2.777	108.0	8.3	0.9	3.44
80	0	10.0	130.3	0.712	86.5	9.5	2.1	1.06
80	0	19.9	95.6	1.212	79.1	9.7	2.9	2.04
80	0	29.8	74.9	1.841	85.8	8.6	3.0	3.35
20	10	3.0	133.2	0.895	99.6	8.5	1.5	1.25
20	10	5.9	102.8	1.484	93.8	8.6	2.1	2.29
20	10	8.9	78.0	1.877	84.3	9.0	2.8	3.23
40	10	5.0	138.4	0.767	94.1	9.1	1.5	1.04
40	10	9.9	109.2	1.453	96.6	8.5	1.9	2.15
40	10	14.8	85.4	1.997	94.8	8.3	2.3	3.25
80	10	4.9	148.7	0.334	78.7	10.6	2.1	0.48
80	10	9.7	128.2	0.642	94.7	8.2	2.3	1.06
80	10	14.5	113.0	0.991	99.0	7.8	2.3	1.67
20	20	3.0	127.0	0.926	93.3	8.9	1.8	1.34
20	20	6.0	99.2	1.801	99.2	8.2	1.9	2.73
20	20	9.0	80.9	2.701	104.2	7.7	1.9	4.22
40	20	5.0	121.5	0.536	72.7	10.4	3.3	0.93
40	20	9.9	89.8	0.872	74.4	9.3	4.2	1.83
40	20	14.8	72.2	1.234	72.5	9.4	4.4	2.66
80	20	6.3	130.9	0.320	65.0	11.3	4.0	0.59
80	20	10.8	110.7	0.534	74.8	9.3	4.1	1.11
10	40	1.0	136.7	0.358	81.2	9.3	3.0	0.63
10	40	2.0	115.2	0.747	98.0	7.5	2.7	1.40
10	40	3.0	94.4	0.981	92.1	7.5	3.3	2.04
20	40	3.0	116.0	0.524	82.9	8.4	3.6	1.08
20	40	5.0	96.2	0.928	98.0	6.9	3.3	2.02
39	40	7.0	94.3	0.484	57.5	11.1	6.2	1.18
39	40	13.9	63.6	0.911	61.9	9.7	6.5	2.54
39	40	20.7	47.1	1.307	64.0	8.9	6.7	4.01
80	40	9.9	104.3	0.290	54.6	10.8	7.5	0.84
80	40	14.8	87.7	0.350	51.1	10.8	8.7	1.14
10	80	1.0	142.1	0.164	63.6	10.9	4.9	0.34
10	80	2.0	119.9	0.249	71.5	8.2	5.8	0.72
10	80	3.0	100.5	0.274	56.4	9.7	8.1	0.92
20	80	4.0	101.3	0.261	58.3	9.1	8.1	0.93
20	80	6.0	83.3	0.330	52.0	9.8	9.4	1.27
39	80	5.9	103.2	0.204	46.0	11.7	10.0	0.70
39	80	8.9	85.8	0.297	56.2	8.5	9.3	1.30
79	80	8.0	108.7	0.135	50.1	9.0	11.0	0.67
79	80	24.7	58.6	0.416	51.7	8.1	11.2	2.37

either [CTACl] or [NaCl] (Table 1). This is within experimental error of the value of $8 \times 10^6 \text{ s}^{-1}$ that can be calculated from the earlier steady-state fluorescence measurements⁵. In contrast to the constancy of k_q , there is a clear increase in k for exit of $\text{S}_2\text{O}_3^{2-}$ from the CTACl micelle with increasing [NaCl].

Several groups have reported that k values for counterionic quenchers increase with increasing detergent concentration¹³⁻¹⁷. This increase was initially attributed to an additional exchange process involving a direct intermicellar transfer of the counterion of the type¹⁴:



The experimental rate constant for micellar exit (k) would then be the sum of an intrinsic rate constant for micellar exit (k') and the rate of intermicellar exchange ($k_{\text{ex}}[\text{M}]$):

$$k = k' + k_{\text{ex}}[\text{M}]$$

and k' and k_{ex} could be determined from the dependence of k on $[\text{M}]$. Subsequent studies suggested, however, that the dependence of k on $[\text{M}]$ is electrostatic in origin^{13,14,16,17}. The data of Table 1 show that, in addition to a modest dependence on the detergent concentration, the experimental values of k for micellar exit of $\text{S}_2\text{O}_3^{2-}$ are strongly dependent on [NaCl]. This dependence on [NaCl] cannot be readily explained on the basis of an intermicellar exchange process alone, pointing to an electrostatic origin for both dependences.

Since the cationic CTACl micelle and the counterion $\text{S}_2\text{O}_3^{2-}$ are oppositely charged, the rate constant for exit of the latter from the micelle must depend on the counterion charge and the magnitude of the micellar surface potential (Ψ^0)¹²:

$$k = k^0 \exp[-2\beta F\Psi^0/RT]$$

where F is the Faraday and R the ideal gas constant. The magnitude of the pre-exponential term k^0 is determined by the chemical part of the free energy barrier, while β represents the fraction of the electrostatic work of attraction that must be overcome in order for $\text{S}_2\text{O}_3^{2-}$ to escape from the micelle¹⁸.

The micellar surface potential (Ψ^0) is logarithmically related to the free counterion concentration ($[\text{Cl}^-_{\text{aq}}]$) in the intermicellar aqueous phase¹⁹:

$$F\Psi^0/2.303RT = K - \log[\text{Cl}^-_{\text{aq}}]$$

Consequently, $\log k$ should be a linear function of $\log [\text{Cl}^-_{\text{aq}}]$, with a slope equal to 2β :

$$\log k = K' + 2\beta \log[\text{Cl}^-_{\text{aq}}]$$

Indeed, as shown in Fig. 2, $\log k$ correlates linearly with values of $\log [\text{Cl}^-_{\text{aq}}]$, the latter calculated in straightforward fashion from the conventional pseudophase ion exchange relationship^{1,19,20}:

$$[\text{Cl}^-_{\text{aq}}] = \alpha C_D + \text{cmc} + [\text{NaCl}]$$

The slope of the best-fit regression line in Fig. 2 provides a value of $2\beta = 0.92 \pm 0.06$.

The present results demonstrate that salt effects on the quenching of pyrene fluorescence by the thiosulfate ion in aqueous micellar solutions of CTACl are due to an electrostatic effect on the rate constant for exit of $\text{S}_2\text{O}_3^{2-}$ from the micelle. The experimental value of $\beta = 0.46$ implies that the electrical contribution to the free energy barrier for escape of $\text{S}_2\text{O}_3^{2-}$ from the CTACl micelle is equivalent to about half of the overall electrostatic work for complete transfer of the thiosulfate ion from the micelle surface to the aqueous phase.

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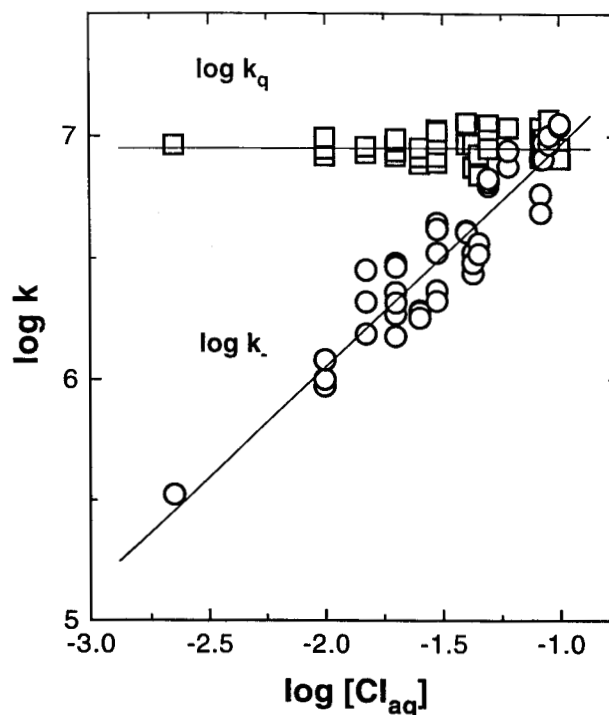


Figure 2. Correlation of $\log k_q$ for intramicellar quenching and $\log k$ for micellar exit of the thiosulfate ion with $\log [\text{Cl}^-_{\text{aq}}]$ in micellar CTACl.

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