

Perturbation of Polyelectrolyte–Surfactant Binding by Cationic Quenchers and Its Effects on Fluorescence Quenching Determinations of Aggregation Numbers

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Cationic alkylpyridinium halide surfactants have been used as quenchers of pyrene fluorescence in polyelectrolyte–surfactant systems such as sodium polyacrylate–alkyltrimethylammonium halide. We use ideal mixing theory to demonstrate that for quencher molecules more strongly bound than the surfactant, the mole fraction of quencher in the micelles may be significantly greater than the mole fraction in the bulk mixture. As well, the mixed surfactant system has a lower critical aggregation concentration and a higher degree of binding than the pure surfactant system. These effects should be considered both when planning experiments and when calculating aggregation numbers. In cases of significant perturbations, the use of pyrene excimer quenching or neutral quenchers may be preferable.

Introduction

Time-resolved fluorescence quenching (TRFQ) has been widely applied to measure surfactant aggregation numbers in polymer–surfactant systems.^{1,2} Cationic surfactant–anionic polyelectrolyte systems present experimental difficulties: the critical aggregation concentration (cac) can be quite small, and one must work at low polymer and surfactant concentrations and low binding ratios to avoid precipitation of neutral complexes. An important contribution to solving such problems has been presented in a series of papers.^{3–9} Cationic alkylpyridinium surfactants were used to quench pyrene fluorescence, generally using a quencher Q of the same alkyl chain length as the surfactant S. Quantification of the amount of bound quencher, crucial to the determination of aggregation number, was handled by assuming identical micelle–water distribution of quencher and surfactant of similar critical micelle concentration (cmc).⁴ Ideal mixing theory¹⁰ was used to demonstrate that the mole fraction of quencher bound in the micelles X_q could be approximated by the mole fraction of quencher in the bulk mixture α_q when most of the surfactant is in the bound state.⁵ For quenchers of longer chain length than the surfactant, 100% binding of the quencher has been assumed.⁵ Publications from the same group^{11,12} have discussed the effects of nonideal micellar mixing (applying a Bragg–Williams type description to the micellar mixture) of surfactant and surfactant quencher in TRFQ aggregation number determinations in the absence of polymers.

In this paper we will show that for the case of polymer–surfactant systems using a surfactant as quencher, such that the system surfactant + quencher represents a mixed micelle system in the presence of polyelectrolyte, the effect of the mixed surfactant on the critical aggregation concentration (cac) and binding isotherm of the system also needs to be taken into account. Such effects have recently been reported in the binding of mixtures of decylammonium chloride (DeAC) and tetra-

TABLE 1: Surfactant cmc and cac Values at 30 °C

surfactant	DTAB	DPC	TTAB	TPB	CPC
cmc (mM) ^a	14.7	16.5	3.6	3.3	0.9 ^c
cac (μm) ^b	333	186	48	26	3 ^d

^a From ref 16, in the absence of electrolyte. ^b From refs 14 and 15, for binding to 0.5 mM NaPA in 10 mM NaCl. ^c 25 °C. ^d Estimated.

decylpyridinium chloride (TPC) to sodium poly(L-glutamate).¹³ The substantial decrease in the cac with addition of TPC, and a synergistic decrease above the cac in the free concentration of mixed surfactant at low degrees of binding β , were well predicted by ideal mixing theory. The amount of DeAC bound increased in the presence of TPC, which suggests that predictions of the amount of surfactant and quencher bound based solely on the surfactant binding isotherm in the absence of quencher may be substantially in error. Our calculations will show that these effects are largest for systems at lower degrees of binding, at higher levels of quencher loading, and with a quencher of longer chain length than the surfactant. These calculations still use the simplest ideal mixing model for the polymer-bound micelle consisting of bound surfactant and surfactant quencher.

Results and Discussion

To demonstrate these effects, we present ideal mixing theory calculations of the mole fraction of quencher in the mixed micelles $X_q = [Q]_b/[C]_b$, mixed surfactant binding ratio $\beta' = [C]_b/[P]$, and mixed surfactant cac $[C]_{cac}$ for several quenchers added at fixed bulk ratio $\alpha_q = [Q]_t/[C]_t$ to complexes of dodecyltrimethylammonium bromide (DTAB) with sodium polyacrylate (NaPA). The subscript t indicates the total concentration of the species in the sample, b indicates species bound to the polymer, [P] is the concentration of polymer charge sites, and C denotes the mixed surfactant system S + Q. The cac values (the bulk concentration of surfactant at the onset of cooperative binding) in Table 1 are derived from published binding isotherms of DTAB,¹⁴ tetradecyltrimethylammonium bromide (TTAB),¹² dodecylpyridinium chloride (DPC),¹⁵ and tetradecylpyridinium bromide (TPB)¹³ to 0.5 mM NaPA in the presence of 10 mM NaCl. The value for cetylpyridinium chloride

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(CPC) is estimated on the basis of those for DPC and TPB. Note that the cac values of the alkylpyridinium surfactants are nearly half those of the corresponding alkyltrimethylammonium surfactants, even though their cmc values¹⁶ are nearly identical. Thus a quencher binds to the polymer in preference to a surfactant of equal chain length, and we expect $X_q > \alpha_q$.

Ideal mixing theory gives the mole fraction of quencher in mixed micelles by the following quadratic equation,⁵ which is algebraically simpler than but identical to the quadratic equation in free quencher concentration $[Q]_f$ given by Clint¹⁰

$$DX_q^2 + EX_q - [Q]_t = 0 \quad (1)$$

where $D = [S]_{\text{cmc}} - [Q]_{\text{cmc}}$, the difference between the cmc values of the two components, and $[Q]_t$ is the total quencher concentration. The total concentration of mixed surfactant in the system is denoted $[C]_t = [Q]_t + [S]_t$, and $E = [C]_t - D$. In applying this theory to micelle formation in the field of a polyelectrolyte, Hansson and Almgren arrived at the same result except that in such a system

$$D = ([S]_f^* + [S]_c^*) - ([Q]_f^* + [Q]_c^*) \quad (2)$$

where the subscripts f and c refer to concentrations of components free in solution and condensed on the polyelectrolyte, and the asterisks denote values at the same binding ratio in the absence of the other surfactant.⁵ This is only equivalent to the difference between the cac values of the two components when the system is actually at the cac. When the condensed concentrations are small, they may be neglected and the difference between the free concentrations may be used. The free concentrations of the two components in the mixed system are given by $[Q]_f = X_q[Q]_t^*$ and $[S]_f = (1 - X_q)[S]_t^*$, from which the bound concentrations, and thus the percentage of the total added quencher present in the bound state % Q_b and the binding ratio of mixed surfactant β' , may be determined. Ideal mixing theory also predicts that the cac of the mixed surfactant will be intermediate between those of the two components, according to the relation^{10,11}

$$\frac{1}{[C]_{\text{cac}}} = \frac{\alpha_q}{[Q]_{\text{cac}}} + \frac{1 - \alpha_q}{[S]_{\text{cac}}} \quad (3)$$

The average number of quenchers per micelle $\langle Q \rangle$ measured by TRFQ is multiplied by the ratio of bound surfactant to bound quencher to calculate the aggregation number N_s

$$N = \langle Q \rangle \frac{[S]_b}{[Q]_b} \quad (4)$$

When using a surface active quencher, this ratio can be replaced by the inverse of the mole fraction of quencher in the mixed micelle $1/X_q$, such that the result is the total aggregation number of quencher and surfactant.⁵ It has been shown that for surfactant and quencher of the same chain length, X_q may be substituted by α_q when the percentage of surfactant-bound % S_b is high.⁵

For the calculations presented in Table 2, we have fixed the total mixed surfactant concentration $[C]_t$ at the value of $[S]_t^*$, where $\beta = 0.2$ or 0.5 , and then varied the bulk mole fraction and chain length of quencher. For DPC, the quencher of the same chain length as the surfactant, the binding ratio and cac of the mixed system change only slightly, but X_q is substantially higher than α_q . The discrepancy decreases with increasing binding ratio, but since % S_b is only 41% at $\beta = 0.5$, the condition that most of the surfactant must be bound is not met,

TABLE 2: Ideal Mixing Theory Calculations of the Effects of Quenchers on the Interactions of DTAB with 0.5 mM NaPA in 10 mM NaCl

quencher	β	$[C]_t$ (μM)	α_q	X_q	% Q_b	β'	$[C]_{\text{cac}}$ (μM)
DPC	0.2	447	0.0050	0.0081	37	0.203	332
DPC	0.2	447	0.0100	0.0162	37	0.206	330
DPC	0.2	447	0.0300	0.0486	38	0.217	325
DPC	0.5	620	0.0050	0.0068	55	0.502	332
DPC	0.5	620	0.0100	0.0137	55	0.505	330
DPC	0.5	620	0.0300	0.0416	56	0.514	325
TPB	0.2	447	0.0050	0.0179	84	0.212	314
TPB	0.2	447	0.0100	0.0344	85	0.222	298
TPB	0.2	447	0.0300	0.0921	87	0.260	246
TPB	0.5	620	0.0050	0.0113	92	0.508	314
TPB	0.5	620	0.0100	0.0225	92	0.516	298
TPB	0.5	620	0.0300	0.0653	93	0.546	246
CPC	0.2	447	0.0050	0.0204	97	0.214	215
CPC	0.2	447	0.0100	0.0388	97	0.227	159
CPC	0.2	447	0.0300	0.1005	98	0.269	77
CPC	0.5	620	0.0050	0.0121	99	0.509	215
CPC	0.5	620	0.0100	0.0239	99	0.518	159
CPC	0.5	620	0.0300	0.0689	99	0.551	77

and α_q should not be used in place of X_q . As the DTAB–NaPA complex tends to phase separate above a polymer concentration of about 1 mM,¹⁷ only 3 times the free surfactant concentration, this condition is probably not achievable in this system.

For quenchers of longer chain length than the surfactant, X_q is 2–3 times higher than α_q , as expected. More dramatic still is the lowering of the cac with increasing quencher mole fraction. The results for % Q_b confirm that practically 100% of the quencher is micellized, and substitution of $[Q]_t$ for $[Q]_b$ in eq 4 should yield reasonable aggregation numbers. However, as the quencher loading in micelles will be much higher than the bulk ratio of quencher to surfactant would suggest, one must be careful when preparing samples not to overload the micelles with too many quenchers. The results also show that the degree of binding of the mixed surfactant β' increases with the quencher loading, more so at lower binding ratios. Thus when measurements are made over a range of quencher concentrations, as is necessary to check for micelle polydispersity or mobility of quencher, the samples are not at precisely the same binding ratio and may not have the same true mean aggregation number or size distribution. It would be useful to measure binding isotherms at these low levels of added quencher to verify the amounts of surfactant and quencher bound.

We therefore call attention to the need for a careful assessment of the effects of these perturbations when preparing samples for TRFQ measurements. In free micelle systems where measurements are performed well above the cmc, D is relatively small and eq 1 can be reduced to $X_q = \alpha_q$. This limit is achieved in a polyelectrolyte–surfactant system only when the cac value is relatively low compared to the amount of surfactant bound, such as the sodium poly(vinyl sulfate) and dextran sulfate systems,⁶ the cetyltrimethylammonium bromide/CPC/poly-(acrylic acid) system,⁸ and also the NaPA gel system.⁹ In a study of the DTAB–sodium carboxymethylcellulose system,⁷ which has a relatively high cac, the increase of X_q over α_q was clearly noted and X_q values were used to calculate aggregation numbers. However, in the DTAB–NaPA system,^{4,5} the limit does not appear to be reached, and the use of α_q in the calculation should overestimate N_s .

Conclusions

We find that the use of a cationic quencher of the same chain length as the surfactant requires attention to the preferential

binding of the quencher relative to the surfactant, while a more hydrophobic quencher, though 100% bound, greatly perturbs the binding isotherm. Although there has been concern that the solubility of aromatic compounds in polyelectrolyte-surfactant complexes may be somewhat reduced by the interaction of the hydrophobic portions of the polymer with the micelle surface,⁵ there are conditions where the use of pyrene excimer quenching or a strongly hydrophobic neutral quencher molecule may be preferable to the binding perturbations caused by charged quenchers in these systems. We have successfully used excimer quenching to measure aggregation numbers in mixtures of DTAB with NaPA (53 ± 3 at $\beta = 0.22$, 66 ± 9 at $\beta = 0.38$, in the absence of salt) and with acrylamide-sodium acrylate copolymers, as will be discussed in more detail in a later publication.

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