Determination of Micellar Aggregation Numbers in Dilute Surfactant Systems with the Fluorescence Quenching Method.

Per Hansson,*,† Bengt Jönsson,‡ Cecilia Ström,‡ and Olle Söderman‡

Department of Physical Chemistry, Uppsala University, Box 532, S-751 21 Uppsala, Sweden and Department of Physical Chemistry, Center for Chemistry and Chemical Engineering, Lund University, P. O. Box 124, S-221 00 Lund, Sweden

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This work addresses the problem of determining micellar aggregation numbers for dilute ionic surfactant systems by means of the time-resolved fluorescence quenching method. We argue that the use of quenchers that are themselves surfactants gives us two advantages. First, the altering of the micelles caused by the solubilization of quencher molecules is minimized. Second, the distribution of the quencher between the micelles and the aqueous subphase can be obtained. The latter point is particularly important for the case of dilute micellar systems and when the micelles are adsorbed at interfaces or associated with polymers. We describe a method to obtain the partitioning of the quencher for various surfactant/quencher combinations. The method is based on a detailed thermodynamic model of mixed micelles supported by Poisson−Boltzmann cell model calculations. It is shown that ideal mixing of surfactant and quencher in the micelles simplifies the analysis of effects related to polydispersity and probe distribution among the micelles. The method is applied to quaternary ammonium surfactants, both mono- and divalent, with various chain lengths, using the corresponding alkyl pyridinium ions as quenchers. Aggregation numbers at concentrations close to the critical micelle concentration (cmc) are presented and discussed.

Introduction

The propensity of surfactants to self-aggregate into micelles in solvents is perhaps the most fascinating aspect of these molecules, and micelles remain one of the central topics of study within surface and colloid chemistry. Important characteristics of micelles are the concentration where they are formed, i.e., the critical micelle concentration (cmc), kinetic features such as the micellar lifetime, and their aggregation numbers (N).[1] The most frequently applied methods to determine N are various scattering methods and the fluorescence quenching (FQ) technique. The two techniques are based on different principles but provide complementary information. While scattering methods have the advantage of giving essentially model-free estimates of the molecular weight or radius, from which N can be obtained, the FQ approach relies on models in the interpretation of the data.

An advantage with the FQ method is that N can be obtained also when the micelles interact with, for instance, interfaces[2−4] or polymers in solution.[5−8] This is because the method does not rely on diffusive properties, concentration fluctuations, etc. On the other hand, an obvious drawback is the necessity of adding a fluorescent probe and a quencher to the system. With FQ, as with all "invasive" methods, the effect of these molecules on the system under study must be kept at a minimum. In the present paper we shall deal with the choice of quencher. A major goal is to find a method that can be used to determine the aggregation numbers of ionic surfactants adsorbed at interfaces between solids and water. This is an important problem where FQ is particularly useful,[2,3] since conventional techniques fail to give this information.

There are several efficient quenchers available. However, as these are present at rather high concentrations (typically 1 per 100 surfactant molecules) the choice is important in order not to introduce artifacts. Another important aspect is that the partitioning of the quencher between the micelles and the surrounding solution must be known with sufficient accuracy. For concentrated micellar solutions the free concentration of quencher can often be neglected, even when the quencher is rather hydrophilic.[9,10] However, in dilute solutions a substantial amount may be in the aqueous subphase. Furthermore, to determine the partitioning of the quencher has turned out to be difficult.

Recently, the advantage of using quenchers with properties similar to the surfactant of interest has been recognized.[11] Clearly, the ideal quencher would be identical to the surfactant under study. This is of course not realizable in practice. However, for the commonly used alkyltrimethylammonium bromides (C_nTAB) the corresponding alkylpyridinium bromides (C_nPB) are good candidates. A comparison shows that, for homologues of the two surfactants, the cmc values are of the same order of magnitude and the concentration dependence of the aggregation number is similar. Furthermore, they have been found to mix almost ideally in the micelles.[12] Recently, C_{12}PB was used as quencher in C_{12}TAB micelles formed in complexes with oppositely charged polyelectrolytes.[11−15] As inferred from the above, there are several advantages with this choice of quencher. First, artifacts are reduced to a minimum as the quencher has properties similar to the surfactant under study. Second, the ideal mixing in the micelles ensures a random distribution of the quencher among the micelles, which simplifies the analysis of FQ data.[16−18] Third, the distribution of the quencher (and the surfactant) between the micelles and the aqueous subphase, at any concentration, can be calculated from

* Corresponding author.
† Uppsala University.
‡ Lund University.

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models of mixed micelles. This is of special importance for the case of dilute micellar systems, such as surfactant systems close to the cmc, and for the important problem of determining aggregation numbers of micelles bound to surfaces in equilibrium with a bulk aqueous solution.

In the present paper we use a detailed thermodynamic model to investigate C_nTAB/C_nPB (n = 12, 14, 16) mixed micelles. In particular, we show how Poisson−Boltzmann (PB) calculations can be used as a tool in the analysis of FQ data. The outline of the paper is the following. After a presentation of the FQ method, we give as a background an example which shows the importance of treating the electrostatic interactions properly. In the three subsequent sections we present the thermodynamic model and how it can be used to calculate the mole fraction of quencher in the micelles, X_Q. In separate sections we discuss polydispersity effects and the influence of the probe on the aggregation numbers determined with FQ and how to calculate X_Q for nonionic and monovalent quenchers in micelles of divalent surfactants. The latter problem was encountered in a previous paper.[19] Finally, we use the presented method to determine the aggregation numbers for C_nTABs in solutions close to the cmc. In a subsequent paper it will be applied to ionic surfactants adsorbed at the charged silica interface.[4]

Experimental Section

Chemicals. Dodecyltrimethylammonium bromide (C_{12}TAB), tetradecyltrimethylammonium bromide (C_{14}TAB), and hexadecyltrimethylammonium bromide (C_{16}TAB), all from Serva, and *N*-hexadecylpyridinium chloride (C_{16}PC) from Merck, were used as supplied. *N*-dodecylpyridinium chloride (C_{12}PC) from Aldrich was recrystallized several times from acetone. Pyrene from Aldrich was recrystallized twice from ethanol.

Preparation of Samples. C_nPC was mixed with C_nTAB before pyrene was added. Pyrene was dissolved in the surfactant solutions in the following way. An appropriate amount of a pyrene/ethanol stock solution was added to a flask. The alcohol was evaporated by letting nitrogen gas gently flow over the solution. After adding the surfactant solution the sample was stirred for at least 24 h prior to measurements. In the case of C_{16}TAB these steps were carried out at an elevated temperature to prevent crystallization, since the Krafft point of C_{16}TAB is close to 25 °C. The pyrene concentration was kept low (≈1 pyrene for 50 micelles) to prevent excimer formation.

Time-Resolved FQ. Time resolved (TR) fluorescence decays were recorded with the single-photon counting technique using an experimental setup described elsewhere.[20] All measurements were made at 25 °C. The excitation wavelength was 325 nm and the emission was detected at 395 nm using a monochromator in front of the detector. The width of the laser pulse was short enough (≈0.2 ns) to be considered as a dirac pulse in the present experiments. Thus, the decays were analyzed without deconvolution of the signal with the pulse.

For each sample the fluorescence lifetime, τ_0, was estimated in a separate experiment by fitting a single-exponential function to a decay recorded in the absence of quencher. The average number of quenchers per micelle, $\langle n \rangle$, was obtained from a fit of eq 1 (see below) to the decays in the presence of quencher.

Fluorescence Quenching

Models describing the time evolution of the fluorescence intensity of an excited probe have been derived for systems of different degrees of complexity.[10,21] The situation relevant here is the rapid quenching observed in small discrete micelles containing probes and quenchers. It is sufficient to consider the case where the interactants are stationary, i.e., their residence time in the micelle is much longer than the fluorescence lifetime, τ_0. The fluorescence decays can then be analyzed with the following equation:[17,18]

$$F(t) = F(0)\exp\{-t/\tau_0 + \langle n \rangle [\exp(-k_q t) - 1]\} \qquad (1)$$

where $F(0)$ is the fluorescence intensity at the excitation event (t = 0), $\langle n \rangle$ is the average number of quenchers per micelle, and k_q is the first-order quenching rate constant; nk_q is the quenching frequency in a micelle with n quenchers.

While k_q derives from an approximate description of the intramicellar quenching kinetics,[22] $\langle n \rangle$ is independent of the kinetic description but related to the assumption of a poissonian distribution of the quenchers among the micelles. In fact, at long times ($t \gg 1/k_q$) eq 1 becomes single-exponential and can be written in the general form[9]

$$F(t) = F(0)\exp\{-t/\tau_0\}P(0) \qquad (2)$$

where $P(0)$ denotes the fraction of quencher free micelles. Equation 2 is the contribution to the fluorescence decay curve (for all t) from excited probes in quencher-free micelles. With a Poisson distribution $P(0) = \exp(-\langle n \rangle)$. Note that, as long as $F(0)$ can be accurately estimated from the quenched curve, $\langle n \rangle$ can be obtained even if the description of the actual quenching process is poor.

The Poisson distribution was introduced by Turro and Yekta[16] when analyzing static fluorescence data. Other distributions have also been used.[10] However, in most cases the Poisson (or random) distribution appears to be a good approximation. Deviations are expected when there are net interactions between the quenchers confined to the same micelle. This was demonstrated by Bales and Stenland[23] and has been further analyzed by Almgren and co-workers.[24,25] One important conclusion from the latter studies was that only large interactions result in serious deviations from the Poisson distribution. However, the problem can, in principle, always be avoided by extrapolation to zero quencher concentration.

In the following sections we shall investigate the use of surfactant molecules as quenchers. Due to the chemical resemblance to the main surfactant, the effect on the system is expected to be small. As noted elsewhere,[13] ideal mixing in the micelles of the components in a binary surfactant mixture results in a binomial distribution, which in the limit of a large excess of one of the components becomes identical to the Poisson distribution.[9]

When employing surfactant molecules as quenchers it is convenient to treat them as cosurfactants. The average aggregation number is then given by

$$N = \frac{\langle n \rangle}{X_Q} \qquad (3)$$

where X_Q is the mole fraction of quenchers in the micellar subphase. Thus,

$$X_Q = \frac{C_{m,Q}}{C_{m,Q} + C_{m,S}} \qquad (4)$$

where $C_{m,Q}$ and $C_{m,S}$ are the concentration of quencher Q and surfactant S in micelles, respectively. For polydisperse micelle systems, N in eq 3 is a function of X_Q and the micelle size

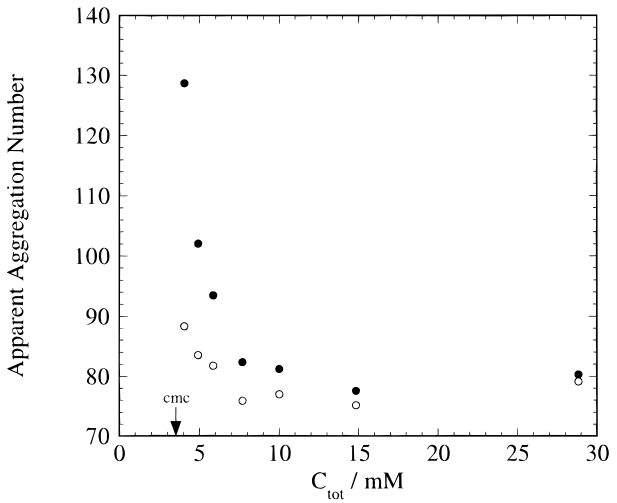

Figure 1. Apparent aggregation numbers for C_{14}TAB obtained from TRFQ with C_{16}PB as quencher. The aggregation numbers are calculated from experimental estimates of $\langle n \rangle$ using eq 3 with X_Q calculated from eqs 6 and 7 with $\beta = 0$ (dots) and $\beta = -1.08$ (circles).

distribution.[26,27] As will be shown in a subsequent section, these effects can be neglected for the systems studied in the present paper.

Another quantity we shall use is the total mole fraction of quencher, α_Q, defined as

$$\alpha_Q = \frac{C_{tot,Q}}{C_{tot,Q} + C_{tot,S}} \tag{5}$$

where $C_{tot,i}$ is the total concentration of component i.

To summarize, time-resolved fluorescence quenching (TR FQ) experiments provide accurate estimates of $\langle n \rangle$, from which N can be calculated if X_Q is known. In subsequent sections we will consider different approaches of calculating X_Q.

Background

It is common to describe the distribution of the components in a binary surfactant mixture using the regular solution approximation. In this model[28] the concentration $C_{f,i}$ of component i in the aqueous subphase is related to the mode fraction X_i in the micelles

$$C_{f,i} = f_i X_i \mathrm{cmc}_i \tag{6}$$

where cmc_i is the cmc of pure i, and f_i is an activity factor defined as

$$f_i = \mathrm{e}^{\beta(1-X_i)^2} \tag{7}$$

The interaction parameter β is zero in the ideal case, giving activity factors equal to one.

When two surfactants of the same charge are mixed one would suppose that the excess free energy of mixing in the micelles is zero (i.e., $\beta = 0$). The reason for this is that the chemical difference between the headgroups is of only minor importance when the long-range electrostatic repulsion between neighboring headgroups prevents them from making molecular contact. Despite this, attempts to use eq 6 to calculate X_Q in charged micelles can give large errors. Figure 1 shows the result from a TR FQ experiment where C_{16}PB was used as quencher in C_{14}TAB micelles. The aggregation numbers were calculated from eq 3, using the experimental estimates of $\langle n \rangle$ (see below), and X_Q was calculated from eq 6 with $\beta = 0$ ($f_i = 1$). The apparent sharp increase of the aggregation number upon dilution must be attributed to artifacts. In principle, there can be two contributions to this. First, the long chain quencher may alter the packing of the hydrocarbon chains in such a way that N actually increases. Second, eq 6 describes the partitioning of S and Q between the subphases in an incorrect way. Effects of the first type can be ruled out since the mean number of Q per micelle, $\langle n \rangle$, was close to 1 for all samples. Furthermore, theoretical investigations suggest that the effects of chain length mismatch on N should be negligibly small for the present X_Q values.[29] Thus, we conclude that the error derives from eq 6. In the model behind eq 6 the standard free energy change of transferring one molecule from the aqueous solution to a micelle is assumed to be the identical for the pure component micelles and the mixed micelles. This quantity, which includes both nonelectrostatic and electrostatic contributions, is equal to $-kT\ln\{\mathrm{cmc}_i\}$, where k is Boltzmann's constant and T is the absolute temperature. This expression is expected to be a fairly good approximation for the main component (C_{14}TAB), since the cmc for the mixture is very close to that of the pure S system ($\mathrm{cmc}_s = 3.5$ mM). However, the electrostatic free energy of the quencher (C_{16}PB) in the mixed micelles is considerably smaller than in the pure C_{16}PB micelles (cmc = 0.58 mM). This is because the mixed micelles are in equilibrium with a more concentrated electrolyte solution than the pure Q micelles are. This difference, which is not corrected for in eq 6, must be taken into account also when the excess free energy of mixing S and Q in the micelle is zero (i.e., when there is "ideal" mixing in the micelles). It is possible to make a correction by introducing eq 7 with an appropriate value of β. Holland and Rubingh have described how β can be determined from cmc values of the mixture measured at different α_Q. At first sight, this appears to be a useful concept. However, the treatment is not rigorous for charged systems (see below), and the resulting values of β fail to predict the correct value of X_Q. In Figure 1 we have included the result obtained with $\beta = -1.08$, which is the value of the interaction parameter obtained using the procedure described in ref 28.

In the following sections we show that a thermodynamic model of mixed micelles, in which the different free energy contributions are considered explicitly, can provide accurate estimates of X_Q.

Thermodynamic Model

A model which is capable of predicting the distribution of the various molecules in a micellar system and thus gives access to X_Q was developed by one of the present authors.[30,31] In this model the chemical potential for an amphiphile in a micelle, μ_{am}^{mic}, is given by a sum of contributions

$$\mu_{am}^{mic} = \mu_{am}^{0,mic} + \mu_{surf} + \mu_{el} + \mu_{mix} \tag{8}$$

where the first term represents the standard state contribution to the chemical potential of a surfactant in a micelle. μ_{surf} is the free energy of the hydrocarbon/water contacts at the micelle surface and is set equal to γa_0, where γ is the free energy per unit area and a_0 is the area per surfactant at the interface. μ_{el} is the electrostatic free energy per monomer (or mole monomer) in the micelle. The latter contribution will be calculated from numerical solutions of the PB equation, by using a specially written software "PBcell".[32]

The term μ_{mix} deserves some comments. In the case of a mixed surfactant system it has two contributions, one of which derives from the free energy of mixing the micelles in the

solution. This contribution (per mole of monomer), which for dilute systems can be written as $(RT/N)\ln(C_{mic})$, where C_{mic} is the concentration of micelles, is present both in single and mixed surfactant systems. However, it is almost constant in the concentration regime considered here and is therefore incorporated in $\mu_{am}^{0,mic}$. The other contribution, $RT\ln X_i$ (where i is Q or S in the present case), represents the (ideal) mixing of the surfactant and the quencher in the micelle and is of great importance in mixed surfactant systems.

In the general case we shall apply a cell model, in which the chemical potential of an ionic compound in the solution is related to the concentration at the cell boundary, $C_i(L)$, and the standard contribution to the chemical potential, $\mu_i^{0,w}$ as[33]

$$\mu_i^w = \mu_i^{0,w} + \ln C_i(L) \tag{9}$$

Starting with eq 9 and throughout this paper, the chemical potential is expressed in units of RT.

At equilibrium the chemical potential for the surfactant is equal everywhere. Thus, for component i

$$\ln C_i(L) = -\ln K_i + \mu_{i,surf} + \mu_{i,el} + \ln X_i \tag{10}$$

where

$$-\ln K_i = \mu_i^{0,mic} - \mu_i^{0,w} \tag{11}$$

When applied to both components in a mixture of surfactant S and quencher Q, eq 10 gives

$$\frac{C_Q(L)}{C_S(L)} = \frac{K_S}{K_Q}\frac{e^{\mu_{Q,el}+\mu_{Q,surf}}}{e^{\mu_{S,el}+\mu_{S,surf}}}\frac{X_Q}{1-X_Q} \tag{12}$$

The surfactant monomers in the aqueous part of the cell are Boltzmann distributed in the electrostatic potential field. Thus, when Q and S have the same charge, $C_Q(L)$ and $C_S(L)$ are related to $C_{f,Q}$ and $C_{f,S}$, (the concentrations of Q and S in the aqueous subphase), through the relation

$$\frac{C_Q(L)}{C_S(L)} = \frac{C_{f,Q}}{C_{f,S}} \tag{13}$$

Thus we have

$$C_{f,Q} = C_{f,S}R\frac{X_Q}{1-X_Q} \tag{14}$$

where

$$R = \frac{K_S}{K_Q}\frac{e^{\mu_{Q,el}+\mu_{Q,surf}}}{e^{\mu_{S,el}+\mu_{S,surf}}} \tag{15}$$

Conservation of mass gives for X_Q

$$X_Q = \frac{\alpha_Q C_{tot} - C_{f,Q}}{C_{tot} - C_{f,Q} - C_{f,S}} \tag{16}$$

where C_{tot} is the total concentration of (S + Q). By combining eqs 14 and 16 one obtains

$$X_Q = \frac{\alpha_Q C_{tot}}{C_{tot} + C_{f,S}(R-1)} \tag{17}$$

For the limiting case of micelles in equilibrium with an infinite bulk solution of the components we have

$$\frac{C_{bulk,Q}}{C_{bulk,S}} = R\frac{X_Q}{1-X_Q} \tag{18}$$

which is valid for all types of Q/S combinations. Furthermore, since $C_{bulk,i} = \alpha_i C_{tot}$, we get

$$X_Q = \frac{1}{1 + R\left(\frac{1-\alpha_Q}{\alpha_Q}\right)} \tag{19}$$

Equation 19 is appropriate for surfactant micelles formed at interfaces, which is in equilibrium with a bulk aqueous phase containing surfactant unimers. Note that, for small values of α_Q, $X_Q \approx \alpha_Q/(R + \alpha_Q) \approx \alpha_Q/R$.

In the general case, the electrostatic and the surface contributions to the chemical potential of both components in the mixed micelles must be evaluated (cf. eq 15). However, when the surfactant and the quencher have the same charge (e.g., S^+/Q^+), which is the situation of main interest here, $\mu_{S,el} = \mu_{Q,el}$ and $\mu_{S,surf} = \mu_{Q,surf}$ in the mixed micelles. In this case eq 15 simplifies to $R = K_S/K_Q$. As will be demonstrated below, once the ratio K_S/K_Q is known we will be able make good estimates of X_Q at any surfactant concentration without knowing the aggregation number of the surfactant. This is, of course, of great importance since it provides a means to determine the aggregation number from FQ data. Next, we describe how to calculate K_S/K_Q.

Calculations of K_S and K_Q

K_S and K_Q can, in principle, be evaluated for any composition of the pure surfactant systems ($X_i = 1$) where the dimensions of the micelles and the activity of the surfactant monomers are known. For C_nTAB, aggregation numbers obtained from TR FQ experiments carried out at sufficiently concentrated solutions can be used; under such conditions a hydrophobic quencher can be assumed to reside exclusively in the micelles. However, for obvious reasons there is no TR FQ data available for the C_nPB.

From static light scattering there are aggregation numbers and cmc values reported for both types of surfactants obtained under similar conditions. The aggregation number is obtained from the Rayleigh ratio by extrapolating to concentrations equal to the cmc. This is an advantage for us since, at this concentration, $C_i(L)$ is equal to cmc_i, of which the latter is usually known from experiments. Thus, K_i can be calculated from (cf. eq 10)

$$K_i = \frac{e^{\mu_{i,el}+\mu_{i,surf}}}{cmc_i} \tag{20}$$

with $\mu_{i,surf}$ calculated assuming $\gamma = 18$ mJ/m^2,[34] and $\mu_{i,el}$ obtained from numerical solutions of the PB equation; see Appendix 1.

Figure 2 shows C_nTAB and C_nPB aggregation numbers determined with light scattering by various investigators as a function of the total electrolyte concentration, i.e., surfactant plus NaBr/Cl. The aggregation numbers with no added salt (as represented by the lowest electrolyte concentration for each surfactant) are about the same or smaller than the largest possible value for a sphere according to purely geometrical considerations as discussed by Tanford.[35] Therefore, in the calculations of K_S and K_Q we use the "Tanford" values both for S and Q together with the cmc data for salt-free conditions. Note that we use the same aggregation number for C_nTAB and C_nPB when they have the same number of carbon atoms in the tail (see below). The

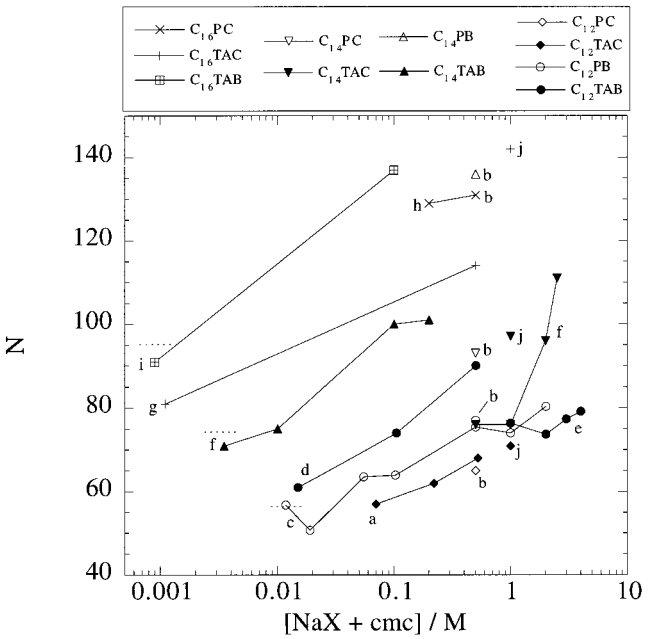

Figure 2. Aggregation numbers at the cmc for the surfactants used in this work obtained from light scattering as a function of total counterion concentration (NaBr/Cl + cmc). Data taken from a: Emerson and Holtzer,[43] b: Jacobs et al.,[44] c: Fujio and Ikeda,[45] d: Anacker et al.,[46] e: Ozeki and Ikeda,[47] f: Imae and Ikeda,[48] g: ref 49, h: Anacker and Ghose,[50] i: Imae et al.,[51] j: TR FQ-data from Swanson-Vethamuthu et al.[52] for 25 mM surfactant plus 1 M NaCl. For each surfactant, the data from one laboratory are connected by solid lines. The dashed lines mark, from left to right, the "Tanford" aggregation numbers for C_{16}, C_{14}, and C_{12} surfactants, respectively, at concentrations corresponding to the cmc in solutions with no added salt.

results are presented in Table 1 together with a description of the parameters used in the calculations. The relations used to calculate the micelle radius and the area per surfactant headgroup from N are given in the footnote to Table 1. Table 2 shows the ratios K_S/K_Q calculated from the data in Table 1.

Our purpose is to find a method that allows the determination of N for the surfactant (C_nTAB) at any concentration, and, in particular in very dilute systems. The key parameter is the ratio K_S/K_Q describing the mutual distribution of S and Q between the micelle and aqueous subphases. However, the calculations of K_S and K_Q depend on the choice of micelle size. Therefore, we find it necessary at this point to further motivate the choice of N and to consider to what extent this affects K_S/K_Q.

There are several remarks that can be made about the data in Figure 2. First of all, the aggregation numbers increase with increasing length of the hydrocarbon chains of the surfactants, but the increase of N with the electrolyte concentration is similar for all systems. Unfortunately, different values have been reported for the same surfactant by different investigators. For example, the aggregation numbers for C_{12}TAB reported by Ozeki and Ikeda are substantially smaller than the values reported by Anacker et al. (see Figure 2). By considering all data in Figure 2, the following can be said about N: C_{12}PB $\leq$ C_{12}TAB, C_{12}PC $\approx$ C_{12}TAC, C_{14}PB $\gtrsim$ C_{14}TAB, C_{14}PC $\geq$ C_{14}TAC, C_{16}PC $\geq$ C_{16}TAC. Included in Figure 2 are also estimates of N from TR FQ for C_nTAC at 1 M added NaCl. A comparison between FQ and light scattering (LS) gives the following result: C_{12}TAC(FQ) $\approx$ C_{12}TAC(LS), C_{14}TAC(FQ) > C_{14}TAC(LS), C_{14}TAC(FQ) $\approx$ C_{14}PC(LS), C_{16}TAC(FQ) > C_{16}TAC(LS), C_{16}TAC(FQ) $\approx$ C_{16}PC(LS). In conclusion, the data in Figure 2 reveal no systematic difference between the aggregation number of C_nTA^+ and C_nP^+. This is the rational for using the same value of N in the calculations of K_S and K_Q when S and Q contain the same number of carbons.

The calculations of K_S and K_Q were made for surfactant concentrations equal to the cmc in the absence of salt, i.e., where we find the smallest aggregation numbers in Figure 2. From the point of view of Poisson−Boltzmann calculations this is an advantage since, at this concentration, the average shape of the micelles is expected to deviate little from a sphere. A drawback is that, in the absence of excess salt, the aggregation numbers obtained from light scattering depend on assumptions regarding the counterion binding and the type of correction for the contribution to the scattering from free surfactant and co-ions. Salt diminishes the importance of these effects but leads to a growth of the micelles and thus to a deviation from a spherical shape. The uncertainty of N obtained in the absence of salt raises the question: to what extent do the ratios K_S/K_Q in Table 2 depend on the particular choice of N in the calculations? To investigate this we calculate K_S and K_Q for micelles of C_{12}TAB and C_{12}PB at the cmc, respectively, with N ranging from 26 to 56. For each N the micelle radius r is defined by N and the volume of a hydrocarbon chain v_{chain} according to the relations given in the footnote to Table 1. As expected, K_S and K_Q are found to be strongly dependent on N. However, the ratio K_S/K_Q changes only by 3% in the entire interval, giving confidence to the data in Table 2. This is very important because it shows that the calculation of X_Q using the present method, and hence N determined in a FQ experiment, is essentially independent of the value of N used in the PB calculations as long as N is the same for pure S and Q micelles.

An error will be introduced if there is a difference between N_S and N_Q. For example, if C_{12}PB has an aggregation number at the cmc which is 17% lower than that of C_{12}TAB (see Figure 2), the calculated value of K_S/K_Q will be 12% larger than the value given in Table 2. The error in N will be largest at infinite dilution with respect to the micelles (cf. eq 17). In this limit the relative error in N (for typical valus of α_Q) will be equal to the error in K_S/K_Q, as shown by eq 19.

Calculations of X_Q

For micelles in equilibrium with an (infinite) bulk solution, X_Q is easily calculated from $R(= K_S/K_Q)$ and α_Q using eq 19. This is useful since the aggregation number can be determined from FQ data (i.e., from $\langle n \rangle$) also when the amount of micellized surfactant is not known. At finite concentrations of micelles we have to use eq 17. Also, in this case X_Q can be directly calculated from α_Q if we find the "ideal" quencher; with $R =$ 1 eq 17 reduces to $X_Q = \alpha_Q$. However, for the majority of S/Q combinations (including C_nTAB/C_nPB) it is necessary to make as good as possible an estimate of the free surfactant concentration. Note that, with the correct value of $C_{f,S}$, eq 17 is exact (within the model). In general, $C_{f,S}$ will not be the same as in the pure surfactant system, but for small values of X_Q the presence of the quencher should have negligible effects on the micellization. Then, if a binding isotherm for the pure surfactant system is available, we expect it to be a good approximation to take $C_{f,S}$ from that and use it in eq 17. When no binding data are available it would be convenient to put $C_{f,S} = \text{cmc}_S$. In the following sections we investigate these approximations. For this purpose we calculate the exact values of X_Q, α_Q, and C_{tot} corresponding to equilibrium within the thermodynamic model. These values, which we obtain from PB calculations, are then used to test the approximate approaches suggested above.

Numerical Calculations. We use C_{12}TAB/C_{12}PB as a model system; see Appendix 1. Within the thermodynamic model the

TABLE 1: Cmc Values and Calculated Parameters for the Surfactants Used in This Work

surfactant	N[a]	r^b (Å)	$v_{surf}{}^c$ (Å3)	$a_0{}^d$ (Å$^{2)}$	cmc (mM)	μ_{el} (RT)	μ_{surf} (RT)	K_i (mM)$^{-1}$
C_{12}TAB	56	19.1	521.2	81.86	15.0	3.971	3.581	127.0
C_{12}PB	56	19.1	521.2	81.86	11.9	4.140	3.581	190.2
C_{14}TAB	74	21.9	594.6	81.45	3.5	5.173	3.564	1779
C_{16}TAB	95	24.7	664.4	80.70	0.90	6.352	3.531	21770
C_{16}PB	95	24.7	664.4	80.70	0.58	6.681	3.531	46830
C_{16}PC	95	24.7	664.4	80.70	0.93	6.327	3.531	20552
C_{12}PPDAC	41[e]	18.4[e]	640[e]	103.8	(48.95)[f]	6.921[f]	5.678[f]	6050[f]
C_{12}PPDAC	20[e]	14.5	640[e]	132.3	48	5.797	7.237	9536

[a] $N = 4\pi r_{core}^3/3v_{chain}$ where $r_{core} = (1.5 + 1.27n_C)$ Å and $v_{chain} = (27.4 + 26.9\ n_C)$ Å^3 is the radius of the hydrocarbon core and the volume per alkyl chain in the micelle, respectively, for a surfactant with n_C carbons in the chain. [b] $r = 1.1 \times (2.1 + 1.27n_C)$ Å. This is the radius of the charged interface in the PB calculations.[31] [c] $v_{surf} = 4\pi r^3/3N$. [d] $0 = 4\pi r^2/N$. [e] Taken from Ström et al.[19] [f] Calculated for 70 mM C_{12}PPDAC using the PB-cell model with a monomer surfactant concentration of 45 mM as reported by Hagslätt et al.[42] $C_S(L) = 48.95$ mM.

TABLE 2: Calculated Ratios of K_S/K_Q

S/Q	K_S/K_Q
C_{12}TAB/C_{12}PB	0.67
C_{14}TAB/C_{16}PB	0.038
C_{16}TAB/C_{16}PB	0.47

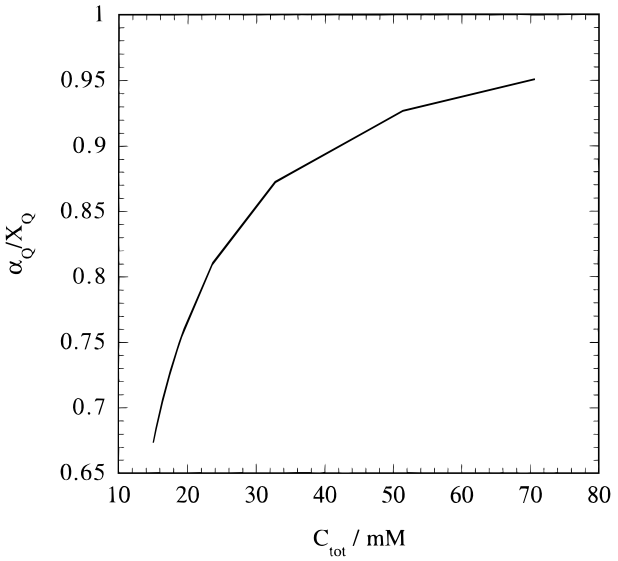

Figure 3. Calculated values of α_Q/X_Q as obtained from Poisson−Boltzmann calculations (see Appendix 1) as a function of C_{tot} for C_{12}TAB/C_{12}PB. The calculations were carried out with a constant value of X_Q equal to 1/56.

system is in chemical equilibrium when eq 10 is satisfied for both components. To find the equilibrium distribution of S and Q in the system we use the PB-cell model from which $\mu_{i,el}$ and $C_i(L)$ are obtained. The most intuitive approach is perhaps to choose a value of α_Q and then calculate the corresponding value of X_Q for a range of surfactant concentrations. However, this would make the PB calculations tedious. To simplify the calculations, we fix the composition of the mixed micelles and calculate the equilibrium concentrations of S and Q in the aqueous subphase. From this, in turn, α_Q and C_{tot} are calculated. We assume that the mixed micelles contain exactly one C_{12}PB (=Q) and 55 C_{12}TAB, i.e., $X_Q = 1/56$. This is reasonable since, in a typical TR FQ experiment the amount of quencher is adjusted to give $\langle n \rangle \approx 1$. The procedure used for the calculation of C_{tot} and α_Q from given values of C_m, N, X_Q, K_Q, and K_S is described in Appendix 1. The calculated values of α_Q/X_Q as a function of C_{tot} are shown in Figure 3. Since $K_S < K_Q$ (Table 1), α_Q/X_Q is less than unity. The ratio is close to unity at concentrations well above the cmc, but increases upon dilution, i.e., the micelles are enriched in the quencher.

Test of Approximations. To determine the aggregation number in a TR FQ experiment we have to calculate X_Q from the total concentrations of S and Q in the sample, i.e., from α_Q and C_{tot}. To test the various approximate approaches outlined above we calculate X_Q for the sets of α_Q and C_{tot} given in Figure 3 and compare the result with the theoretical value $X_Q = 1/56$. The result is given in Figure 4. Please note that the plot shows the relative deviation of X_Q from the true value, i.e., the values have been divided with 1/56.

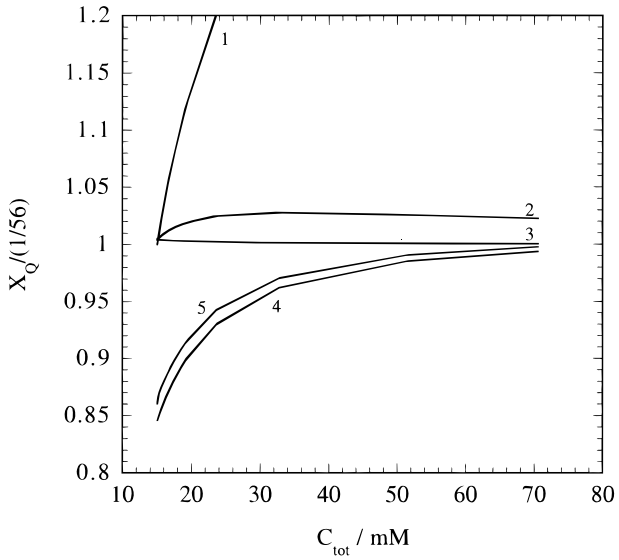

Figure 4. X_Q vs the total concentration of surfactant for the surfactant/quencher combination C_{12}TAB/C_{12}PB. Five different approaches (see text for details) were used; curve 1: eq 19, curve 2: eq 17 with $C_{f,S}$ constant at 15 mM and $R = K_S/K_Q$, curve 3: eq 17 with $C_{f,S}$ from Figure 5, curve 4: the "ideal mixing model" eq 6 with $f_S = f_Q = 1$, curve 5: the regular solution approach eqs 6−7 with $\beta = -0.024$ (see text for details).

Curve 1 is calculated from eq 19. As expected, the correct value of X_Q is obtained in the limit of infinite dilution of the micelles. However, the error increases rapidly with increasing concentration. As shown by the curve 2, it is a better approximation to put $C_{f,S} = cmc_S = 15$ mM in eq 17. The deviation from the theoretical value is less than 3% in the entire concentration range, which is smaller than what is possible to detect with the TR FQ method. This result is perhaps better than expected, considering the substantial decrease of $C_{f,S}$ with increasing surfactant concentration above the cmc for ionic surfactants.[36] The latter feature is illustrated in Figure 5 where the concentration of $C_{12}TA^+$ ions in the aqueous subphase in equilibrium with *pure* C_{12}TAB micelles is given as a function of the total surfactant concentration. These data are obtained from PB cell model calculations with parameters for the surfactant taken from Table 1. Curve 3 in Figure 4 is the result

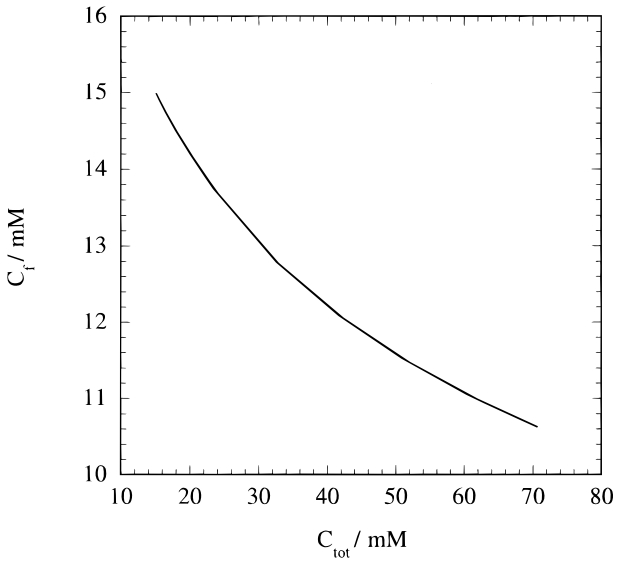

Figure 5. The concentration of $C_{12}TA^+$ unimers in the aqueous subphase as a function of the total surfactant concentration. The data were obtained from Poisson−Boltzmann calculations using parameters relevant for the pure $C_{12}TAB$/water system taken from Table 1.

of taking $C_{f,S}$ from Figure 5 and using it in eq 17. The agreement with the theoretical value is very good. This demonstrates that Q has negligible effects on $C_{f,S}$.

Included in Figure 4 is also the prediction of eq 6 with $f_S = f_Q = 1$. The result is represented by curve 4, which is obtained by inserting eq 6 in eq 16. While the model is expected to give a reasonable description of a mixture of nonionic surfactants (the situation for which it was originally derived[37]) it fails in the present case due to the neglect of electrostatic free energy changes. In the present case it underestimates the driving force of the quencher to solubilize in the micelle.

In the regular solution approach (eqs 6, 7) β is evaluated using experimental cmc values for the mixture (here denoted cmc*) determined with α_Q in the range from zero to unity.[28] With the present notations, this involves a calculation of X_Q at cmc* from α_Q, cmc_S, cmc_Q, and cmc* (see eq 18 in ref 28). β is obtained from a plot of cmc* vs X_Q through a fitting of the relation cmc* $= f_Q X_Q cmc_Q + f_S(1 - X_Q)cmc_S$, where f_S and f_Q are defined by eq 7. To test this approach in the present case we calculate from the thermodynamic model (eq 10) cmc* and X_Q as a function of α_Q for $C_{12}TAB/C_{12}PB$ mixtures and estimate β using the procedure described above. The quality of the fit is very good, but the resulting value ($\beta = -0.024$) is too small to improve the ideal mixing model; see curve 5 in Figure 4. When the same type of calculation is made for $C_{14}TAB/C_{16}PB$ mixed micelles we reach the same conclusion (see Background section). It can be mentioned that, for small X_Q, eqs 6 and 7 give reasonable values of X_Q when β is equal to -0.17 and -1.5 for $C_{12}TAB/C_{12}PB$ and $C_{14}TAB/C_{16}PB$, respectively. These values cannot be obtained from experimental cmc* data within the regular solution model. However, they can be calculated from the above thermodynamic model. Insertion of eq 20 into eq 10 and comparing with eqs 6 and 7 reveal that

$$\beta(1 - X_i)^2 = \mu_{i,el}(\text{mixed}) - \mu_{i,el}(cmc_i) + \mu_{i,surf}(\text{mixed}) - \mu_{i,surf}(cmc_i) \quad (21)$$

where the left-hand side originates from the regular solution model and the right-hand side from eq 10. Here "mixed" and "cmc_i" refer to mixed micelles at any concentration and pure i micelles at the cmc, respectively. In the limit as X_Q goes to zero, where cmc* goes to cmc_S, we obtain the above values of β when using the data in Table 1.

Polydispersity Effects and Probe Distribution

In the previous sections, where our primary interest has been the partitioning of the quencher and the surfactant *between* the micelles and the aqueous subphase, we have restricted the calculations to one type of micelle with a composition representing the average over all micelles in the system. This is expected to be a good approximation for that purpose. For instance, the corresponding approximation for single surfactant systems gives a good prediction of the free concentration of monomers in equilibrium with the micelles.[36] In the present section we discuss briefly how a polydispersity in the micelle population influences the distribution of surfactant, quencher, and fluorescent probe among the micelles. Here, it is important to note that the fluorescence from the solution in an FQ experiment comes exclusively from the micelles containing excited probes, i.e., from the "photo selected" population.[26,27] The object is to find the fraction of Q-free micelles in that population.

Let us consider first the micelle system before the probe is added. For S/Q combinations where S and Q are equivalent with respect to the packing in the micelles (ideal mixing), the distribution of S and Q among the micelles is independent of the distribution of N. By defining a "set" of micelles as all micelles with the same N, we have that the *average* mole fraction of Q within a set (here denoted $\langle X_Q \rangle$) is the same for all sets of micelles, independent of N. Furthermore, the fraction of quencher-free micelles in each set is equal to $(1 - \langle X_Q \rangle)^N$. This follows from the binomial distribution, consistent with a random mixing of S and Q.[24] Thus, in the absence of probe molecules the fraction of micelles with no quencher can be written (cf. eq 2)

$$P_{\langle N \rangle, \langle X_Q \rangle}(0) = \sum_N (1 - \langle X_Q \rangle)^N P_{\langle N \rangle}(N) \quad (22)$$

where $P_{\langle N \rangle}(N)$ is the fraction of micelles with aggregation number N in a distribution of micelles with the average aggregation number $\langle N \rangle$. For narrow distributions[38] of N and with $\langle X_Q \rangle$ typical for a TR FQ experiment, the sum in eq 22 is to a good approximation equal to $(1 - \langle X_Q \rangle)^{\langle N \rangle}$. Thus, the fraction of Q-free micelles in a population with a characteristic $\langle N \rangle$ is approximately the same as for a monodisperse population of micelles with $N = \langle N \rangle$.

When the fluorescent probe is present the situation is more complicated. Pyrene, which is most frequently used, has a very strong tendency to associate with surfactant assemblies.[39] This has the advantage that the pyrene concentration in the aqueous subphase can usually be neglected. Furthermore, thanks to the sensitivity of the available fluorescence detectors, pyrene needs to be present only at very low concentrations (10^{-7} to 10^{-6} M). As a consequence, the effect on the macroscopic properties of the system is small. In fact, to avoid self-quenching due to excimer formation the pyrene concentration is adjusted so that there is never more than one probe in a micelle (there is typically 1−2 pyrene per 100 micelles). Thus, in a typical TR FQ experiment there are two populations of micelles: a major one comprising micelles free from probe, and a minor one with micelles containing exactly one probe. Importantly, for mixtures where S and Q have the same affinity for micelles containing the probe (probably a good assumption for C_nTAB/C_nPB), $\langle X_Q \rangle$

has the same value in the two populations. From this it follows that S and Q are binomially distributed within each set of micelles with a given N also when the probe is present. Thus, the distribution of the probe among the micelles can be described as if there were no Q present. Note that, this is not expected to be the case for nonionic Q in ionic micelles.

Before proceeding with the polydispersity effects we recall that an FQ experiment gives information only about the probe-containing population. Since we are interested in the probe-free micelles, this is a fundamental problem that cannot be neglected. In fact, aggregation numbers obtained with FQ always represent the (average) number of surfactant molecules in micelles containing *one* solubilized probe molecule. The intriguing question is thus, to what extent does the probe influence the optimal aggregation number? It is possible to investigate the problem theoretically by extending the model behind eq 8 to mixtures of chemically very different species.[40,41] For the present purpose, it would be interesting to calculate the size distribution of the micelles containing a probe and to compare that with the probe-free distribution. However, this requires extensive PB calculations and will not be pursued here. To appreciate the effect, comparisons with other techniques have been made[10] for conditions where the partitioning between the aqueous and micelle subphases represents no problem in TR FQ. It is generally found[10] that the aggregation numbers determined with TR FQ agree well with estimates from more direct methods. The conclusion is that the presence of a single pyrene molecule has only negligible effects on the optimal aggregation number.

When the probe has no effect on the micelle size distribution it is possible to analyze the polydispersity effects in a simple way. For example, with a Gaussian size distribution[38] the fraction of micelles in the photoselected population with aggregation number N should be proportional to $\exp\{-\mu_{\text{probe}}(N)\}\exp\{-(N - \langle N\rangle)^2/2\sigma^2\}$, where $\mu_{\text{probe}}(N)$ is the free energy of a probe in micelles with aggregation number N. The size distribution of the photoselected population is given by the relationship

$$P^*_{\langle N\rangle} = \frac{N e^{-\mu_{\text{probe}}(N)} e^{-(N-\langle N\rangle)^2/2\sigma^2}}{\sum_N N e^{-\mu_{\text{probe}}(N)} e^{-(N-\langle N\rangle)^2/2\sigma^2}} \quad (23)$$

The fraction of Q-free micelles in the photoselected population can be calculated from eq 22 if $P_{\langle N\rangle}(N)$ is replaced by $P^*_{\langle N\rangle}(N)$. Recall that this is the quantity we obtain from the fluorescence decays. Thus, when the decays are analyzed with eq 1 we expect the apparent aggregation number, N_{app}, to be given by the relationship (cf. eq 3)[24]

$$N_{\text{app}} = -\frac{\ln \sum_N P^*_{\langle N\rangle}(1 - \langle X_Q\rangle)^N}{\langle X_Q\rangle} \quad (24)$$

Here, $\mu_{\text{probe}}(N)$ can be calculated separately for each N that gives an important contribution to the size distribution function. To investigate the magnitude of the effect we consider a nonionic probe solubilized in the headgroup region of the micelles, where it occupies an area equal to the effective headgroup area of the surfactant molecule in a micelle with aggregation number $N = \langle N\rangle$. The electrostatic contribution to $\mu_{\text{probe}}(N)$ can be obtained from PB calculations within the thermodynamic model.[40] The result from such calculations for C_{12}TAB micelles containing one probe gives that $\mu_{\text{el,probe}}(N) \approx N^{0.27}$. This relation is valid for $30 < N < 120$ at an electrolyte concentration in the bulk equal to the cmc for C_{12}TAB. The probability of a micelle of aggregation number N to host a probe is then proportional to $\exp\{-\mu_{\text{el,probe}}(N) - \ln(1/(N+1))\} \approx N e^{N^{0.27}}$, where the second term in the exponent describes the entropy of mixing the probe with the surfactant (cf. eq 8). In Figure 6 we have used this expression to calculate N_{app} from eq 24 with $P^*_{\langle N\rangle}$ given by eq 23. $\langle N\rangle$ and σ^2 were both equal to 56. The result, as represented by curve 1, indicates that the preference of the probe for the micelles with large N has only a negligible effect on the apparent aggregation number. In fact, as long as σ is small the effect will be small unless the probe has a very strong preference for micelles with certain aggregation numbers.

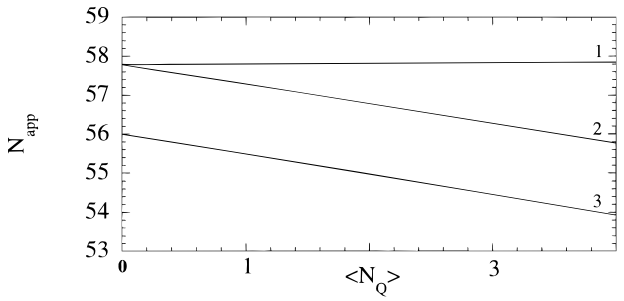

Figure 6. The effect of polydispersity on aggregation numbers determined with TR FQ.The curves represent theoretical calculations of the apparent aggregation numbers (N_{app}) for a polydisperse micelle system as a result of analyzing the decays with models valid for monodisperse micelles. The model system has a Gaussian micelle size distribution ($\langle N\rangle = \sigma^2 = 56$) and a binomial distribution of S and Q among the micelles. There are on the average $<N_Q>$ quenchers per micelle. Curve 1: The probability of the probe to be in a micelle of aggregation number N is proportional to $N \exp\{N^{0.27}\}$ (see text). Q is assumed to be Poisson distributed among the micelles (eqs 23−24). Curve 2: Same as in 1 but with a binomial distribution of S and Q ($\langle X_Q\rangle$ replaced by $-\ln(1 - \langle X_Q\rangle)$ in eq 24). Curve 3: The probability of a micelle to host a probe is independent of N (no photoselection). Binomial distribution of S and Q.

Equation 1 is based on the assumption of a Poisson distribution of Q. In principle, the binomial distribution should be used. To see the effect of that we repeat the above calculation of N_{app} and replace $\langle X_Q\rangle$ in eq 24 with $-\ln(1 - \langle X_Q\rangle)$. As shown by curve 2 in Figure 6 the assumption of a Poisson distribution gives negligible errors. For the sake of comparison we have also calculated N_{app} for a (hypothetical) case where the photoselected size distribution is identical to the one in the absence of probe; curve 3. In this case the number average aggregation number is obtained in the limit as $<N_Q>$ goes to zero.

In their analysis of polydispersity effects, Almgren and Löfroth[26] assumed that the probability of a micelle to host a probe is directly proportional to N. This should be a good approximation for nonionic quenchers in nonionic micelles. In the case of a poissonian distributed quencher they found that N_{app} is equal to $\langle N\rangle + \sigma^2/\langle N\rangle$, in the limit as $\langle X_Q\rangle$ goes to zero. This is equal to the weight-average aggregation number $\langle N\rangle_w$. The same result is obtained with a binomial distribution of S and Q, since this distribution is identical to a Poisson distribution of Q in this limit. However, the value of N_{app} obtained by extrapolating to zero quencher concentration in Figure 6 is larger than $\langle N\rangle_w$. This is due to the electrostatic contribution to $\mu_{\text{probe}}(N)$.

In conclusion, there are advantages with quenchers that are similar to the surfactant under study also in the analysis of

polydispersity effects. The effects on the aggregation number determined with FQ can be expected to be small for S/Q pairs such as C_{12}TAB/C_{12}PB.

Quenchers for Micelles of Divalent Surfactants

In a previous paper[19] we determined aggregation numbers for the divalent surfactant dodecyl-1,3-propylene-pentamethyl-bis(ammonium chloride) (C_{12}PPDAC) using a nonionic quencher, dimethylbenzophenone (DMBP). To calculate the amount of quencher in the micelles we used a distribution constant K_D describing the partitioning of DMBP between C_{12}TAB micelles and water, obtained from spectroscopic measurements on solutions saturated with DMBP.[13] In the present section we use the thermodynamic model presented in this paper to check the result of this procedure, and, in addition, we investigate the possibility of using C_{16}PC as quencher in C_{12}PPDAC micelles.

We wish to investigate how the ratio R defined by eq 15 changes upon dilution of a C_{12}PPDAC/DMBP mixture. This amounts to estimating K_S, K_Q, and the electrostatic and surface contributions to the chemical potentials of both components in the mixed micelles.

K_S can be calculated from eq 20. The result is given in Table 1. In the present case the calculations correspond to a 70 mM solution containing 25 mM of the surfactant in the micelles. There are two motives for this choice of "reference state". First, the concentration of micellized surfactant is so large that the free concentration of DMBP is negligible. Thus, the aggregation number obtained from TR FQ ($N = 41$[19]) is independent of models describing the distribution of the quencher between water and micelles. Second, the free surfactant concentration in equilibrium with the micelles is available from NMR measurements.[42] The dimension of the micelle used in the PB calculation is the same as in our previous paper.[19] In particular, the interfacial free energy per unit area, γ, is equal to 22.5 mJ/m^2. Note that, this value differs from the value of 18 mJ/m^2 used for the monovalent surfactants.

The experiments in our previous study revealed a pronounced decrease in the aggregation number for C_{12}PPDAC upon dilution. Close to the cmc, N was found to be about 20. To check the effect of N on K_S for this surfactant we repeat the above calculation for a micelle with $N = 20$ in equilibrium with a 48 mM (= cmc) surfactant solution. As can be seen in Table 1, the resulting value of K_S is of the same order of magnitude as obtained with $N = 41$ at 70 mM C_{12}PPDAC.

It is more problematic to calculate K_Q since DMBP does not form micelles, and hence, there is no obvious choice of reference state. However, it is possible to make an estimate of R for DMBP/C_{12}PPDAC from the distribution constant K_D for DMBP/C_{12}TAB. This procedure is described in Appendix 2. As a result, R is found to be between 4×10^{-3} and 7×10^{-3} for C_{12}PPDAC concentrations in the range from the cmc to 70 mM. We use this estimate of R in the Experimental Section to check our previous determinations of N for C_{12}PPDAC. It should be stated that the correction turns out to be very small.

Turning now to C_{16}PC as quencher in C_{12}PPDAC micelles, it is straightforward to calculate the ratio K_S/K_Q; see Table 2. However, to calculate $\mu_{Q,el}$ and $\mu_{Q,surf}$ (and from that, R) we need to know the $C_{16}P^+$ headgroup area when the quencher is taking part of a C_{12}PPDAC micelle. Calculations described in Appendix 2 show that R is between 4.2×10^{-4} and 4.6×10^{-4} when a_0 takes on values typical for pure C_{16}PC and C_{12}PPDAC micelles. For such small R it is often a good approximation to assume that there is no free quencher. In a related paper we make use of this when investigating C_{12}PPDAC aggregates formed at the silica/water interface.[4]

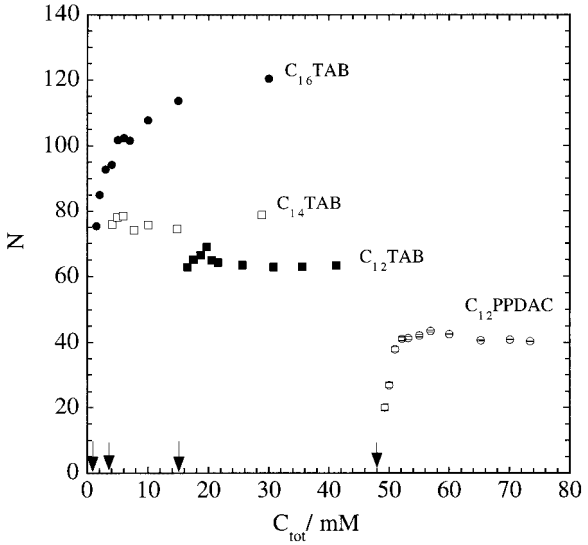

Figure 7. Aggregation numbers obtained from TR FQ for the indicated surfactants. See text for details. The cmc values for the pure surfactant systems are indicated by arrows. The arrows correspond to (from left to right): C_{16}TAB, C_{14}TAB, C_{12}TAB, and C_{12}PPDAC.

The above calculations point to the problems of describing the distribution of Q when it has a charge different from S. Therefore, if possible, such S/Q combinations should be avoided. An investigation of such mixtures will be presented in a coming article.

Experimental Results

Figure 7 shows N for C_{12}TAB, C_{14}TAB, and C_{16}TAB obtained with C_{12}PB, C_{16}PB, and C_{16}PB as quenchers, respectively. α_Q was always on the order of 0.01, which means that the fact that the quenchers were actually added to the solution as chloride salts should have no effect. N was calculated from $\langle n \rangle$ as obtained from the experimental fluorescence decay curves and X_Q using eq 3, where X_Q was obtained from eq 17 using $C_{f,S}$ equal to cmc$_S$ and R equal to K_S/K_Q. This corresponds to the approach resulting in curve 2 of Figure 4. According to the discussion above, this is an excellent approximation. In fact, judging from Figure 4 the error in X_Q (and as a consequence N) should be less than a few percent.

A recalculation of the aggregation numbers reported earlier[19] for C_{12}PPDAC using the present estimate of the relevant value of R gives the results included in Figure 7. A comparison shows that the correction of the previous estimates is very small (ca 10% close to the cmc, and about 1% at 70 mM).

The following features of Figure 7 are noteworthy. Starting with C_{16}TAB the aggregation number at a surfactant concentration of roughly 1.5 times cmc is 75 while it is 120 at 30 times the cmc. We note that the value from light-scattering studies of C_{16}TAB extrapolated to concentrations close to the cmc is 90 (cf. Figure 1). However, this estimate is not model independent (see discussion above). The method developed in this paper thus provides new information complementary to that from light scattering. The increase in aggregation number as the concentration increases close to the cmc can be attributed to an increased shielding of the headgroup interactions at the micellar surface. This is due to the increase in counterion concentration in the aqueous subphase as the surfactant concentration is increased. In terms of the thermodynamic model described above, the

increase in the aggregation number reflects the strong dependence of μ_{el} on the electrolyte concentration at low salt concentrations.[19]

Turning to the C_{12}TAB data, it shows a different behavior. The first aggregation number is obtained very close to the cmc (at ≈1.1 times the cmc). The aggregation number here is 60. It remains constant at least up to concentrations of roughly 3 times the cmc. The growth in aggregation number with concentration is thus less pronounced in the C_{12}TAB case as compared to C_{16}TAB. The reason for this difference is the higher value of the cmc for the former. The surfactant unimers and counterions in the solution serve as a background electrolyte. Thus, μ_{el} is much less sensitive to changes of the ionic strength in this concentration regime, which can explain the almost constant value of N. C_{14}TAB shows the same qualitative behavior as C_{12}TAB. C_{14}TAB has a cmc roughly 4 times that of C_{16}TAB, and thus the explanation for its behavior may be the same as for the behavior of C_{12}TAB. However, it must be remarked that the C_{14}TAB values were obtained using $C_{16}P^+$ as quencher. Thus the surfactant and the quencher are not matched with respect to the hydrocarbon chain length. This effect is not explicitly accounted for in the estimation of R (but is expected to be very small[29]). One way to check this would obviously be to use $C_{14}P^+$ as quencher. Unfortunately this molecule is not available to us.

We now turn to the divalent surfactant C_{12}PPDAC. In view of the discussion above one would perhaps expect that C_{12}PPDAC would behave similar to C_{12}TAB given its high cmc. However, the fact that the surfactant is divalent strongly affects its self-assembly as compared to the monovalent case. This can be qualitatively accounted for within the PB-cell model as shown in a previous paper.[19] The divalent charge of the surfactant is responsible for the high cmc and small aggregation numbers close to the cmc. In fact, the aggregation number (20 at the cmc and 41 at the plateau of N vs C_{tot} in Figure 7) is smaller than that expected for the maximum size consistent with a spherical micelle of a C_{12} surfactant, the value of which is roughly 60. The increase in N from 20 to 41 can be attributed to the fact that each surfactant contributes two counterions to the water subphase, which means that the headgroup screening increases rapidly with increasing surfactant concentration.

Conclusions

We have treated the problem of determining micellar aggregation numbers with the FQ method at concentrations close to the cmc and shown that this can indeed be done. Two things are required. First, the use of quenchers that are in themselves surfactants that resemble the surfactants under study. Second, the distribution of the quencher between the micelles and the water subphase should be calculated from the ratio K_S/K_Q. When applied to several monovalent cationic surfactants and one divalent surfactant, the proposed method provides aggregation numbers over a broad concentration range starting from concentrations close to the cmc values. The obtained values of N can be rationalized from a combination of electrostatic effects and the hydrophobic effect. Finally, we note that one main application of this work lies in the characterization of surface bound micelles, a problem of considerable interest.

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Appendix 1

Model System. As a system representative of C_{12}TAB/C_{12}PB we use a spherical cell with a micelle of aggregation number 56 positioned at the center. The radius of the cell is given by the concentration of micelles so that the cell has the same composition as the macroscopic system. The micelle, containing one $C_{12}P^+$ (Q) and 55 $C_{12}TA^+$ ($X_Q = 1/56$), is in equilibrium with the aqueous region of the cell, where the counterions to the charged interface and a certain amount of the neutral salts of both surfactants are dissolved ($\langle n \rangle \approx 1$ is typical for a TR FQ experiment). We assume that it is possible to replace a C_nTA$^+$ with a C_nP^+ in a C_nTAB micelle without changing the structure of the micelle. Thus, both components are assumed to occupy the same volume in the micelle core and the same area at the charged interface.

PB Cell Model Calculations. A self-consistent solution of the PB equation gives with appropriate boundary conditions the electrostatic potential and the equilibrium distribution of all ions in the cell. The boundary conditions depend on the amount of salt in the system. Here, the salt is the surfactant unimers and their counterions. At chemical equilibrium the activity, which is equal to $C_i(L)$ in the model, and $\mu_{i,el}$ must satisfy eq 10 for both surfactants. The "PB-cell" software calculates $C_i(L)$ and C_i(ave) for all ionic species in the cell and $\mu_{i,el}$ for an amphiphile in the micelle. C_i(ave) is the average concentration of i in the aqueous region. C_Q(ave) and C_S(ave) are related to $C_{f,Q}$, $C_{f,S}$, C_{tot}, α_i, and the volume fraction of micelles Φ through

$$C_{f,i} = (1 - \Phi)C_i(\text{ave}) \tag{A1}$$

$$C_{tot} = NC_m + C_{f,Q} + C_{f,S} \tag{A2}$$

$$\alpha_i = \frac{NX_iC_m + C_{f,i}}{C_{tot}} \tag{A3}$$

The following scheme permits the calculation of C_Q(ave) and C_S(ave) from X_Q and C_m.

(1) Assume a value of the activity of a 1:1 electrolyte in the cell (or in a solution in equilibrium with the cell).

(2) Solve the PB equation numerically and calculate $C^+(L)$, $C^-(L)$, C^+(ave), C^-(ave), $\mu_{Q,el}$, and $\mu_{S,el}$.

(3) Use $\mu_{Q,el}$ and $\mu_{S,el}$ to calculate $C_Q(L)$ and $C_S(L)$ from

$$C_Q(L) = \frac{\mu_{Q,el} + \mu_{Q,surf}}{K_Q} \tag{A4}$$

$$C_S(L) = (1 - X_Q)\frac{e^{\mu_{S,el} + \mu_{S,surf}}}{K_S} \tag{A5}$$

(4) Repeat step 1−3 by choosing a new value of the activity until $C_Q(L)$, $C_S(L)$ and the result in step 2 satisfy

$$C^+(L) = C_Q(L) + C_S(L) \tag{A6}$$

(5) Calculate C_S(ave) and C_Q(ave) from

$$C_S(\text{ave}) = \frac{C^+(\text{ave})}{1 + \frac{X_Q \quad K_S}{1 - X_QK_Q}} \tag{A7}$$

$$C_Q(\text{ave}) = C^+(\text{ave}) - C_S(\text{ave}) \tag{A8}$$

Appendix 2

Calculation of R for DMBP/C_{12}PPDAC. The distribution constant K_D is defined by the relationship (cf. eq 6)[41]

$$\frac{C_{m,Q}}{C_{m,S}} = K_D C_{f,Q} \quad \text{(A9)}$$

A comparison of eq A9 with eq 10 shows that K_Q is related to K_D through the relationship

$$K_Q = K_D\{e^{\mu_{Q,el}} + e^{\mu_{Q,surf}}\}_{C_{12}TAB} \quad \text{(A10)}$$

where the index "C_{12}TAB" indicates that the quantity inside the parentheses corresponds to DMBP solubilized by C_{12}TAB micelles at the cmc. A combination of eqs 10, 20, and A10 gives

$$R = \frac{1}{cmc_S K_D} \times \frac{\{e^{\mu_{S,el}} + e^{\mu_{S,surf}}\}_{pure C_{12}PPDAC}\{e^{\mu_{Q,el}} + e^{\mu_{Q,surf}}\}_{mix}}{\{e^{\mu_{Q,el}}\, e^{\mu_{Q,surf}}\}_{C_{12}TAB}\{e^{\mu_{S,el}}\, e^{\mu_{S,surf}}\}_{mix}} \quad \text{(A11)}$$

where the index "pure C_{12}PPDAC" indicates that the quantity inside the parentheses corresponds to pure C_{12}PPDAC micelles at the cmc. Likewise, "mix" refers to DMBP/C_{12}PPDAC mixed micelles.

R can be calculated from eq A11 by assuming that the solubilization site for DMBP is the same in C_{12}PPDAC and C_{12}TAB micelles. It is sufficient to consider two extreme situations. (i) the quencher is embedded in the core with no contact with water ($\mu_{Q,surf} = 0$), and (ii) it resides strictly in the micelle/water interface occupying zero volume in the core. PB calculations (with parameters taken from Table 1) give for case (i) that $\mu_{Q,el}$ (in units of RT) is equal to 0.7 both in a C_{12}TAB micelle at the cmc and in a C_{12}PPDAC micelle in a 70 mM solution of the surfactant. (At the cmc for C_{12}PPDAC we find that $\mu_{Q,el} \approx 1$.) In case (ii) the calculations again show that $\mu_{Q,el}$ is about the same (≈ -5) when DMBP is solubilized in C_{12}TAB and C_{12}PPDAC micelles. $\mu_{Q,surf}$ is not known, but since it is mainly an intrinsic property of DMBP it can be considered as a system-independent constant. As a result, $\{e^{\mu_{Q,el}}\, e^{\mu_{Q,surf}}\}_{C_{12}TAB}$ and $\{e^{\mu_{Q,el}}\, e^{\mu_{Q,surf}}\}_{mix}$ cancel each other in eq A11 no matter if DMBP is solubilized according to (i) or (ii). As regards the free energy of C_{12}PPDAC, the quantities denoted "pure C_{12}PPDAC" and "mix" will cancel each other since the change in $\mu_{S,el}$ and $\mu_{S,surf}$ when adding small amounts of the quencher to the micelle is negligible. All of these simplifications give that $R \approx (cmc_S K_D)^{-1}$ at the cmc for C_{12}PPDAC. Calculations made for several C_{12}PPDAC concentrations in the range from the cmc to 70 mM reveal that R is in the range from 4×10^{-3} to 7×10^{-3}. In these calculations cmc_S in eq A11 is replaced by $C_{S,f}$ from NMR measurements.[42]

Calculation of R for C_{16}PC/C_{12}PPDAC. We consider two extreme situations: (i) a_0 for $C_{16}P^+$ is the same as in a pure C_{16}PC micelle, and (ii) a_0 is the same as for C_{12}PPDAC in a pure micelle. Calculations show that $\mu_{Q,surf}$ increases from 2.3 to 4.5 and $\mu_{Q,el}$ decreases from 3.9 to 1.6 as a_0 increases from 52 to 104 Å^2. The net change in $\mu_{Q,el} + \mu_{Q,surf}$ being -0.1. This gives values of R between 4.2×10^{-4} and 4.6×10^{-4}. The calculations were made for $N = 41$, but the result is little dependent of this choice.

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