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Surfactant-Induced Modulation of Fluorosensor Activity: A Simple Way to Maximize the Sensor Efficiency

Arabinda Mallick, Malay C. Mandal, Basudeb Haldar, Alok Chakrabarty, Paramita Das, and Nitin Chattopadhyay*

Department of Chemistry, Jadavpur University, Calcutta 700 032, India

Received December 20, 2005; E-mail: pcnitin@yahoo.com

Tuning of the sensory capability of a potentially bioactive indoloquinolizine system, namely, 3-acetyl-4-oxo-6,7-dihydro-12*H*-indolo-[2,3-a]-quinolizine (AODIQ), is described in a biomimicking micellar nanocage. It has been shown that surfactant concentration dictates the sensing behavior of the fluorophore toward physiologically essential trace metals, such as Cu^{2+}. This is a simple and efficient technique that allows one to utilize the sensor to its maximum efficiency.

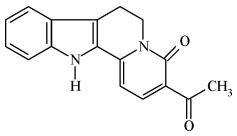
The development of fluorescence chemosensors for sensing of metal ions is an important goal in present day chemistry and biology.[1−6] The growing interest in this field can be rationalized by considering the ever-increasing air and water pollution and the consequent need to monitor the polluting species, such as Pb^{2+}, As^{3+}, etc. This area receives attention, particularly in the context of studies of metallic species in natural water and biological systems.[7,8] Useful biochemosensors are expected to be specific, have high sensitivity, and be able to operate in aqueous medium. There are some methods, such as liquid chromatography, which are frequently used for the detection of metal ions. However, in the case of detection of trace amount of metal ions, most of these methods suffer some limitations.

The fluorosensor, AODIQ (Scheme 1), used in the present experiment has recently been shown to be an excellent probe as a polarity calibrator for biomimicking and biological environments, such as micelles, reverse micelles, and proteins.[9−11] AODIQ belongs to the group of bioactive indole family and has been synthesized from 1-methyl-3,4-dihydro-β-carboline in the laboratory following the method described elsewhere.[12] Copper is one of the elements that has most extensively been detected through fluorescence sensing technique. This is not surprising since on one hand it is an essential trace element in the physiological system[13−15] and on the other hand fluorescence signaling technique offers the advantage of high sensitivity.[16]

A major effort on sensor research has focused on tuning the sensory capability by rational designing and synthesis of suitable probes. For example, the emission wavelength and fluorescence quantum yield can be tuned by changing the chemical structure of the sensor molecule. This approach often involves frightening synthetic efforts. Hence, a suitable but simple and powerful technique to tune the sensory capability without synthesizing new chemical structure is much welcome.

Surfactants are central to biosensor application since they stabilize DNA/DNA and protein/protein interactions.[17] In addition, surfactants, because of their ability to solubilize the membrane proteins, are extremely important in simulating the complex environmental condition present in larger bioaggregates, such as biological membranes.[18] Micellar effects on reactivity and equilibrium have been exploited to modify and improve a variety of important analytical methods. Works in the area of micellar, reverse micellar, monolayer, and metal chelating nanoparticle environments are of growing importance to modify and improve the sensing capability of fluorosensors.[19−21]

Scheme 1. Structure of AODIQ



Interaction of Cu^{2+} with AODIQ leads to the quenching of the fluorescence of the fluorophore and allows detection of the former in the micro or submicromolar range. This fluorescence quenching technique can be exploited to measure the concentration of the essential trace metals in biological environments. An enhanced efficiency in the fluorescence quenching leads to a better sensitivity of the sensor.[22] Appreciating the importance of this aspect, in the present communication, we report the modulation of sensing efficiency of a bioactive probe, AODIQ, toward Cu^{2+} simply by altering its environment by the use of a suitable surfactant. We find that the quenching efficiency of AODIQ increases enormously up to a critical surfactant concentration, after which the efficiency decreases again with further addition of the surfactant. This allows one to tune the sensing ability of the sensor and exploit it to its maximum efficiency level.

Quenching of fluorescence of AODIQ due to the physiologically important trace element Cu^{2+} (heavy metal ion) has been studied as a function of concentration of an anionic surfactant, sodium dodecyl sulfate (SDS). In aqueous medium, the sensor molecule absorbs appreciably in the blue region (at 420 nm) and emits in the green region (broad emission around 520 nm). In SDS environment, the emission maximum is blue shifted to 500 nm along with an enhancement in the fluorescence yield and fluorescence lifetime. A broad and unstructured band, ascribed to the intramolecular charge transfer transition,[23] characterizes the fluorescence spectrum of AODIQ in aqueous SDS medium. Figure 1 depicts the effect of the addition of Cu^{2+} on the fluorescence intensity of AODIQ.

As is evident from Figure 1, gradual addition of metal ion (Cu^{2+}) to the aqueous solution of AODIQ (ca. 4×10^{-6} M) at a particular concentration of SDS results in the quenching of the fluorescence of AODIQ without an appreciable shift in the emission maximum.

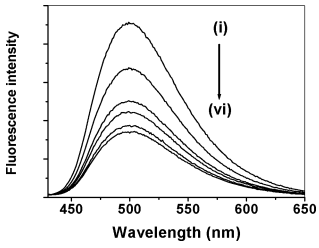


Figure 1. Emission spectra of AODIQ in micellar solution as a function of $[Cu^{2+}]$ (λ_{exc} = 420 nm, [SDS] = 4.8 mM). Curves (i) → (vi) correspond to $[Cu^{2+}]$ = 0, 11, 22, 33, 44, and 55 μM, respectively.

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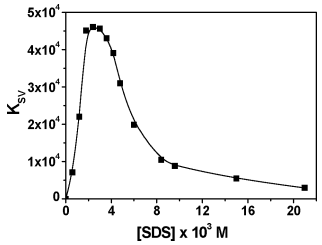

Figure 2. Variation of K_{SV} as a function of SDS concentration.

The effect obtained for the quenching of the AODIQ fluorescence upon addition of Cu^{2+} in SDS medium is in accordance with the Stern−Volmer equation, which can be expressed as follows

$$F_0/F = 1 + K_{SV}[Cu^{2+}] \quad \text{(i)}$$

F_0 and F being the fluorescence intensities of AODIQ in the absence and presence of quencher (metal ion). The slope of the plot of F_0/F against $[Cu^{2+}]$ gives the Stern−Volmer quenching constant (K_{SV}), which is an indicator of the degree of sensitivity of the fluorosensor for the detection and estimation of the quencher metal ion.

Anionic SDS micellar environments have been exploited to enhance the sensor efficiency for reasons discussed later (vide infra). K_{SV} has been determined in the presence of various concentrations of SDS, and they are plotted as a function of SDS concentration in Figure 2. The variation of K_{SV} with SDS concentration makes a bell-like pattern, that is, as the SDS concentration increases, K_{SV} increases up to [SDS] $\approx$ 2.5 mM and then it decreases with further increase in the SDS concentration. It is important to mention here that in 2.5 mM SDS environment the K_{SV} value is enhanced to nearly 2000 times its value in pure aqueous medium. Considering the fact that the fluorescence lifetime of the fluorophore in SDS micellar medium ($\tau_f = 2.0$ ns) is enhanced only slightly (relative to the huge enhancement in the K_{SV} value) from its value in aqueous solution ($\tau_f = 800$ ps), we can conclude that the higher the value of K_{SV}, the greater is the sensitivity of the sensor.[11,24]

Figure 2 reveals that the quenching efficiency of Cu^{2+} is maximum at ~2.5 mM SDS concentration. In this condition, presence of only 10 μM Cu^{2+} in the solution quenches the fluorescence of AODIQ to 50% of the original. This fluorescence quenching is large enough to consider this simple system as an efficient fluorescent sensor for the detection of copper ion, and it can be compared favorably to most of the known copper-specific chemosensors.[19,25] Similar experiment performed with Ca^{2+} ion reveals that the fluorescence of AODIQ is not affected by these interfering ions, commonly present in physiological fluids.

Before making an attempt to explain the variation of the sensitivity parameter (K_{SV}) of the fluorosensor with SDS concentration, it is important to remember two known facts: (i) in the presence of free ions, critical micellar concentration (cmc) of SDS decreases appreciably from its usual value of 5−8 mM in the absence of electrolyte;[26] and (ii) AODIQ molecule locates itself in the micelle−water interfacial region.[10] The indifference in the absorption spectra and shortened fluorescence lifetime of the sensor upon addition of quencher rule out complex formation with Cu^{2+} and reflect that the quenching process is dynamic. Fluorescence quenching of AODIQ with Cu^{2+} gives K_{SV} of 4.8×10^4 M^{-1} at 2.5 mM SDS. Considering dynamic quenching mechanism, the quenching constant is estimated to be $k_q = K_{SV}/\tau_f \approx 2 \times 10^{13}$ M^{-1} s^{-1}, which is 3 orders of magnitude higher than a value expected for simple diffusion control quenching.[24] An effective electrostatic interaction between the positively charged metal ion and the negatively charged micellar surface appears to be responsible for the higher value of K_{SV}.[27]

The modulation of the activity of the fluorosensor as a function of SDS concentration is thus rationalized by considering two competing processes: electrostatic interaction between the anionic SDS micellar surface and the positive metal ion (Cu^{2+}) and lesser accessibility of the probe molecules toward the metal ions within the micellar environment. The first factor leads to an increase in the local concentration of the metal ions in the near vicinity of the probe. The close proximity of the fluorophore and the metal ions in micellar aggregates ensures effective communication between the active components responsible for quenching. Thus with the formation of the micellar units, the efficiency of quenching is enhanced. Further addition of SDS, after the formation of the micelle, leads to the swelling of the micellar units allowing the penetration of the fluorophore within the apolar micellar phase. This restricts the accessibility of the probe molecules toward the metal ions, resulting in a reduction in the quenching efficiency.

In conclusion, we have shown that the metal sensing ability of a fluorosensor can be modulated simply by using commercially available anionic surfactants. One can thus tune the sensing ability of a system to its maximum value. With a proper choice of suitable surfactants, the method has the potential to be utilized conveniently in general for the purpose of detection of essential metal ions in real biological environments.

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