A Nanoreactor for Tuning the Chemical Reactivity of a Solute

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · AUGUST 2008

Impact Factor: 3.3 · DOI: 10.1021/jp8050802 · Source: PubMed

5 AUTHORS, INCLUDING:

Prabhat Singh
Bhabha Atomic Research Centre
37 PUBLICATIONS **491** CITATIONS
SEE PROFILE

Manoj Kumbhakar
Government of India
65 PUBLICATIONS **1,548** CITATIONS
SEE PROFILE

Haridas Pal
Bhabha Atomic Research Centre
193 PUBLICATIONS **4,933** CITATIONS
SEE PROFILE

Sukhendu Nath
Bhabha Atomic Research Centre
81 PUBLICATIONS **1,434** CITATIONS
SEE PROFILE

THE JOURNAL OF PHYSICAL CHEMISTRY B LETTERS

2008, *112,* 11447–11450
Published on Web 07/09/2008

A Nanoreactor for Tuning the Chemical Reactivity of a Solute

Prabhat K. Singh,[†] Ashis K. Satpati,[‡] Manoj Kumbhakar,[†] Haridas Pal,[†] and Sukhendu Nath*,[†]

Radiation & Photochemistry Division and Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Received: June 10, 2008; Revised Manuscript Received: June 24, 2008

Present results demonstrate that the redox potential and hence the chemical reactivity of a solute dissolved in a polymer−surfactant supramolecular assembly, considered as a nanoreactor, can be tuned substantially by changing the composition of the supramolecular assembly. It is understood from detailed study that, on changing the polymer−surfactant composition of the supramolecular assembly, the probe undergoes a change in its location in these nanoreactors and accordingly its physical and chemical properties can be modulated.

Microheterogeneous media like micelles can be considered as nanoreactors and nanocontainers and have been used widely in various applications, e.g., as a confined media for organic synthesis,[1–3] as a template for nanostructures,[4–7] as drug carrier systems,[8–10] etc. In all of these applications, the solute of interest is dissolved into the nanosized confined micellar media, and the efficiency of the desired process is determined largely by the physical and chemical properties of the entrapped solute in these nanoreactors. Among other chemical processes, redox reactions are the most important processes involved in many of these applications. Even the pharmacological activity of certain molecules is believed to be related to their redox properties.[11] Thus, controlling the reactivity of a chemical species by changing its redox behavior is always a desire to chemists. The most conventional route for modulating the redox behavior of a molecule is the chemical modification/substitution of the species. However, in this chemical route, the other important chemical properties of the species may get changed, which may result in some other unwanted chemical effects. Changing the chemical reactivity by some physical means is always a challenging task to chemists. In this Letter, we report the use of a nanosized supramolecular assembly to tune the redox potential and hence the chemical reactivity of an entrapped solute.

Since a wide range of microenvironments exist in a single micellar phase, a solubilized molecule can in principle show a wide range of physical as well as chemical properties in these media depending on its position in the micelle. The main strategy of the present work is to see if by any physical means it is possible to change the location of the dissolved solute in a micelle and thus to tune its physical as well as chemical properties. For this purpose, we have used a supramolecular system composed of P123 pluronic polymer and CTAC surfactant, while the dye coumarin-343 (C343) is used as the solute.[12] At the working pH condition, the dye C343 exists in its anionic form.[13,14]

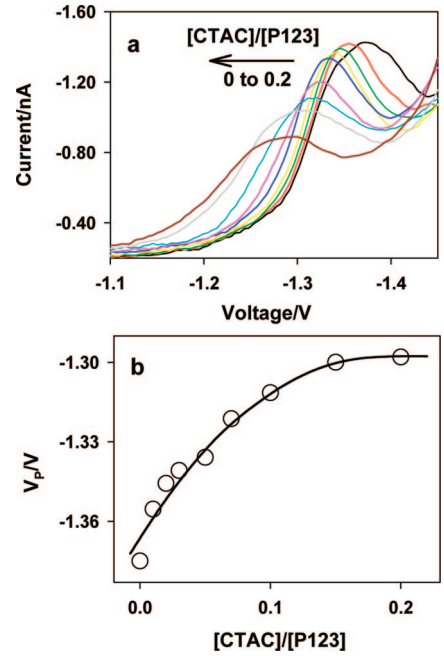


Figure 1. (a) Differential pulse polarograms and (b) variation of the peak potential (V_p) of C343 in P123 micellar solution at different CTAC concentrations. The CTAC/P123 molar ratios used are 0.0, 0.01, 0.02, 0.03, 0.05, 0.07, 0.10, 0.15, and 0.20. The solid line is the best fitted smooth curve among the data points.

Differential pulse polarography studies[12] have been carried out for C343 dye in the P123 micellar solution at different CTAC concentrations to investigate the effect of the cosurfactant on the redox behavior of the solute in the P123 micelle. Differential pulse polarograms for C343 at different CTAC concentrations are presented in Figure 1a. The peak potential of C343 in pure P123 micelle appears at −1.381 V. However, as we gradually increase the CTAC concentration, the polarographic peak gradually shifts toward the less negative potential. Thus, the peak potential of the dye measured at a CTAC/P123 molar ratio of ∼0.2 is about −1.298 V. The variation in the peak potential (V_p) for the dye as a function of CTAC concentration in P123 micelle is shown in Figure 1b. A

* To whom correspondence should be addressed. Phone: 91-22-25590306. Fax: 91-22-25505151. E-mail: snath@barc.gov.in.
† Radiation & Photochemistry Division.
‡ Analytical Chemistry Division.

10.1021/jp8050802 CCC: $40.75

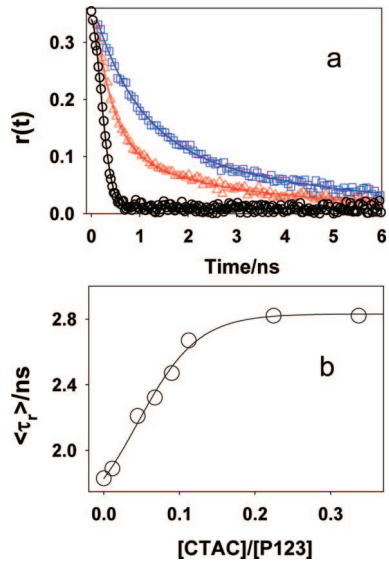


Figure 2. (a) Decay of fluorescence anisotropy, $r(t)$, for C343 in water (○) and in P123 micelle at different CTAC/P123 molar ratios: (△) 0.0 and (□) 0.34. (b) Variation of the average reorientation time, $\langle\tau_r\rangle$,[12] for C343 in P123 micelle with varying CTAC/P123 molar ratios. The solid line is the best fitted smooth curve among the data points.

gradual change in the peak potential clearly indicates that the solute C343 gradually becomes a stronger oxidant as we increase the CTAC concentration in P123 micellar solution. It is also evident from Figure 1b that the redox potential of the solute tends to reach a limiting value at a CTAC/P123 molar ratio of ~0.15. This implies that the property of the present solute does not change any further beyond a CTAC/P123 molar ratio of ~0.15.

The change in the redox characteristics of the solute is associated with only a little change in the absorption and fluorescence spectra of the solute. These results indicate that the addition of CTAC to the P123 micellar solution does not cause any change in the chemical nature of the dye, and it is believed that the changes in the redox characteristics of the solute is due to the changes in the microenvironment around the solute in P123 micelle as a function of CTAC concentration. To substantiate this further, we have carried out the rotational relaxation dynamic studies of C343 in the P123 micellar system at different CTAC concentrations using time-resolved fluorescence anisotropy measurements.[12] The typical fluorescence anisotropy decays of C343 in P123 micelle with varying CTAC concentrations are shown in Figure 2a. For comparison, the anisotropy decay for C343 in water is also shown in Figure 2a.

The slow rotational relaxation in the micellar media compared to that in pure water as shown in Figure 2a suggests that the solute C343 is solubilized in the micellar phase rather than in the bulk water phase. From Figure 2a, it is also evident that, as we increase the concentration of CTAC in the micellar media, the anisotropy decay gradually becomes slower. The changes in the average reorientation time, $\langle\tau_r\rangle$,[12] for the C343 dye in the micellar media at different CTAC concentrations are shown in Figure 2b. These results suggest that, as we increase the CTAC concentration, the rotation of the solute, C343, gradually becomes more restricted in the present system.

To understand whether the observed changes in the redox potentials are correlated with the changes observed in the reorientation times, we have plotted in Figure 3 the changes in the peak potential vs the changes in the reorientation time of the probe due to the addition of CTAC in the P123 micellar

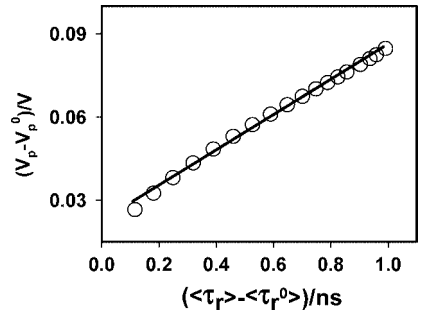


Figure 3. Variation of the changes in the peak potential, $(V_p - V_p^0)$, with the changes in the reorientation time $(\langle\tau_r\rangle - \langle\tau_r^0\rangle)$ of C343 due to the addition of CTAC in P123 micellar solution.[15] V_p^0 and $\langle\tau_r^0\rangle$ are the peak potential and average reorientation time of C343 in P123 micellar solution in the absence of CTAC, and their values are −1.381 V and 1.83 ns, respectively. The solid line is the best fitted straight line through the data points.

solution. It is clearly evident from this figure that the changes in the peak potential and the changes in reorientation time are linearly correlated to each other. This observation clearly indicates that the reason for the observed changes in the peak potentials is the same as that of the observed changes in the reorientation times of the probe in the present system.

The above electrochemical and rotational relaxation results can be explained on the basis of the structure of the supramolecular assembly formed due to the addition of CTAC to the P123 micellar solution. Detailed X-ray and light scattering studies on the P123 micellar system in the presence of CTAC suggest the formation of a kind of supramolecular assembly.[16,17] Ganguly et al. have proposed a unique structure for these supramolecular assemblies based on their results from detailed neutron scattering studies.[18] According to these authors, in these supramolecular assemblies, the long hydrocarbon chains of the ionic surfactants are embedded into the hydrophobic core of the pluronic micelles and the charged head groups of the surfactants reside at the interfacial region between the micellar core and the corona region. Such an arrangement resulted in a supramolecular assembly that contains a charged layer inside the micellar phase, and the charge density of this layer increases gradually as the surfactant to polymer molar ratio increases.

We infer that the changes in the electrochemical and rotational relaxation characteristics of the present solute is a manifestation of the electrostatic interaction between the anionic probe C343 and the positively charged layer inside the supramolecular assembly. In P123 micellar solution, as C343 exists in its anionic form, it prefers to reside at the micellar surface rather than entering deep into the micellar phase.[13,14] With a gradual increase in CTAC concentration, as the positive charge density gradually increases in the interior of the micelle due to the formation of the supramolecular assembly, the anionic probe C343 will gradually be dragged into the interior of the micelle. Our studies on the solvent relaxation dynamics also support this movement of the probe inside the supramolecular assembly on addition of surfactant, CTAC.[19] Under such a situation, the increase in the reorientation time with CTAC concentration can be due to the following two reasons. First, the microviscosity in the micellar interior is much higher than that at the micelle−water interface. Second, the mobility of the ionic probe will also be restricted due to the electrostatic interaction between the negatively charged probe and the positively charged layer inside the micelle. The decrease in the polarographic current with an increase in the CTAC concentration (cf. Figure 1a) is a manifestation of the formation of a supramolecular assembly

with P123 micelle. As we increase the CTAC concentration, we are adding more and more CTAC molecules to the existing P123 micelles. This addition of CTAC molecules in the P123 micelle results in the increase in the average molecular weight of the micelle. Due to the increase in the average weight of the micelle, the diffusion of the latter will be sluggish. As the polarographic current is directly related to the diffusion of the micelle,[20] the observed current decreases with the increase in the CTAC concentration. The increase in the oxidation power of the probe, C343, on gradual increase in the CTAC concentration, is also a manifestation of the electrostatic interaction between the headgroup of CTAC and the reduced form of the probe molecule.[21] On reduction, the probe C343 becomes more negetively charged and hence gets stabilized in the P123−CTAC supramolecular assembly due to the electrostatic attraction between oppositely charged species. This additional stabilization of the reduced form of C343 leads to an increase in the oxidation power in the supramolecular assembly in the presence of CTAC.

The changes in the reorientation time of the probe due to any major structural change in the micelle on addition of CTAC can easily be ruled out based on the following considerations. The detailed structural study by Jansson et al.[16,17] has shown that the changes in the micellar characteristics, like the core and the micellar radius, are only marginal even up to the CTAC/P123 molar ratio of ~0.5. Recently, Mali et al.[22] have suggested that the addition of CTAC does not change the characteristics of the P123 micelle significantly. These authors have shown that the reorientation time of a cationic dye, which resides at the micellar surface, remains almost unchanged on addition of CTAC up to ~0.5 CTAC/P123 molar ratio. This clearly indicates that even if there is a marginal change in the P123 micellar characteristic due to the addition of CTAC, it does not cause any significant change in the reorientation time for a probe residing at the surface of the micelle. As the anionic probe, C343, is also reported to reside at the micellar surface under normal circumstances,[13,14] the observed increase in the reorientation time with CTAC concentration certainly suggests that it is not related to the changes in the micellar characteristics but is due to the changes in the location of the probe in the supramolecular assembly formed by the special arrangement of CTAC into the P123 micelle.

Surfactant induced changes in the pK_a values have been reported in the literature.[23] The probe that we have used can also change its prototropic equilibrium due to the changes in the micellar characteristics. To confirm whether the observed changes are due to the changes in the prototropic equilibrium of the dye, we have also measured its pK_a value in three different conditions, namely, in neat water, in P123 micellar solution, and in P123−CTAC mixed micellar solution with a [CTAC]/[P123] ratio of ~0.4. The pH dependent changes in the absorbance for the neutral form of C343 in these three media are shown in Figure 4. The pK_a values are calculated from the inflection points of the curves and are found to be 4.5, 6, and 4.9 in water, P123, and P123−CTAC medium, respectively. These results clearly indicate that, at the experimental condition (pH 8.1), C343 is always present in the anionic form in the present system. Although there is a shift in the pK_a value due to the addition of CTAC in P123 micellar solution, this does not affect the prototropic form of the probe in the experimental solution, because the pK_a is always lower in P123−CTAC solution than in P123 solution. Thus, it may be inferred that the observed changes in the redox potentials and reorientation times due to the addition of CTAC surfactant in P123 micellar solution cannot be due to the changes in the prototropic form of the probe.

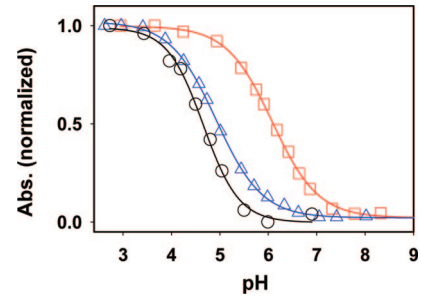
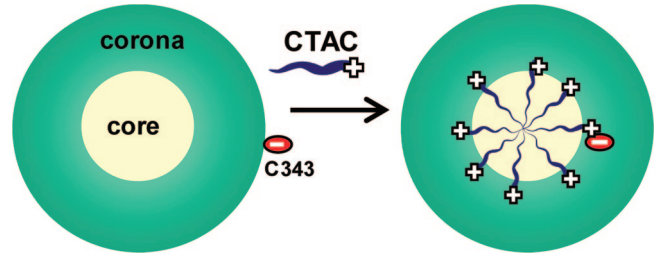


Figure 4. Variation in the absorbance for the neutral form of C343 at different pHs in (○) water, (□) P123 micellar solution, and (△) P123−CTAC mixed solution with a [CTAC]/[P123] value of 0.4. The absorbances of C343 in solution at the lowest pH used for the three systems were normalized to unity for comparison.

SCHEME 1: Schematic Representation of the Changes in the Location of an Anionic Solute with the Addition of a Cationic Co-Surfactant in a Neutral Micelle



In conclusion, the present study indicates that the location of a suitable probe can be changed in a confined nanosize media simply by the addition of an ionic surfactant to a polymer micelle. These changes in the probe location in the supramolecular assembly with an increase in the CTAC concentration can be presented as in Scheme 1.

The present study shows that, in the supramolecular assembly, which can be considered as a nanoreactor, the location of the solute and consequently its redox potential can be tuned by changing the composition of these assemblies. As the chemical reactivity of a solute largely depends on its redox potential, the former can be controlled by suitable choice of the composition of these nanoreactors. This phenomenon can also be utilized in other polymer−surfactant systems and can find possible applications in various applied areas, like chemical synthesis in micellar media, biological activity of drugs, etc.

Acknowledgment. The authors are thankful to Dr. G. B. Dutt and Dr. R. Ganguly for many valuable suggestions.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Vriezema, D. M.; Aragonès, M. C.; Elemans, J. A. A. W.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M. *Chem. Rev.* **2005**, *105*, 1445.
(2) Lindström, U. M. *Chem. Rev.* **2002**, *102*, 2751.
(3) Klier, J.; Tucker, C. J.; Kalantar, T. H.; Green, D. P. *Adv. Mater.* **2000**, *12*, 1751.
(4) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.
(5) Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.
(6) Förster, S.; Konrad, M. *J. Mater. Chem.* **2003**, *13*, 2671.
(7) Sakai, T.; Alexandridis, P. *Langmuir* **2005**, *21*, 8019.

(8) Kataoka, K.; Harada, A.; Nagasaki, Y. *Adv. Drug Delivery Rev.* **2001**, *47*, 113.

(9) Kabanova, A. V.; Batrakovaa, E. V.; Alakhovb, V. Y. *J. Controlled Release* **2002**, *82*, 189.

(10) Lavasanifar, A.; Samuel, J.; Kwon, G. S. *Adv. Drug Delivery Rev.* **2002**, *54*, 169.

(11) Sereda, G.; Heukelom, J. V.; Koppang, M.; Ramreddy, S.; Collins, N. *Beilstein J. Org. Chem* **2006**, *2*, 26.

(12) See the Supporting Information for molecular structures of all chemicals used and details of the experimental procedure.

(13) Riter, R. E.; Undiks, E. P.; Levinger, N. E. *J. Am. Chem. Soc.* **1998**, *120*, 6062.

(14) Grant, C. D.; DeRitter, M. R.; Steege, K. E.; Fadeeva, T. A.; Castner, E. W., Jr *Langmuir* **2005**, *21*, 1745.

(15) The data points in Figure 3 are obtained from the best fitted solid curve, as shown in Figure 1b and Figure 2b.

(16) Jansson, J.; Schillen, K.; Nilsson, M.; Soderman, O.; Fritz, G.; Bergmann, A.; Glatter, O. *J. Phys. Chem. B* **2005**, *109*, 7073.

(17) Jansson, J.; Schillen, K.; Olofsson, G.; da Silva, R. C.; Loh, W. *J. Phys. Chem. B* **2004**, *108*, 82.

(18) Ganguly, R.; Aswal, V. K.; Hassan, P. A.; Gopalakrishnan, I. K.; Kulshreshth, S. K. *J. Phys. Chem. B* **2006**, *110*, 9843.

(19) Singh, P. K.; Kumbhakar, M.; Pal, H.; Nath, S. *J. Phys. Chem. B* **2008**, *112*, 7771.

(20) Parry, E. P.; Osteryoung, R. A. *Anal. Chem.* **1965**, *37*, 1634.

(21) Prado-Gotor, R.; Jimenez, R.; Perez-Tejeda, P.; Lopez-Lopez, M.; Sanchez, F. *Chem. Phys.* **2001**, *263*, 139.

(22) Mali, K. S.; Dutt, G. B.; Mukherjee, T. *J. Chem. Phys.* **2007**, *127*, 154904.

(23) Kalyanasundaram, K. *Photochemistry in Microheterogeneous systems*; Academic Press Inc.: Orlando, FL, 1987.

JP8050802