# **Excited State Proton Transfer in Gemini Reverse Micelle and**

# **Cationic Alkyl Quaternary Ammonium Reverse Micelles**

# **: A Comparative Study**

Dr. Romen Chutia­a and Dr. Aparajita Phukonb

aChemistry Department, Debraj Roy College, Golaghat-785621, Assam, India

bIndian Institute of Technology Guwahati, Guwahati-781039, Assam, India

[aorkromen@gmail.com](mailto:aorkromen@gmail.com)

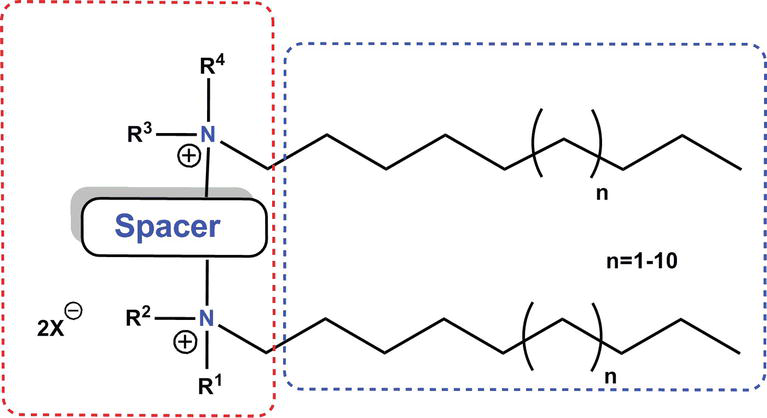
**Abstract**

Gemini cationic surfactants are compounds with two hydrophilic head groups and two hydrophobic tails linked by a spacer at the head. How do the interfacial properties (e.g. interfacial hydration or headgroup packing) of a Gemini reverse micelle differ from those of a cationic reverse micelle? For this, we investigated excited-state proton transfer (ESPT) and fluorescence anisotropy decay of an interface localized negative fluorophore, 8-hydroxypyrene-1,3,6-trisulphonate (HPTS), and its methyl analogue, 8-methoxypyrene-1,3,6-trisulfonate (MPTS), within the reverse micellar interfaces. Two Gemini surfactants (G-12-2-12 and G-16-2-16) and two cationic surfactants (DTAB and CTAB) with matching alkyl tails were selected for an effective comparison. The steady state, time resolved fluorescence as well as anisotropy studies clearly reveal about the compact and highly packed less hydrophilic nature of Gemini reverse micelle.

**Key words**: ESPT, HPTS, Gemini Surfactant, Reverse micelle, Anisotropy.

**Introduction**

Gemini surfactants are dimeric surfactant molecule, with two hydrophilic head groups and two hydrophobic groups covalently joined together through a spacer (Figure 1).Quaternary ammonium gemini surfactants have a nomenclature of the type m-s-m where m indicates the number of carbons atoms in the hydrophobic chain, and s indicates those in the spacer.These surfactants possess surface active properties superior to those of corresponding conventional surfactants with one hydrophilic and one hydrophobic group like lower critical micelle concentration (CMC), low Kraft temperature.[1](#_ENREF_1)The CMC values of gemini surfactants depends on the length of spacer; longer spacer decreases the CMC value. Therefore, Gemini surfactants can be broadly applied in various fields, like soil remediation, separation of biomaterials, enhanced oil recovery and drug entrapment and release, skin careeither as micelle, reverse micelle, vesicles etc.



**Scheme 1: Schematic representation of Gemini surfactant structure.**

Reverse micelle is one of the surfactant assemblies containing an inner core of water molecules, dispersed in acontinuous organic solvent medium. Similar to cationic surfactants, such as cetyltrimethylammoniumbromide (CTAB), gemini surfactants need assistance ofco-surfactant in order to form stable RMs.The water trapped in the reverse micelle is used to study as a model of specific water in biologicalsystems because the properties of encaged water can be easily tuned just by changing size of reverse micelles by injecting different amount of water using the relation,w0 = [H2O]/ [surfactant]. The FT-IRexperiments revealed presence of four different water typesinside the RMs: bulk-like water, cation-bound water, or anionboundwater and free water, which structures depend on the W0value.[2](#_ENREF_2)

Excited state proton transfer (ESPT) offers many importantinsights about the nature and dynamics of water inside variousself-assemblies. The photo-acid 8-hydroxypyrene-1,3,6-trisulphonate (HPTS)bears strong negative charges (-3 and -4,respectively, in the protonated and deprotonated forms). Thereby, HPTS acts as a prototype of a large anion whichcan be accommodated at the interface of cationic reverse micelle. The emission of HPTS isvery sensitive to local hydration inside reversemicelles.[3](#_ENREF_3) The optical properties of the protonated (ROH) anddeprotonated (RO-) forms are quite distinct, which allows theESPT dynamics to be conveniently followed.[4](#_ENREF_4),[5](#_ENREF_5)

Here, we compare the ESPT dynamics of HPTS inside cationicand Gemini reverse micelles. In addition, we used amethyl analogueof HPTS, 8-methoxypyrene-1,3,6-trisulfonic acid (MPTS),to monitor the fluorescence anisotropy decay. The lack of an ESPTprocess for MPTS is advantageous for the fluorescence anisotropymeasurement. A detailed comparison of the results obtainedfor the two reverse micelles may shed light on the organization of the surfactants at the micelle interfaces. Interestingly, we found astonishing similarity, as well as, notable dissimilarity between the two types of reverse micelles.

# **Experimental Section**

* 1. ***Materials used:*** 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS, pyranine),8-Methoxypyrene-1,3,6-trisulfonic acid trisodium salt (MPTS) cetyltrimethylammonium bromide (CTAB, 98%) and *n*-pentanol (99%), 1,2-bis(dimethylamino)ethane, 1-bromododecane, 1-bromohexadecanewere purchased from Sigma-Aldrich. Benzene (HPLC grade), n-pentanol, ethanol, ethyl-acetate, ethyl ether, chloroform were purchased from Spectrochem, India. Water (resistivity 18.2 MΩ cm) from a Millipore system was used in the study.The Gemini surfactants (G12-2-12, G16-2-16) were synthesized[6](#_ENREF_6),[7](#_ENREF_7).
  2. ***Instruments and detection methods:***Absorption and emission spectra were measured in a Perkin-Elmer Lamda-750 spectrophotometer and Jobin-Yvon FluoroMax4 spectrofluorometer, respectively. The time-resolved fluorescence were recorded by a time-correlated single photon counting (TCSPC) setup (Horiba Instruments) using a picosecond laser diode 375 (Horiba Instruments) with an excitation wavelength of 375 nm. The FWHM of the set up was typically ~160 ps. The fluorescence decays were fitted using DAS6 software. The fluorescence transients were recorded by keeping the analyzer at the magic angle (55°) with respect to the polarizer.

To measure fluorescence anisotropy decays, the analyzer was rotated at regular intervals to obtain parallel () and perpendicular () decay components of a fluorescence decay separately. The anisotropy function, r(t) was constructed using the expression

(1)

The G value of the set up was determined at 440 nm emission wavelength of HPTS and was found to be 0.68.Fluorescence anisotropy decays were fitted using DAS6 software.

* 1. ***Preparation of reverse micelle solution****:* To prepare reverse micelle, first 0.1 M surfactant solution in benzene was prepared. The co-surfactant pentanol is added maintaining the pentanol to surfactant ratio (p0) at 7. Reverse micelles at various w0s was prepared by injecting a requisite amount of water (using the relation, w0 = [H2O]/ [surfactant]) into the above mentioned solution. The benzene/Gemini/n-pentanol systems require a minimum amount of water to solubilize the surfactant[8](#_ENREF_8), for [Gemini] = 0.1M the minimum w0 value required is w0min = 5.To incorporate the probe into the reverse micelle (RM) solution, a required amount of a stock solution of HPTS/MPTS in water were injected into the reverse micelle solution and this amount of water was included in the w0 calculation. In all the experiments, we kept the HPTS/MPTS concentration at ∼8μM.MPTS is used in the anisotropy measurement to avoid ESPT, i.e. mixing of de-protonated band to the protonated one.

## **Results:**

### **Steady State Spectroscopy:**

The absorption spectra of HPTS inside all the reverse micelles are verysimilar with a common absorption maximum at ~ 405 nm. The absence of any absorbance at higherwavelengths (<430 nm) eliminates the possibility of any groundstatedeprotonation of HPTS at a bulk pH of 5.6.



**Figure 1:Comparison of the absorption spectra of HPTS in the cationic and Gemini reverse micelle at p0 = 7.**

****

**Figure 2:Comparison of Emission spectra (normalized at the protonated emission band) of HPTS insidedifferent reverse micelles at w0 = 6, 20. The black line for G12-2-12, red for DTAB, blue for G16-2-16 and orange for CTAB reverse micelle at p0 = 7n-pentanol to surfactant concentration.**

### The emission spectra of the fluorophore HPTS highly dominated by protonated band at 430nm for cationic reverse micelle and 433nm for Gemini reverse micellar medium. The deprotonated band becomes prominent on increasing w0 value, at expense of protonated emission band. The deprotonated band appear at 520nm at low w0 (=6) and undergo red shift to 525 nm at higher w0 (=20) value for cationic reverse micelle. However, for Gemini (G12-2-12, G16-2-16) reverse micelle the deprotonated emission band arise at 525nm. Noted ESPT dynamics is quite slow in the Gemini reverse micelle even at higher w0 value unlike the cationic reverse micelle (**Figure 2**).

### **Time-Resolved Fluorescence*.***

To investigate the ESPT dynamics of HPTS inside the cationic and Gemini reverse micelle, we record fluorescence transients of HPTS at two selective emission wavelengths representative of the protonated (425 nm) and deprotonated (570 nm) emission band. The selected wavelength,425 nm is slightly higher in energy compared to the protonated emission maxima (), whereas, 570 nm is lower in energy compared to the de-protonated emission maxima (). We intentionally pick these wavelengths to avoid undesirable mixing of the contribution of the two respective forms.[9](#_ENREF_9),[10](#_ENREF_10)



**Figure 3a: Fluorescence transients of the protonated form of HPTS inside different reverse micelles of w0 = 6, 20(λem= 425 nm).**

The fluorescence transients of HPTS monitored at 425nm is slightly faster in the cationic DTAB RM than in G12-2-12 and almost similar for CTAB and G16-2-16. However, we observe notable variation at higher w0 (= 20) value (**Figure3a**).

A clear ultraslow rise component is observed inthe deprotonated emission transients indicative of the ESPTphenomena. The rise times of the deprotonated form are ofsimilar magnitude to that of the decay times of the correspondingprotonated emission (**Table 1**).

The rise times alsobecome longer for the Gemini reverse micelles than those of thecationic reverse micelles for the same tail length of the surfactants.Thus, the ESPT dynamics in the Gemini reverse micelles are more retardedthan those of the corresponding cationic reverse micelles. The emission decays for both protonate and de-protonated form are fitted by a tri-exponential fitting function.

ROH\*(t)] or [] = +



**Figure 3b: Fluorescence transients of the de-protonated form of HPTS inside different reverse micelles of w0 = 6, 20 (λem= 570 nm).**

**Table 1. Fitting parameters of the protonated (ROH\*, λem = 425 nm) and deprotonated (ROH-\*,**

**λem = 570 nm) emission transients of HPTS inside different reverse micelles with matching decay and rise time.**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **ROH\*** | | | | | **RO-\*** | | | |
| **w0 = 6** | **τ1(ps)** | **τ2 (ps)** | **τ3 (ps)** | **χ2** | **τ1(ps)** | **τ2 (ps)** | **τ3 (ps)** | **χ2** |
| ***DTAB*** | 315  (0.17) | 2165  (0.53) | 3605  (0.30) | 1.21 | 315  (-0.96) | 2165  (-4.74) | 4065  (6.70) | 1.16 |
| ***G12-2-12*** | 545  (0.12) | 2775  (0.66) | 4150  (0.22) | 1.04 | 545  (-0.71) | 2775  (-1.73) | 4385  (3.44) | 1.09 |
| ***CTAB*** | 330  (0.07) | 2125  (0.58) | 3900  (0.35) | 1.1 | 330  (-0.68) | 2125  (-4.03) | 4125  (5.71) | 1.1 |
| ***G16-2-16*** | 605  (0.04) | 2580  (0.71) | 4180  (0.25) | 1.1 | 605  (-0.41) | 2580  (-0.81) | 4480  (2.22) | 1.1 |
| **w0 = 20** | **τ1(ps)** | **τ2 (ps)** | **τ3 (ps)** | **χ2** | **τ1(ps)** | **τ2 (ps)** | **τ3 (ps)** | **χ2** |
| ***DTAB*** | 330  (0.13) | 1995  (0.68) | 3185  (0.20) | 1.1 | 330  (-0.34) | 1995  (-5.06) | 4735  (6.40) | 1.1 |
| ***G12-2-12*** | 580  (0.23) | 2765  (0.74) | 5470  (0.03) | 1.1 | 580  (-1.08) | 2765  (-4.23) | 4715  (6.31) | 1.1 |
| ***CTAB*** | 560  (0.20) | 2450  (0.78) | 5935  (0.03) | 1.1 | 560  (-1.09) | 2450  (-6.77) | 4565  (8.86) | 1.1 |
| ***G16-2-16*** | 690  (0.19) | 2815  (0.78) | 5350  (0.03) | 1.1 | 690  (-1.10) | 2815  (-3.86) | 4710  (5.96) | 1.07 |

The higher life time constant of the protonated form of HPTS and slower rise time of de-protonated form in Gemini RM imply to HPTS tendency to stay more time in the protonated form at the Gemini RM interface unlike in the cationic RM (**Table 1**). This observation is consistent even for higher w0 values.

The fluorescence transients measured at particular wavelength representing the protonated and the de-protonated emission give a qualitative idea of the time scale of ESPT, but emission spectrum at different time may be more convenient and more informative. Time resolved emission spectra (TRES) or time resolved area normalized emission spectra (TRANES) are better representation of the ESPT phenomenon. TRES denotes emission spectrum at different times, reconstructed from fluorescence decays measured at regular interval of wavelengths (5nm interval) across the steady state emission and the steady state emission intensity distribution. TRANES are obtained just by dividing the TRES by its area. This simple construct simplifies interpretation of ESPT process greatly. The emission intensity (or excited state population) of the protonated form decays as a result of proton transfer (conversion to the deprotonated form) and relaxation to the ground state. On the other hand, the intensity of the deprotonated form can develop from the protonated form and simultaneously can also decay to the ground state. In TRANES, total area (excited state population of protonated and de-protonated forms) is fixed and thus, more clearly display the inter-conversion of the two forms.

We found discernible difference in the ESPT dynamics for different micelles depending on the type of headgroup, the length of the alkyl tail or the counterion. Fluorescence transient measurements and the reconstructed TRANES clearly revealed a less favorable ESPT inside the gemini reverse micelles compared with those of the cationic reverse micelles with the same alkyl tail. The slower ESPT may be attributed to the lesser availability of water inside the gemini reverse micelle interface compared with the cationic surfactant reverse micelles.



**Figure 3. Time-resolved area normalised emission spectra (TRANES) of HPTS inside the cationic and Gemini RM of w0 = 6 and 20 at t = 5ns.**

Additionally, the ESPT process is found to be more restricted for surfactants with longer tails within the same surfactant series. This implies that a modification of the tail length of the surfactant may also influence the interfacial organization of the reverse micelles. Slower ESPT usually indicates a higher confinement of HPTS with less access to water.

**Fluorescence Anisotropy Decay.**

The anisotropy decays can be fitted by a bi-exponential function retaining a constant residual anisotropy

(5)

Where r0 is initial anisotropy; τs and τfare the slow and fast rotational time constants, respectively and *a*s is the amplitude of the slow component. We further analyzed the fitting parameters using the “wobbling-in-cone (WIC)” model. According to the model, the fluorophore may undergo a wobbling motion traversing a cone with a semi-cone angle of θ and may also diffusion along the interface.Assigning time constants for these motions as τW, τD respectively, the anisotropy decay may be modelled as

(6)

Where S is an order parameter and is related to the semi-cone angle θas

(7)

Equating (6) and (7) one obtains

(8)

(9)

(10)

Finally, we obtained the diffusion coefficient for wobbling (DW) of HPTS inside the CTAB RM interface using the relation



**Figure 4. Fluorescence anisotropy decay of MPTS inside different reverse micelles (λem= 430 nm). The probe can rotate freely in cationic RM compare to in Gemini surfactant.**

The anionic fluorophore MPTS binds loosely to the polarhead group of the cationic (CTAB, DTAB) RM and rotate with faster time constant in the both in low and high w0 values.However, as the Gemini RM interface possess moreelectropositive nature, MPTS binds strongly; which leads to slower rotation time(**Figure 4**).

The wobbling time constants (τW), the semi-cone angle (θ), and the wobbling diffusion coefficient (DW) are shown in **Table 2**. The relatively small semi-cone angle in the Gemini RM refer to strong probe binding into the interface; unlike in thecationic RM. The diffusion co-efficient decreases in the Gemini RM than in the cationic RM with similar long alkyl chain length. This values indicate the lesser interfacial fluidity in the Gemini RM.Notably, the wobbling and the translational time constants differ significantly among different micelles. In the Gemini RM, the wobbling time constants and the translational time constants are longer than the corresponding cationic reverse micelles. The wobbling diffusion constants are higher for the cationic reverse micelles than the gemini reverse micelles of the same chain length. The results indicate that the interface of the gemini reverse micelles is more compact compared to the cationic reverse micelles having identical tail length.

**Table 2. Fitting Parameters of the Anisotropy Decays of MPTS (λem= 430 nm) inside different reverse Micelles for w0 values 6 and 20**.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **w0 = 6** | ***a*s** | ***r*α** | ***r*0** | ***τf (ns)*** | ***τs (ns)*** | | ***τw (ns)*** | ***ϴ*** | | ***Dw(ns*)-1** | ***x2*** |
| **CTAB** | 0.66 | 0.001 | 0.32 | 0.450 | 1.845 | | 1.68 | 41.2 | | 0.0425 | 1.05 |
| **G16-2-16** | 0.83 | -0.018 | 0.28 | 0.875 | 4.655 | | 0.928 | 28.1 | | 0.0214 | 1.05 |
| **DTAB** | 0.45 | 0.001 | 0.30 | 0.540 | 2.67 | | 1.19 | 55.1 | | 0.130 | 0.986 |
| **G12-2-12** | 0.82 | -0.011 | 0.27 | 0.555 | 3.96 | | 1.55 | 29 | | 0.0144 | 0.983 |
| **w0 = 20** |  |  |  |  |  | |  |  | |  |  |
| **CTAB** | 0.56 | 0.0072 | 0.31 | 0.445 | | 2.065 | 1.76 | | 47.9 | 0.063 | 1 |
| **G16-2-16** | 0.78 | 0.0179 | 0.29 | 0.705 | | 3.615 | 1.14 | | 32.3 | 0.029 | 1.1 |
| **DTAB** | 0.47 | 0.0066 | 0.31 | 0.495 | | 2.67 | 1.65 | | 53.8 | 0.090 | 1.03 |
| **G12-2-12** | 0.75 | 0.0342 | 0.32 | 0.6 | | 3.57 | 1.39 | | 34.6 | 0.031 | 1.03 |

The fluorescence anisotropy decay of MPTS also dramaticallyslows down upon binding to the reverse micelles. The extent of retardationof the rotational dynamics is more dramatic for the Gemini surfactant reverse micelles compared to that of the cationic reverse micelles with an equalchain length. The result implies a better packing of the Gemini surfactant headgroups at the interfacial region of the reverse micellescompared to that of the cationic reverse micelles. With the increase in thesurfactant chain length, the rotational dynamics was found to befaster within a specific surfactant series. This is in agreement withthe results of Chakrabarty et al.[11](#_ENREF_11) They also found that therotational dynamics of coumarin 102 inside alkyl-tri-methyl-ammoniumbromide micelles become slower with an increasein the alkyl chain lengths of the surfactant. They concluded thatthe increase in the length of the alkyl chain leads to a morecompact interface.[11](#_ENREF_11) Thus, the increase in the chain length mayindirectly affect the headgroup packing, which resulted in amore confined environment for the fluorophore (HPTS orMPTS) to exert slower ESPT or rotational dynamics.

## **Conclusion:**

In summary, we compared the interfacial properties, in particular,the nature of the interfacial hydration and rigidity, of two differenttypes of reverse micelles using the ESPT behavior and rotationalanisotropy of two negative fluorophores, HPTS and MPTS. Boththe ESPT and rotational dynamics are found to be slower insidethe Gemini reverse micelles compared with that of the cationic reverse micelles with the same tail length. Thus, the interface of Gemini reverse micelles is more packed and less hydratedcompared to cationic alkyl-ammonium reverse micelles with an identicalalkyl tail. Inside the densely packed interface, water moleculesmay form strong H-bonds with the headgroups, reducing themobility of water and resulting in slower ESPT.

## **References:**

(1) Menger, F. M.; Littau, C. A.: Gemini-surfactants: synthesis and properties. *J. Am. Chem. Soc.***1991**, *113*, 1451-1452.

(2) Zhao, J.; Deng, S.; Liu, J.; Lin, C.; Zheng, O.: Fourier transform infrared investigation on the state of water in reverse micelles of quaternary ammonium gemini surfactants C12-s-C12⋅2Br in n-heptane. *J. Colloid Interface Sci.***2007**, *311*, 237-242.

(3) Phukon, A.; Sahu, K.: The strikingly different miscibility of n-octanol in highly-confined and quasi-confined water. *Chem. Commun.***2015**, *51*, 14103-14106.

(4) Phukon, A.; Ray, S.; Sahu, K.: Effect of Cosurfactants on the Interfacial Hydration of CTAB Quaternary Reverse Micelle Probed Using Excited State Proton Transfer. *Langmuir***2016**, *32*, 10659-10667.

(5) Phukon, A.; Barman, N.; Sahu, K.: Wet Interface of Benzylhexadecyldimethylammonium Chloride Reverse Micelle Revealed by Excited State Proton Transfer of a Localized Probe. *Langmuir***2015**, *31*, 12587-12596.

(6) Zana, R.; Benrraou, M.; Rueff, R.: Alkanediyl-.alpha.,.omega.-bis(dimethylalkylammonium bromide) surfactants. 1. Effect of the spacer chain length on the critical micelle concentration and micelle ionization degree. *Langmuir***1991**, *7*, 1072-1075.

(7) Danino, D.; Talmon, Y.; Zana, R.: Alkanediyl-.alpha.,.omega.-Bis(Dimethylalkylammonium Bromide) Surfactants (Dimeric Surfactants). 5. Aggregation and Microstructure in Aqueous Solutions. *Langmuir***1995**, *11*, 1448-1456.

(8) Cuenca, V. E.; Falcone, R. D.; Silber, J. J.; Correa, N. M.: How the Type of Cosurfactant Impacts Strongly on the Size and Interfacial Composition in Gemini 12-2-12 RMs Explored by DLS, SLS, and FTIR Techniques. *J. Phys. Chem. B***2016**, *120*, 467-476.

(9) Roy, D.; Karmakar, R.; Mondal, S. K.; Sahu, K.; Bhattacharyya, K.: Excited state proton transfer from pyranine to acetate in a CTAB micelle. *Chem. Phys. Lett.***2004**, *399*, 147-151.

(10) Mondal, S. K.; Sahu, K.; Sen, P.; Roy, D.; Ghosh, S.; Bhattacharyya, K.: Excited state proton transfer of pyranine in a γ-cyclodextrin cavity. *Chem. Phys. Lett.***2005**, *412*, 228-234.

(11) Chakrabarty, D.; Chakraborty, A.; Seth, D.; Hazra, P.; Sarkar, N.: Effect of alkyl chain length and size of the headgroups of the surfactant on solvent and rotational relaxation of Coumarin 480 in micelles and mixed micelles. *J. Chem. Phys.***2005**, *122*, 184516.