Electronic Supporting Information

Detailed study of interactions between eosin yellow and gemini pyridinium surfactants

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Annexure SI

1. Methods

1.1 Conductivity measurements. The Conductivity measurements were carried out using a digital Systronics conductivity meter model 306 with a dip-type conductivity cell at 298.15 K having a cell constant of 1.01 cm^{-1}. All the solutions were prepared in deionised double distilled water having specific conductivity of $2.0\text{-}3.0 \ \mu\text{S cm}^{-1}$.

1.2 UV-visible measurements. The absorption spectra of eosin yellow (EY) and EY-gemini pyridinium surfactants mixed systems were recorded on a UV-1800 Shimadzu spectrophotometer with a quartz cuvette having a path length of 1 cm. The titrations were performed at 298.15 K by successive additions of stock solutions of surfactants directly into the quartz cuvette containing 2.0 mL of $0.001 \text{ mmol dm}^{-3}$ EY solution. The spectra were recorded in the range of 400-650 nm.

1.3 Fluorescence measurements. Fluorescence measurements were carried out using F-1600 Hitachi spectrophotometer using a quartz cuvette having an optical length of 10 mm at 298.15 K. The emission spectrum of EY was recorded in the range of 530-650 nm at an excitation wavelength of 518 nm. The titrations were performed same as done in UV-visible measurements.

1.4 Voltammetric measurements. The voltammetric measurements were carried out on a PC controlled CHI660D (Austin, USA) electrochemical workstation equipped with a conventional three electrode system comprising of a working glassy electrode (3.0 mm in diameter), a counter Pt wire and a reference Ag/AgCl electrode. All the solutions were deoxygenated with N_2 and working electrodes were polished with slurry of alumina powder. These voltammetric measurements were carried out in the presence of 0.1 M KCl working as a supporting electrolyte.

1.5 Potentiometric measurements. The potentiometric measurements were done by employing an Equiptronics digital potentiometer, Model EQ-602 employing the following electrochemical cell assembly:

Ag/AgCl	3M KCl	Test Solution	PVC membrane	Internal Reference Solution	3M KCl	Ag/AgCl
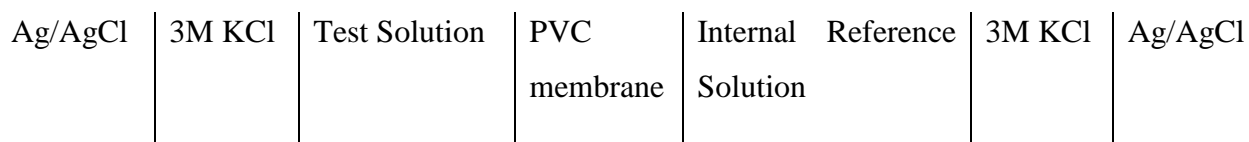
The neutral ion-pair complexes of gemini pyridinium surfactants and sodium dodecylsulfate as $[C_n-3(OH)-C_n]^+DS^-$, where n = 14, 16 were prepared by same procedure as reported [1, 2]. Equimolar aqueous solutions of $[C_n-3(OH)-C_n]$, n = 14, 16 and sodium dodecylsulfate (SDS) were mixed and after continuous stirring for a considerable time, the white precipitates of $[C_n-3(OH)-C_n]^+DS^-$ were obtained . The precipitates so obtained were washed repeatedly with water to remove NaCl and recrystallized thrice from acetone. The PVC (176 mg), ion-pair (5 mg) and plasticizer (550 mg) were mixed and dissolved in minimum quantity of THF. The resulting mixture was poured in 50-mm petri dish after removing the air-bubbles. The solvent THF was allowed to evaporate at room temperature. The resulting membrane was cut to required size and attached to PVC tubes with PVC glue and equilibrated in 1mM of respective surfactant solution. The internal reference solution was 1mM of these surfactants in 1mM NaCl. The given composition of the components used for membrane formation represents the best system in terms of slope values, correlation coefficient, linear range and detection limit. The EMF measurements were performed by titration method at 298.15 K in the presence of 1mM NaCl solution.

1.6 Dynamic light scattering measurements. Dynamic light scattering measurements were done using a Malvern Nano-ZS Zetasizer instrument employing a He-Ne laser (λ = 632 nm) at a scattering angle of 173˚. The solutions of EY and EY-surfactants mixed systems were prepared in doubly distilled water and filtered through a membrane filter with pore size of 0.45 μm prior to each measurement. The temperature of the measurements was controlled to an accuracy of ±0.1°C using a built-in temperature controller.

Annexure SII

The corrected absorbance (ΔA) represents the difference between the measured absorbance (A_{exp}) and theoretical absorbance (A_{theo}) as per the equation (1) [3]

$$\Delta A = A_{exp} - A_{theo} \tag{1}$$

Where A_{theo} is calculated taking into account the Beer-Lambert's law *i.e.* the two components do not interact with each other and hence the total absorbance of the mixture is equal to the sum of their individual absorbances according to the equation (2)

$$A_{Theo} = \varepsilon_S C_S^0 X_S - \varepsilon_D C_D^0 (1 - X_S) \tag{2}$$

Here ε_s and ε_D are the molar extinction coefficients and C_s^0 and C_D^0 are the concentrations of the stock solutions of the gemini pyridinium surfactants and the dye, EY respectively, whereas, X_s represents the volume fraction of gemini pyridinium surfactants. The formation of dye-surfactant complexes makes the absorbance of the solution to satisfy the following equation (3):

$$A_{exp} = \varepsilon_S C_S + \varepsilon_D C_D + \varepsilon_{S-D} C_{S-D} \tag{3}$$

Where $\varepsilon_{\text{S-D}}$ *is* the molar extinction coefficient of the complex (Dye-surf) and C_S, C_D and $C_{\text{S-D}}$ are the concentrations of the respective species in the mixture.

Table S1. The concentration corresponding to ion-pair formation (C_1), critical micelle concentration C_2 (*cmc*) of gemini pyridinium surfactants, [14-3(OH)-14] and [16-3(OH)-16] surfactants in the absence and presence of EY determined from potentiometric measurements.

System	C_1(mmol dm^{-3})	$C_2 = cmc$(mmol dm^{-3})
[14-3(OH)-14]	-	0.022
EY+[14-3(OH)-14]	0.001	0.017
[16-3(OH)-16]	-	0.003
EY+[16-3(OH)-16]	0.001	0.002

Table S2. Hydrodynamic diameters (D_h) for EY-gemini pyridinium surfactants mixed systems at different concentration of gemini pyridinium surfactants, [14-3(OH)-14] and [16-3(OH)-16] in the absence and presence of EY.

EY + [14-3(OH)-14]			
C / mmol dm^{-3}	0.025[a]	0.002[b]	0.010[b]	0.025[b]
D_h / nm	82.5	58.8	91.3	220.2
EY + [16-3(OH)-16]			
C / mmol dm^{-3}	0.003[a]	0.0005[b]	0.0010[b]	0.0030[b]
D_h / nm	91.3	78.8	122.4	342.0

[a] In the absence of EY, [b] in the presence of 0.001 mmol dm^{-3} EY
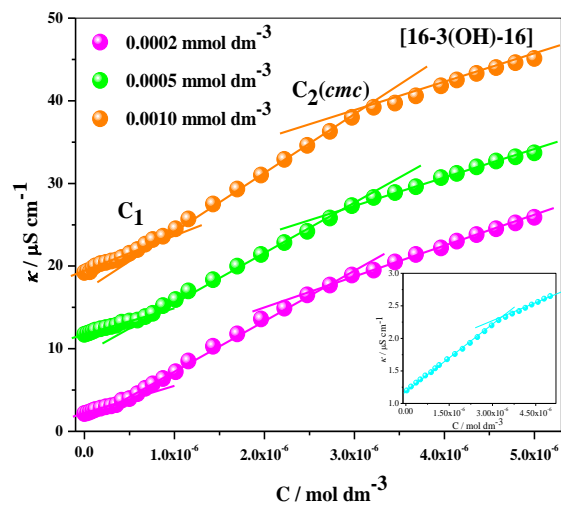
Fig.S1 Variation of specific conductivity (κ) with molar concentration of gemini pyridinium surfactant, [16-3(OH)-16] in the presence of varying amounts of EY and the inset shows the variation of specific conductivity (κ) with molar concentration of pure [16-3(OH)-16] in aqueous solution.
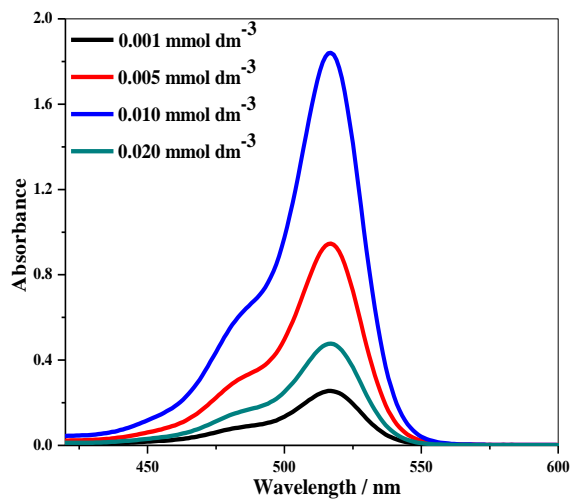

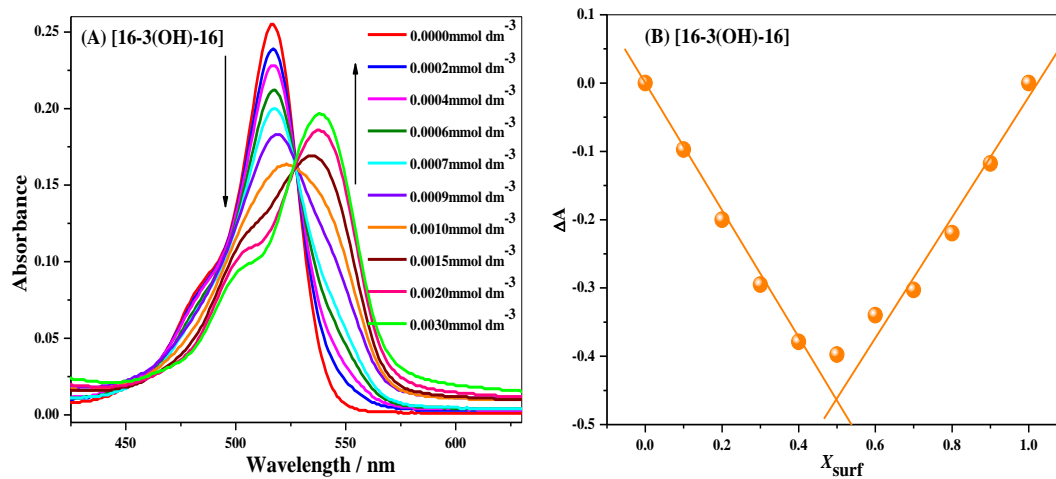Fig.S2 UV-visible spectra of EY at different concentrations

Fig.S3 (A) UV-visible spectra of 0.001 mmol dm^{-3} EY in the presence of increasing concentrations of gemini pyridinium surfactant, [16-3(OH)-16] (B) Job's plot depicting 1:1 stoichiometry of EY-[16-3(OH)-16] mixed system.
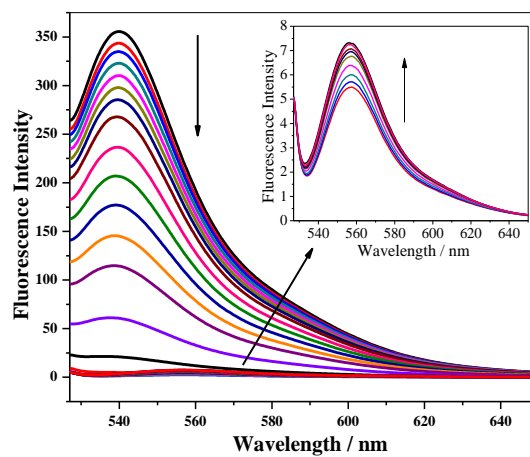
Fig.S4 Fluorescence emission spectra of 0.001 mmol dm^{-3} EY in the presence of increasing concentrations of gemini pyridinium surfactant, [16-3(OH)-16].
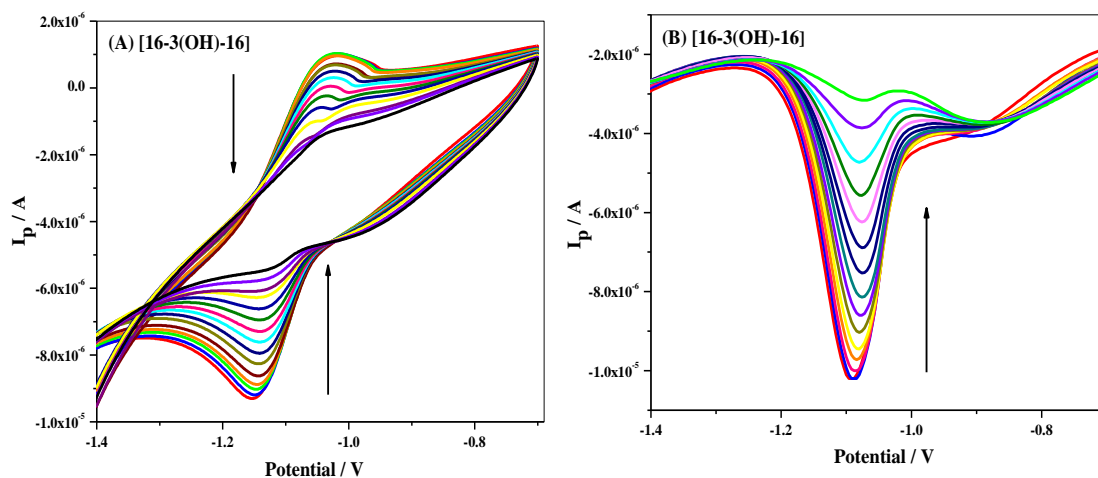
Fig.S5 (A) Cyclic voltammograms of EY in the presence of increasing concentrations of gemini pyridinium surfactant, [16-3(OH)-16] (B) Differential pulse voltammograms of EY in the presence of increasing concentrations of [16-3(OH)-16]
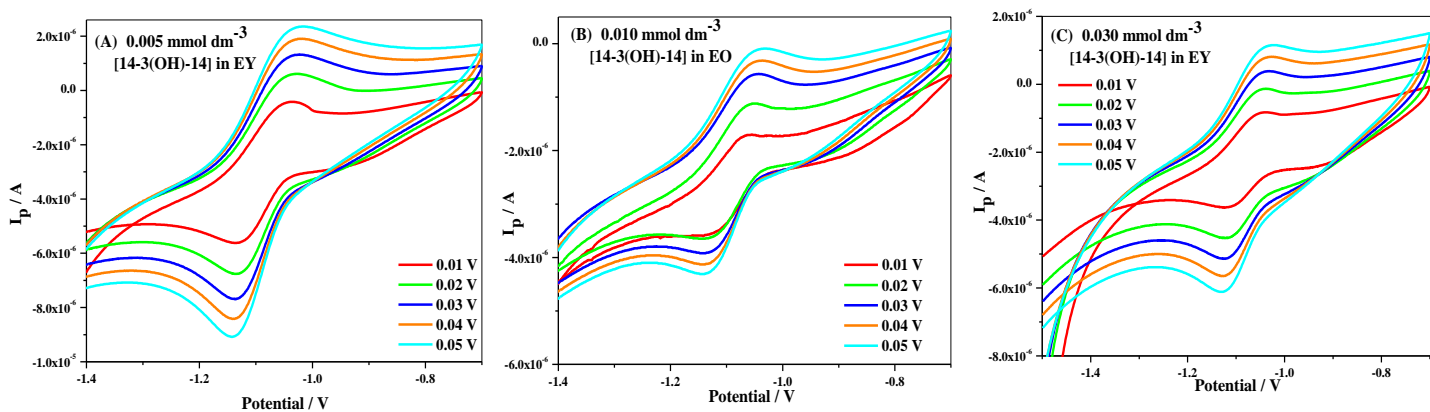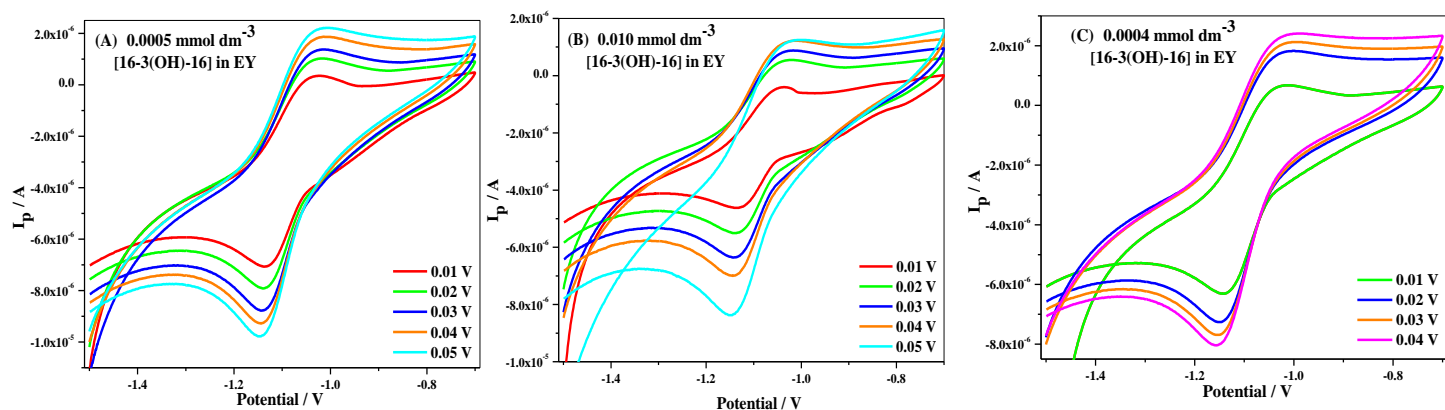

Fig.S6 Cyclic voltammogram (CV) of gemini pyridinium surfactants in EY at various scan rates (A) 0.005 mmol dm^{-3} [14-3(OH)-14] (B) 0.010 mmol dm^{-3} [14-3(OH)-14] (C) 0.030 mmol dm^{-3} [14-3(OH)-14].

Fig.S7 Cyclic voltammogram (CV) of gemini pyridinium surfactants in EY at various scan rates (A) 0.0005 mmol dm^{-3} [16-3(OH)-16] (B) 0.0020 mmol dm^{-3} [16-3(OH)-16] (C) 0.0040 mmol dm^{-3} [16-3(OH)-16]
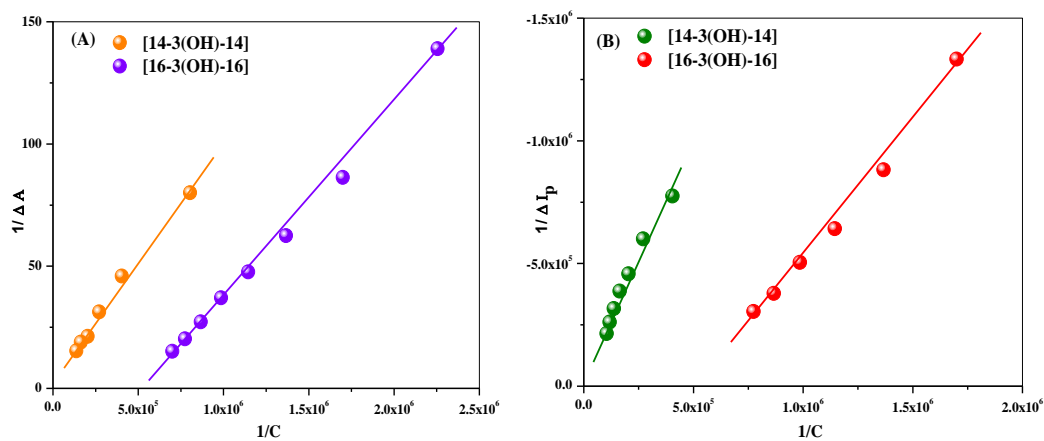

Fig.S8 Binding constant determination for the EY-gemini pyridinium surfactants mixed systems using (A) changes in UV-visible spectra of EY (B) changes in the peak current of EY.
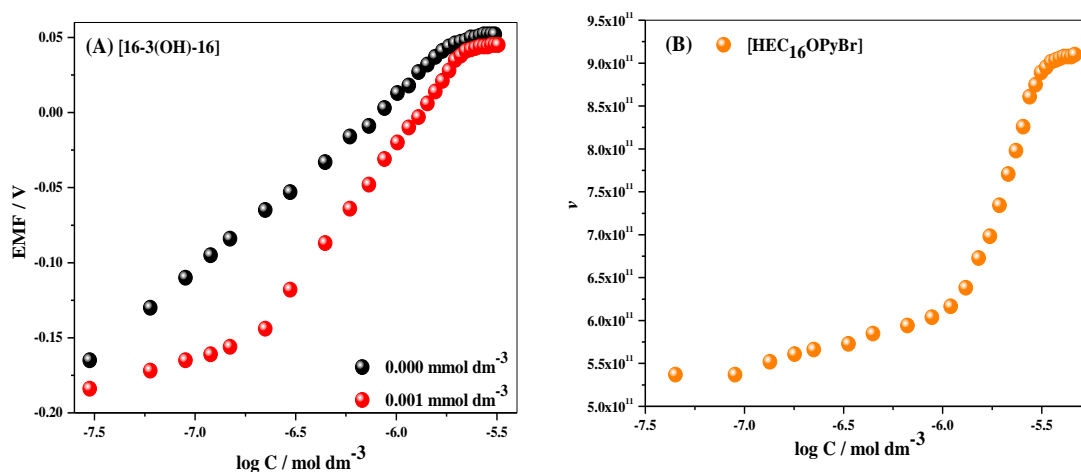
Fig.S9 (A) EMF as a function of logarithm of molar concentration of gemini pyridinium surfactant, [16-3(OH)-16] in the absence and presence of 0.001 mmol dm^{-3} EY (B) Binding isotherms of binding parameter (v) *versus* logarithm of molar concentration of [16-3(OH)-16] in the presence of 0.001 mmol dm^{-3} EY.
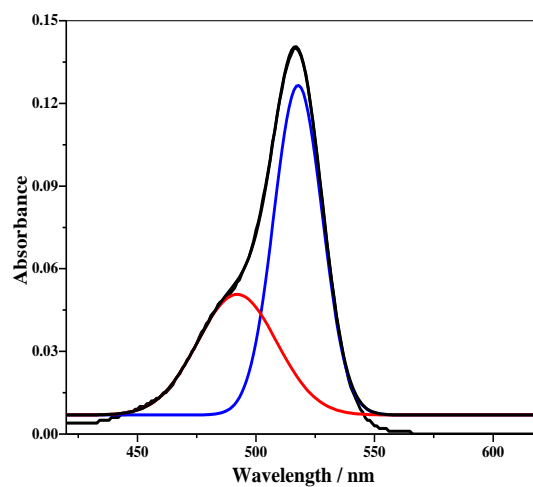

Fig.S10 Representative spectral decomposition stratergy for deconvolution of EY absorbance spectra into Gaussian shapes.

References

[1] A. Shaheen, I. Kaur, R.K Mahajan, Potentiometric studies of micellization behavior of cationic surfactants in the presence of glycol additives and triblock polymer (Pluronic F68), using surfactant-selective sensors based on neutral ion-pair complexes. Ind. Eng. Chem. Res. 2007, 46, 4706-4709.

[2] R.K. Mahajan, A. Shaheen, Effects of various additives on the performance of a newly developed PVC based potentiometric sensor for anionic surfactants. J. Colloid Interface Sci. 2008, 326, 191-195.

[3] S. Gokturk, M. Tuncay, Dye-surfactant interaction in the pre-micellar region. J. Surf. Deterg. 2003, 6, 325-330