Electronic Supporting Information

A quantitative appraisal of the binding interactions between anionic dye, Alizarin Red S and alkyloxypyridinium surfactants: a detailed micellization, spectroscopic and electrochemical study

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Annexure SI

## 1. Methods (Detailed Description)

1.1 Conductivity measurements. Conductivity was measured using a digital Systronics conductivity meter model 306 with a dip-type conductivity cell having a cell constant of 1.01 cm^{-1} at 298.15 K. The specific conductivity of deionised double distilled water used in present study was measured to be 2.0-3.0 µS cm^{-1}.

1.2 Surface tension measurements. Surface tension measurements have been performed using Kruss (Hamburg, Germany) Easy dyne tensiometer using ring detachment method with an accuracy of ± 0.15 mN m^{-1} at room temperature of 298.15 K. A mixing time of two minutes followed by an equilibration time of 5 minutes was adopted before each measurement

1.3 UV-visible measurements. The absorption spectra 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 small aliquots of stock solutions of alkyloxypyridinium surfactants directly into the quartz cuvette containing 2.0 mL of 0.02 mmol dm^{-3} ARS solution. After every addition, the solution was equilibrated for 5 minutes to reach thermal equilibrium. The spectra were recorded in the range 350-700 nm.

1.4 Voltammetric measurements. Voltammetric measurements were performed 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. The voltammetric measurements were carried out in the presence of 0.1 M phosphate buffer having pH of 7.4 as a supporting electrolyte.

1.5 Potentiometric measurements. The potentiometric measurements were carried out by using 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
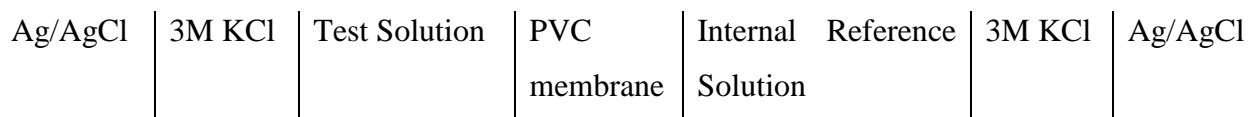
The neutral ion-pair complexes of alkyloxypyridinium surfactants and sodium dodecylsulfate as [HEC$_n$OPy] +DS⁻were prepared by the procedure earlier reported by our laboratory [1, 2]. Equimolar aqueous solutions of [HEC$_n$OPyBr], n = 14, 16 and sodium dodecylsulfate (SDS) were mixed and after continuous stirring for a considerable time, the white precipitates of HEC$_n$OPy+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 1 mmol dm⁻³ of respective surfactant solution. The internal reference solution was 1mM of these surfactants in 1 mmol dm⁻³ 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 carried out by titration method at 298.15K in the presence of 1 mmol dm⁻³ NaCl solution.

1.6 Dynamic light scattering measurements. Dynamic light scattering measurements were performed using a Malvern Nano-ZS Zetasizer instrument employing a He-Ne laser (λ = 632 nm) at a scattering angle of 173˚ using quartz cuvette having path length of 1 cm. The temperature of the measurements was controlled to an accuracy of ±0.1°C using a built-in temperature controller.

1.7 ¹H NMR measurements. ¹H NMR experiments were performed on a 500 MHz JEOL-FT NMR-AL spectrometer using CD$_3$CN as solvent. The NMR titration experiments were performed by titrating one equivalent of ARS prepared in CD$_3$CN with increasing equivalents of alkyloxypyridinium surfactants. Chemical shifts were given on the δ scale.

Annexure SII.

The maximum surface excess concentration (Γ_{max}) and minimum area per molecule [3, 4] at the air-solution interface can be calculated using equation (1) and (2) as follows:

$$\frac{d\gamma}{d\ln C_T} = -nRT\Gamma_{max} \tag{1}$$

$$A_{min} = 10^{20}/(N_A \cdot \Gamma_{max}) \tag{2}$$

The Gibbs free energy of adsorption (ΔG°_{ads}) [5] is calculated using the equation (3)

$$\Delta G^\circ_{ads} = \Delta G^\circ_{mic} - \Pi_{cmc}/\Gamma_{max} \tag{3}$$

Table S1. The concentration corresponding to ion-pair formation (C_1), critical micelle concentration (*cmc*) of alkyloxypyridinium surfactants, [HEC$_{14}$OPyBr] and [HEC$_{16}$OPyBr] surfactants in the absence and presence of ARS determined from potentiometric measurements.

System	C_1(mmol dm^{-3})	$C_2 = cmc$(mmol dm^{-3})
ARS	-	-
[HEC$_{14}$OPyBr]	-	0.83
ARS+[HEC$_{14}$OPyBr]	0.05	0.78
[HEC$_{16}$OPyBr]	-	0.16
ARS+[HEC$_{16}$OPyBr]	0.02	0.13

Table S2. Hydrodynamic diameter (D_h) for ARS-alkoxypyridinium surfactants, [HEC$_{14}$OPyBr] and [HEC$_{16}$OPyBr] mixed systems at varying mole fractions of ARS (x_{ARS}).

ARS + [HEC$_{14}$OPyBr]						
x_{ARS}	0.0	0.1	0.3	0.5	0.7	0.9
D_h / nm	1.2	4.50	11.7	25.8	18.6	10.4
ARS + [HEC$_{16}$OPyBr]						
x_{ARS}	0.0	0.1	0.3	0.5	0.7	0.9
D_h / nm	1.5	6.20	13.5	28.2	21.3	12.8

Table S3. Chemical shifts and observations determined by ^{1}H-NMR titrations of alizarin red S (ARS) with increasing equivalents of alkyloxypyridinium surfactant, [HEC$_{14}$OPyBr].

ARS-[HEC$_{14}$OPyBr] system	^{1}H-NMR chemical shift range in δ (ppm) for aromatic protons of ARS	Observations after addition of surfactant solution	^{1}H-NMR chemical shift range in δ (ppm) for aromatic and aliphatic protons of surfactants	Observations after addition of surfactant solution
ARS	11.52 (s, H1) 11.79 (s, H2)		3.99 (m, Hy),4.23 (t, Hn), 4.65 (m, Hx), 8.38 (d, Hq), 8.53 (s, Hr)	
1 equivalent ARS+ 0.25 equivalent of [HEC$_{14}$OPyBr]	11.51 (s, H1) 12.79 (s, H1)	Upfield shift for H1 proton.	3.96 (m, Hy),4.22 (t, Hn), 4.64 (m, Hx), 8.37 (d, Hq), 8.51 (s, Hr)	Upfield shift for all the protons.
1 equivalent ARS+ 0.5 equivalent of [HEC$_{14}$OPyBr]	11.49 (s, H1) 12.79 (s, H1)	Upfield shift for H1 proton.	3.98 (m, Hy),4.23 (t, Hn), 4.67 (m, Hx), 8.40 (d, Hq), 8.57 (s, Hr)	Downfield shift for all the protons.
1 equivalent ARS+ 1.0 equivalent of [HEC$_{14}$OPyBr]	11.48 (s, H1) 12.79 (s, H1)	Upfield shift for H1 proton.	3.98 (m, Hy),4.25 (t, Hn), 4.69 (m, Hx), 8.42 (d, Hq), 8.60 (s, Hr)	Downfield shift for all the protons.
1 equivalent ARS+ 1.5 equivalent of [HEC$_{14}$OPyBr]	11.47 (s, H1) 12.79 (s, H1)	Upfield shift for H1 proton.	3.99 (m, Hy),4.23 (t, Hn), 4.70 (m, Hx), 8.43 (d, Hq), 8.61 (s, Hr)	Downfield shift for all the protons.

Table S4. Chemical shifts and observations determined by ^{1}H-NMR titrations of alizarin red S (ARS) with increasing equivalents of alkyloxypyridinium surfactant, [HEC$_{16}$OPyBr].

| ARS-[HEC$_{16}$OPyBr] system	^{1}H-NMR chemical shift range in δ (ppm) for aromatic protons of ARS	Observations after addition of surfactant solution	^{1}H-NMR chemical shift range in δ (ppm) for aromatic and aliphatic protons of surfactants	Observations after addition of surfactant solution
ARS	11.52 (s, H1) 11.79 (s, H2)		3.99 (m, Hy),4.23 (t, Hn), 4.65 (m, Hx), 8.38 (d, Hq), 8.53 (s, Hr)	
1 equivalent ARS+ 0.50 equivalent of [HEC$_{16}$OPyBr]	11.53 (s, H1) 12.79 (s, H1)	Upfield shift for H1 proton.	3.97 (m, Hy),4.21 (t, Hn), 4.57 (m, Hx), 8.39(s, Hq)	Upfield shift for all the protons.
1.0 equivalent ARS+ 1.0 equivalent of [HEC$_{16}$OPyBr]	11.49 (s, H1) 12.79 (s, H1)	Upfield shift for H1 proton.	3.98 (s, Hy),4.23 (t, Hn), 4.64 (s, Hx), 8.35 (d, Hq), 8.52 (s, Hr)	Downfield shift for all the protons.
1.0 equivalent ARS+ 1.5 equivalent of [HEC$_{16}$OPyBr]	11.48 (s, H1) 12.79 (s, H1)	Upfield shift for H1 proton.	3.98 (s, Hy),4.23 (s, Hn), 4.66 (s, Hx), 8.39 (s, Hq), 8.55 (s, Hr)	Downfield and upfield shift for protons.
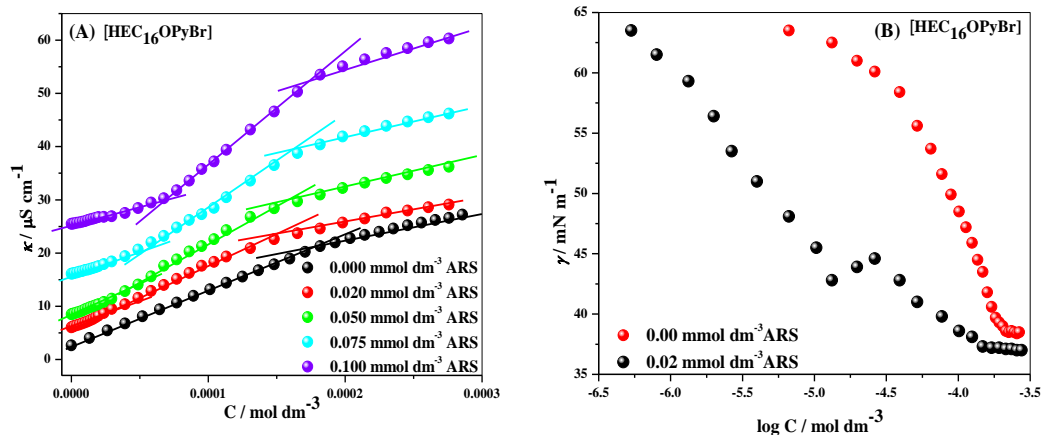
Fig.S1 (A) Variation of specific conductivity (κ) with molar concentration of [HEC$_{16}$OPyBr] in the absence and presence of varying amounts of ARS. (B) Variation of surface tension (γ) as a function of logarithm of molar concentration of alkyloxypyridinium surfactant, [HEC$_{16}$OPyBr] in the absence and presence of 0.02 mmol dm^{-3} ARS.
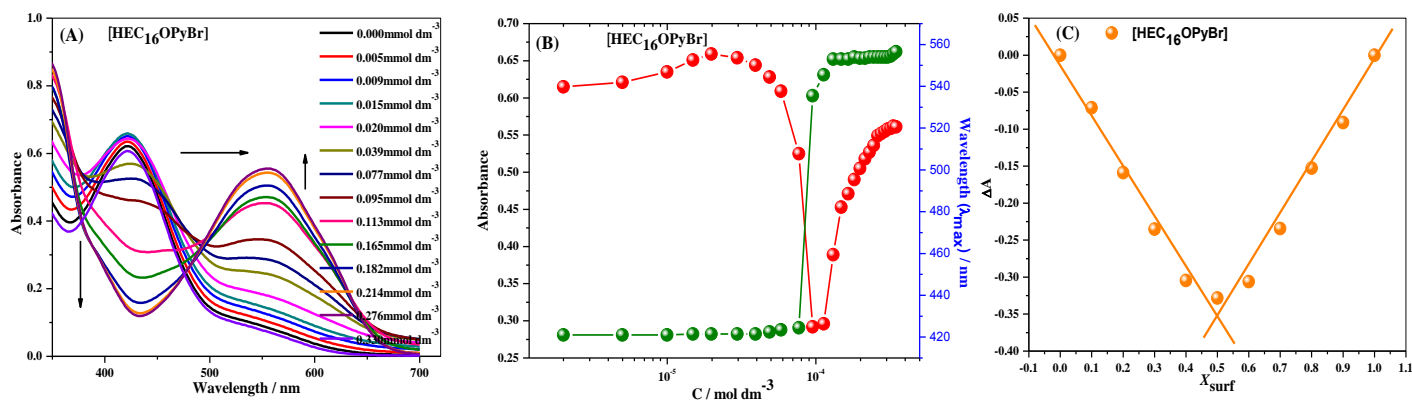

Fig.S2 (A) UV-visible spectrum of 0.02 mmol dm^{-3} ARS in the presence of increasing concentrations of alkyloxypyridinium surfactant, [HEC$_{16}$OPyBr] (B) Plot of Absorbance and λ_{max} vs increasing concentration of [HEC$_{16}$OPyBr] (C) Job's plot depicting 1:1 stoichiometry of ARS-[HEC$_{16}$OPyBr] mixed system.
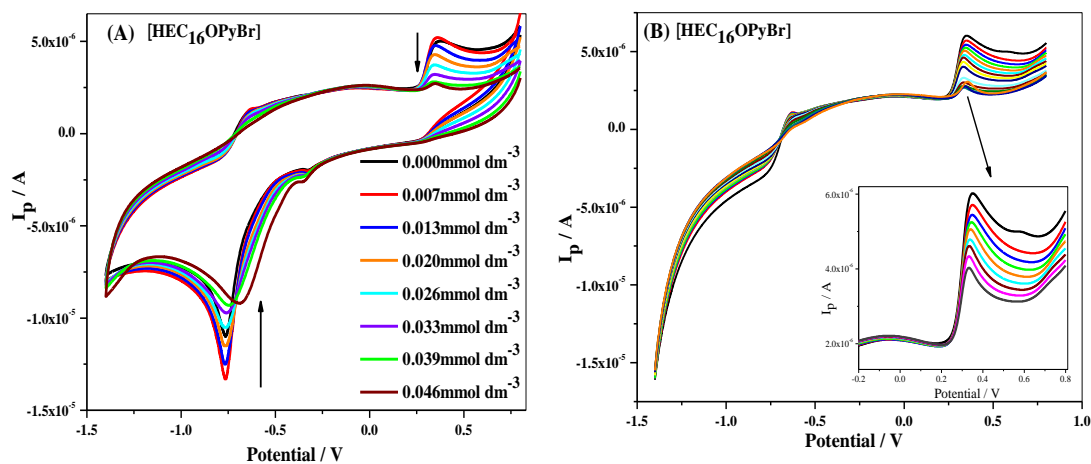
Fig.S3 (A) Cyclic voltammograms of ARS in the presence of increasing concentrations of alkyloxypyridinium surfactant, [HEC$_{16}$OPyBr] (B) Linear sweep voltammograms of ARS in the presence of increasing concentrations of [HEC$_{16}$OPyBr]
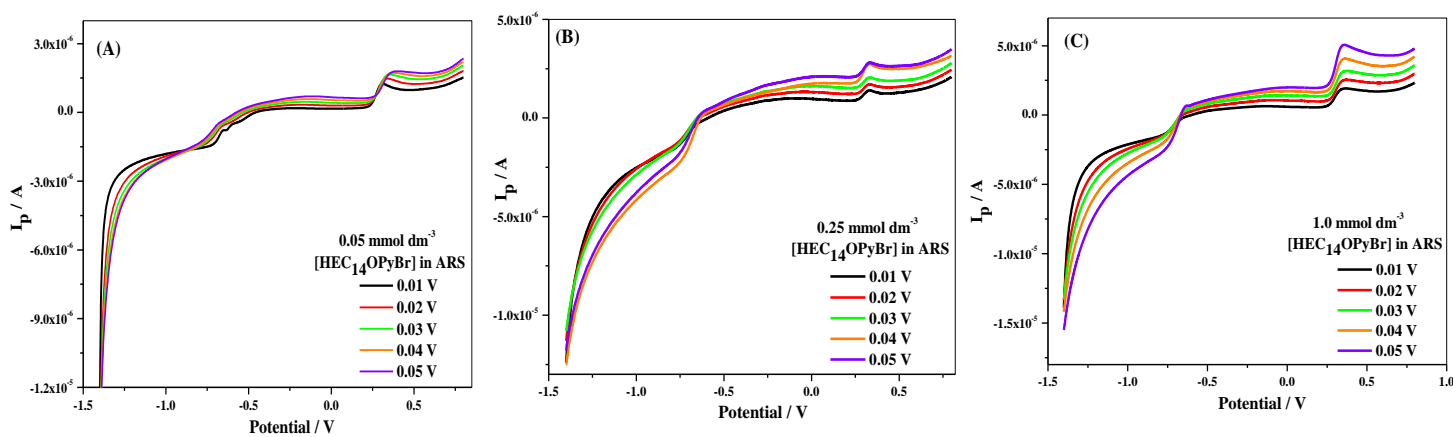

Fig.S4 (A) Linear sweep voltammograms (LSV) of 0.05 mmol dm^{-3} alkyloxypyridinium surfactant, [HEC$_{14}$OPyBr] in ARS at various scan rates of potential (B) LSV of 0.25 mmol dm^{-3} [HEC$_{14}$OPyBr] in ARS at various scan rates of potential (C) LSV of 1.0 mmol dm^{-3} [HEC$_{14}$OPyBr] in ARS at various scan rates of potential
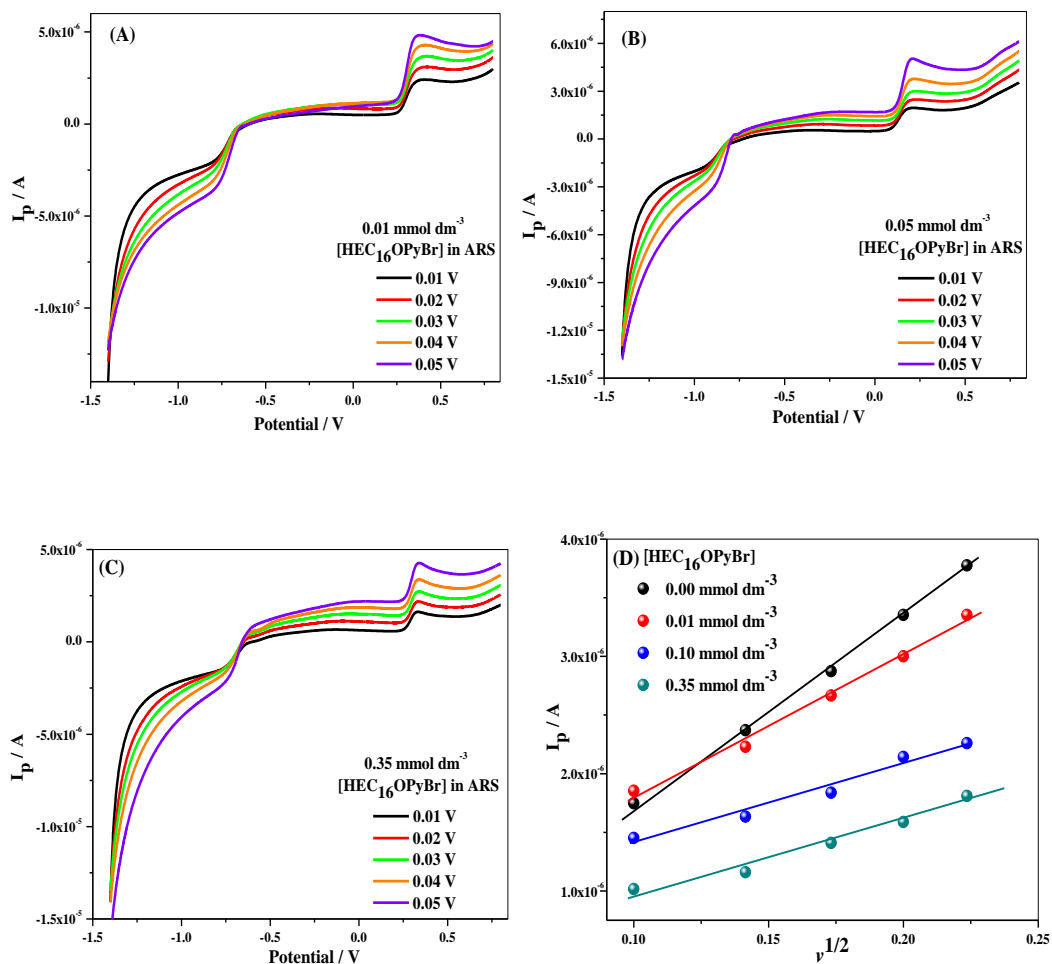
Fig.S5 (A) LSV of 0.01 mmol dm^{-3} [HEC$_{16}$OPyBr] in ARS at various scan rates of potential (B) LSV of 0.05 mmol dm^{-3} [HEC$_{16}$OPyBr] in ARS at various scan rates of potential (C) LSV of 0.35 mmol dm^{-3} [HEC$_{16}$OPyBr] in ARS at various scan rates of potential (D) Variation of I_p (A) vs $v^{1/2}$ for ARS in the absence and presence of increasing concentrations of [HEC$_{16}$OPyBr].
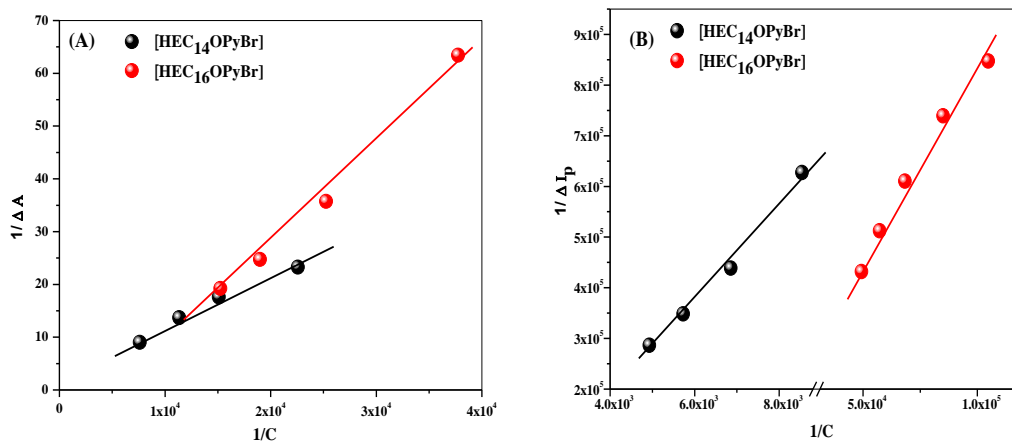
Fig.S6 Binding constant determination for the ARS-[HEC$_n$OPyBr] mixed systems using (A) changes in UV-visible spectra of ARS (B) changes in the peak current of ARS.
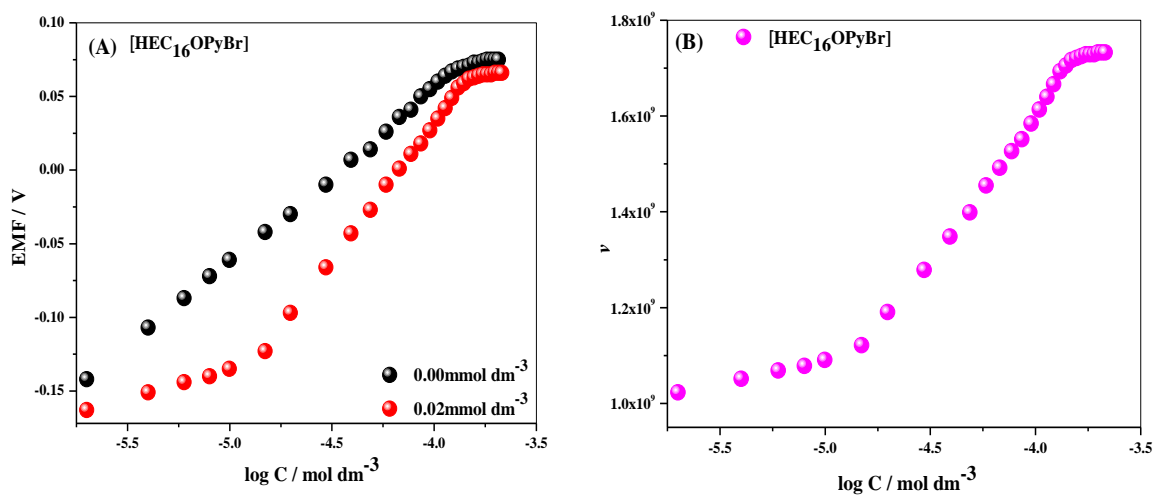

Fig.S7 (A) EMF as a function of logarithm of molar concentration of alkyloxypyridinium surfactant, [HEC$_{16}$OPyBr] in the absence and presence of 0.02 mmol dm^{-3} ARS (B) Binding isotherms of binding parameter (v) versus logarithm of molar concentration of [HEC$_{16}$OPyBr] in the presence of 0.02 mmol dm^{-3} ARS.
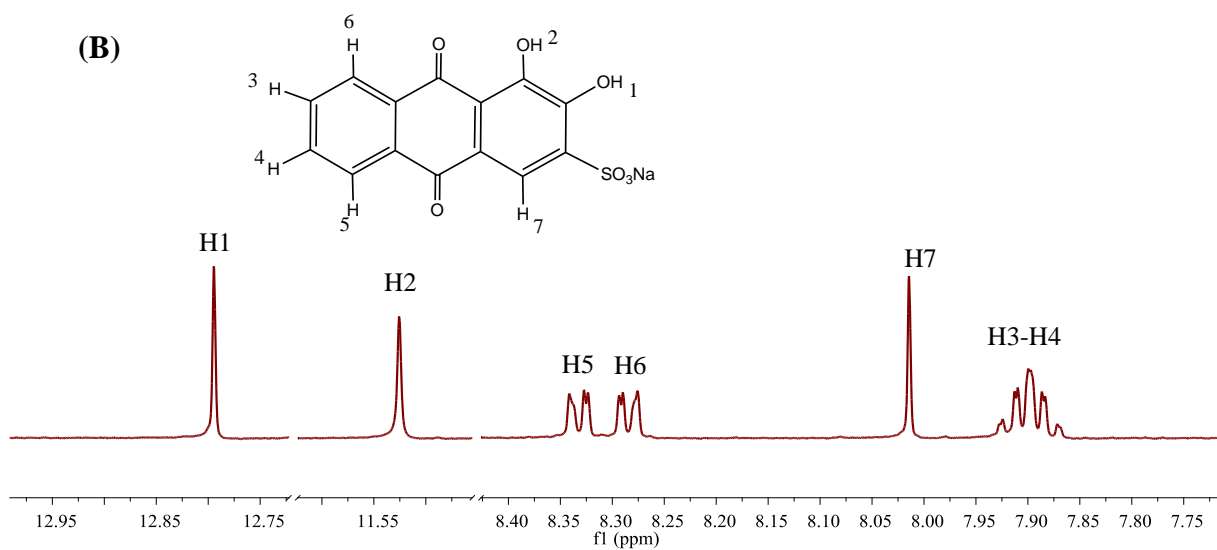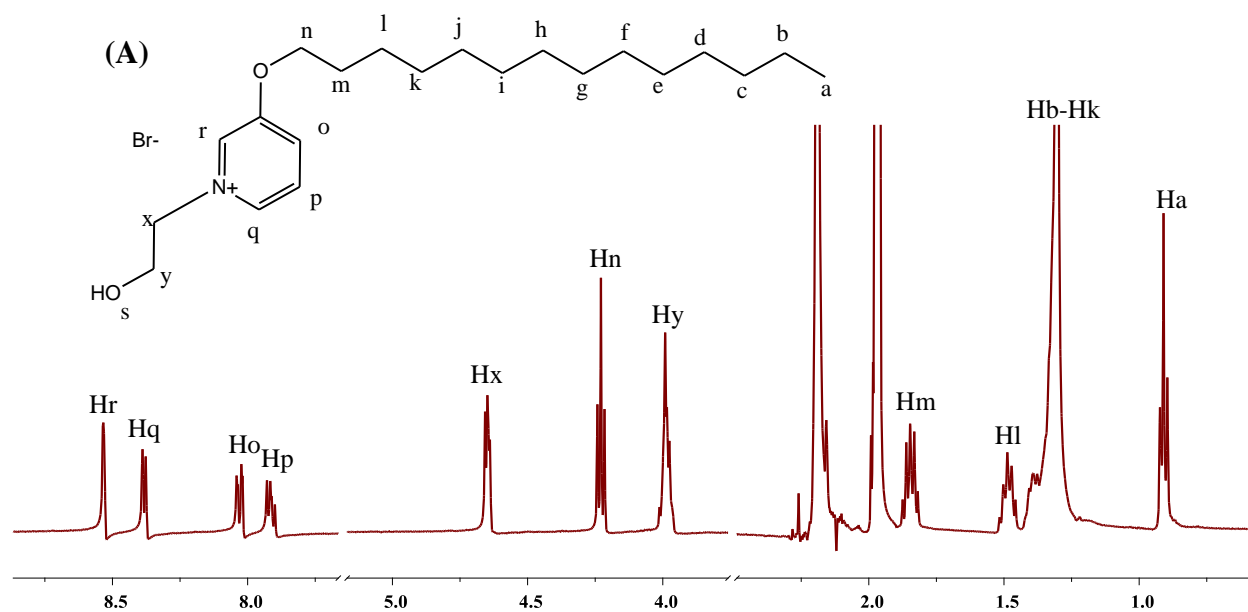
Fig.S8 (A) ^{1}H-NMR spectra of pure alkyloxypyridinium surfactant, [HEC$_{14}$OPyBr] (B) ^{1}H-NMR spectra of pure ARS
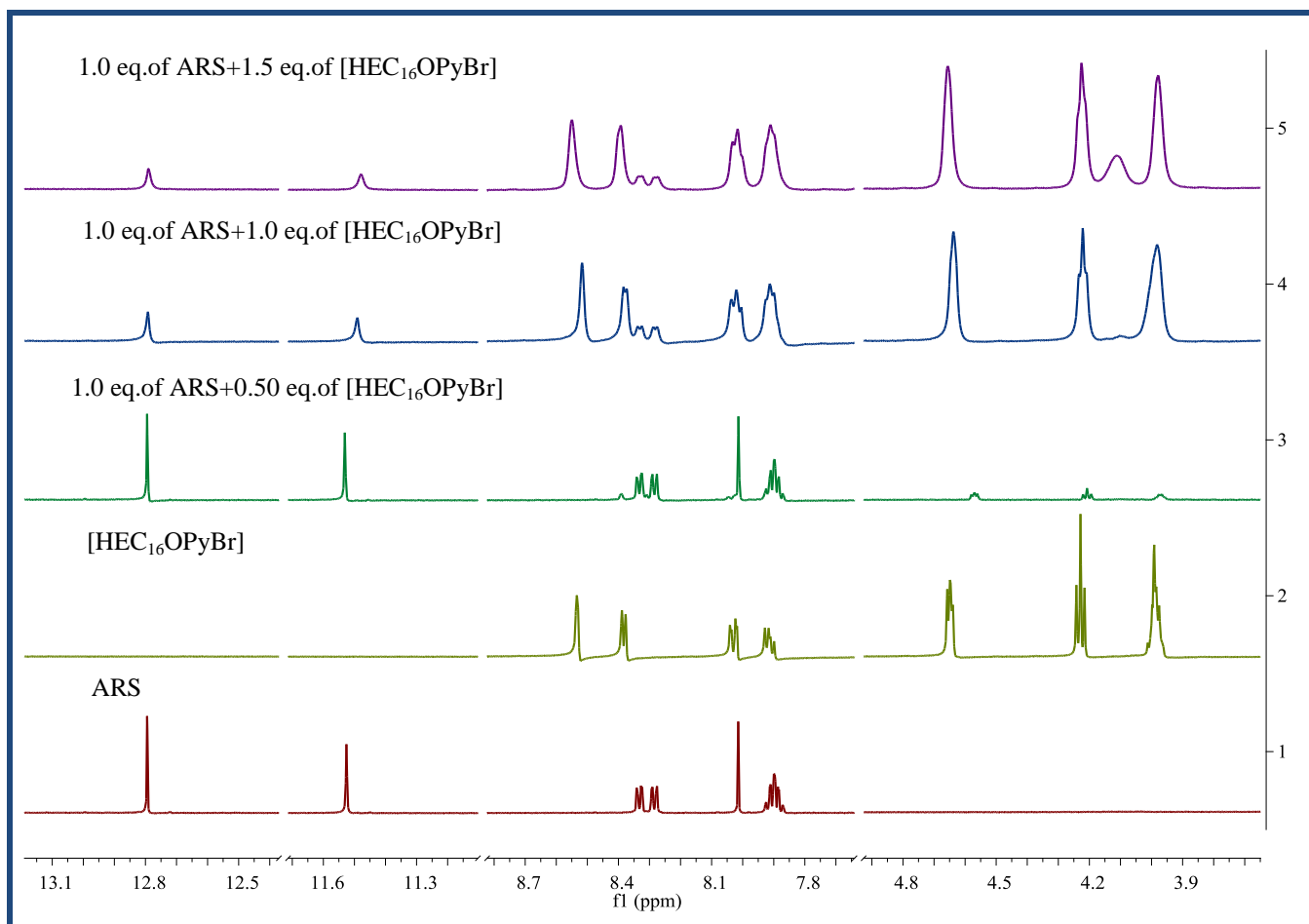
Fig.S9 ^{1}H-NMR titrations of ARS with increasing equivalents of alkyloxypyridinium surfactant, [HEC$_{16}$OPyBr]

References

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