Supporting Information

Probing the self-aggregation behavior and counter ion distribution of a copper surfactant complex

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Cyclic Voltammograms for cmc determination

Cyclic voltammograms for copper surfactant complex are recorded at different concentrations to evaluate cmc. A typical cyclic voltammogram of the copper surfactant at 5mM concentration and scan rate of 100mV/s is shown in Figure 1. The redox peaks in the region -0.2 to -0.7 correspond to the reduction and oxidation of H^+ and OH^- ions from water molecule [1]. The copper surfactant complex shows the oxidation peak at 1.04 V and correspondingly a reduction peak is observed at 0.70V. The overall redox potential of the system comes out to be 0.87 V.

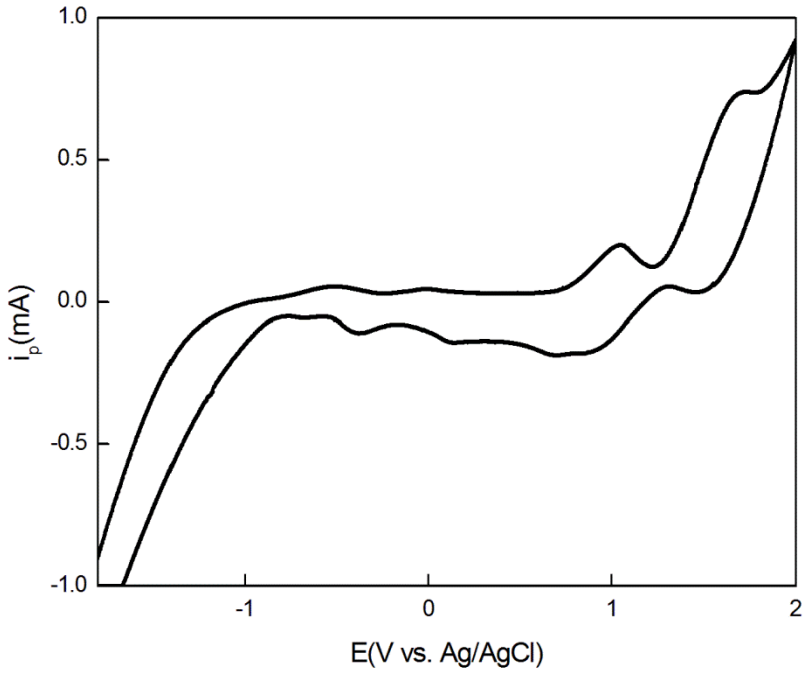

Figure 1 Cyclic voltammograms of copper surfactant complex at the scan rate of 100mV/s.

Calculations for Ellipsometric analysis:

The values for surface density of each chemical species, used are $\Gamma_{\mathrm{DTA}} = 1.855\ \mu\mathrm{mol\ m^{-2}}$, $\Gamma_{\mathrm{Br}} = 1.03\ \mu\mathrm{mol\ m^{-2}}$, $\Gamma_{\mathrm{Cl}} = 0.22\ \mu\mathrm{mol\ m^{-2}}$ as determined in the manuscript (last section). Γ_{DTA} has been estimated from the peak height of ERA-FTIR (This value was almost half of that at 9.5 mM). Γ_{Br} and Γ_{Cl} are estimated with assumption that the composition of adsorbed film is equal to that at 9.5 mM.

- *Calculation of* (TMA) : Volume fraction of TMA, for head groups in the layer is calculated using eq.1 given below:

$$\phi(\mathrm{TMA}) = \frac{\Gamma(\mathrm{TMA}) \times V_m\,(\mathrm{TMA})}{d_h} \tag{1}$$

where, $\Gamma(\mathrm{TMA})/d_h$ expresses the number of moles of TMA per m^3. The value of $\Gamma(\mathrm{TMA}) = \Gamma_{\mathrm{DTA}} = 1.855$ μmol m^{-2}, V_m (TMA) $= 62.3$ cm^3 mol^{-1} (as estimated previously [2]) and $\varepsilon_{\mathrm{w}} = 1.776$.

- *Calculation of* r_D : In case of multivalent ions and in bulk solution, the equation used to calculate Debye length or r_{D} is:

$$r_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r RT}{2FI}} \tag{2}$$

where $I = (1/2)\sum_i z_i^2 c_i$ is ionic strength (z_i is the valence of ion i, and c_i is the molality of ion,i) which is calculated to be 17.5 mol m^{-3}, $\varepsilon_0 = 8.85419 \times 10^{-12}$ J^{-1} C^2 m^{-1}, $\varepsilon_r = 78.36$ (relative permittivity of water) , $R = 8.314$ J mol^{-1} K^{-1}, $T = 298.15$ K and $F = 96484.56$ C mol^{-1}. Substituting the values in eq. (2) above, the value of $r_D = 2.2975 \times 10^{-9}$ m.

[1] Li Y., Hao J., Li G., J. Disp. Sci. Tech., 27 (2006) 781.

[2] Wilkinson K.M., Bain C.D., Matsubara H., Aratono M., Chem. Phys. Chem., 6 (2005) 547.