

Facile Solubilization of Organochalcogen compounds In Mixed Micelle Formation of Binary and Ternary Cationic-Nonionic Surfactant mixtures

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Solubility determination

Batch tests for solubilization of organochalcogen in surfactant solution were performed in single and equimolar bi and ternary combinations of C16Br, C16Cl and Brij 58 with 16 carbon hydrophobic groups. Single/ mixed surfactant solutions in the total surfactant concentration range above cmc were placed in 8-10 glass vials of 25 ml capacity and organochalcogenides were separately added to each tube in amounts slightly more than required to saturate the solution. The vials were sealed and then rotated at 150 rpm at 25⁰C for 24 h. After this, subsequent centrifugation for 15 min was performed to remove the undissolved solid organochalcogenides. The concentration of dissolved solute was determined spectrophotometrically with UV-vis spectrophotometer following appropriate dilution of an aliquot of the supernatant with surfactant-water solution. The surfactant concentration was kept the same in both the reference and the measurement cells to eliminate the effect of surfactant on UV absorbance. Duplicate tests were performed for each surfactant concentration.

1. cmc determination by the dye micellization method. a. UV spectrophotometry.

Acridine orange (AO) has a UV peak at 491nm corresponding to the π electronic transitions which remained unaltered in the presence of single as well as mixed surfactant systems used in the study. However, surfactant addition results in an increase of the absorbance at 491nm. It has been suggested that the inflection point in the λ_{max} should be treated as the cmc.¹ However, not all dyes show a distinct shift in λ_{max} (e.g. merocyanine).² Therefore, λ_{max} of the micellized dye is sufficiently different from the

aqueous dye, the absorbance at this wavelength can be followed as a function of surfactant concentration to measure the extent of dye uptake [Figure S1(a)]. Below cmc, the rise in absorbance is small, where as above cmc, the rise is sharp. Since the micellization process is known to be less sharp for nonionic surfactant than for ionic surfactants, the rise in absorbance varies strongly over a range of surfactant concentration. At high enough surfactant concentrations, the absorbance vs concentration curve flattens again as most of the dye shifts to the micelles, depleting the continuous phase dye. The linear portion near the inflection point is extrapolated to the point where the absorbance matches that of the dye in the absence of any surfactant [represented by the horizontal dashed line in Figure S1 (a)], and this concentration is defined as the cmc. The obtained cmc values of single as well as mixed surfactant systems are presented in Table I (supporting data).

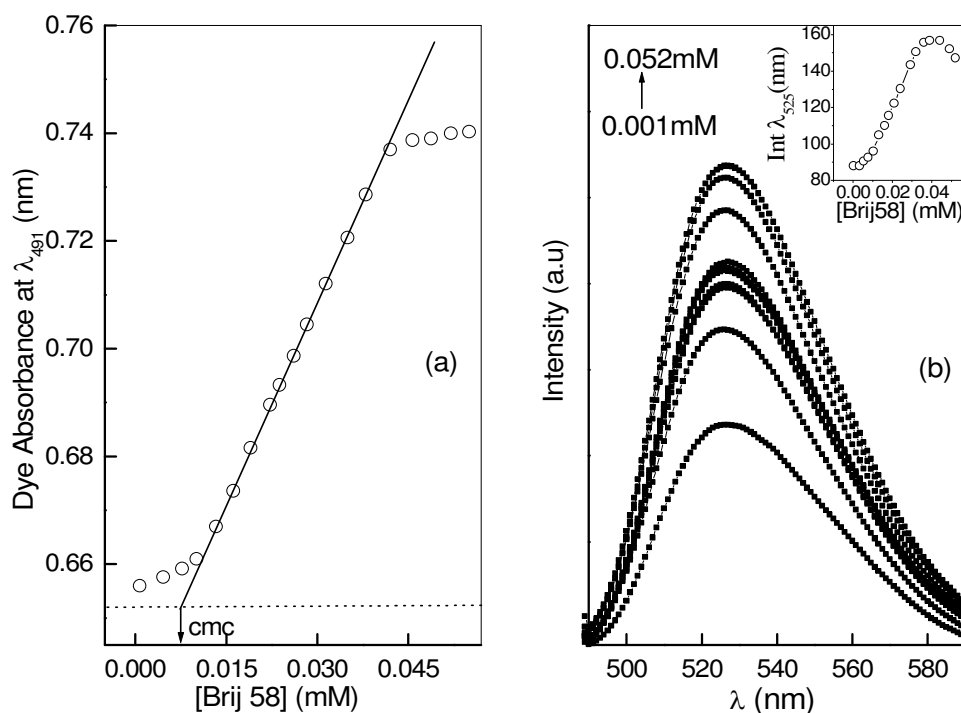


Figure S1. Critical micelle concentration (cmc) determination of Brij 58 using (a) absorbance and (b) fluorescence spectral measurements at 298.15 K. The inset shows the fluorescence intensity values with dilution of Brij 58.

b. Fluorimetry. The fluorescence intensity of AO was also used to determine the cmc values of single as well as binary and ternary surfactant mixtures. The fluorescence spectrum of Brij 58 is presented in Figure S1(b). The inset Figure S1(b) shows the fluorescence intensity profile for Brij 58. The fluorescence spectra of C₁₆Br and C₁₆Cl are also shown in Figure S2 and S3 (supporting information). The profiles are very similar to those observed in the UV-vis spectroscopy discussed above. The inflection point in the fluorescence intensity should be treated as cmc. The increasing fluorescence intensity on increasing [surfactant] up to cmc reflected the exposure of the dye upon interaction with surfactant monomers that attained a maximum at cmc. Further addition of surfactant shielded the dye from exposure to the radiation by the amphiphile aggregates.

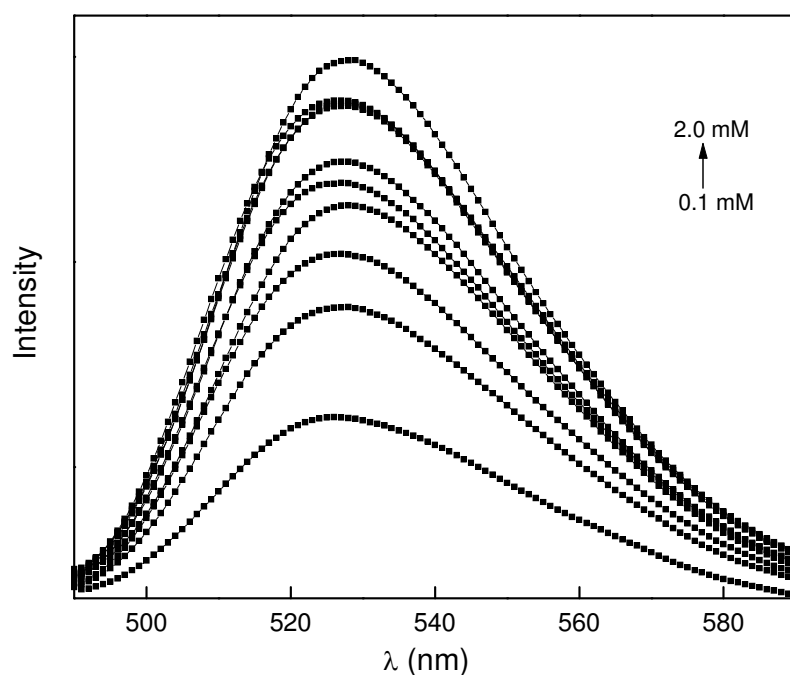


Figure S 2. Fluorescence spectrum of AO as a function of [C₁₆Br].

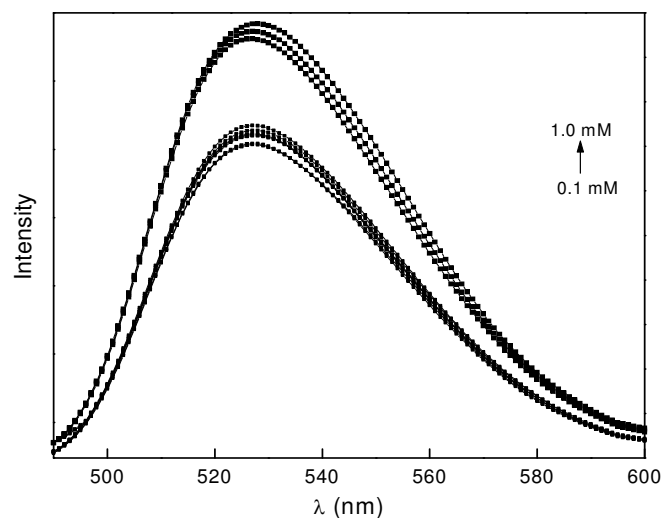


Figure S3. Fluorescence spectrum of AO as a function of $[C_{16}Cl]$.

Table I: Critical micellar concentration values of single as well as binary and ternary surfactant mixtures determined using spectrophotometric techniques.

| Surfactant system | UV-vis spectroscopy cmc (mM) | fluorescence spectroscopy cmc (mM) |
|---------------------------------|---------------------------------|---------------------------------------|
| $C_{16}Br$ | 0.87 | 0.85 |
| $C_{16}Cl$ | 1.36 | 1.31 |
| Brij58 | 0.007 | 0.0069 |
| $C_{16}Br$ - $C_{16}Cl$ | 1.04 | 1.03 |
| $C_{16}Br$ -Brij58 | 0.012 | 0.011 |
| $C_{16}Cl$ -Brij58 | 0.013 | 0.011 |
| $C_{16}Br$ - $C_{16}Cl$ -Brij58 | 0.022 | 0.022 |

Error estimation for cmc values is $\pm 2\%$ and 1.5% in UV-vis and Fluorescence methods respectively.

2. cmc determination by the conductivity measurements: The electrical conductivity measurements have been found to be highly useful to study the association behavior and probe the structural changes occurring in the system. The conductometric profile for pure $C_{16}Br$ is shown in Figure S4. The plot shows single break point. The cmc value is obtained from the intersection of the fitting lines of the conductivity-concentration plot above and below the break point as suggested by Williams.³ For the criterion of fit, best correlation coefficient was chosen. The obtained cmc values were further counter checked by using differential conductivity plot (Figure S4), which is derived from the differential of specific conductance as a function of concentration (i.e $d\kappa/dc$ vs c). The Phillips⁴ method was also applied to verify the obtained cmc value (inset Figure S4). Similar plots were obtained for other single as well as mixed cationic surfactant systems (not shown here) and the cmc values corresponding to the breakpoints in the specific conductance (κ) vs [surfactant] plots for the studied systems were calculated. The values for pure surfactants are in good agreement with the literature^{5,6} values.

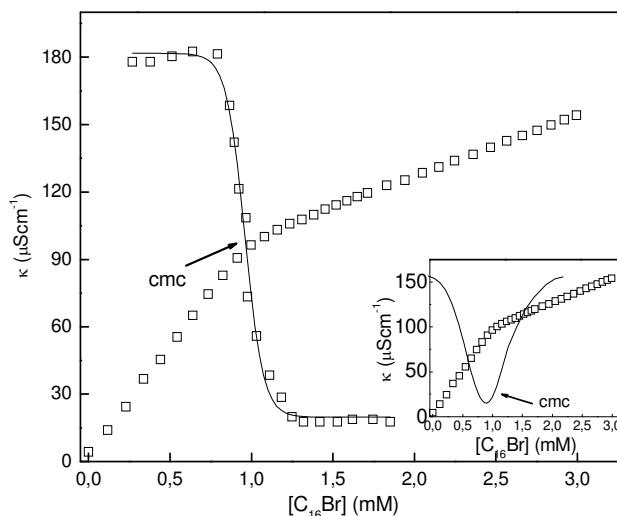


Figure S4. Differential derivative plot of specific conductivity, κ , vs the total surfactant concentration of $C_{16}Br$ in aqueous micellar media at 298.15 K. The inset of this figure shows the application of the Phillips (solid line) and Williams (dotted line) method for $C_{16}Br$ micellar media.

$$\frac{(X_1^M)^2 \ln(cmc_{12}\alpha_1 / cmc_1 X_1^M)}{(1 - X_1^M)^2 \ln\{cmc_{12}(1 - \alpha_1) / cmc_2(1 - X_1^M)\}} = 1 \quad (A)$$

where cmc_1 , cmc_2 and cmc_{12} denote the experimental cmc values of the surfactant 1,2 and their equimolar binary mixture respectively; X_1^M is the micellar mole fraction of surfactant 1 in the mixed micelle.

Table II Gibbs surface excess at cmc (Γ_{\max}) and area of exclusion per monomer at the saturated air/water interface (A_{\min}) for single as well as binary and ternary surfactant mixtures determined using surface tension method.

| Surfactant system | $(\Gamma_{\max}) \times 10^6$ (mole m ⁻²) | A_{\min} (nm ² molecule ⁻¹) |
|--|--|---|
| C ₁₆ Br | 3.87 | 0.44 |
| C ₁₆ Cl | 5.17 | 0.34 |
| Brij58 | 2.93 | 0.58 |
| C ₁₆ Br- C ₁₆ Cl | 4.85 | 0.35 |
| C ₁₆ Br-Brij58 | 1.69 | 1.00 |
| C ₁₆ Cl-Brij58 | 2.66 | 0.64 |
| C ₁₆ Br-C ₁₆ Cl-Brij58 | 1.16 | 1.46 |

Table III ΔG_s° for single as well as binary and ternary surfactant mixtures

| Surfactant system | ΔG_s° (kJmol ⁻¹) | |
|--|---|-----------------------------|
| | $[(C_6H_5)_2CHSe]_2$ | $[C_{12}H_{10}N_2Se_2Br_2]$ |
| C ₁₆ Br | -7.249 | -12.274 |
| C ₁₆ Cl | -5.537 | -10.618 |
| Brij58 | -9.648 | -13.529 |
| C ₁₆ Br- C ₁₆ Cl | -9.077 | -12.902 |
| C ₁₆ Br-Brij58 | -13.187 | -13.301 |
| C ₁₆ Cl-Brij58 | -11.189 | -13.30 |
| C ₁₆ Br-C ₁₆ Cl-Brij58 | -10.504 | -13.073 |

References

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