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ARTICLE

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Acid−Base Equilibrium at an Aqueous Interface: pH Spectrometry by Heterodyne-Detected Electronic Sum Frequency Generation

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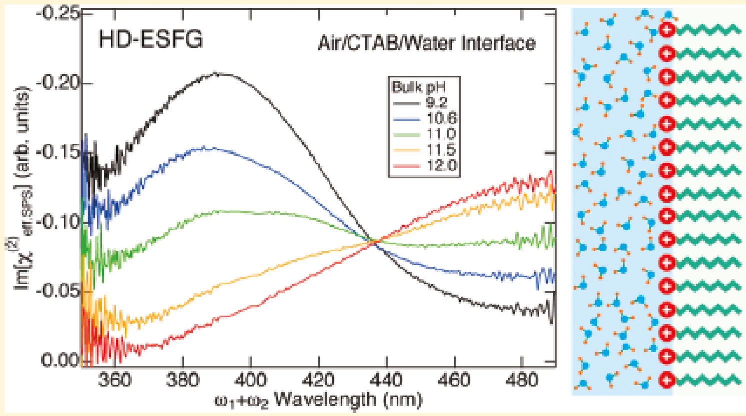
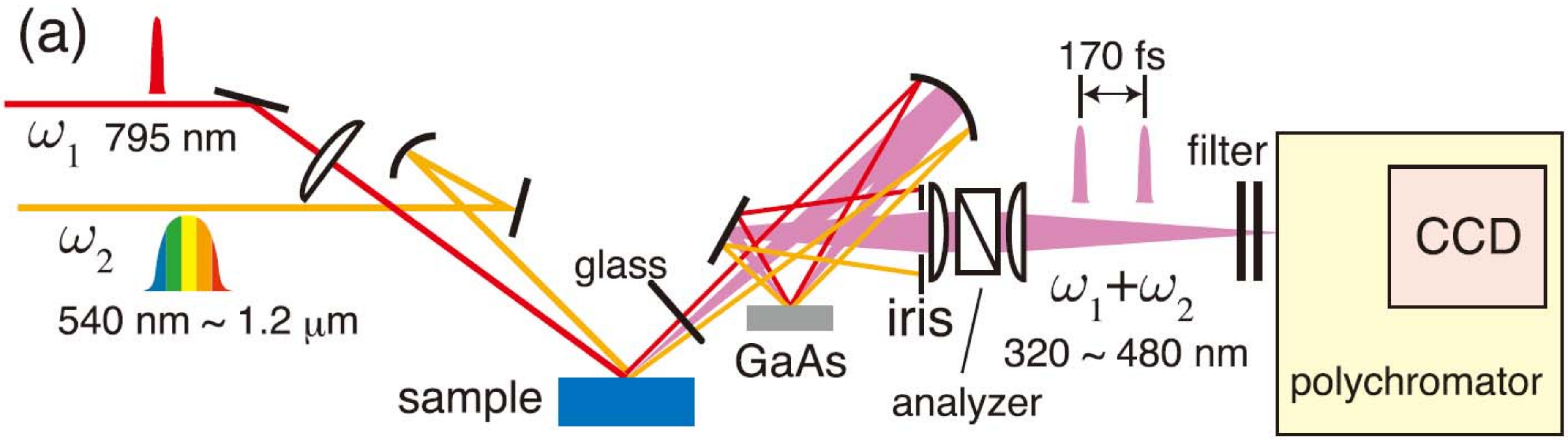
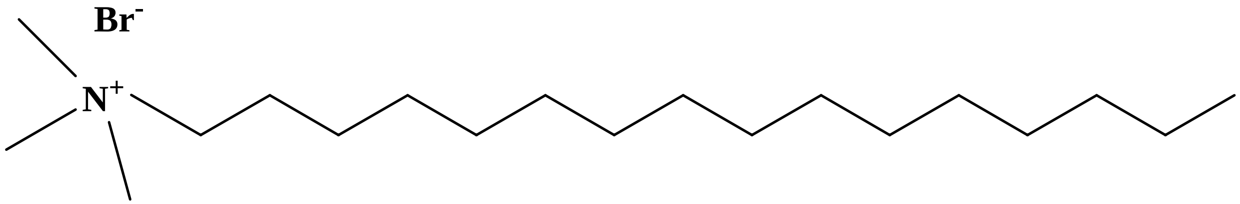
ABSTRACT: We applied interface-selective heterodyne-detected electronic sum frequency generation (HD-ESFG) to the pH spectrometry of an air/cationic surfactant/water interface in order to obtain insight into an acid−base equilibrium at the interface. We used an indicator molecule adsorbed at the interface to probe local pH and local effective polarity. We obtained unprecedentedly high quality spectral data of the interfacial pH spectrometry, which clearly indicates that this interface has higher pH than the bulk owing to the positive charge of the head group of the surfactant. In addition, we found that the air/surfactant/water interface and the micelle interface of the same surfactant are essentially equivalent in local pH and local effective polarity.



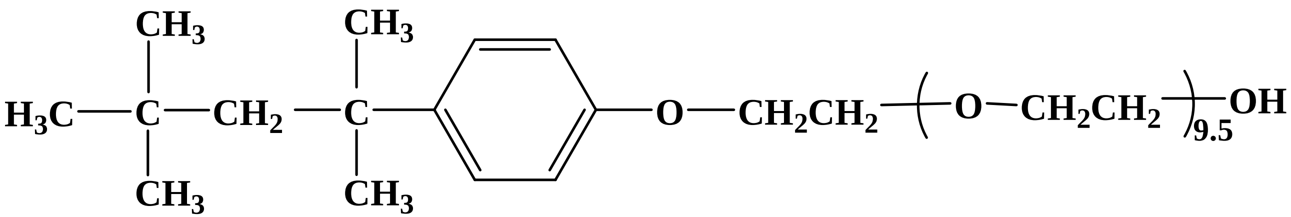


HD-ESFG experimental setup

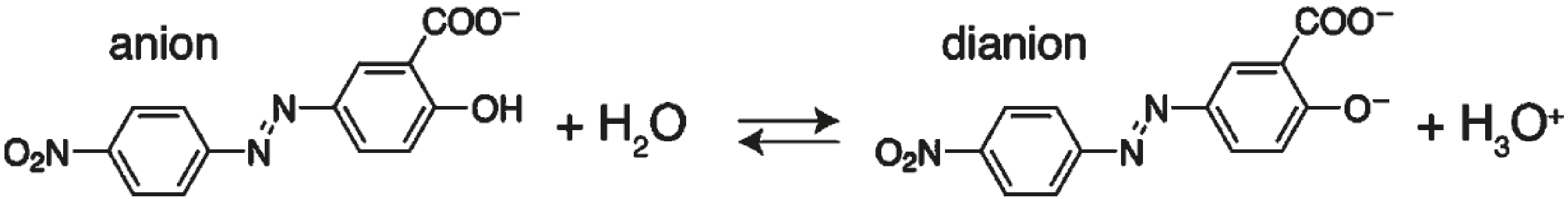
Experimental Materials



Cationic Surfactant: CTAB



Nonionic Surfactant: Triton X-100

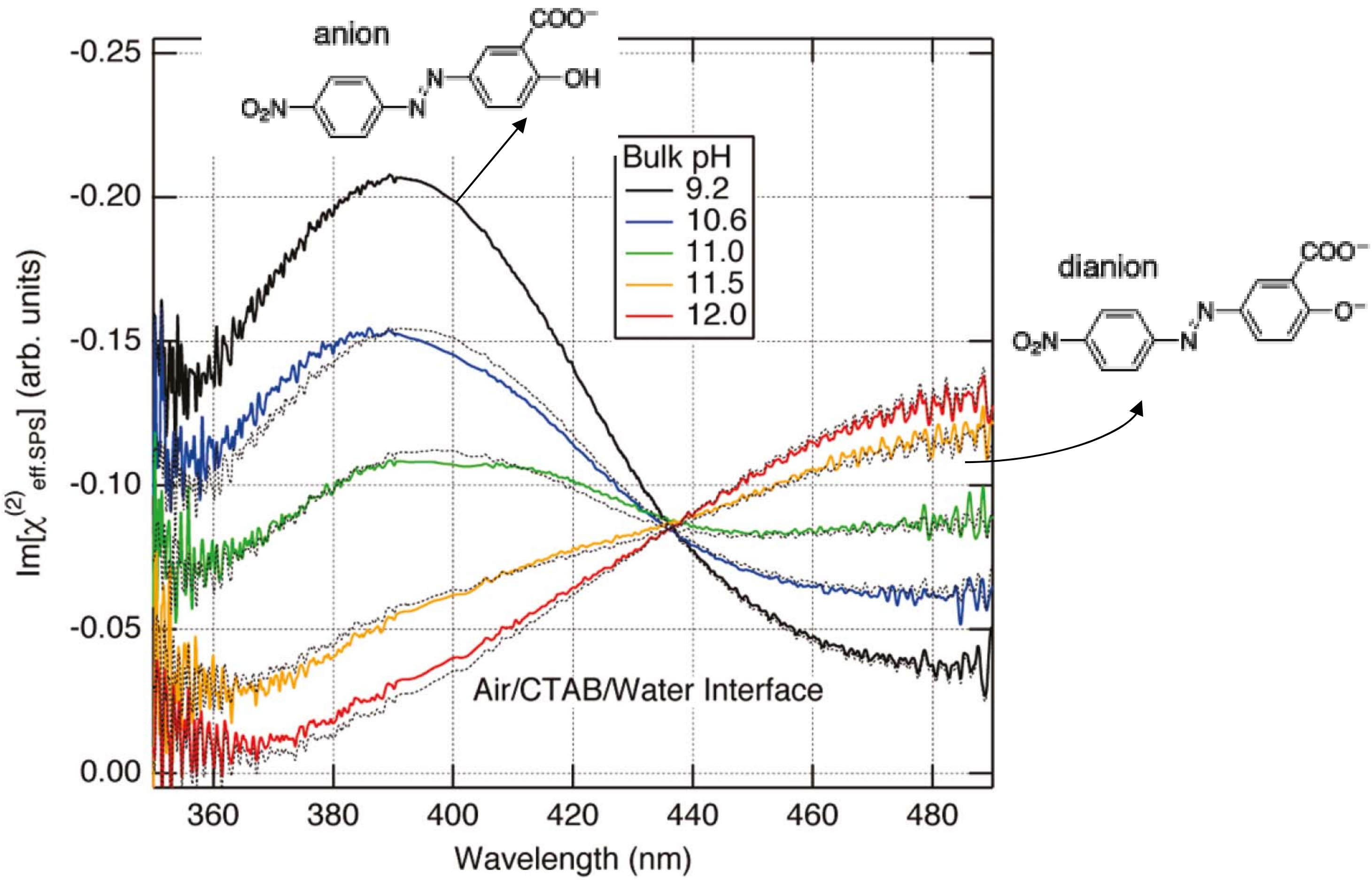


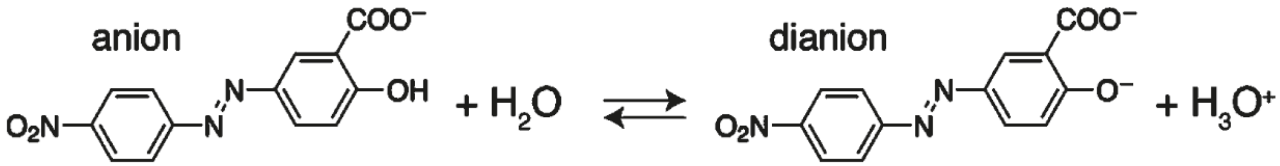
Acid-base indicator molecule: AYR

Experimental Systems

- Air/ CTAB/ Water Interface
- CTAB Micelle Interface
- Triton X-100 Micelle Interface

pH Spectrometry of AYR at the Air/CTAB/Water Interface by HD-ESFG





HA **A-**

$$f_{\mathrm{HA}}(\mathrm{pH}) = \frac{[\mathrm{HA}]}{[\mathrm{HA}] + [\mathrm{A}^-]} = \frac{1}{1 + 10^{\mathrm{pH} - \mathrm{p}K_a}} \quad (1)$$

$$f_{\mathrm{A}}(\mathrm{pH}) = \frac{[\mathrm{A}^-]}{[\mathrm{HA}] + [\mathrm{A}^-]} = \frac{10^{\mathrm{pH} - \mathrm{p}K_a}}{1 + 10^{\mathrm{pH} - \mathrm{p}K_a}} \quad (2)$$

$$S_{\mathrm{HA}}(\lambda) = c^1_{\mathrm{HA}} S^1(\lambda) + c^N_{\mathrm{HA}} S^N(\lambda) \quad (3)$$

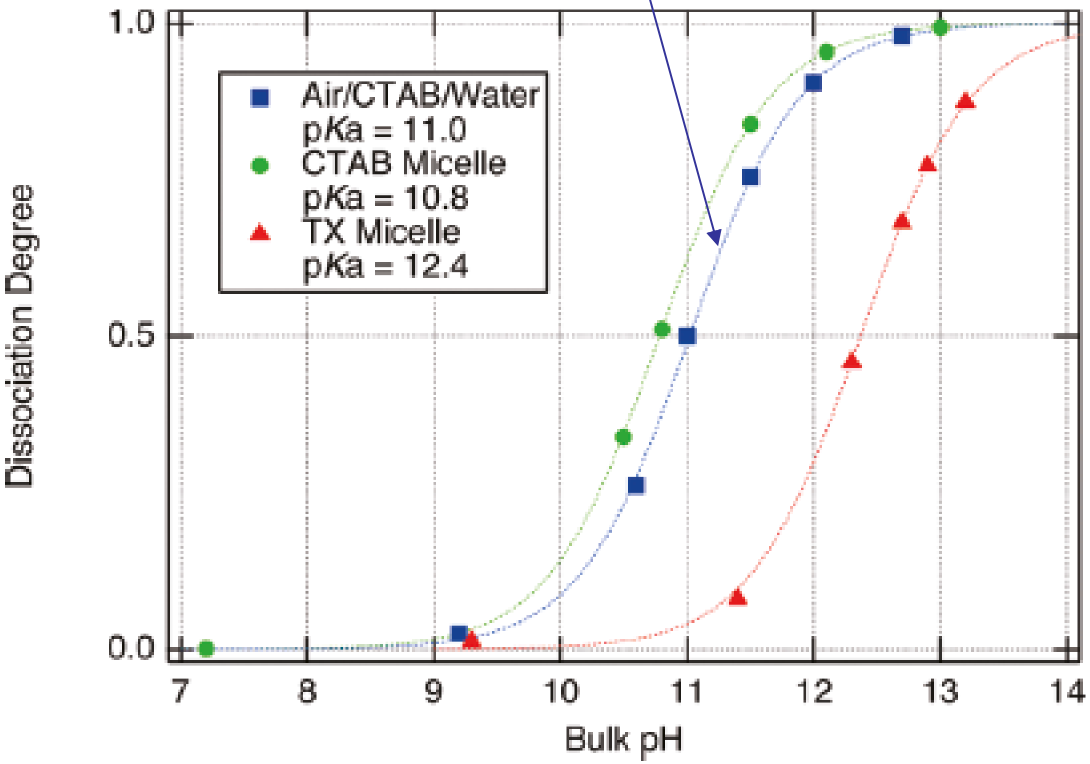
$$S_{\mathrm{A}}(\lambda) = c^1_{\mathrm{A}} S^1(\lambda) + c^N_{\mathrm{A}} S^N(\lambda) \quad (4)$$

$$S^i(\lambda) = f_{\mathrm{HA}}(\mathrm{pH}^i) S_{\mathrm{HA}}(\lambda) + f_{\mathrm{A}}(\mathrm{pH}^i) S_{\mathrm{A}}(\lambda) \quad (5)$$

Air/CTAB/Water interface: pKa = 11, obtained by fitting analysis

$$f_A(\mathrm{pH}) = \frac{[A^-]}{[HA] + [A^-]} = \frac{10^{\mathrm{pH} - \mathrm{p}K_a}}{1 + 10^{\mathrm{pH} - \mathrm{p}K_a}} \quad (2)$$

Air/CTAB/Water interface: **pKa = 11**



Interface pH should be different from the bulk pH

bulk pH → apparent pKa → pKa =11

interface pH → intrinsic pKa → pKa =?

$$\text{intrinsic p}K_a = -\log_{10}\frac{[H^+]_{int}[A^-]_{int}}{[HA]_{int}} = \text{interfacial pH} - \log_{10}\frac{[A^-]_{int}}{[HA]_{int}} \quad (7)$$

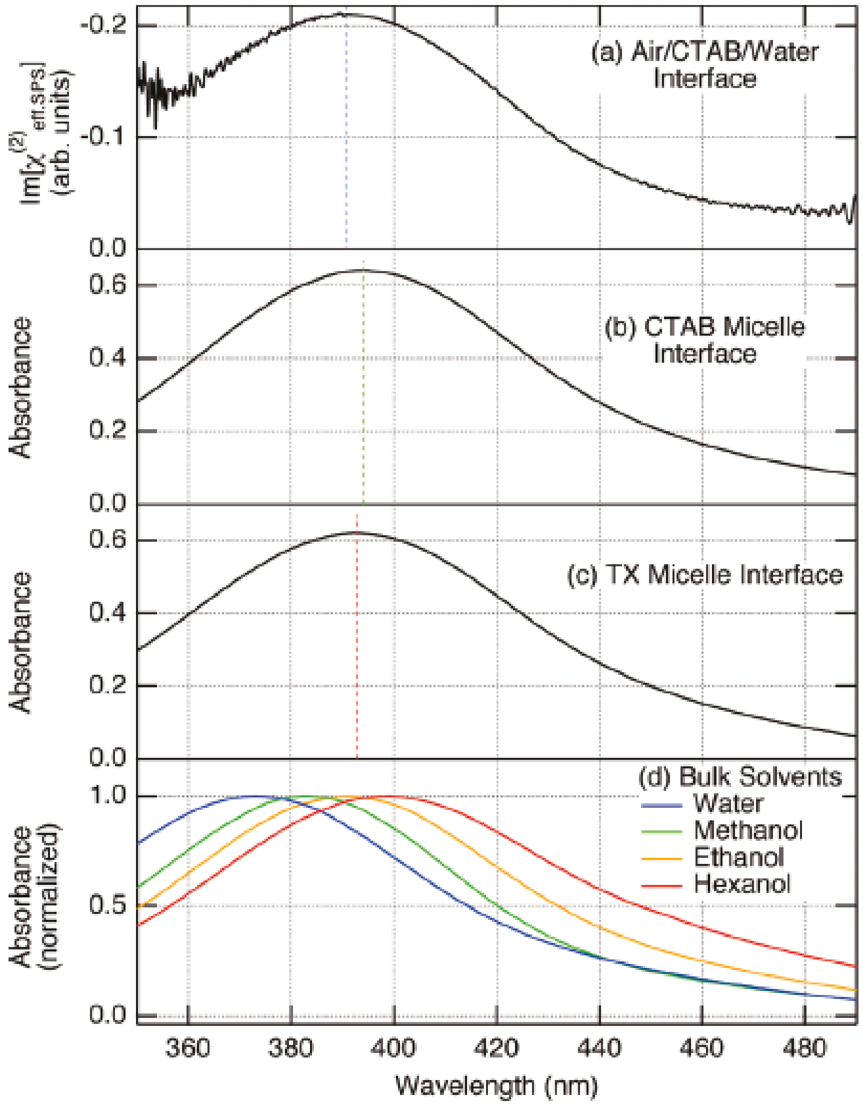
$$\text{apparent p}K_a = \text{bulk pH} - \log_{10}\frac{[A^-]_{int}}{[HA]_{int}} \quad (8)$$

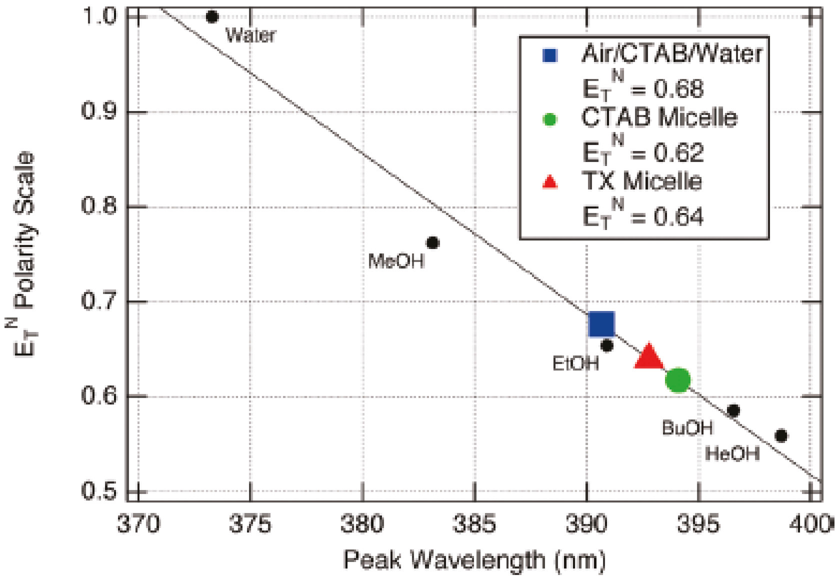
$$\text{apparent p}K_a - \text{intrinsic p}K_a = \text{bulk pH} - \text{interfacial pH} \quad (9)$$

↓

apparent pKa = 11, intrinsic pKa = ?

Intrinsic pKa is estimated by the local effective polarity at the interface



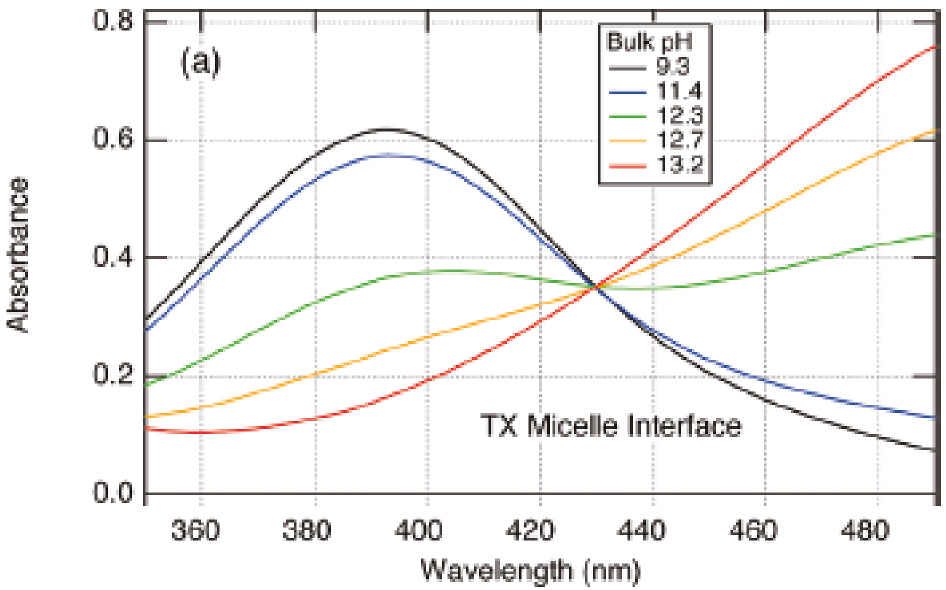


AYR at the air/CTAB/water interface has almost the same intrinsic pKa as that at the CTAB and TX micelle interfaces

TX-100 micelle interface: interfacial pH = bulk pH

TX-100 micelle interface: intrinsic pKa = apparent pKa

Intrinsic pKa: TX-100 micelle = air/CTAB/water = CTAB micelle



TX-100 micelle interface:

intrinsic pKa = apparent pKa = 12.4

Air/CTAB/Water interface:

intrinsic pKa=12.4

Local pH at air/CTAB/water interface

$$\text{apparent p}K_a - \text{intrinsic p}K_a = \text{bulk pH} - \text{interfacial pH} \quad (9)$$

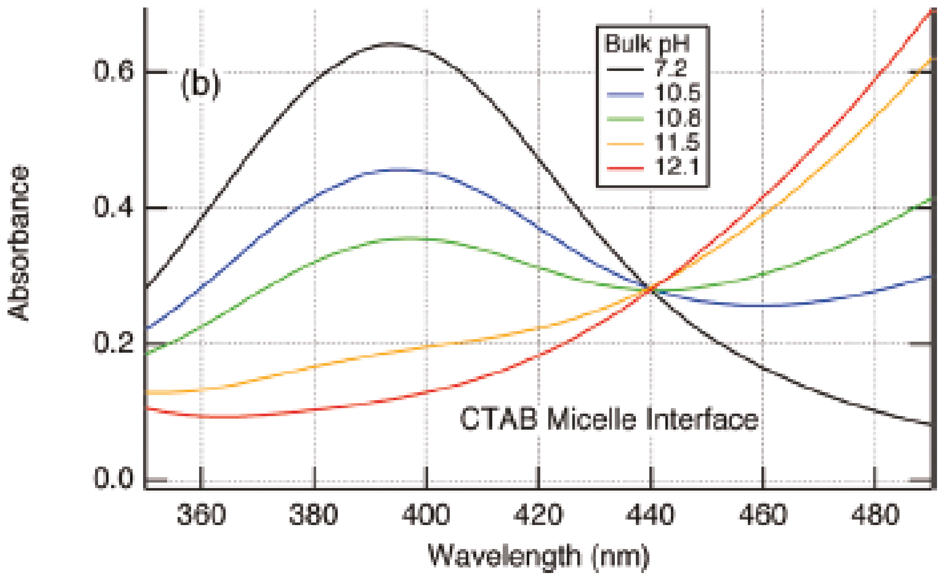
↓

11.0 – 12.4 = -1.4

↓

Air/CTAB/Water interface is more basic than the bulk

Local pH at CTAB micelle interface



CTAB micelle interface:

apparent pKa = 10.8

$$\text{apparent p}K_a - \text{intrinsic p}K_a = \text{bulk pH} - \text{interfacial pH} \qquad (9)$$

10.8 – 12.4 = -1.6

CTAB micelle interface is more basic than the bulk