

ELECTRONIC SUPPLEMENTARY INFORMATION

Interfacial properties modulated by the water confinement in Reverse Micelles created by the Ionic liquid-like surfactant bmim-AOT

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EXPERIMENTAL SECTION

Methods

RM_s preparation: The stock solutions of bmim-AOT in the organic solvent (benzene and chlorobenzene) were prepared by mass and volumetric dilution. To obtain optically clear solutions, they were shaken in a sonicating bath. The amount of water present in the system is expressed as the molar ratio between water and surfactant ($W_0 = [\text{H}_2\text{O}]/[\text{surfactant}]$). The W_0 was varied between 0-6 for bmim-AOT RM_s. It was not possible to obtain higher values of W_0 due to turbidity problems. The lowest value for W_0 ($W_0 = 0$), corresponds to a system without water addition. The appropriate amounts of H₂O (D₂O for ²H NMR experiments) were incorporated into RM_s solutions by means of microsyringes.

Similar procedures were performed by the Na-AOT RM_s experiments.

For the absorption experiments, a 1×10^{-2} M solution of QB in methanol (Sintorgan HPLC quality) was prepared. The appropriate amount of this solution to obtain a concentration of 2×10^{-4} M for QB in the RM_s was transferred into a volumetric flask, and the methanol was evaporated by bubbling dry N₂; then, the surfactant RM_s stock solution was added to the residue and agitated in a sonicating bath until the RM_s was optically clear. For the experiments varying the surfactant concentration at W_0 constant, a stock solution of surfactant 0.2 M was used. Thus, to the cell baring 2 mL of QB of the same concentration in the nonpolar solvent, was added the appropriate amount of surfactant and molecular probe stock solution to obtain a given concentration of surfactant in the micellar media. Therefore, the absorbance values of the molecular probe were not affected by dilution. For the experiments varying the water content, an RM_s solution prepared at $[\text{surfactant}] = 0.06$ M was employed. Similar procedure was employed for the experiments using $[\text{Cu}(\text{acac})(\text{tmen})][\text{B}(\text{C}_6\text{H}_5)_4]$.

General

The absorption spectra were measured by using Shimadzu 2401 equipment at 25 (0.1 °C unless otherwise indicated). The path length used in the absorption experiments was 1 cm. λ_{max} was measured by taking the midpoint between the two positions of the spectrum where the absorbance is equal to $0.9 \times \text{Abs}_{\text{max}}$.

The ^2H NMR spin-lattice relaxation times, T_1 , were obtained on a Bruker Avance II 300 spectrometer operating at a deuterium Larmor frequency of 46.05 MHz. The measurements were performed using the inversion-recovery pulse sequence, $(\pi)_x - \tau - (\pi)_{x,-x} - \text{Acq}$, as reported previously¹, where τ indicates the magnetization recovery period. The dependence of the normalized measured signal intensity with τ is $I(\tau) = 1 - 2\exp(-\tau/T_1)$.^{2,3} All NMR data were processed using MestReC 4.8.6 for window and plotted and fitted using Microcal OriginPro 7.

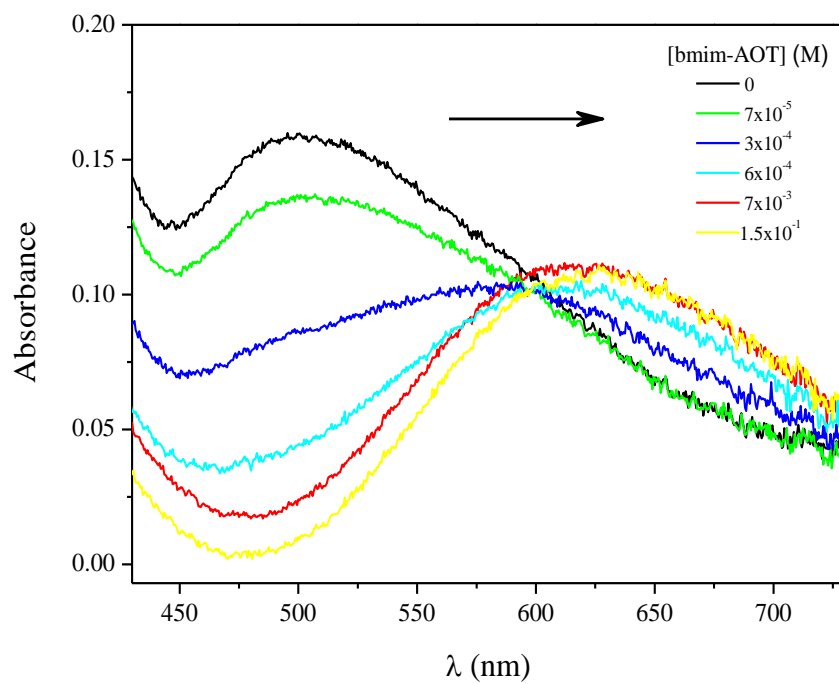


Figure S1. Absorption spectra of $[\text{Cu}(\text{acac})(\text{tmen})][\text{B}(\text{C}_6\text{H}_5)_4]$ complex in chlorobenzene/bmim-AOT RMs varying [bmim-AOT] at $W_0 = 0$. $[[\text{Cu}(\text{acac})(\text{tmen})][\text{B}(\text{C}_6\text{H}_5)_4]] = 1 \times 10^{-3}$ M.

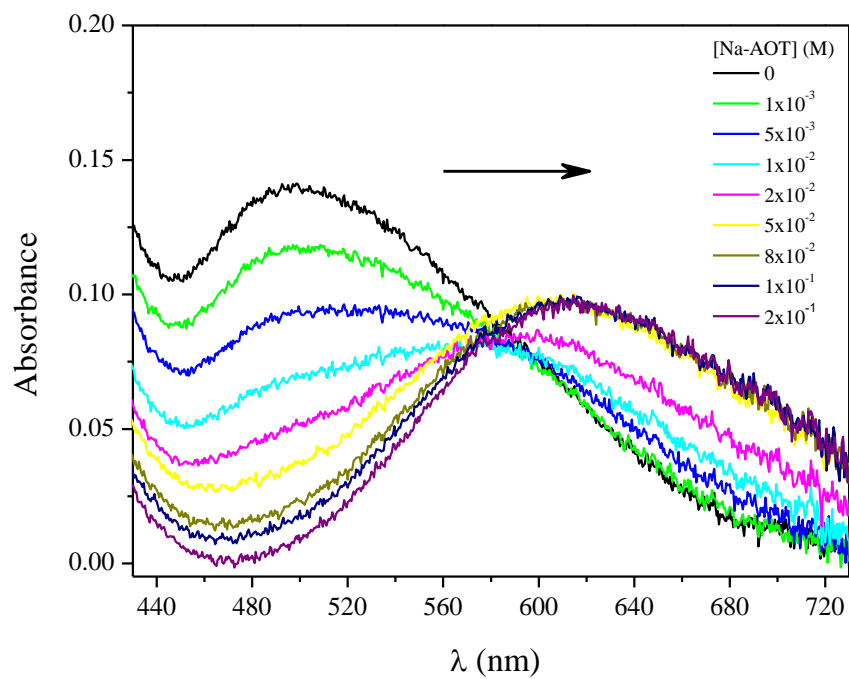


Figure S2. Absorption spectra of $[\text{Cu}(\text{acac})(\text{tmen})][\text{B}(\text{C}_6\text{H}_5)_4]$ complex in chlorobenzene/Na-AOT RMs varying $[\text{Na-AOT}]$ at $W_0 = 0$. $[[\text{Cu}(\text{acac})(\text{tmen})][\text{B}(\text{C}_6\text{H}_5)_4]] = 1 \times 10^{-3} \text{ M}$.

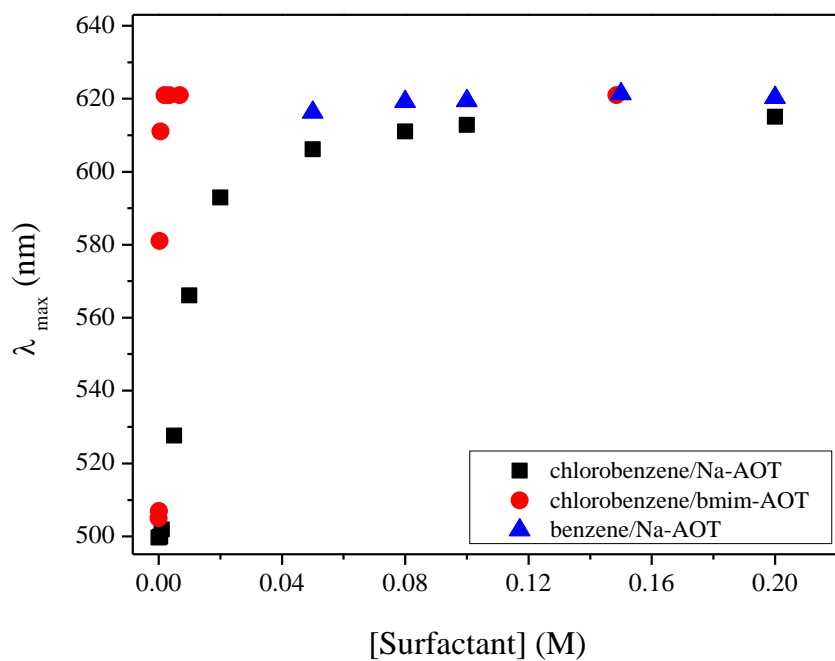


Figure S3. Absorption maxima shifts (λ_{\max}) values of $[\text{Cu}(\text{acac})(\text{tmen})][\text{B}(\text{C}_6\text{H}_5)_4]$ in different RMs as a function of [surfactant] at $W_0 = 0$. $[[\text{Cu}(\text{acac})(\text{tmen})][\text{B}(\text{C}_6\text{H}_5)_4]] = 1 \times 10^{-3} \text{ M}$.

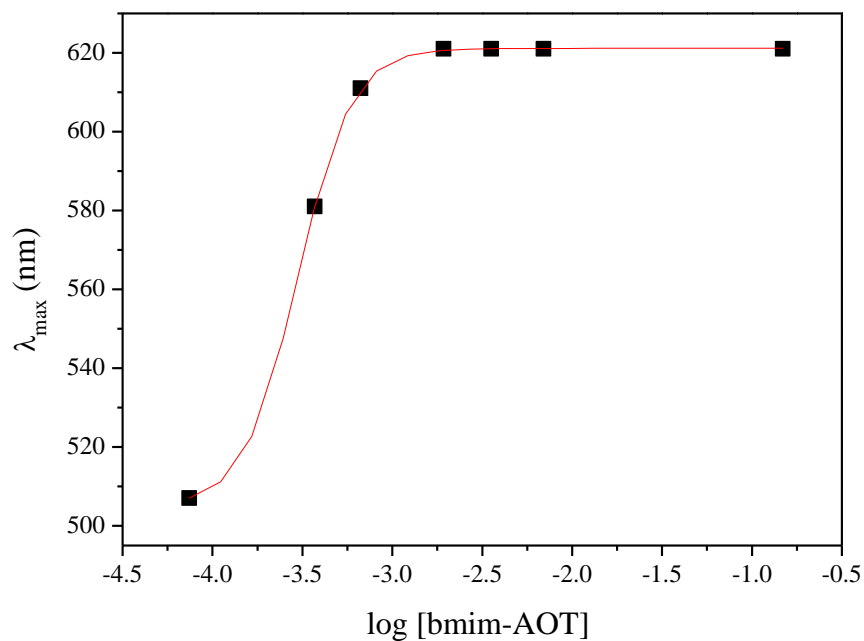


Figure S4. Variation of the λ_{\max} of $\text{Cu}(\text{acac})(\text{tmen})\text{B}(\text{C}_6\text{H}_5)_4$ as a function of $\log[\text{bmim-AOT}]$ in chlorobenzene/bmim-AOT RMs at $W_0 = 0$. $[\text{Cu}(\text{acac})(\text{tmen})\text{B}(\text{C}_6\text{H}_5)_4] = 1 \times 10^{-3}$ M. The solid lines represent the sigmoidal fit using Sigmoidal–Boltzmann equation.

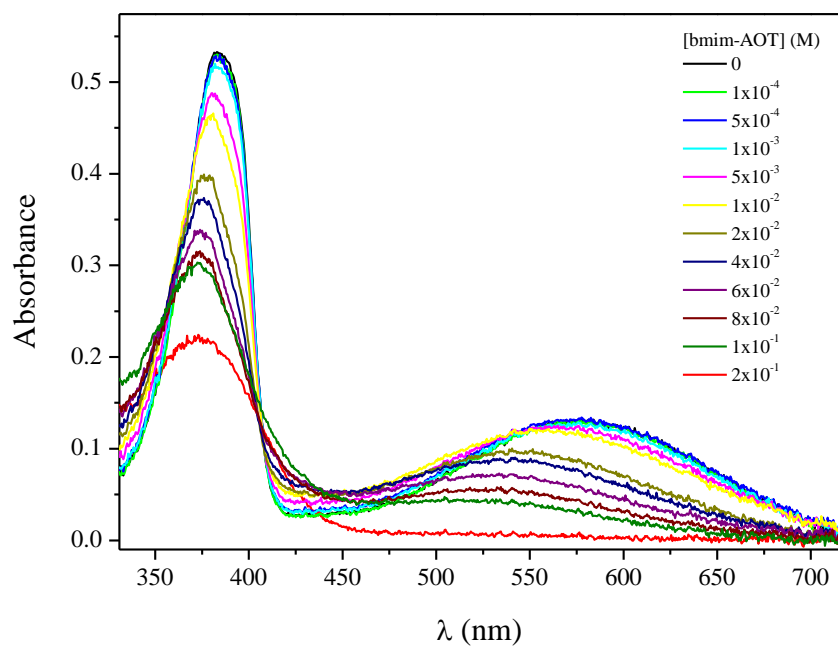


Figure S5. Absorption spectra of QB in benzene/bmim-AOT RMs varying [bmim-AOT] at $W_0 = 0$.

$[QB] = 2 \times 10^{-4}$ M.

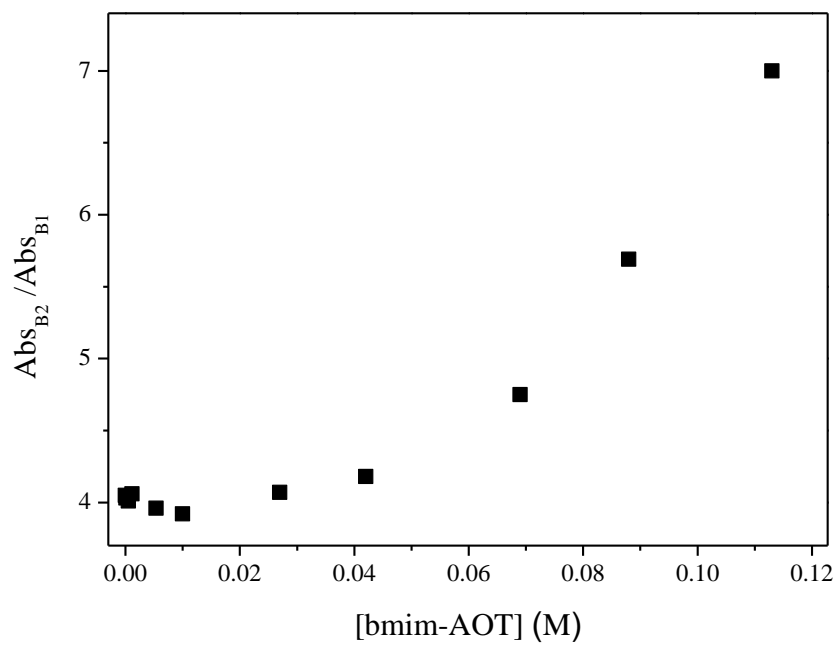


Figure S6. Variation of $\text{Abs}_{\text{B2}}/\text{Abs}_{\text{B1}}$ ratio values in benzene/bmim-AOT as a function of [bmim-AOT] at $W_0 = 0$.

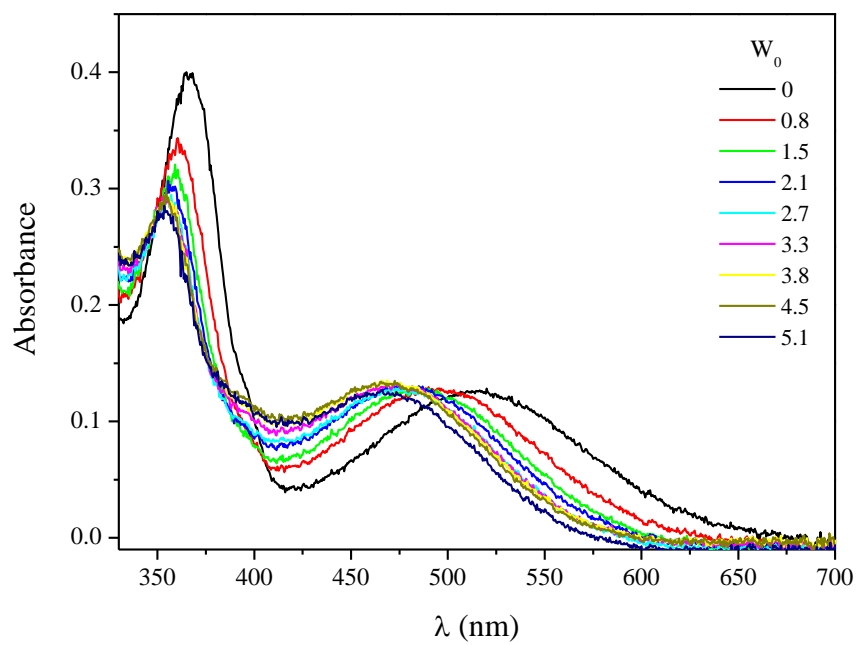


Figure S7. Absorption spectra of QB in benzene/Na-AOT/water RMs varying W_0 . [Na-AOT] = 0.06 M, [QB] = 2×10^{-4} M. T = 25 °C.

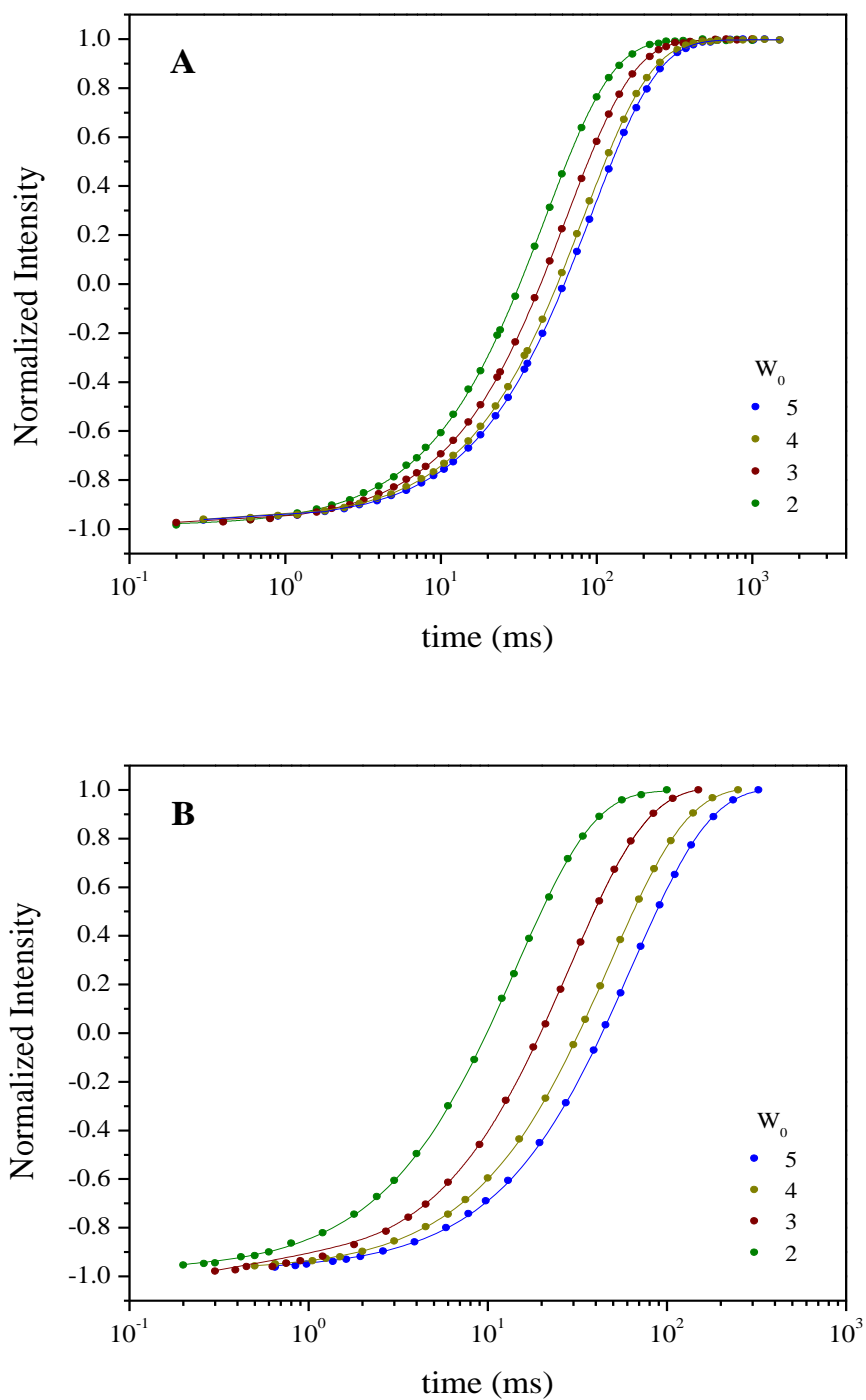


Figure S8. Monoexponential fit of the longitudinal relaxation decay for benzene/surfactant/D₂O RMs as a function of D₂O content. A) bmim-AOT and B) Na-AOT. [Surfactant] = 0.2 M.

References

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