Supporting Information

Singularities on the physicochemical properties of spontaneous AOT-BHD

unilamellar vesicles in comparison with DOPC vesicles

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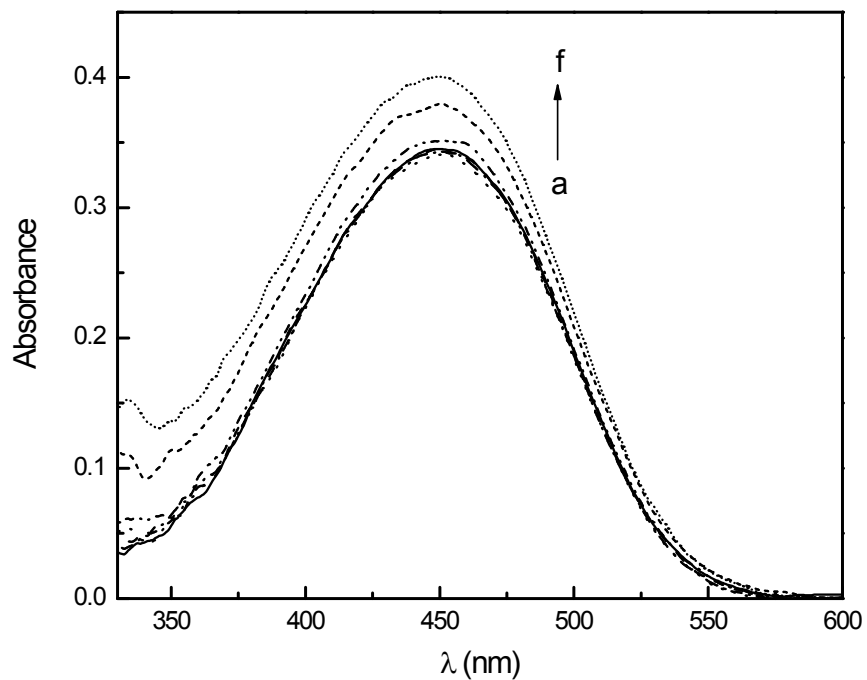Dr. R. Darío Falcone. Corresponding-Author, E-mail: rfalcone@exa.unrc.edu.ar

Figure S1. Absorption spectra of HC in AOT-BHD unilamellar vesicles varying [AOT-BHD]. [AOT-BHD]: a) 0 mg/mL, b) 0.1 mg/mL, c) 0.5 mg/mL, d) 1 mg/mL, e) 3 mg/mL, f) 5 mg/mL. [HC] = 1 x 10^{-5} M.
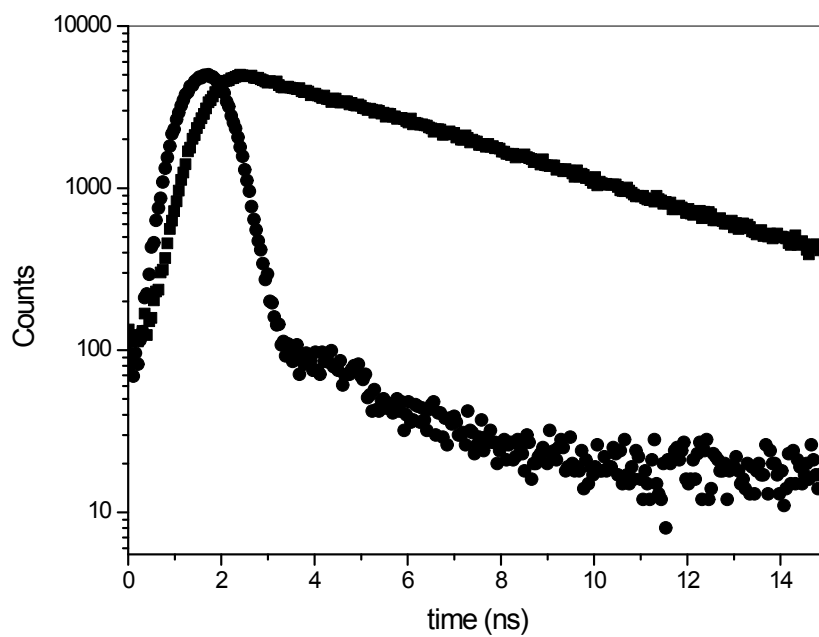
Figure S2. Fluorescence decay profiles of HC in AOT-BHD vesicles at [AOT-BHD] = 2 mg/mL, λ_{exc} = 450 nm and λ_{em} = 600 nm. [HC] = 1×10^{-5} M. (∞) Lamp profile and (O) fluorescence intensities measured.
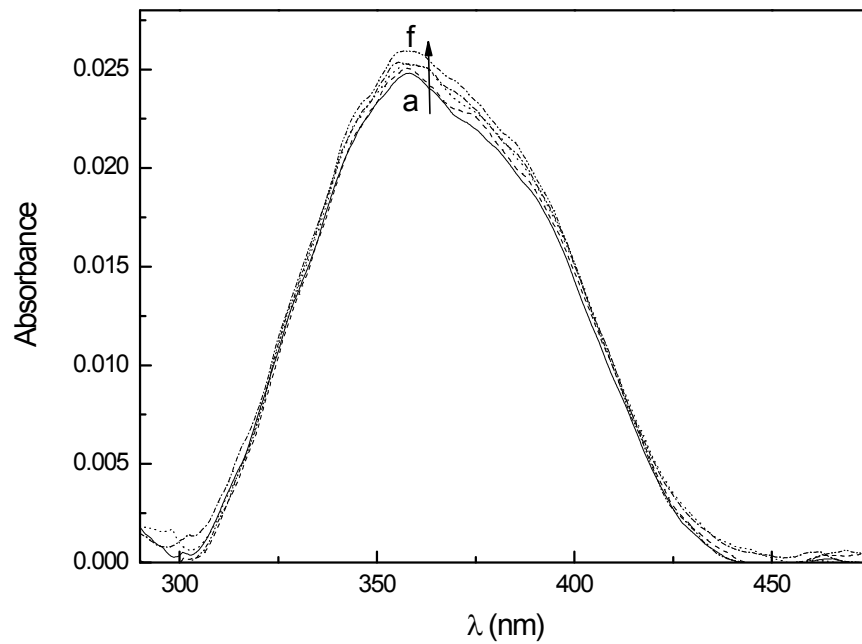
Figure S3. Absorption spectra of PRODAN in AOT-BHD unilamellar vesicles varying [AOT-BHD]. [AOT-BHD]: a) 0 mg/mL, b) 0.1 mg/mL, c) 0.5 mg/mL, d) 1 mg/mL, e) 3mg/mL, f) 5mg/mL. [PRODAN] = 5 x 10^{-6} M.

PRODAN and HC partition constants (K_p) Calculation

To evaluate the HC and PRODAN partition constants, K_p, we use the changes in its emission spectra with the AOT-BHD concentration (Figures 1 and 5) following a procedure used in other organized media.[S1-2]

The HC and PRODAN partition between the AOT-BHD vesicles and water will be treated within the framework of the pseudophase model.[S3-4] This model considers the vesicle as a distinct pseudophase whose properties are independent of the AOT-BHD concentration. In this model, only two solubilization sites are considered, that is, the water and the vesicle (ie. all the AOT-BHD molecules). In this way, the distribution of PRODAN or HC between the bilayer and the water pseudophase defined in equation S1 can be expressed in terms of the partition constant K_p showed in equation S2:

$$MP_w \underset{\leftarrow}{\rightarrow} MP_b^{\#} \tag{S1}$$

$$K_p = \frac{[MP]_b^{\#}}{[MP]_w} \tag{S2}$$

The terms in brackets represent the molecular probe (MP) in water (w) and bound (b) to the bilayer in terms of local concentrations. Thus, $[MP]^{\#}_b$ can be expressed taking into account the analytical (bulk) concentration of vesicle bound substrate, $[MP]_b$, as equation S3 show.

$$[MP]_b^{\#} = \frac{[MP]_b}{[AOT-BHD]} \tag{S3}$$

Hence K_p can be defined as in equation S4:

$$K_p = \frac{[MP]_b}{[MP]_w[AOT - BHD]}$$

(S4)

Where $[MP]_b$ is the analytical concentration of the substrate (PRODAN or HC) incorporated to the bilayer, $[MP]_w$ is the concentration of the substrate in the water pseudophase, and $[AOT-BHD]$ is the catanionic surfactant concentration. This equation applies when $[MP]_t \ll [AOT-BHD]$.

As it was previously reported,[S4,5] the K_p value can be determined from the change in the MP's fluorescent intensity (at a given wavelength) with the AOT-BHD concentration. If the analytical concentration of the MP is kept constant and the absorbance of the sample at the working excitation wavelength is constant[S5], equation S5 can be deduced:

$$I = \frac{I_0(\phi_w + \phi_b K_p[AOT - BHD])}{(1 + K_p[AOT - BHD])}$$

(S5)

Where, I is the fluorescence intensity at [AOT-BHD] considered, I_0 is the incident light and ϕ_w, ϕ_b, are the fluorescent quantum yield of the MP in water and bound to the AOT-BHD bilayer, respectively. Figure S1 A and B show the increments of I values when increase the AOT-BHD concentration for HC and PRODAN, respectively. Thus, using a least-square fit of equation S5 we calculate the K_p values for HC and PRODAN (Table 3).
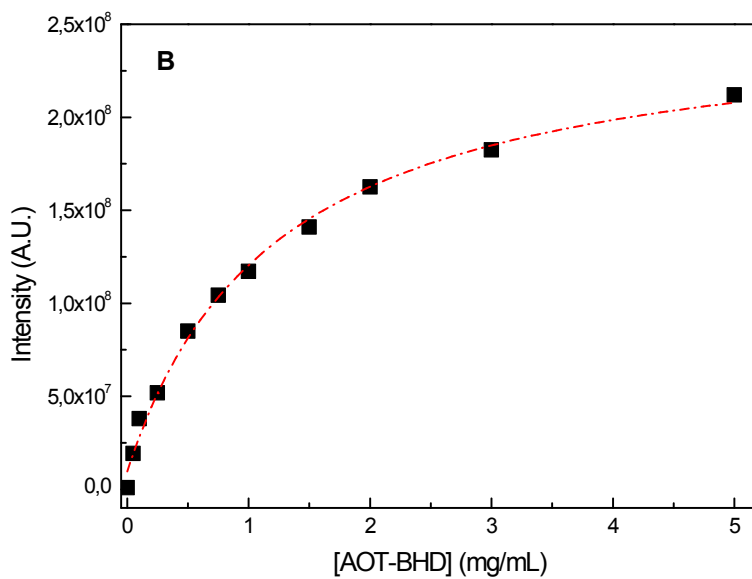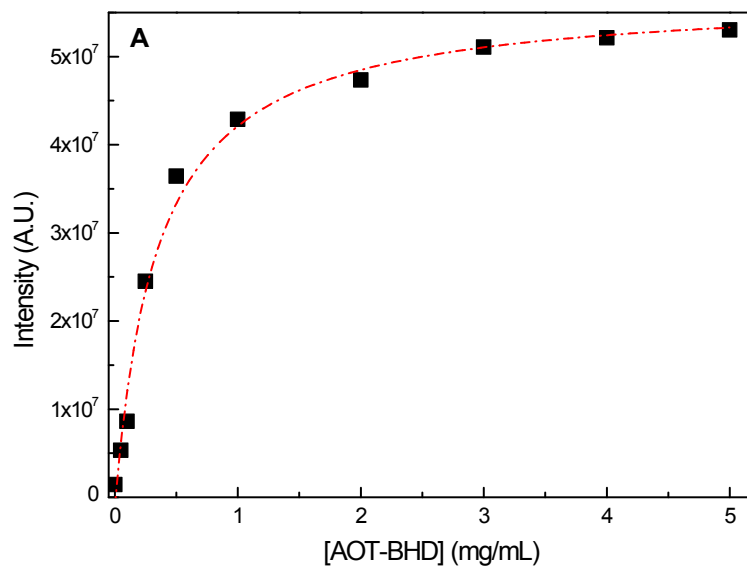
Figure S4. (A) Variation of HC in emission intensity at 584 nm by varying [AOT-BHD]. λ_{exc} = 450 nm. [HC] = 1 x 10^{-5} M. (B) Variation of PRODAN emission intensity at 448 nm by varying [AOT-BHD]. λ_{exc} = 350 nm. [PRODAN] = 5 x 10^{-6} M. All data in Figures A and B were fitted using equation S5.

References

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