

## Supporting Information

### **How TOPO Affects the Interface of the Novel Mixed Water/AOT:TOPO/*n*-heptane Reverse Micelles. A Dynamic Light Scattering and Fourier Transform Infrared Spectroscopy Study**

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### ***Stretching Band of P=O ( $\nu_{P=O}$ )***

Figure S1 shows the  $\nu_{P=O}$  in the 1240-1100  $\text{cm}^{-1}$  region for TOPO in *n*-heptane,  $\text{CCl}_4$  and also the TOPO spectrum for the solid it was included. As it was observed long time ago,<sup>1,2</sup> the shape of the band depends strongly on the solvent. In *n*-heptane the band split into two components of similar intensity at 1197 and 1176  $\text{cm}^{-1}$  while in  $\text{CCl}_4$  the band is single, with a maximum around 1168  $\text{cm}^{-1}$  and shoulders at higher frequency.<sup>1,2</sup> Searching in the literature it is not possible to find an explanation about the splitting of the band in some solvents while in others, as in the solid state, there is a single band. A possible explanation is that the splitting is due to the aggregation of TOPO forming RMs in solvents like *n*-heptane while in  $\text{CCl}_4$  the surfactant only forms a solution without surfactants' organization. To corroborate that, we have prepared a TOPO solution in  $\text{CCl}_4$  and tested the capacity of dissolved water that it was practically negligible. Moreover, DLS experiments performed on this system confirms the existence of a homogeneous solution since no counts and no correlation could be obtained. Thus, it seems that when TOPO forms RMs, the molecules are located in different zones within the interface some more into the polar part and others into the oil side and consequently a splitting of the band is observed. Similar behavior presents AOT with its  $\text{SO}_3^-$  group which, the asymmetric mode splits only when the surfactant makes RMs.<sup>3,4</sup>

Figure S2 A shows the FT-IR spectra corresponding of P=O band region of TOPO in TOPO/*n*-heptane RMs upon increasing the  $W_0$  values and Figure S2 B shows the shift of the lower frequency band with the water content. One of the band shifts almost 12  $\text{cm}^{-1}$  to lower frequency when  $W_0$  value increases from 0 to 0.8 while the band at higher frequency remains constant. These facts show two different things: i) water effectively interacts by H-bond with the P=O group of TOPO located at the polar side of the RMs interface, shifting

the band to lower frequencies and ii) TOPO molecules at the nonpolar part of the interface do not interact with water molecules.

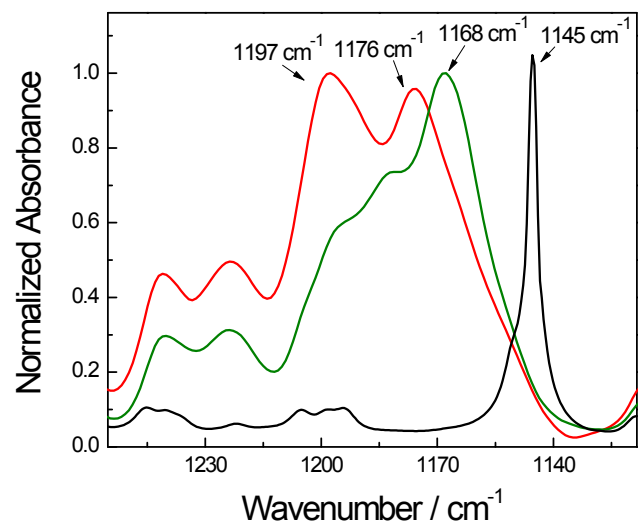
### ***Stretching Band of C=O ( $\nu_{C=O}$ )***

Figure S7 shows the spectra of the AOT C=O stretching region upon increasing the  $W_0$  at  $X_{\text{TOPO}} = 0.7$  value in mixed RMs. An asymmetric broad peak around  $1738\text{ cm}^{-1}$  and a less intense shoulder at  $\sim 1720\text{ cm}^{-1}$  is observed. As shown, the intensity and position of the main peak does not change with the water content. It seems to us that there is no perturbation due to H-bond interaction between water and the C=O group in the mixed RMs even in the presence of TOPO. Thus, as it was suggested before for AOT RMs the interaction between water with the AOT polar head group is with the  $\text{SO}_3^-$  group and the  $\text{Na}^+$  counterions.<sup>5,6</sup>

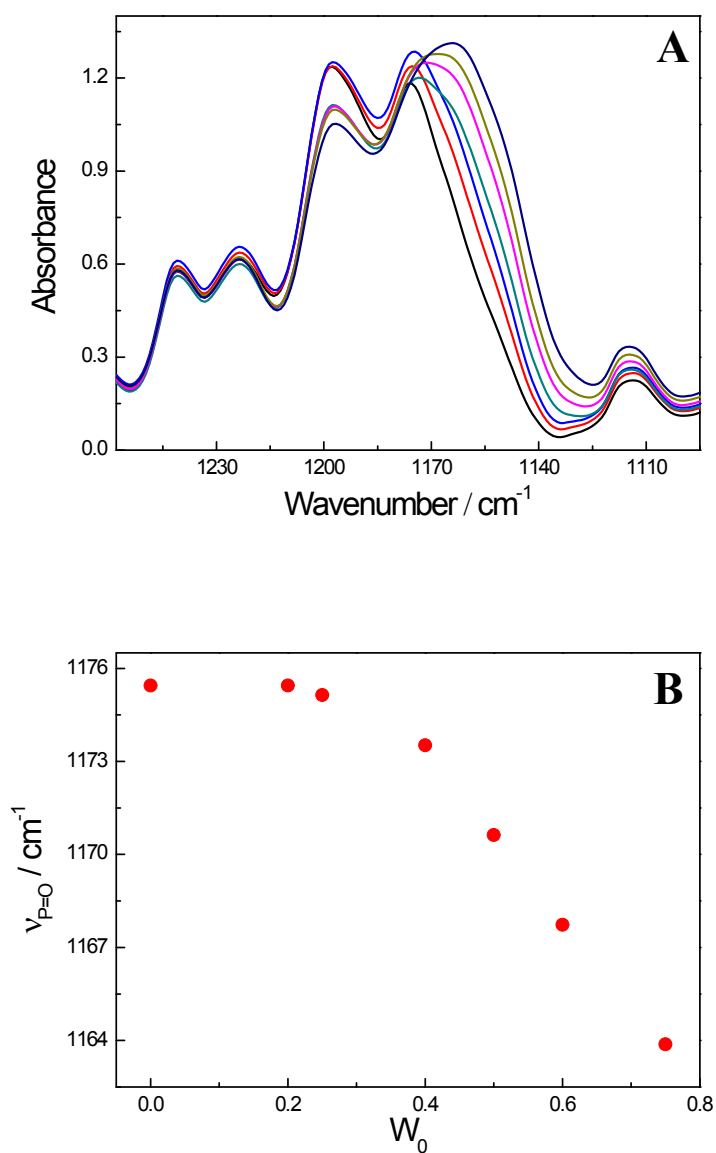
With regard to the C=O band shape, it is not clear the causes of these asymmetry. Different explanation can be found in the literature but none of them are conclusive.<sup>3,7-7</sup> For example, it was claim that these bands arise from a mixture of the AOT predominant rotational isomers, in particular the *gauche* ( $\nu_{C=O}$  around  $1720\text{ cm}^{-1}$ ) and *trans* ( $\nu_{C=O}$  around  $1730\text{ cm}^{-1}$ , see Scheme S1).<sup>8</sup> The ratio of the conformers should vary with the nature of the microenvironment. In a polar media, the *gauche*-like conformer is expected to be favored because in this conformation the whole polar group remains directly toward the polar side of the RMs interface. On the other hand, in a nonpolar media the *trans*-like rotamer is favored because the neighboring C=O group to  $\text{SO}_3^-$  group moves from the polar side to the nonpolar region of the interface.<sup>7</sup> However, when polar solvents are encapsulated inside AOT RMs<sup>6,7</sup> and inside the mixed RMs (Figure S7) the  $1720\text{ cm}^{-1}$  band does not decrease

as it is expected for a rotamer equilibrium shift. So, it seems that other effects are affecting the AOT C=O asymmetric band.<sup>3,4</sup> Other possible explanation arises considering that AOT has two C=O groups that are not symmetrically equivalent.<sup>9</sup> Nevertheless, the data found in this work, let us think that other explanation never considered before, should be considered as possible explanation for the asymmetry of the C=O band.

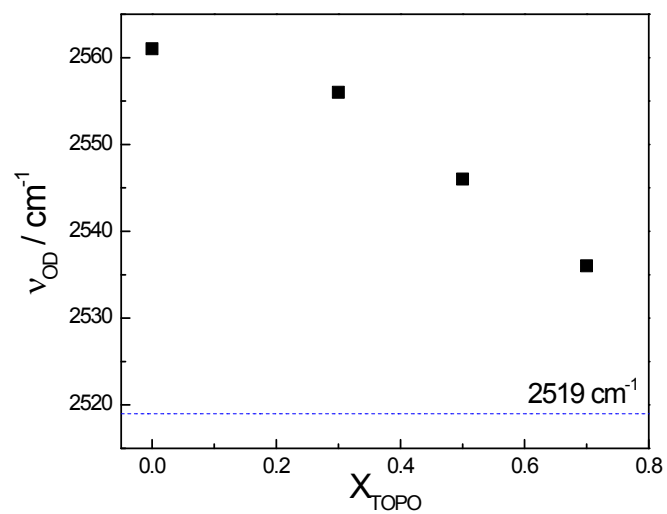
Herein, we will discuss the effect of the changes in the TOPO composition at constant  $W_0$  value. Figure S8 shows the FT-IR spectra of the AOT C=O stretching region in the mixed RMs for different  $X_{\text{TOPO}}$  at  $W_0 = 0$ . As shown, the intensity and position of the main peak located at  $1738 \text{ cm}^{-1}$  does not change with the increases of  $X_{\text{TOPO}}$ . However, the intensity of the shoulder at  $1720 \text{ cm}^{-1}$  gradually decreases increasing the TOPO content. Spectra and similar behavior (data not shown) were obtained for different  $W_0$  and  $X_{\text{TOPO}}$  analyzed. As it was discussed, TOPO makes strong complex with the  $\text{Na}^+$  counterions separating it from the AOT  $\text{SO}_3^-$  group. In this way, it is very likely that the interaction between  $\text{Na}^+$  and the  $\text{SO}_3^-$  group may have impact in the C=O asymmetry of the band. Once TOPO makes complex with the counterion, the C=O band is considerably more symmetric.



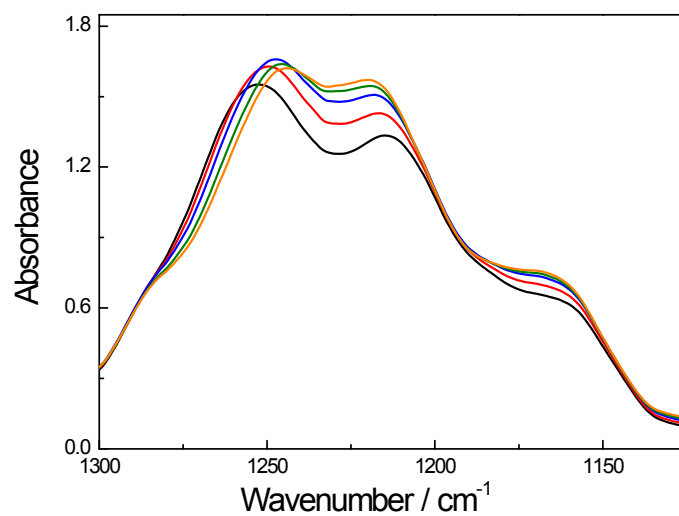
**Figure S1:** FT-IR spectra corresponding to the phosphoryl group stretching band of TOPO in TOPO/*n*-heptane (—), TOPO/CCl<sub>4</sub> (—) at  $W_0 = 0$  and solid TOPO (—).



**Figure S2:** (A) FT-IR spectra corresponding to the phosphoryl group stretching band of TOPO in water/TOPO/*n*-heptane reverse micelles upon increasing the  $W_0$  value.  $W_0$ : 0 (—), 0.2 (—), 0.25 (—), 0.4 (—), 0.5 (—), 0.6 (—), 0.8 (—). (B) Shift of the phosphoryl group stretching frequency ( $\nu_{P=O}$ ) of TOPO in water/TOPO/*n*-heptane reverse micelles upon increase the  $W_0$  value. [TOPO] = 0.1 M.

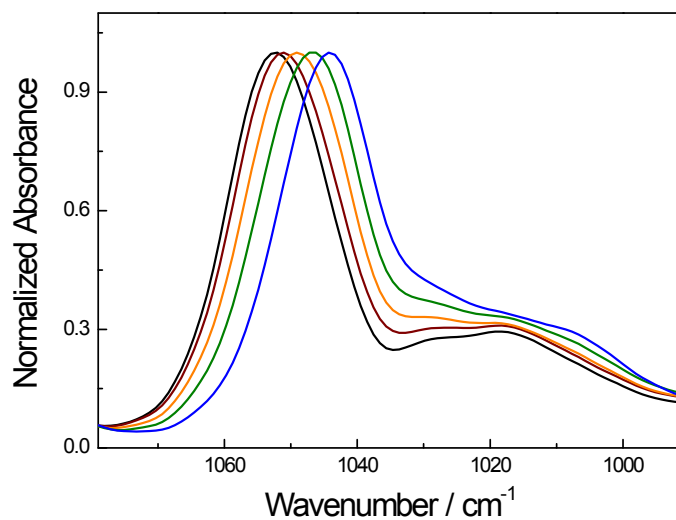


**Figure S3:** Shift of O-D stretching frequency ( $\nu_{\text{OD}}$ ) for HOD upon increasing the  $X_{\text{TOPO}}$  in water/AOT:TOPO/*n*-heptane mixed reverse micelles at  $W_0 = 2$ . The  $\nu_{\text{OD}}$  value for pure HOD (---) is included for comparison.<sup>8</sup>  $[\text{Surf.}]_{\text{T}} = 0.2 \text{ M}$ .

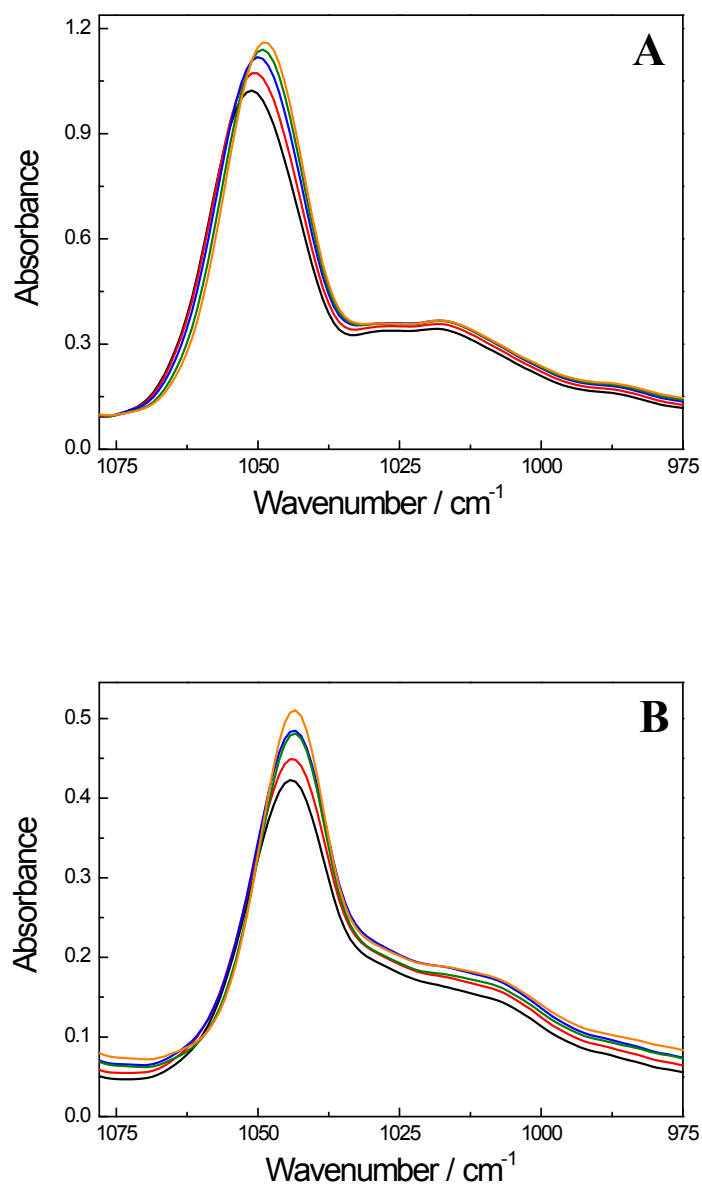


**Figure S4:** FT-IR spectra in the region of 1100-1300 cm<sup>-1</sup> for AOT upon increasing the  $W_0$  value at  $X_{\text{TOPO}} = 0.1$  in water/AOT:TOPO/*n*-heptane mixed reverse micelles.  $W_0$ : 0 (—), 0.5 (—), 1.0 (—), 1.5 (—), 2.0 (—).  $[\text{Surf}]_{\text{T}} = 0.05$  M.

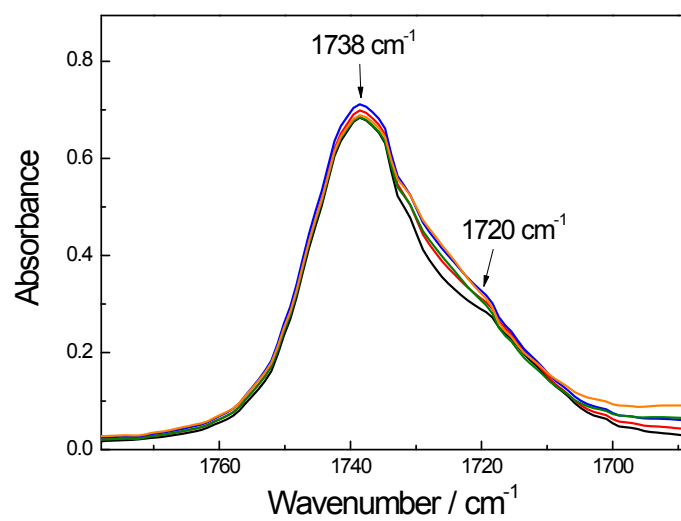




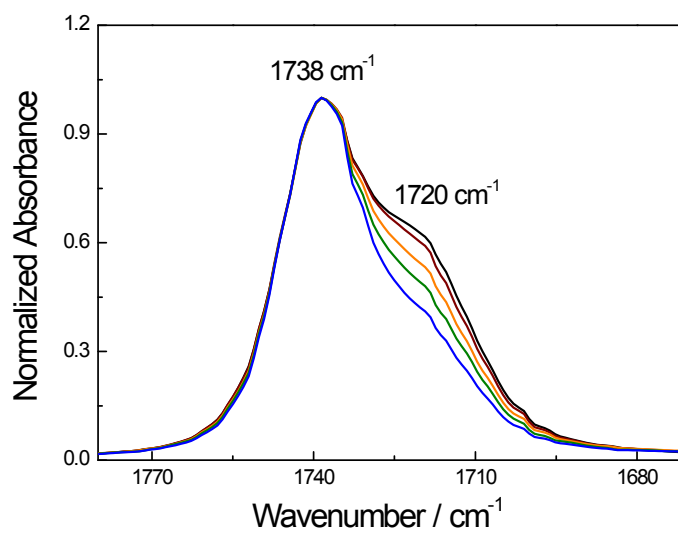
**Figure S5:** Normalized FT-IR spectra corresponding to the symmetric sulfonate stretching band of AOT upon increasing the  $X_{\text{TOPO}}$  at  $W_0 = 0$  in AOT:TOPO/*n*-heptane mixed reverse micelles.  $X_{\text{TOPO}}$ : 0 (—), 0.1 (—), 0.3 (—), 0.5 (—), 0.7 (—).  $[\text{Surf.}]_{\text{T}} = 0.05 \text{ M}$ .



**Figure S6:** FT-IR spectra corresponding to the symmetric sulfonate stretching mode of AOT upon increasing the  $W_0$  value at (A)  $X_{\text{TOPO}}=0.1$  and (B)  $X_{\text{TOPO}}=0.7$  in water/AOT:TOPO/*n*-heptane mixed reverse micelles.  $W_0$ : 0 (—), 0.5 (—), 1.0 (—), 1.5 (—), 2.0 (—).  $[\text{Surf}]_1=0.05$  M.



**Figure S7:** FT-IR spectra corresponding to the carbonyl stretching mode of AOT upon increasing the  $W_0$  value at  $X_{\text{TOPO}}=0.7$  in water/AOT:TOPO/*n*-heptane mixed reverse micelles.  $W_0$ : 0 (—), 0.5 (—), 1.0 (—), 1.5 (—), 2.0 (—).  $[\text{Surf}]_{\text{T}}=0.05$  M.



**Figure S8:** FT-IR spectra of AOT:TOPO/*n*-heptane mixed reverse micelles at  $W_0 = 0$ , in the region of 1800 - 1600  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ).  $X_{\text{TOPO}}$ : 0 (—), 0.1 (—), 0.3 (—), 0.5 (—), 0.7 (—).  $[\text{Surf.}]_{\text{T}} = 0.05 \text{ M}$ .

**Scheme S1.** Preferred rotational conformers of AOT in reverse micelles.

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