

## Electronic Supplementary Information

### Combination of protic ionic liquid-like surfactant and biocompatible solvents to generate environmentally friendly anionic reverse micelles

Nahir Dib<sup>[a]</sup>, Juana J. Silber<sup>[a]</sup>, N. Mariano Correa<sup>[a]</sup>, R. Dario Falcone<sup>[a]\*</sup>

<sup>[a]</sup> Dr. N. Dib, Prof. J. J. Silber, Dr. N. M. Correa and Dr. R. D. Falcone.

Instituto para el Desarrollo Agroindustrial y de la Salud (IDAS), CONICET. Departamento de Química. Universidad Nacional de Río Cuarto. Agencia Postal # 3. C.P. X5804BYA Río Cuarto. ARGENTINA.

\* Corresponding-Author: Dr. R. Dario Falcone. E-mail: [rfalcone@exa.unrc.edu.ar](mailto:rfalcone@exa.unrc.edu.ar)

## EXPERIMENTAL SECTION

### Methods

*RMs preparation:* Stock solutions of imim-DEHP (0.25 M) in the IPM and ML in absence of water were prepared by mass. Then, to make each of the RMs solutions with different amount of water, defined as  $W_0 = [\text{water}] / [\text{surfactant}]$ , aliquots of those stock solutions were used. The incorporation of water into each RMs solutions was performed by calibrated microsyringes. To obtain optically clear solutions they were shaken in a sonicating bath until the observation of a single phase. Similar procedure was used to prepare Na-AOT RMs.

The maximum amount of water ( $W_0^{\text{max}}$ ) able to be dispersed in the systems investigated was evaluated at different surfactant concentrations (0.05-0.25 M), using individual stock solutions prepared in both biocompatible nonpolar solvents (Table S1). Larger values of  $W_0$  than reported in Table S1 were not possible to obtain due to turbidity problems. The smallest value for  $W_0$  ( $W_0 = 0$ ), corresponds to a system without water addition.

In the DLS and SLS experiments the surfactant concentration was keep constant and equal to 0.25 M. For the FT-IR measurements two surfactant concentrations were employed in order to optimize the experiments: 0.2 M in the O-D stretching modes and 0.06 M for C-H stretching modes. HOD (10 %) and D<sub>2</sub>O (100 %) were used as polar solvent, respectively.

### General

A dynamic light scattering equipment (DLS, Malvern 4700 with a goniometer) with an argon-ion laser operating at 488 nm was used to determine the apparent diameters of the different imim-DEHP RMs. In order to obtain reliable and reproducible data in the DLS experiments, a meticulous cleanliness procedure of the cuvettes was performed.<sup>1</sup> Thus, cuvettes were washed with ethanol, and then with doubly distilled water and finally dried with acetone. Prior to use and to avoid dust or particles presents in the original solution, the RMs samples were filtered three times using an Acrodisc with 0.2  $\mu\text{m}$  PTFE membrane (Sigma). Before introducing each sample to the

cuvette, it was rinsed with pure nonpolar solvent twice, then with the surfactant stock solution, and finally with the sample to be analyzed. Prior to making measurements on a given day, the background signals from air and IPM (or ML) were collected to confirm cleanliness of the cuvettes. Prior to data acquisition, the samples were equilibrated in the DLS instrument for 10 min at 25 °C. To obtain valid results from DLS measurements requires knowledge of the system refractive index and viscosity in addition to well-defined conditions. Since we worked with dilute solutions, the refractive indices and viscosities for the RMs solutions were assumed to be the same as neat IPM and ML. Multiple samples at each size were made, and thirty independent size measurements were made for each individual sample at the scattering angle of 90°. The equipment was calibrated before and during the course of experiments using several different size standards. Thus, we are confident that the magnitudes obtained by DLS measurements can be taken as statistically meaningful for all the systems investigated. To analyze the data the algorithm CONTIN was used and the DLS results have shown have experimental errors on the sizes less than 5 %.

The aggregation numbers ( $N_{agg}$ ) of the imim-DEHP RMs were determined by static light scattering (SLS) technique in the same DLS equipment. All the measurements were made at an angle of 90° and due to the small size of the RMs droplets, the data analysis of SLS was done using the Rayleigh expression<sup>2</sup> (eq. 1):

$$\frac{KC}{R_{\theta}} = \frac{1}{M_w} + 2A_2C \quad (1)$$

where  $C$  is the surfactant concentration,  $R_{\theta}$  is the Rayleigh ratio of the sample intensity to the incident intensity at the angle  $\theta$ ,  $M_w$  is the molecular weight of the sample in weight average,  $A_2$  is the 2<sup>nd</sup> virial coefficient and  $K$  is an optical constant that accounts for the experimental parameters:

$$K = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_a} \left( \frac{dn}{dc} \right)^2 \quad (2)$$

where  $\frac{dn}{dc}$  is the increment in the refractive index with concentration,  $n_0$  is the solvent refractive index,  $\lambda_0$  is the wavelength of the incident light and  $N_a$  is the Avogadro number. Calibration was performed using toluene, for which the reported Rayleigh ratio at  $90^\circ$  and at a wavelength of 488 nm ( $R_{90}^{tol}$ ) is  $3.96 \times 10^{-5} \text{ cm}^{-1}$ .<sup>3</sup> Debye plots were created using solutions with different surfactant concentrations at fixed  $W_0$  for all the RMs studied. The micellar molecular weights ( $M_w$ ) were determined and the  $N_{agg}$  values for all the systems investigated were calculated according the procedure detailed in the literature.<sup>2</sup> To perform the SLS measurements, was essential to determine the  $\frac{dn}{dc}$  values of the different RMs explored, to do that a differential refractometer (Brookhaven Instruments Corporation, BI-DNDCW model) with a tungsten lamp operating at 470 nm and  $30^\circ\text{C}$  was used.

To obtain the FT-IR spectra a Nicolet IMPACT400 FT-IR spectrometer and IR cell of the type Irtran-2 (1 mm of path length) from Wilmad Glass (Buena, NJ) were used. 200 spectra at a resolution of  $0.5 \text{ cm}^{-1}$  were co-added for all the FT-IR spectra.

**Table S1.** Maximum amount of water solubilized ( $W_0^{\max}$ ) for imim-DEHP in IPM and ML at different [imim-DEHP]. T = 25 °C.

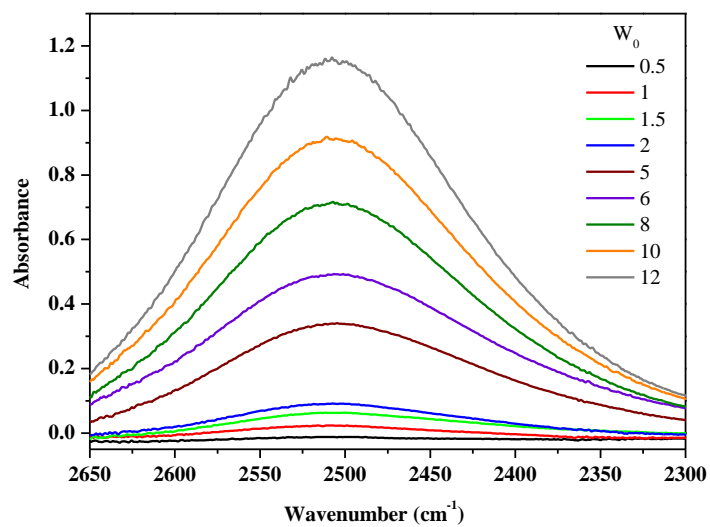
[imim-DEHP] (M)	$W_0^{\max}$	
	IPM	ML
0.05	11 ± 2	24 ± 2
0.10	12 ± 2	26 ± 2
0.15	13 ± 1	26 ± 1
0.20	15 ± 1	30 ± 1
0.25	16 ± 1	30 ± 1

**Table S2.** Apparent diameter ( $d_{app}$ ) and polydispersity index (PDI) values of IPM/imim-DEHP/water and ML/imim-DEHP/water RMs obtained at 25 °C varying  $W_0$ . [imim-DEHP] = 0.25 M.

IPM/imim-DEHP/water			ML/imim-DEHP/water		
$W_0$	$d_{app}$ (nm)	PDI	$W_0$	$d_{app}$ (nm)	PDI
8	$6.6 \pm 0.4$	0.3	9	$6.8 \pm 0.4$	0.2
10	$7.6 \pm 0.5$	0.02	10	$7.8 \pm 0.5$	0.09
11	$8.7 \pm 0.5$	0.02	11.5	$10.9 \pm 0.4$	0.03
12	$10.7 \pm 0.5$	0.03	13	$10.8 \pm 0.5$	0.02
13	$12.0 \pm 0.5$	0.01	14.5	$13.6 \pm 0.6$	0.07
14	$15.3 \pm 0.5$	0.004	16	$13.9 \pm 0.5$	0.03
15	$20.2 \pm 0.6$	0.003	19	$20.6 \pm 0.6$	0.06
16	$36.6 \pm 0.7$	0.06	21	$22.4 \pm 0.5$	0.02
-	-	-	23	$27.2 \pm 0.8$	0.04

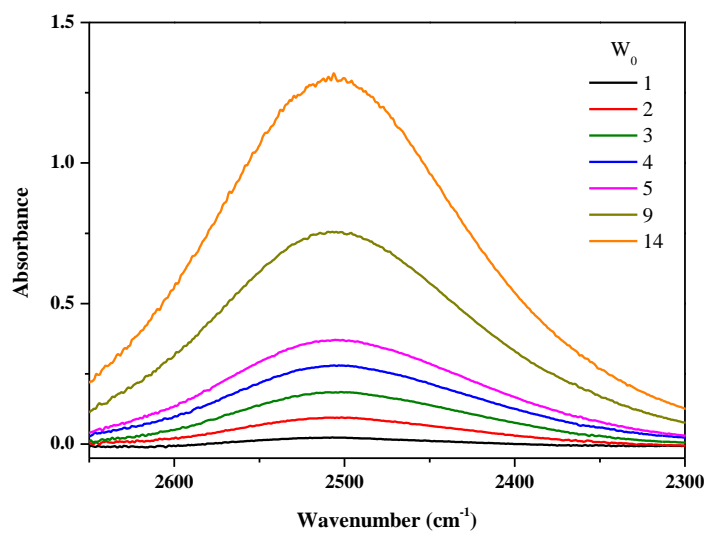
**Table S3.** Aggregation numbers ( $N_{\text{agg}}$ ) and apparent hydrodynamic diameters ( $D_{\text{app}}$ ) values for imim-DEHP RMs in IPM and ML at  $W_0 = 10$ .  $T = 25\text{ }^\circ\text{C}$ .

	<b>imim-DEHP/IPM</b>	<b>imim-DEHP/ML</b>
<b><math>D_{\text{app}}</math> (nm)</b>	$7.6 \pm 0.4$	$7.8 \pm 0.4$
<b><math>N_{\text{agg}}</math></b>	$94 \pm 5$	$160 \pm 7$

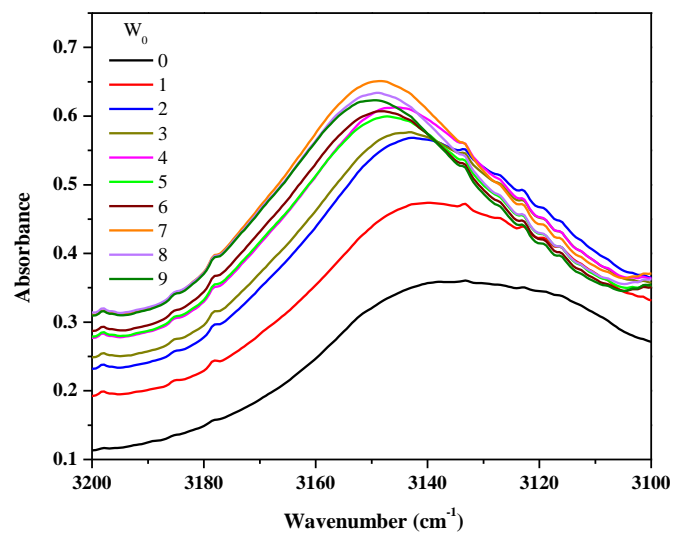


**Figure S1.** FT-IR spectra in the region of O-D stretching mode of HOD in IPM/imim-DEHP/HOD RMs upon increasing the  $W_0$  values. The IPM bands have been subtracted.  $[\text{imim-DEHP}] = 0.2 \text{ M}$ .

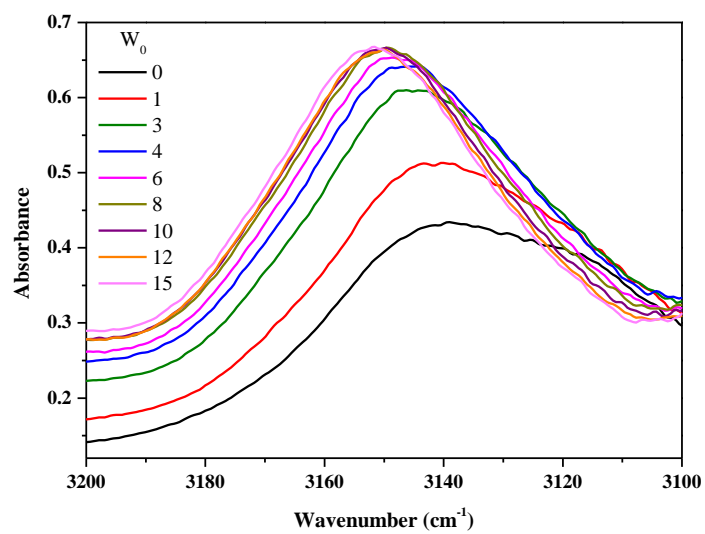




**Figure S2.** FT-IR spectra in the region of O-D stretching mode of HOD in ML/imim-DEHP/HOD RMs upon increasing the  $W_0$  values. The ML bands have been subtracted. [imim-DEHP] = 0.2 M.



**Figure S3.** FT-IR spectra of IPM/imim-DEHP RMs at different  $W_0$  values, in the region of 3200-3100  $\text{cm}^{-1}$ . [imim-DEHP] = 0.06 M. The IPM bands have been subtracted.



**Figure S4.** FT-IR spectra of ML/imim-DEHP RMs at different  $W_0$  values, in the region of 3200-3100  $\text{cm}^{-1}$ .  $[\text{imim-DEHP}] = 0.06 \text{ M}$ . The ML bands have been subtracted.

## REFERENCES

- 1 M. A. Sedgwick, A. M. Trujillo, N. Hendricks, N. E. Levinger and D. C. Crans, *Langmuir*, 2011, **27**, 948–954.
- 2 C. A. Gracia, S. Gómez-Barreiro, A. González-Pérez, J. Nimo and J. R. Rodríguez, *J. Colloid Interface Sci.*, 2004, **276**, 408–413.
- 3 T. M. Bender, R. J. Lewis and R. Pecora, *Macromolecules*, 1986, **19**, 244–245.