

Electronic Supplementary Information

Improvement of the Amphiphilic Properties of a Dialkyl Phosphate by Creation of a Protic Ionic Liquid-like Surfactant

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EXPERIMENTAL SECTION

Materials

Bis-(2-ethylhexyl) phosphoric acid (HDEHP) from Fluka (> 95% purity) was used as received. 1-methylimidazole from Sigma Aldrich (> 99 % purity) was distilled under vacuum before using. Ultrapure water was obtained from Labonco equipment model 90901-01. Benzene, *n*-heptane, CDCl₃ and toluene, all from Sigma Aldrich (HPLC quality) were used without prior purification.

imim-DEHP preparation: The protic IL-like surfactant used, 1-methylimidazolium bis-(2-ethylhexyl) phosphate (imim-DEHP), was formed under inert conditions by mixing equimolar quantities of the base (1-methylimidazole) and the acid (HDEHP) as is shown in supplementary information section (Scheme S1). Dropwise addition of base to acid was carried out for complete neutralization in an ice bath in order to avoid heat generation. The reaction mixture was stirred for 24 hs at room temperature and then unreactive starting materials and volatile impurities were removed from imim-DEHP under reduced pressure at 60 °C for 8 hs. Thus, the product (imim-DEHP) obtained was a colorless and highly viscous liquid (mp < -18 °C). The formation of imim-DEHP was confirmed by ¹H, ³¹P NMR and FT-IR techniques as it is shown in supplementary information section. Figure S1 show that all protons corresponding to the anionic (DEHP) and to cationic (imim⁺) components are present. The chemical shifts values of the most important protons of imim-DEHP (Scheme S2) obtained in CDCl₃ are included in Table S1. Moreover, ³¹P NMR has the advantage of providing a single signal (+0.12 ppm) that allows us to monitor only the DEHP component of imim-DEHP in CDCl₃ as Figure S2 show. It is important to mention that HDEHP in CDCl₃ appears in different region (+1.82 ppm).¹ Additionally, the FT-IR spectrum of imim-DEHP plotted in Figure S3 demonstrate that the main stretching modes (aromatic C-H and P=O) of the IL are observed.

Prior to use, imim-DEHP was dried under vacuum for 4 hours.

Methods

RMs preparation: Stock solutions of imim-DEHP (0.2 M) in the nonpolar solvent (toluene, *n*-heptane or benzene) 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. The W_0 was varied between 0-39 for imim-DEHP in *n*-heptane and between 0-16 in toluene (15 for benzene) RMs. Larger values of W_0 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.

The maximum amount of water (W_0^{max}) able to be dispersed in the systems investigated was evaluated using the 0.2 M stock solutions prepared in the nonpolar solvents (*n*-heptane, toluene and benzene).

In the DLS and SLS experiments the surfactant concentration was keep constant and equal to 0.1 M.

Vesicles preparation: Stock solutions of imim-DEHP in pure water were prepared by mass and volumetric dilution and these samples were used directly in the DLS and TEM experiments without any other procedure.

General

To determine the apparent diameters of the different imim-DEHP RMs and vesicles, a dynamic light scattering equipment (DLS, Malvern 4700 with goniometer) with an argon-ion laser operating at 488 nm was used. In order to obtain reliable and reproducible data in the DLS experiments, a meticulous cleanliness procedure of the cuvettes was performed.² 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 and vesicles samples were filtered three times using an Acrodisc with 0.2 μm PTFE and 0.45 μm nylon membrane (Sigma), respectively. Before introducing each sample to the cuvette, it was rinsed with pure

nonpolar solvent (or water) twice, then with the surfactant stock solution, and finally with the sample to be analyzed. Prior making measurements on a given day, the background signals from air and toluene 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 toluene and *n*-heptane.³ 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 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 expression⁴ (eq. 1):

$$\frac{KC}{R_{\theta}} = \frac{1}{M_w} + 2 A_2 C \quad (1)$$

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

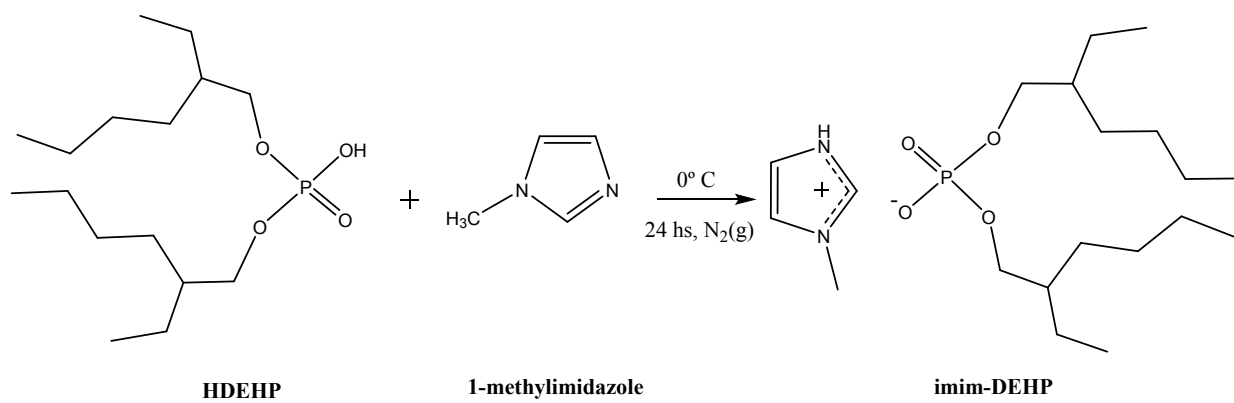
$$K = \frac{4\pi^2 n_0^2}{\lambda_0^4 N_a} \left(\frac{dn}{dC} \right)^2 \quad (2)$$

where dn/dC is the increment in the refractive index with concentration, n_0 is the solvent refractive index, λ_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° and at a wavelength of 488 nm (R_{90}^{tol}) is $3.96 \times 10^{-5} \text{ cm}^{-1}$.⁵ 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.⁴ To perform the SLS measurements, was essential to determine the 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°C was used.

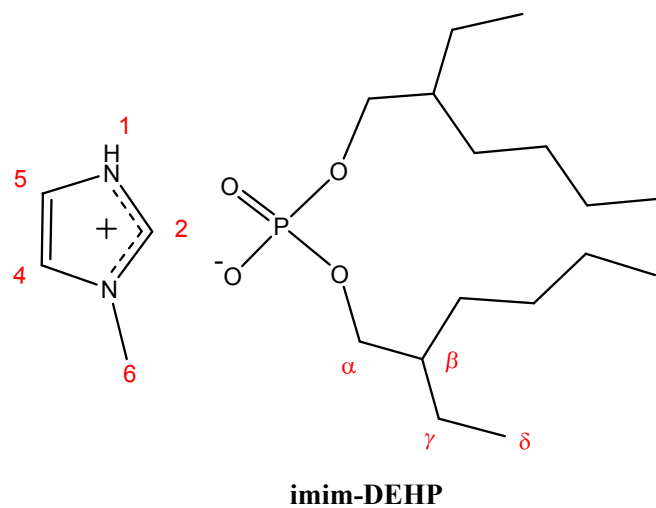
Zeta potential of the imim-DEHP vesicles were measured using a dynamic light scattering (ZetasizerNano ZS Malvern Instrument Ltd) operating at 633 nm.

To obtain the FT-IR spectra a Nicolet IMPACT400 FT-IR spectrometer and IR cell of the type Irtran-2 (0.015 mm of path length) from Wilmad Glass (Buena, NJ) were used. 200 spectra at a resolution of 0.5 cm^{-1} were co-added for all the FT-IR spectra. For the ^1H and ^{31}P NMR experiments a Bruker 400 NMR spectrometer was used. The ^1H NMR chemical shifts were measured relative to internal TMS and the values were reproducible within 0.01 ppm. The ^{31}P NMR spectra were recorded at 121 MHz and measured using a single-pulse sequence with WALTZ decoupling during acquisition; usually, 128 or 256 scans were collected. In this case, the chemical shift values were referenced to 85% H_3PO_4 (0 ppm) as an external standard. MestReC 4.8.6 and Microcal OriginPro 7 for window were used to process and plotted all NMR data, respectively.

For the TEM experiments, the micrographs were obtained with a JEOL 1200 EXII transmission electron microscope at a working voltage of 80 kV. The TEM samples were prepared by the negative-staining method. Phosphotungstic acid solution (2%) was used as the staining agent.



Scheme S1: Synthesis of imim-DEHP.



Scheme S2. Molecular structure of the imim-DEHP surfactant and the specific protons observed in ¹H NMR spectra.

Table S1. ^1H NMR chemical shifts (in ppm) for imim-DEHP, 1-methylimidazole and HDEHP in Cl_3CD . [imim-DEHP] = 0.05 M.

H	Chemical shifts (ppm)		
	imim-DEHP	HDEHP	1-methylimidazole
H₁	12.31	12.05	-
H₂	8.92	-	7.38
H₄	7.21	-	6.86
H₅	7.04	-	7.01
H₆	3.90	-	3.64
H_{α}	3.83	3.93	-
H_{β}	1.54	1.57	-
H_{γ}	1.48 – 1.27	1.46 – 1.31	-
H_{δ}	0.87	0.90	-

Table S2. Apparent diameter (d_{app}) and polydispersity index (PDI) values of toluene/imim-DEHP/water and *n*-heptane/imim-DEHP/water RMs obtained at 25 °C varying W_0 . [imim-DEHP] = 0.1 M.

toluene/imim-DEHP/water			<i>n</i> -heptane/imim-DEHP/water	
W_0	d_{app} (nm)	PDI	d_{app} (nm)	PDI
0	2.2 ± 0.5	0.46	3.6 ± 0.3	0.31
0.5	-	-	2.9 ± 0.2	0.17
1	2.6 ± 0.3	0.39	3.9 ± 0.2	0.05
2	3.2 ± 0.2	0.35	5.0 ± 0.1	0.03
3	3.7 ± 0.2	0.32	6.2 ± 0.1	0.02
4	4.3 ± 0.1	0.18	7.7 ± 0.1	0.03
5	4.4 ± 0.1	0.05	12.5 ± 0.1	0.05
6	5.3 ± 0.1	0.03	14.3 ± 0.1	0.08
7	5.9 ± 0.1	0.04	19.1 ± 0.1	0.05
8	6.3 ± 0.1	0.03	21.0 ± 0.1	0.07
9	6.8 ± 0.1	0.04	24.8 ± 0.1	0.08
10	7.7 ± 0.1	0.03	-	-
11	8.3 ± 0.1	0.03	-	-
12	8.8 ± 0.1	0.03	-	-
13	9.5 ± 0.1	0.03	-	-

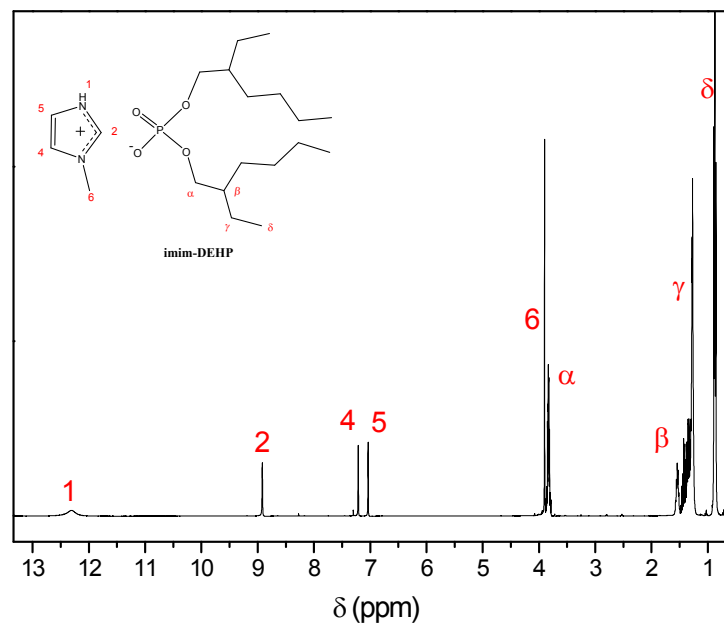


Figure S1. ¹H NMR spectrum of imim-DEHP in Cl₃CD. [imim-DEHP] = 0.05 M.

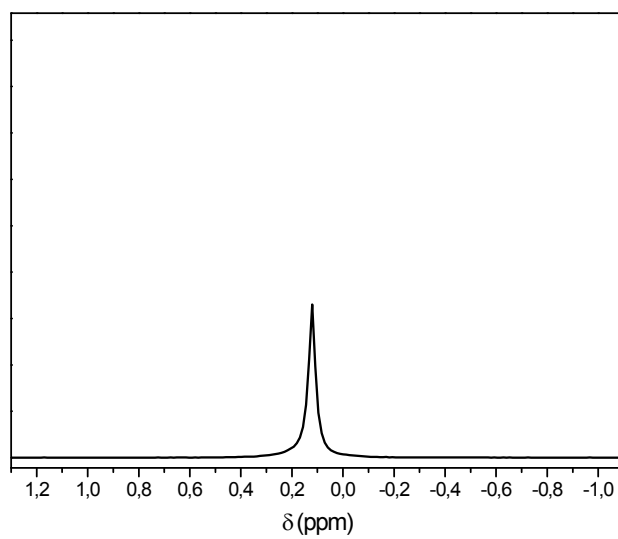


Figure S2. ^{31}P NMR spectrum of imim-DEHP in CDCl_3 . $[\text{imim-DEHP}] = 0.1 \text{ M}$.

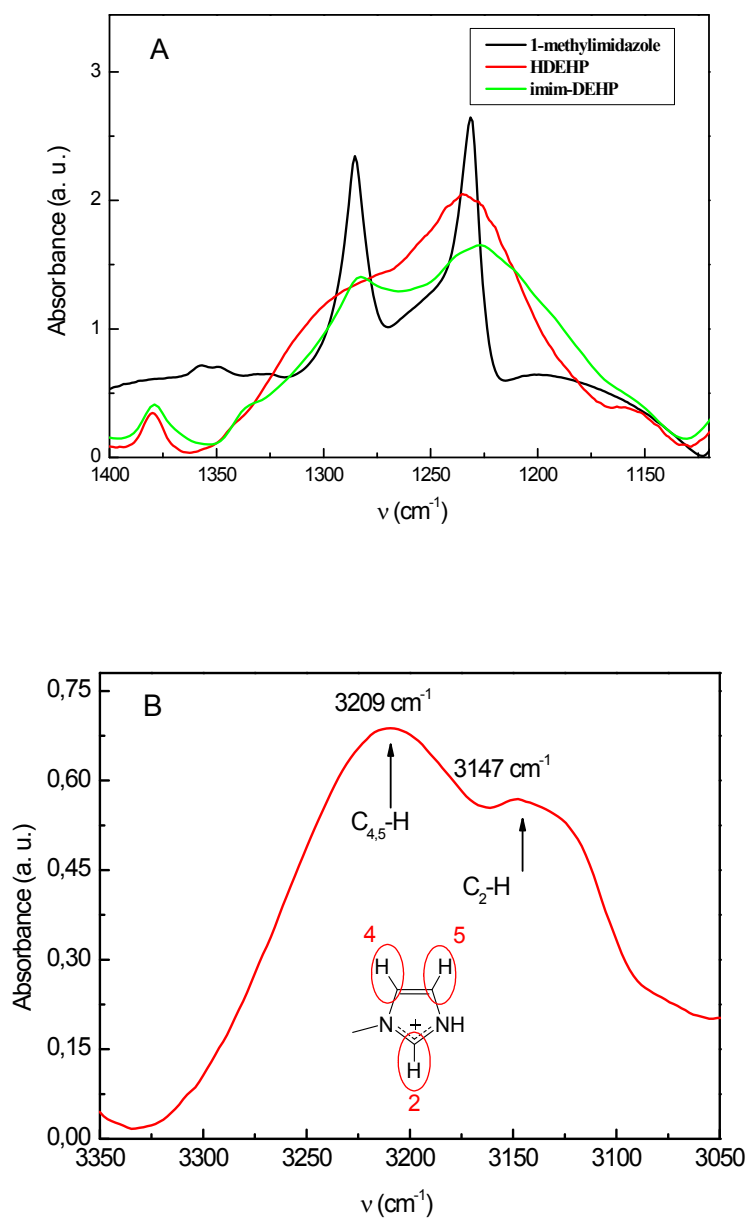


Figure S3. FT-IR spectrum of neat imim-DEHP, HDEHP and 1-methylimidazole in the region of 1400-1120 cm⁻¹ (A) and neat imim-DEHP in the region of 3350-3050 cm⁻¹ (B).

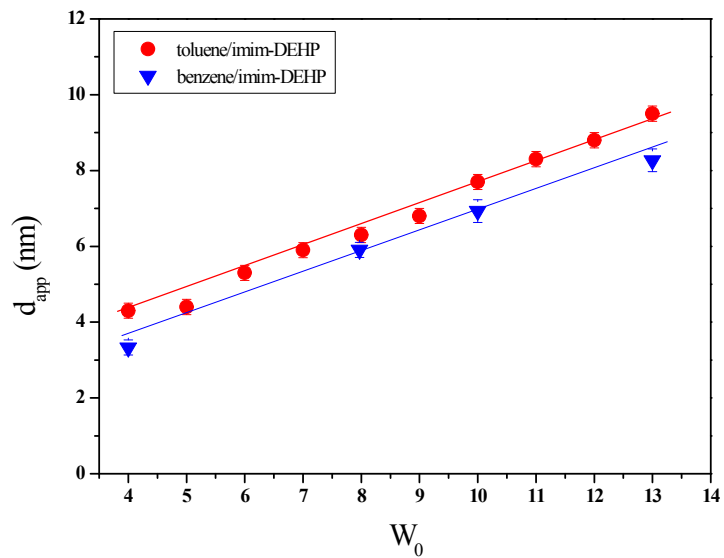


Figure S4. Apparent diameter (d_{app}) values of the (●) toluene/imim-DEHP/water RMs and (▼) benzene/imim-DEHP/water RMs obtained at 25 °C varying W_0 . The straight line is plotted to guide the eye. [imim-DEHP] = 0.1 M.

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