Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Interfacial Dynamic of Liquid-Liquid Extraction, a Second Harmonic Generation Investigation

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Supporting information

Experimental details

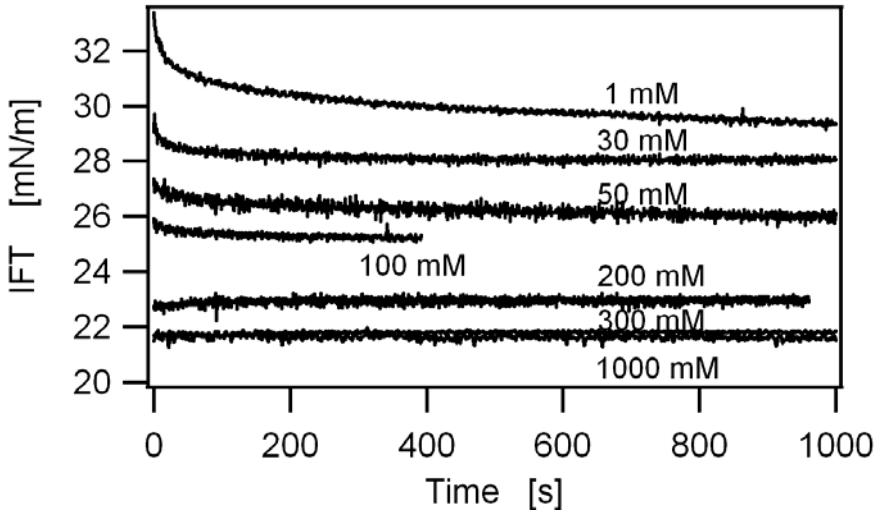

Figure 1: Time evolution of IFT measurements at various DEHiBA concentrations. Pre-equilibration with nitric acid is done before measurements.

Below 200 mM DEHiBA concentration, time is needed to reach the IFT equilibrium. The criteria of 1000 seconds is chosen for all measurements in order to record an IFT value for IFT slop less than 10^{-3} $mN.m^{-1}.s^{-1}$.

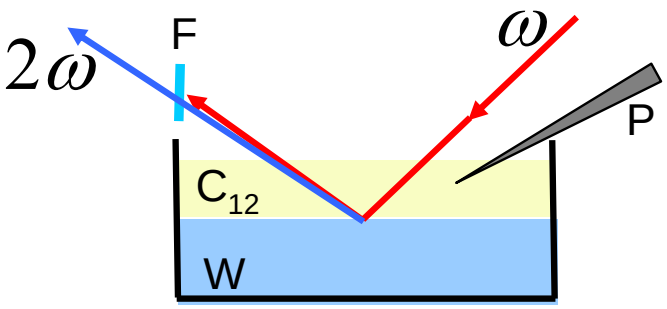

Figure 2 : Schematics of the experimental setup. The Petri dish is represented with the water phase (W) and the organic dodecane phase (C_{12}). Filter (F) allows a separation between fundamental beam reflexion (red beam at 800nm wavelength) and second harmonic generation (blue beam at 400 nm wavelength). The micropipette (P) permits the extractant or acid addition.

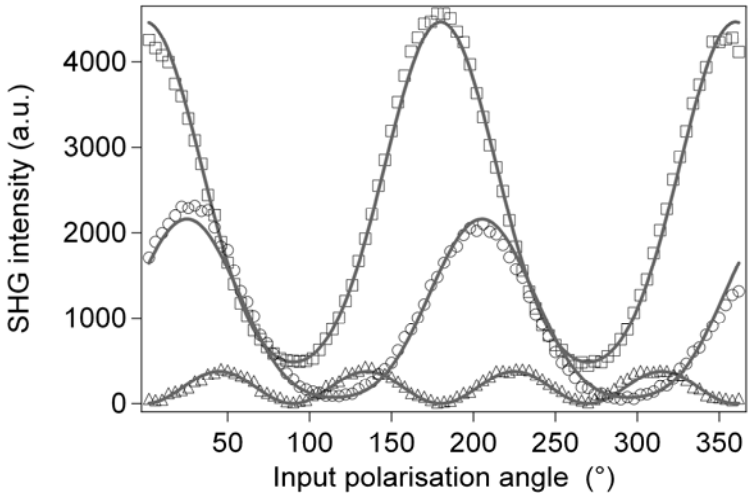

Figure 3 : Output SSHG intensity as a function of the input polarization angle for neat water/dodecane interface. S-out intensity experimental data corresponds to triangles, P-out intensity to the squares and 45° angle-out intensity to the circles. Lines are the fitted curve.

The output S- and P-polarized harmonic intensities as a function of the input polarization angle γ are fitted as

$$I_s^{DE} \propto \left| a_1 \chi_{yyz} \sin(2\gamma) \right|^2$$

$$I_p^{DE} \propto \left| \begin{matrix} (a_2 \chi_{xxz} + a_3 \chi_{zxx} + a_4 \chi_{zzz}) \cos^2 \gamma \\ + a_5 \chi_{zxx} \end{matrix} \quad \sin^2 \gamma \right|^2$$

Where a_i are non linear Fresnels factors. The 45-polarized harmonic intensity makes possible sign determination. More details are in the Brevet's book[1].

The most noticeable think is that the two ratio $\frac{\chi_{xxz}}{\chi_{zzz}} = 0.27$ and $\frac{\chi_{zxx}}{\chi_{zzz}} = 0.31$ are not modified for all experiments. So, we conclude that no polarisation dependence is observed in any measurements presented in this publication.

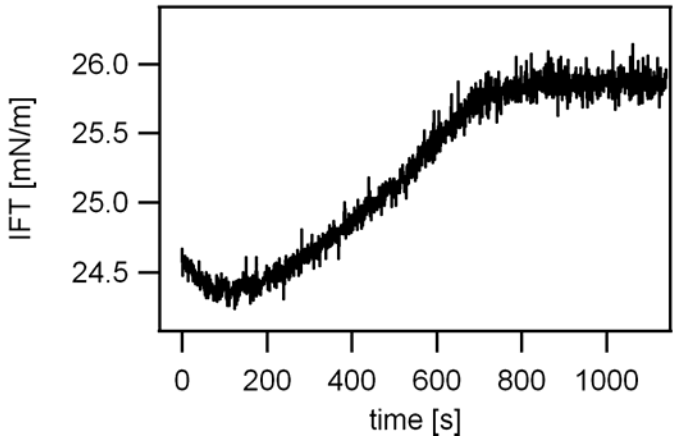

Figure 4: Time evolution of IFT measurements at 150 mM DEHiBA concentration. Pre-equilibration with water and nitric acid 3M is not done before measurement in order to see first contact time evolution.

In this Figure 4, a first IFT decrease shows DEHiBA coming to the interface. It is then followed by an increase corresponding to the acidic transfer from the water phase to the organic phase. No extra fluctuation is detected with IFT measurements during the transfer.

Bibliography:

1. P. F. Brevet, *Surface Second Harmonic Generation*, Presses Polytechniques Universitaires Romandes, Lausanne, 1997.