A drop Fabry Perot interferometer for the study of liquid-liquid interfaces: surface dynamics close to the fluid-gel transition

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The new interferometric technique, recently improved to study a surfactant monolayer absorbed at the interface of a gas bubble in water[1], is extended here to the case liquid-liquid interfaces, namely to the interface of an oil drop pending in mixed concentrated ionic solutions of controlled pH. The drop is attached to an electrode and a second electrode is placed below the drop. In presence of an electrical charge at the interface, an alternating electric field (in the range of a few Volt/cm) applies an alternating force to the drop in the vertical direction. The deformation from the unperturbed shape is detected by the change of the optical path of a laser beam traversing the drop it in the horizontal direction. Refractive index mismatch causes light reflection at the liquid-liquid interfaces, which act as the mirrors of a confocal Fabry Perot interferometer. At the surface, the "periodic" boundary conditions naturally provided by its closed geometry allow only a discrete spectrum of drop stationary oscillation modes with Lorentzian frequency dispersion harmonic series. For a given geometry of the drop, the resonance frequency is determined by the elastic force acting to restore the un-deformed shape. This resonance frequency is reduced on lowering interfacial tension, and is increased in the presence of an elastic modulus. As an example, we show in the figure the measured frequency response of a 1mm drop containing a concentrated solution of surface active extractant (TODGA:dodecane = 30:70 bw), contacted with solutions of increasing concentration of europium nitrate in nitric acid. Europium salt adsorbs at the interface. Charge adsorption at the interface causes the initial decrease in frequency until saturation, then frequency is stationary until enough europium salt gets into the drop to form a thin layer of liquid crystal phase beyond the interface (i.e. the problematic and elusive interphase in chemical engineering), with a consequent increase of the resonance frequency. The interpretation of resonance peak amplitude, frequency and quality factor requires to take into account the classically known monolayer and the elusive "interphase". We show in this work an unambiguous detection of surface-induced swelling of a gel, at concentration ten times lower than the bulk phase separation. Amplitudes of the order of nm in a mm-size droplet can be seen for the first time, making this technique hundred times more sensitive than any other one measuring surface waves induced by external fields. Thank to its ultra-sensitivity, this analytical technique will be crucial for investigating resilience of any type of formulation used in liquid-liquid extraction, from metals to advanced extraction of essential oils.

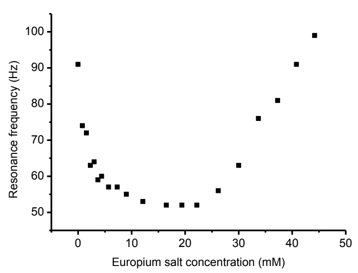

Figure 1. Shift of the resonance frequency of a mm-size droplet of extractant solvent solution in equilibrium with a concentrated solution of Europium nitrate, induced by lowering of surface tension followed at higher concentration by the formation of an interphase above 25 mM of rare earth nitrate.

1) Corti,M.; Pannuzzo,M.; Raudino, *Langmuir* **2014**, *30*, 477-487

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