Interfacial shear micro- and macrorheology of Langmuir monolayers: Fatty acids, fatty alcohols and polymers.

Javier Tajuelo[1], J.M. Pastor[2], F. Ortega[3], R.G. Rubio[3,4], E. Guzmán[3], M.A. Rubio[1].

[1]Department of Fundamental Physics, Universidad Nacional de Educación a Distancia (UNED), Madrid, Spain.
[2]Complex System Group, ETSIAAB, Polytechnical University, Madrid, Spain
[3]Department of Physical Chemistry, Complutense University, Madrid, Spain
[4]Pluridisciplinary Institute, Complutense University, Madrid, Spain

**fortega@quim.ucm.es*

Langmuir monolayers are molecular-thick films formed after the spreading of insoluble low-molecular weight or polymer surfactants at the liquid/vapour interface. Complex phase diagrams have been reported in the case of fatty acid, ester or alcohol monolayers [1]. The effect of monolayers in stabilizing colloidal systems, such as emulsions and foams, strongly depends on their mechanical properties. In the case of foams, the complex shear modulus of the monolayer is key information. Surface shear elasticity and viscosity can change several orders of magnitude in response to changes in temperature or concentration. In the last decade it was found that the values of shear viscosity for polymer monolayers were very different (up to four decades) depending on the type of experimental technique used [2]. More recently, we have shown that this was the result of overlooking the lower limit of the viscosity that can be sensed depending on the actual value of the Boussinesq number of each experiment [3]. With a proper combination of techniques it is possible to eliminate the discrepancies, and measure the viscosity over a range of six orders of magnitude [4].

In this work we have found that, in the case of fatty acids the magnitude of the complex surface viscosity, η^*, increases monotonically with the monolayer concentration. In addition the L_{2d}-L_S phase transition is clearly observed as a step on the value of η^*, whose amplitude depends on the chain length. On the contrary we found that in the case of fatty alcohols η^* presents a maximum in the L'_2 phase. We have also discussed the correlation found between η^* and the chain length.

In the case of polymer monolayers we have compared the results obtained with micro-rheology and with a new magnetic microwire rheometer [4]. The molecular weight dependence of the viscosity definitively confirms that the monolayers follow a Rouse dynamics for very low molecular weights, and a reptation-like dynamics for higher molecular weights. This is in agreement with the behaviour already described for the surface dilational viscosity.

Acknowledgements We are grateful for the financial support of COST MP1106, of CoWet ITN (E.U.), and of MINECO through grants FIS2014-62005-EXP, and FIS2013-47350-C5-5-R and and FIS2012-38231-C02-01.

[1] V.M. Kaganer et al. Rev. Mod. Phys. 71, 3 (1999)
[2] A. Maestro et al. Soft Matter 7, 7761 (2011)
[3] J. Tajuelo et al. Langmuir 31, 1410 (2015)
[4] J. Tajuelo et al. J. of Rheology (2016, to be published)