Polyelectrolyte/surfactant films spread from neutral aggregates

Andrea Tummino^{1,2*}, Boris A. Noskov³, Imre Varga², Richard A. Campbell¹

¹Institut Laue-Langevin, 71 avenue des Martyrs, CS20156, 38.042 Grenoble Cedex 9, France. ²Institute of Chemistry, Eötvös Loránd University, Budapest 112, P. O. Box 32, H-1518 Hungary. ³Institute of Chemistry, St. Petersburg State University, 198904 St. Petersburg, Russian Federation

*tumminoa@ill.fr

Oppositely charged polyelectrolyte/surfactant (P/S) mixtures have generated sustained interest because of the huge commercial value of the formulations we use in our everyday lives [1]. Recently there has been growing awareness that non-equilibrium effects can determine their behavior in the bulk [2], and we have systematically related such effects to the interfacial properties [3,4].

Here we present a new methodology to prepare loaded P/S films out of equilibrium conditions at the air/water interface [5]. Our approach consists of exploiting the dynamic dissociation of hydrophobic neutral aggregates from an aqueous dispersion dropped onto pure water to form a spread film thanks to the Gibbs-Marangoni effect. The system studied is poly(sodium styrene sulfonate)/dodecyltrimethylammonium bromide (NaPSS/DTAB) mixtures. A systematic investigation of the interfacial composition as well as the mechanical properties of the films with respect to the sample history has been carried out using ellipsometry, Brewster angle microscopy and specular neutron reflectometry (NR) in combination with surface pressure-area isotherms. A new implementation of NR was used thanks to use of the FIGARO reflectometer with greatly improved time resolution compared with traditional approaches.

We found that the membranes behave like perfectly insoluble Langmuir-like films over five consecutive cycles with an initial surface excess more than four times higher than layers formed from bulk adsorption. The components bind in a one-to-one molar ratio independently of the sample history, which is rationalized in terms of the entropy of counterion release due to the low ionic strength of the solution. To our knowledge, this is the first time in which the dynamic interfacial stoichiometry of a binary system has been resolved in situ during mechanical cycling. Lastly, we discuss how our findings may open up new possibilities in the fields of preparation of films at the air/water interface for coating technologies as well as encapsulation of functional molecules such as drugs.



Figure 1- left: Ellipsometry measurements: A and C are spread films while B and D are adsorbed layers with equivalent compositions, 100 ppm, 17k NaPSS with (A) 6 mM and (C) 0.4 mM DTAB; E is just the pure surfactant; **centre:** Langmuir isotherms of five cycles of spread films where each cycle is displayed darker in shading; **right:** Interfacial composition resolved using NR where the maxima full mark compression and minima mark full expansion.

- [1] G. Agam, "Industrial chemicals: Their characteristics and development"; Elsevier: Amsterdam, 1994.
- [2] A. Naderi et al. Colloid Surf. A, 2005, 253, 83 & A. Mezei et al. J. Phys. Chem. B, 2008, 112, 9693.
- [3] R. A. Campbell et al. J. Phys. Chem. Lett. 2010, **1**, 3021 & J. Phys. Chem. B 2011, **115**, 15202.
- [4] R. A. Campbell et al. J. Phys. Chem. B 2012, 116, 7981 & Langmuir 2014, 30, 8664.
- [5] R. A. Campbell et al. Soft Matter 2016, under review.