Formation of solid metal stearate layers at the decane/water interface

R. de Ruiter, R.W. Tjerkstra, M.H.G. Duits*, F. Mugele

Physics of Complex Fluids, Faculty of Science and Technology, IMPACT and MESA+
Institutes, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
* e-mail: m.h.g.duits@utwente.nl

We study how solid layers are formed at the interface between aqueous salt solutions and decane with stearic acid, by monitoring the evolution of their mechanical, optical and chemical properties from the moment that the two liquids are exposed to each other. Using aqueous phases at various pH and containing different combinations of mono- and/or divalent cations, the following general trends were found. For pH < pKa, stearic acid hardly displays any interfacial activity. At higher pH it deprotonates at the interface and forms metal stearate layers. This becomes evident via a remarkable signature of the time-dependent interfacial tension, which successively shows an instantaneous drop, a (lag time) plateau, a sharp decrease and finally an increase. The decrease in IFT after the lag time is accompanied by an increase in the dilatational storage modulus $E'$ and the formation of a visible layer.

Variation of the cationic composition (at high pH) is found to have strong effects. Layer formation is particularly pronounced in artificial seawater (ASW), in which the groups of mono- and divalent cations interact synergistically. Also individual cations have distinct contributions: layers formed in presence of Ca$^{2+}$ or Mg$^{2+}$ develop a large transient $E'$, whereas for Na$^+$ such behavior is hardly observable. In layers obtained from ASW, almost exclusively Ca$^{2+}$ cations are found, in spite of its much lower abundance in ASW than Na$^+$ and Mg$^{2+}$. Our findings strongly suggest that layer formation from ASW is initiated by monovalent cations, while the subsequent growth of the layer is dictated entirely by the Ca$^{2+}$ ions.

Proposed (possible) mechanism for multilayer formation.