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Structural study of ionic liquid aggregates in an aqueous biphasic system using small-angle neutron scattering.

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Phase separation in an aqueous biphasic system is the result of subtle balance between entropy and enthalpy of the system, both varying with temperature. It is highly dependent on the systems, and not clearly understood yet. In order to get more insight into the driving mechanisms of the phase separation, microscopic structural investigations are invaluable information. Small-angle neutron scattering (SANS) techniques are suited for the study of both micro and mesoscopic organisations and have been used to highlight the formation of spherical micelles of ionic liquid (IL) in aqueous solutions[1] . By contrast, very little studies have been done on that subject for aqueous biphasic solutions (ABS) where acid is added to the IL and the water, apart from evidence of similar aggregation behaviors in the IL-rich upper phase[2] . SANS measurements were performed at the ISIS and the ILL neutron sources on ABS samples to study IL micelles form and structure, using P44414Cl ionic liquid along deuterated nitric, hydrochloric and sulfuric acids. The micelles have been found to be cylindrical with a radius around 15 Å similar to the radius of the spherical micelles formed in acid free solutions and a variable length ranging from 50 Å to 1500 Å depending on the acid type, the acid concentration and the solution temperature. The change in the self-aggregation behavior of the ionic liquid as a function of the latter parameters is discussed and correlated to the phase separation phenomenon.

[1] J. Bowers, C. Butts, P. Martin, M. Vergara-Gutierrez , Langmuir 20, 2191-2198 (2004)
[2] N. Schaeffer, G. Pérez-Sánchez, H. Passos, J. Gomes, N. Papaiconomou, J. Coutinho , Phys. Chem. 21, 7462 (2019)

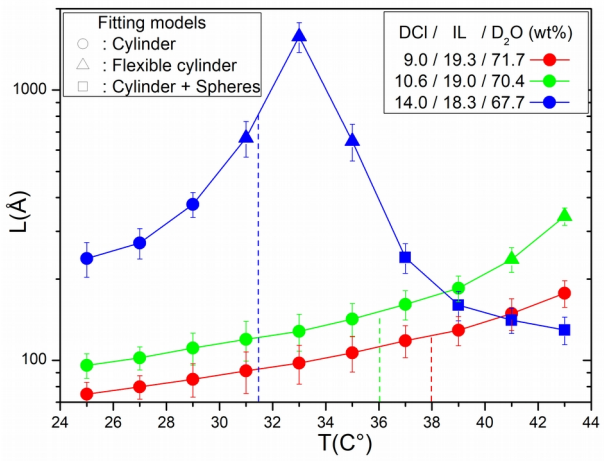

Figure 1 : Cylindrical micelles length evolution as a function of temperature for three hydrochloric acid based ABS.