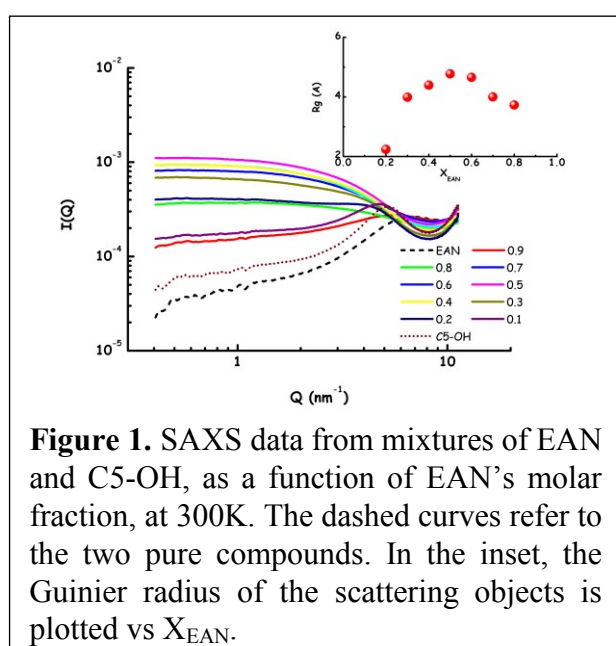


	Experiment title: Amphiphile meets amphiphile: from micro to mesoscopic structure of ionic liquid-molecular liquid mixtures	Experiment number: SC- 3853
Beamline: ID02	Date of experiment: from: 04/03/2015 to: 06/03/2015	Date of report: 25/02/2015
Shifts: 6	Local contact(s): S. Prevost	<i>Received at ESRF:</i>
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Report:



The proposed experiment was focused on characterising the mesoscopic organization in binary mixtures of protic ionic liquids (PILs) and molecular liquids (ML) such as n-alkyl alcohols that share with PILs the characteristic of being amphiphilic.

We have shown in the past that ionic liquids (ILs) are characterised by a distinct degree of mesoscopic order, due to their intrinsic amphiphilic nature.^{1,2} Accordingly they show a diffraction pattern that fingerprints the existence of a polar-vs-apolar alternation centred at ca. $0.2\text{-}0.7 \text{ \AA}^{-1}$. A similar observation can be done on normal alcohols, whose amphiphilic nature is well known. Despite the commonly accepted view that the polar-vs-apolar dualism influences dispersion of a

ML into a IL in terms of the segregation of the ML into the most affine compartment in ILs³, we recently detected the existence of a complex structural behaviour in PIL-alcohols mixtures.⁴

Recent works from other groups confirm such a behaviour^{5,6}. As shown in the data set collected at ID02 (figure 1), ethylammonium nitrate (EAN, the simplest PIL) when mixed with n-pentanol, shows a distinct excess low Q scattering for $Q < 3 \text{ nm}^{-1}$. This feature is no longer related to the polar-vs-apolar alternation, as the two low Q peaks for EAN and pentanol are centred at 7 and 5 nm^{-1} , respectively. The observed low Q excess is related to a larger scale density fluctuation phenomenon, related to criticality.

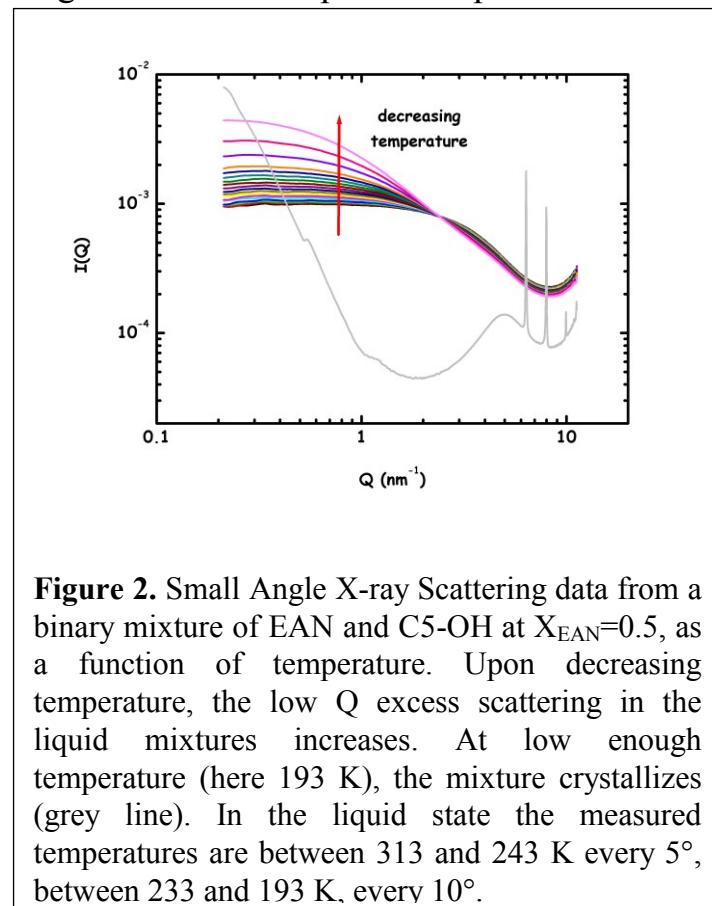


Figure 2. Small Angle X-ray Scattering data from a binary mixture of EAN and C5-OH at $X_{\text{EAN}}=0.5$, as a function of temperature. Upon decreasing temperature, the low Q excess scattering in the liquid mixtures increases. At low enough temperature (here 193 K), the mixture crystallizes (grey line). In the liquid state the measured temperatures are between 313 and 243 K every 5° , between 233 and 193 K, every 10° .

During the ID02 experiment we also explored the temperature dependence of the SAXS pattern and observed that it grows in amplitude upon decreasing T (see Figure 2). We modelled this trend in terms of the Ornstein-Zernicke law and associated these scattering features to critical concentration fluctuations that are precursors for liquid-liquid phase separation.

These results have been just (as of 24.02.2016) accepted for publication on the Journal of Physical Chemistry B (DOI:10.1021/acs.jpccb. 6b01422).

During the experiment we also explored other EAN-alcohol mixtures, namely EAN-hexanol and EAN-heptanol, both as a

function of concentration and temperature. These results are being organised to be published in the near future.

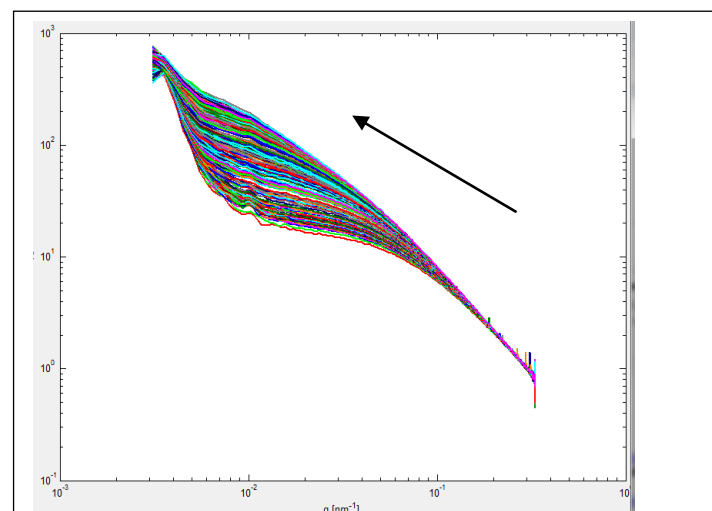


Figure 3. Representative kinetics for off-critical EAN-C7-OH mixture, after inducing phase separation by quenching.

In order to prove the origin of the density fluctuations, the experimental session also was used to explore the kinetics of phase separation when approaching the demixing temperature for the two above mentioned mixtures. This study took advantage of the unique performances of ID02 in terms of access to USAXS Q range and high time resolution. The collected results however are still limited, but prove the assumption of the divergence of critical fluctuations.

Due to the limited time that was available to collect these data, we could not achieve a complete enough set of data to fully account for the Spinodal Decomposition process

occurring in these systems. In Figure 3, we show a representative plot of the measured kinetics of phase separation, obtained by quenching a mixture of EAN and heptanol ($X(\text{EAN})=0.65$) from -14°C down to -14.8°C . The arrow indicates progressive kinetics combined with coarsening that corresponds to a shift of the peak towards lower Q values.

Another representative plot for the phase separation kinetics is shown in Figure 4. This data collection made use of a different setup (wavelength and SSD) and the Frelon Detector that allow reaching lower Qs and higher time resolution. It can be observed that we can nicely follow the kinetics of these phase separations (as witnessed by the progressive shift of the peak towards lower Q values by

increasing time), by wise selection of the quench depth and instrumental parameters. Unfortunately due to time limitation, it was not possible to make a systematic investigation of this interesting phenomenology. Further beam time will be requested to complete the investigation of kinetics of structural changes inside the one-phase region and during the phase transition.

These results are important not only for the intrinsic information that they deliver on the specific phase behaviour of PIL-alcohol mixtures, but also because they univocally determine the complex nature of the mesoscopic organization and reorganization in these mixtures that cannot be interpreted merely in terms of

organized entities such as micelles or microemulsions⁶, but encompasses a more fundamental liquid-liquid phase separation phenomenology. These results may contribute to a solution of the open discussion concerning this point.

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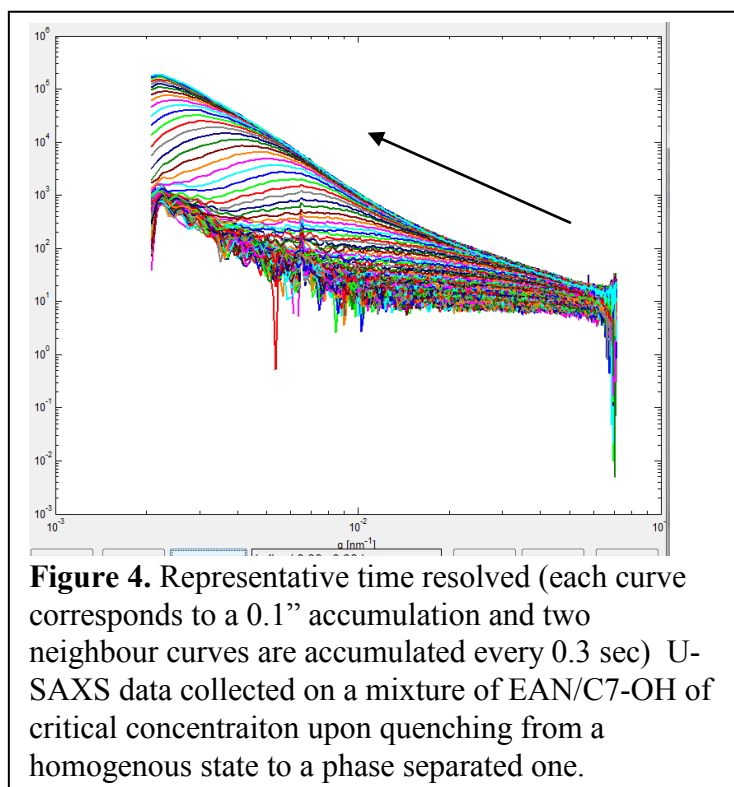


Figure 4. Representative time resolved (each curve corresponds to a 0.1'' accumulation and two neighbour curves are accumulated every 0.3 sec) U-SAXS data collected on a mixture of EAN/C7-OH of critical concentration upon quenching from a homogenous state to a phase separated one.

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