Experimental Report

Proposal: **9-10-1383** **Council:** 4/2014

Title: Study of nanometre-size domains indilutions of eutectic mixtures

This proposal is a new proposal

Researh Area: Chemistry

Main proposer: **DEL MONTE Francisco**

Experimental Team: DEL MONTE Francisco
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Local Contact: HONECKER Dirk

Samples:
Resorcinol/Choline chloride
Resorcinol/hexylresorcinol/choline chloride
resorcinol/choline chloride in benzylalcohol
Resorcinol/hexylresorcinol/choline chloride in benzyl alcohol
resorcinol/choline chloride/phosphoric acid
resorcinol/urea/choline chloride in water

Instrument	Req. Days	All. Days	From	To
D11	1	1	17/12/2014	18/12/2014

Abstract:

Deep eutectic solvents (DESs) offer an interesting alternative to regular amphiphiles. We have studied aqueous dilutions of DESs by NMR spectroscopy and Brillouin scattering. The former revealed that for DES dilutions with low water contents, the chemical shifts of the NMR spectra corresponded to water molecules solvated by DES, whereas the opposite situation (i.e., water solvating the individual components of DES) was found for high water contents. We also found that transitioning from low to high water contents implies the growth of the water domains that, in a first stage, can be yet solvated by DES and, later on, promote the rupture of the DES into its individual components. The use of SANS will let us analyse the main features of this bicontinuous phase, those are, the range of dilutions where it indeed exists and the dimensions of the nanometre-size domains. Our interest in determining these features resides in the capability of DES dilutions to produce materials that also exhibit a bicontinuous structure. Demonstrating that this bicontinuous structure comes from the bicontinuous phase at the solution stage will definitively help for the design of novel materials.

TECHNICAL REPORT FOR EXPERIMENT 9-10-1383

In our previous proposal (experiment 9-10-1383) we mentioned that we have studied aqueous dilutions of DESs by NMR spectroscopy[1, 2, 3] and Brillouin scattering. The former revealed that for DES dilutions with low water contents, the chemical shifts of the NMR spectra corresponded to water molecules solvated by DES, whereas the opposite situation (i.e., water solvating the individual components of DES) was found for high water contents. We also found that transitioning from low to high water contents implies the growth of the water domains that, in a first stage, can be yet solvated by DES and, later on, promote the rupture of the DES into its individual components.

We have also studied DES dilutions (using either water or benzyl alcohol as solvents) by Brillouin scattering. In these experiments, the sound wave travels through the solution with a velocity that depends on the particular solvent nature. For instance, Figure 1 shows the velocity of the sound wave versus the DES content in the aqueous solution for a DES composed of resorcinol and choline chloride. Interestingly, velocity decreases upon dilution following two linear fits, one for DES contents ranging from 100 to ca. 70 wt% and a different one from ca. 70 to 0 wt%. We have ascribed this behaviour to the presence of a continuous aqueous phase for diluted samples whereas for DES contents above 70 wt%, the aqueous phase is not continuous any more and sound has to travel through the continuous DES phase.

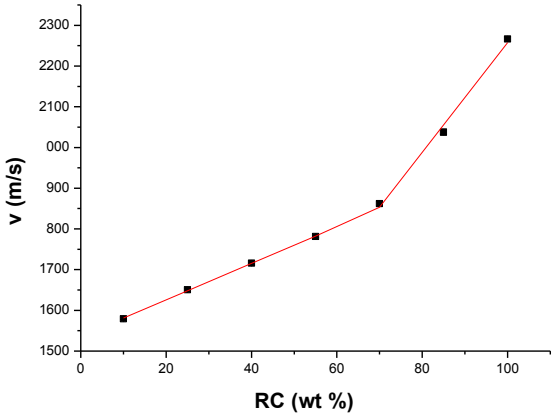

Figure 1: Plot of sound velocity versus resorcinol-choline chloride content (RC, in wt%) in water.

On Dec-2014, we carried out at Grenoble the experiment 9-10-1383 with a DES composed of resorcinol and choline chloride and its respective D_2O dilutions (e.g. 90, 80, 70 and 50 wt%), this is, the same samples studied above by Brillouin scattering. First of all, we found that the scattering was significant in all the dilutions (even for the most diluted one, e.g. 50 wt%) and decreased along with the dilution (Figure 2, left). In a further step and under the assumption that adding D_2O simply dilutes the system without changing the structure, we represented I_total-(1-x)*I_D20)/x versus q. In this plot (see Figure 2, right), samples with DES contents ranging from 100 to ca. 70 wt% exhibited a different pattern than that of the sample with DES contents below 70 wt% (e.g. 50 wt%), this is, in agreement with the trend already observed by Brillouin (see Figure 1).

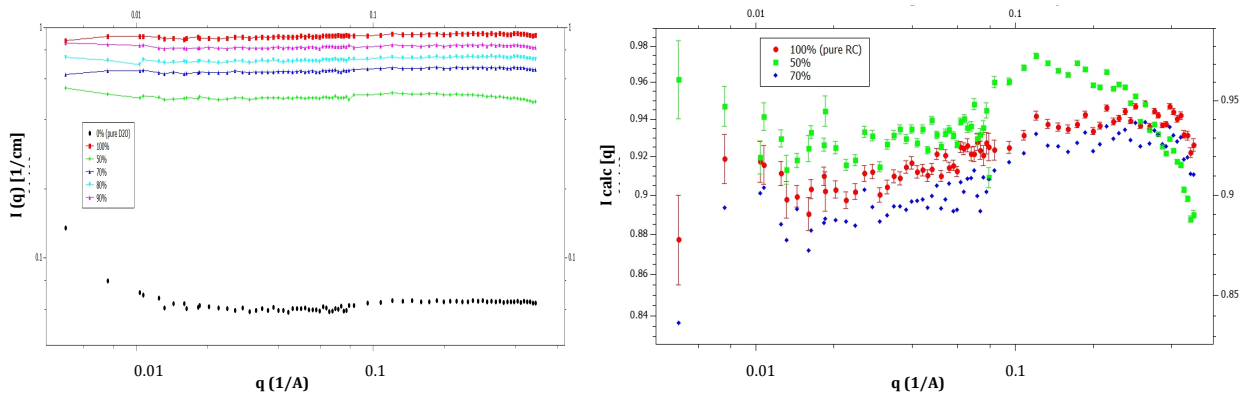

Figure 2: Left, small-angle neutron scattering (SANS) as a function of DES dilution in D_2O. **Right,** a peak appeared in the normalized SANS profile of the dilution with RC content 50 wt%.

More interestingly, we have used a RC aqueous dilution – the RC content was ca. 55 wt% – to prepare porous carbons by (1) polycondensation of resorcinol with formaldehyde and (2) subsequent carbonization.[4] The porous structure of the carbons exhibited a bicontinuous structure with mesopores of ca. 10 nm (see the manuscript enclosed below), this is in range to the q value where there was a peak in the SANS spectrum of the RC aqueous dilution with a RC content of 50 wt%. This correspondence is remarkable and opens interesting perspectives in materials synthesis.

Bibliography

[1] M. C. Gutiérrez, C. R. Mateo, M. L. Ferrer, F. del Monte, "Freeze-drying of aqueous solutions of deep eutectic solvents: a suitable approach to deep eutectic suspensions of self-assembled structures" *Langmuir* **2009**, *25*, 5509–5515

[2] M. C. Gutiérrez, M. L. Ferrer, L. Yuste, F. Rojo, F. del Monte, "Bacteria Incorporation in Deep Eutectic Solvents via Freeze-Drying." *Angew. Chem.* **2010**, *49*, 2158–2162

[3] S. Nardecchia, M. C. Gutiérrez, M. L. Ferrer, M. Alonso, I. M. López, J. C. Rodríguez-Cabello, F. del Monte, "Phase Behavior of Elastin-Like Synthetic Recombinamers in Deep Eutectic Solvents" *Biomacromolecules* **2012**, *13*, 2029−2036

[4] D. Carriazo, M. C. Gutiérrez, M. L. Ferrer, F. del Monte, "Resorcinol-based deep eutectic solvents as both carbonaceous precursors and templating agents in the synthesis of hierarchical porous carbon monoliths" *Chem. Mater.* **2010**, *22*, 6146–6152.