Experimental report

03/11/2020

Proposal:	**DIR-200**	**Council:**	10/2019

Title: Unravelling the interactions of hydrophobic deep eutectic solvents with water

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Paulo RIBEIRO CLARO**

Experimental team:

Local contacts: Monica JIMENEZ RUIZ

Samples:
Glycerol
Urea
Ibuprofen
Choline Chloride
Aspirin
Acetaminophen
Lidocaine
Lactic acid

Instrument	Requested days	Allocated days	From	To
IN1	4	2	10/09/2020	12/09/2020

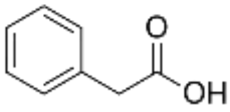
Abstract:

In the recent years, the search for "green solvents" has been intensified and Deep Eutectic Solvents (DESs) have been emerged as an alternative to conventional molecular solvents. DESs are formed by the association of an hydrogen bond acceptor with an hydrogen bond donor. In the eutectic composition, the mixture has a melting point much lower than that of an ideal mixture of its components.
However, the high viscosity of DESs may hinder their practical applications in different industrial processes.
The viscosity of DES systems was found to decrease significantly with the addition of even small amounts of water. Thus, the effect of water on the nanostructural properties of DESs is of utmost importance. Having a firm grasp of how water interacts with binary eutectic mixtures is an essential prerequisite for the design of hydrated DES systems suitable for defined applications - such as food processing, extraction processes, enzyme reactions, and pharmaceutical uses.
This project aims at the understanding of the behaviour of DES with hydrophobic components as a function of increasing water content, using Inelastic Neutron Scattering.

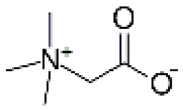
The original proposal aimed at the study of four well-characterized DES systems with different water contents, from the “low water” regime to “medium water” boundary. For each system, it was intended to record the spectra of i) two pure components (HBD, HBA), ii) pure DES (anhydrous), and iii) three selected DES-water mixtures (6 samples) – giving a total number of 24 samples.

Within the 2 days of beam time awarded, it was possible to collect the INS spectra for one system (5 samples), in the low and medium energy regions. The low energy range is of interest due to the expected presence of a water-related band, while the high energy region is better accessible with the optical techniques (IR or Raman).

Among the four systems of the original proposal, the Phenylacetic acid:Trimethyl Glycine (also known as Betaine), PAA:TMG was considered the most amenable for the initial study.



PAA



TMG

The melting point of the PAA:TMG mixture with a molar ratio of 1:2 is -7 ºC.

The INS spectra was obtained for the following samples:

Betain PURE (BET)
Phenyl acetic acid PURE (PAA)
PAA:BET 2:1 0.7%w/w water *mole ratio 2:1:0.15*
PAA:BET 2:1 3.8%w/w water *mole ratio 2:1:0.85*
PAA:BET 2:1 12.9%w/w water *mole ratio 2:1:3.20*

The Inelastic Neutron Scattering (INS) spectra were measured at 5 K in the range of energy transfers up to *ca*. 200 meV, with an energy resolution of $\Delta E/E \approx 2\%$. In the present experiment the energy transfer was calculated by subtracting 4.5 meV, the energy of the PG crystals in the ellipsoid, from the energy of the incoming neutrons selected with a focusing Cu(220) single crystal and bent Si(111) and Si(311) reflections. In order to capture the structure of the liquid phase through INS, the liquid mixtures have been “shock-frozen” (sudden temperature drop using liquid nitrogen), a procedure that has been demonstrated to avoid segregation of DES components.

Figure 1 compares the INS spectra of the pure components and the 1:2 “dry” mixture (0.7% w/w of H_2O). Several bands in the DES spectrum can be assigned from their counterparts in the pure compounds, and the amorphous nature of the sample obtained is also evident in the low wavenumber region. New band profiles observed in the mixture are the matter of interest for assessing the nature of the DES.

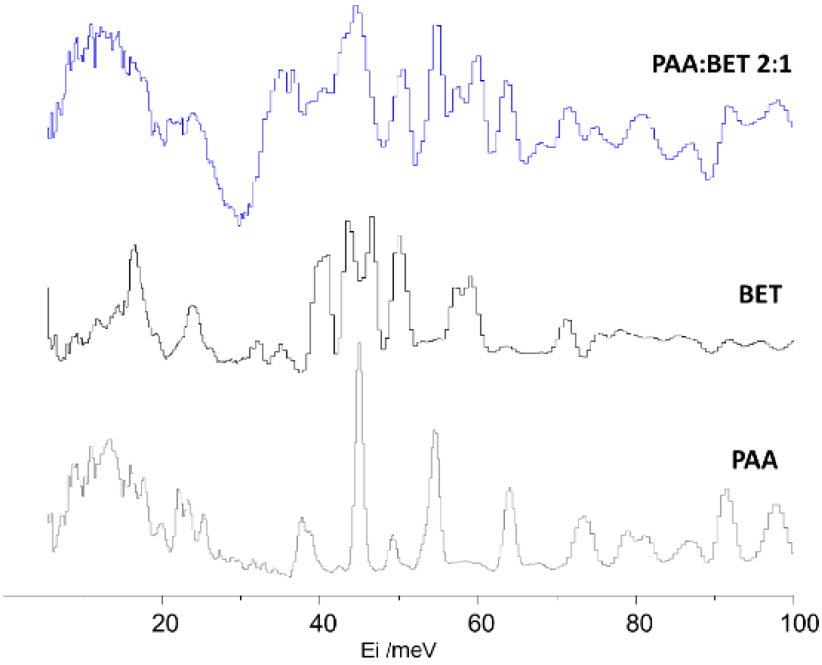


Fig. 1 – INS spectra of PAA, BET and PAA:BET 2:1 mixture, up to 100 meV.

Figure 2 compares the INS spectra of DES mixture in the presence of approximately 0, 1 and 3 water molecules. These samples are within the "low water" regime, where the amount of water is predicted to change the heterogeneous 3D structures of pure DES, but without isolating the DES components. The arrows identify some bands affected by the increasing amount of water. These bands are tentatively related with the torsional motion of methyl groups of BET and deformation modes of PAA.

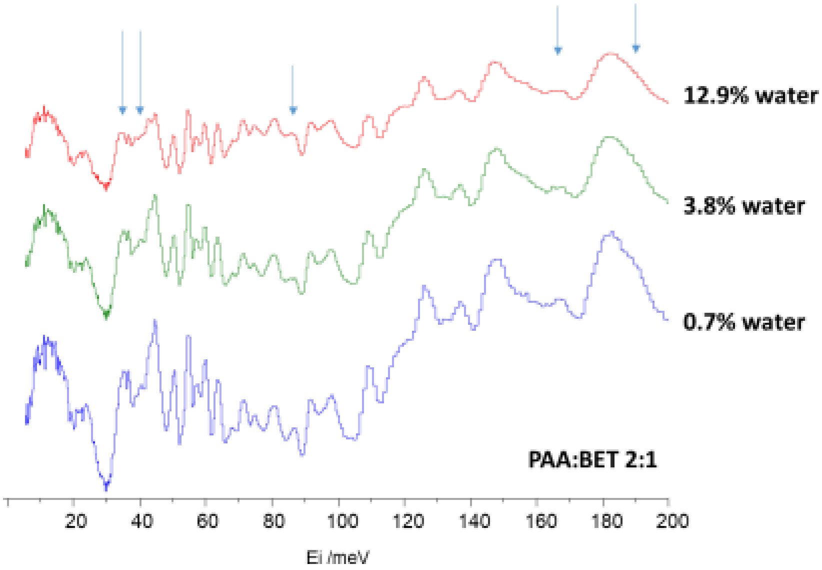


Fig. 2 – INS spectra of PAA:BET mixtures with different water contents, up to 200 meV.

The assignment of the observed INS bands in the pure compounds is of utmost importance for the interpretation of the observed changes in the mixtures. Reliable assignments will be obtained from periodic DFT calculations, using the program *CASTEP* (currently running). Figure 3 reveal the limitations of the calculated spectra obtained with single molecule calculations (*Gaussian 16* program). For the region above *ca*. 500 cm^{-1} (60 meV), a limited match between experimental and calculated bands is observed, allowing the assignment of a few bands. However, in the lower energy region, even above the external mod region, there is no reliable correspondence between calculated and experimental bands. This emphasises the importance of intermolecular interactions in pure systems.

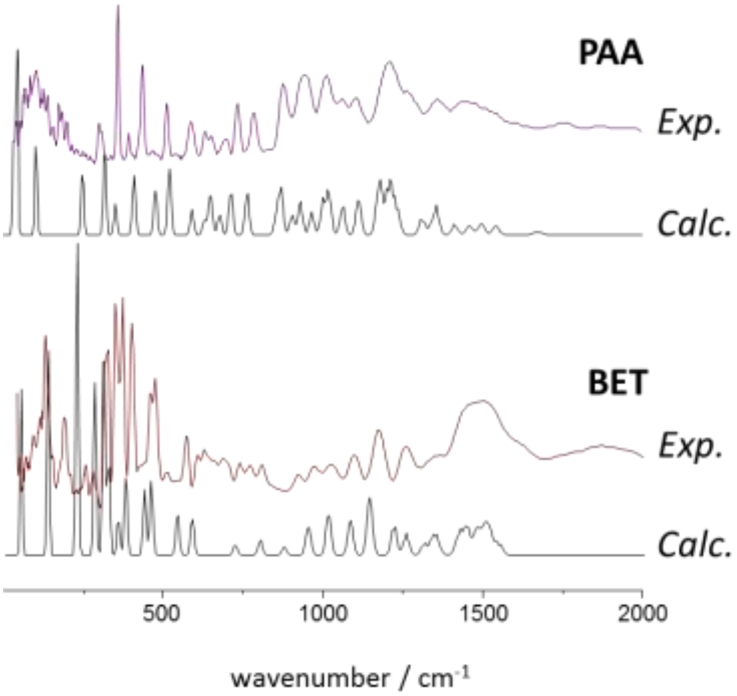


Fig. 3 – Experimental vs. calculated (single molecule) INS spectra of pure PAA (top) and pure BET (bottom).