Experimental report

15/04/2022

Proposal: DIR-224 **Council:** 10/2020

Title: Unravelling the interactions of hydrophobic deep eutectic solvents with water (Cont.)

Research area: Chemistry

This proposal is a continuation of DIR-200

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Samples: Trimethyl Glycine / C5H11NO2
Choline Chloride / C5H14ClNO
Diethylene glycol / C4H10O3
Glycolic Acid / C2H4O3

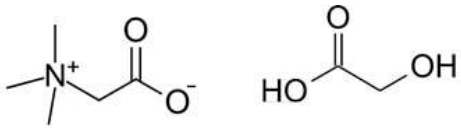
Instrument	Requested days	Allocated days	From	To
IN1 LAG	4	2	24/05/2021	26/05/2021

Abstract:

In the recent years, the search for "green solvents" has been intensified and Deep Eutectic Solvents (DESs) have been emerged as na 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.

This mission resulted from a continuation proposal, following the results obtained for the project entitled "Unravelling the interactions of hydrophobic deep eutectic solvents with water", hereafter referred to as "DIR-200".The original proposal DIR-200 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.

During DIR-200, it was possible to collect the INS spectra for one system (5 samples), in the low and medium energy regions. Among the four systems of the original proposal, the Phenylacetic acid:Trimethyl Glycine (also known as Betaine) DES, was considered the most amenable for the initial study. In this continuation study, the Glycolic acid:Trimethyl Glycine DES system was addressed.



TMG GA

The melting point of the GA:TMG mixture with a molar ratio of 1:2 is -36 ºC.

The INS spectra was obtained for the DES following samples:

Glycolic acid PURE (GA)
Betaine anydrous PURE (TMGa)
GA:TMG 2:1 3%w/w water *mole ratio 2:1:0.6*
GA:TMG 2:1 4.7%w/w water *mole ratio 2:1:0.95*
GA:TMG 2:1 10.3%w/w water *mole ratio 2:1:2.22*
Diethylene Glycol PURE

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 [1,2].

Figure 1 compares the INS spectra of the pure Betaine, in the mono-hydrated and anhydrous forms. The presence of water in the crystalline structure gives rise to a different band profile above 500 cm^{-1}.

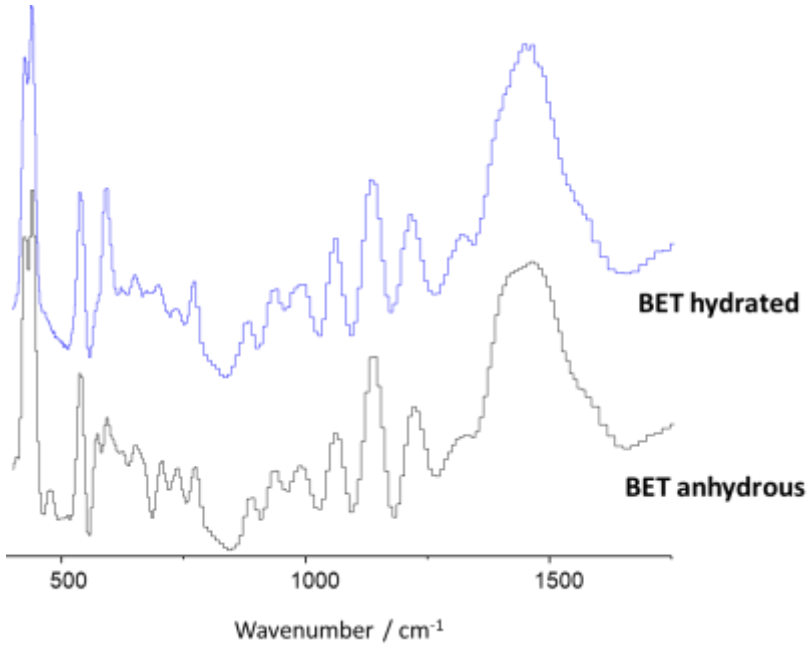


Fig. 1 – INS spectra of BE, mono-hydrated and anhydrous forms.

Figure 2 shows the effect of water content the INS spectra of DES mixture, in the 200-400 cm^{-1} range. This is the region of methyl torsional modes,which give rise to strong INS intensities, and so dominate the 200-300 cm-1 spectral range. The effects of water contents are highlighted through the difference spectra obtained by subtracting the spectrum of the sample with 2:1:0.6 DES:water mole ratio (described as 0w) from the spectra of samples with 2:1:0.95 and 2:1:2.2 DES:water mole rata (described as 1w and 2w, respectively).

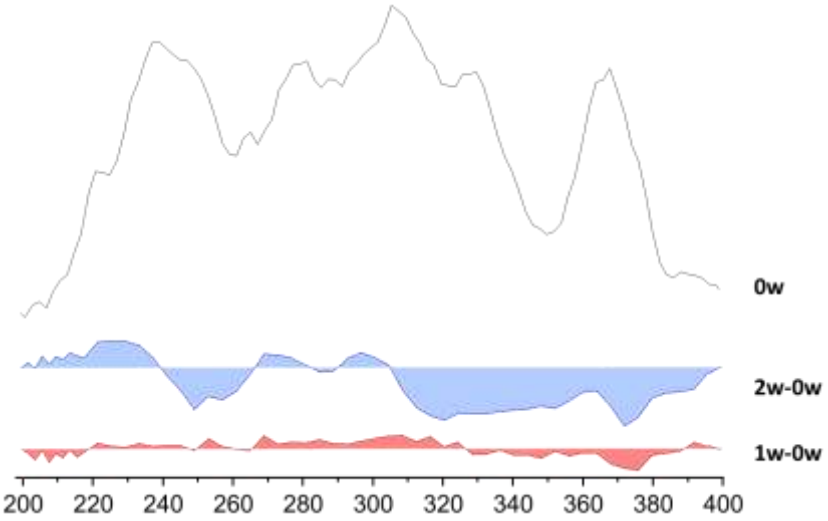


Fig. 2 – The region of methyl torsions in the GA:BET mixture: the difference spectra (wet minus dry) for the DES:water molar ratios of 1:1 (1w-0w), and 1:2(2w-0w), compared with the spectrum of the driest sample (0w)

The patterns of difference spectra can be compared with the ones recently reported [2] for the “Reline” DES, a well-known hydrophilic DES.

As it can be seen from Fig.2,, the red-shift of the lower component of methyl torsion in BET at ca. 240 cm^{-1}, is not present in the 1w sample but becomes quite evident in the 2w sample. The molecular origin of this effect cannot be obtained from these results alone and deserves requires further investigation.

References:

[1] - *Inelastic Neutron Scattering study of Reline: shedding light on the hydrogen bonding network of deep eutectic solvents.* C. Araujo, J. A. P. Coutinho, M. M. Nolasco, S.F. Parker, P. Ribeiro-Claro, S. Rudić, B. I. G. Soares, P. D. Vaz
Phys. Chem. Chem. Phys 19 (2107) 17998-18009

[2] - *Water in Deep Eutectic Solvents: New Insights From Inelastic Neutron Scattering Spectroscopy*
Mariela M. Nolasco,Sónia N. Pedro,Carla Vilela,Pedro D. Vaz,Paulo Ribeiro-Claro, Svemir Rudić, Stewart F. Parker, Carmen S.R. Freire, Mara G. Freire and Armando J. D. Silvestre. Frontiers in Physic, 10 (2022) 834571
DOI: 10.3389/fphy.2022.834571