Poster Number: **CCG09**

Molecular Structure in a Saturated Solution and in the Solid in Equilibrium with that Solution: The Case of the Hydroxynicotinic Acid Family

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Crystallization from solution is one of the oldest methods used to obtain pure solid materials. Yet the molecular mechanisms that underly the process, particularly at the early stages, remain largely a mystery [1]. Achieving a better understanding of how the molecular structure of a solute, and the possible interactions with the solvent, direct the assembling process that results in a specific crystal form, is a fundamental scientific challenge that needs to be overcome if control over the outcome of crystallization is to be achieved. One important aspect within this scope is the possible existence of relationships between the solute conformation favoured in a particular solvent, and the packing motifs observed in the materials crystallized from that solvent. We have previously explored this question for undersaturated solutions of 4'-hydroxyacetophenone in water and ethanol (two protic solvents with different polarity and H-bond interaction ability) [2]. Building up on previous information obtained in our group [3], here we extended these studies to nicotinic acid (NA, Figure 1) and its hydroxy derivatives (HNAs, Figure 1), using the same two solvents, but focusing on saturation conditions.

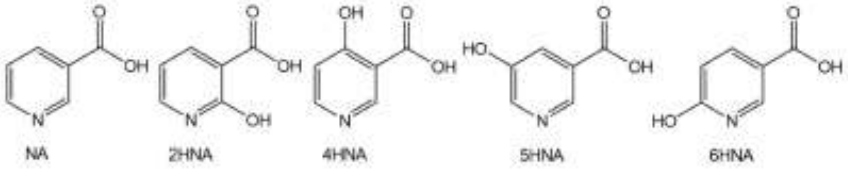

Figure 1. The nicotinic acid (NA) and hydroxynicotinic acids (HNAs).

HNAs solubilities were determined as a function of temperature, by the gravimetric method, and compared to that previously reported for NA [4]. The general trend, NA > 4HNA > 2HNA > 5HNA ≈ 6HNA, was observed. The solids in equilibrium with the saturated solutions were analysed by PXRD. Moreover, the saturated aqueous solutions pH values were measured, at 293±2 K, and used to rationalize about the possible structures, building up on the known protonation constants and the calculated species distribution diagrams. It was found that the molecular structures in the saturated solutions and in the solids in equilibrium with such solutions matched well.

Acknowledgements:

This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal, through Projects PTDC/QUI-OUT/28401/2017 (LISBOA-01-0145-FEDER-028401), UIDB/00100/2020 and UIDP/00100/2020.

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