P5 Insights into solute-solvent interactions guiding crystallization from density measurements: the $OHC_6H_4C(O)R$ ($R = H, CH_3, CH_2CH_3$) family as a model system

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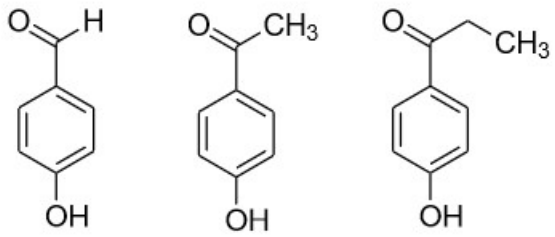
Crystallization from solution is arguably the most important process to obtain highly pure solid products [1,2]. There is still, however, very little knowledge about the early stages of crystallization (the pre-nucleation and nucleation stages) [3]. This is a major factor behind the lack of control over crystallization processes leading to manufacture problems related with polymorphism (the possibility of existence of two or more crystal forms of a molecule with different packing architectures). A particularly important open question within this scope, is how solute-solute and solute-solvent interactions determine the aggregation processes from which crystals emerge.
When evaporative crystallization is in view, insights into this question can be provided by density measurements as a function of concentration. This method was used in this work to investigate the aggregation/solvation of 4'-hydroxybenzaldehyde (HBA), 4′-hydroxyacetophenone (HAP) and 4′-hydroxypropiophenone (HPP) in ethanol (**Figure 1**).



1 **2** **3**

Figure 1. Molecular structures of 4'-hydroxybenzaldehyde (1), 4′-hydroxyacetophenone (2) and 4′-hydroxypropiophenone (3).

In the case of HBA and HPP it was found that the apparent molar volume decreased as the concentration increased, until an approximately constant value was reached. An opposite trend was observed for HAP. This volumetric behavior results from a delicate balance between solvent structure breaking effects and solute-solvent H-bond interactions in very dilute solutions.

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