



Letter to the Editor

Macroscopic Evidence of Inclusion Phenomena in Urea and Thiourea Matrices

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Inclusion compounds actually represent suitable systems for investigating the nature of molecular guest-host interactions. Among such materials urea and thiourea inclusion compounds (i.e., clathrates), have been particularly investigated. X-ray diffraction studies have shown that this type of compound is built up with a hexagonal channel structure. The urea or thiourea matrix is formed by hydrogen bonding and a variety of guest molecules of appropriate size and shape can be included [1–4]. The nature of the vacancies in the host structure and the van der Waals host-guest interactions, as well as the “self assembling” capacity of the system may be considered as a real model for biological systems, e.g., those occurring in cavities containing protein or DNA structures [5].

From such a point of view it is interesting to investigate the conditions determining this type of molecular self-organization. The smallest urea channels are appropriate for example to storing non-branched hydrocarbon chains, while the thiourea channel diameters are large enough to accommodate bulky molecules such as substituted or non-substituted cyclic hydrocarbons [1]. This kind of inclusion phenomenon is attracting much interest in recent papers dealing for instance with guest molecule dynamics [6, 7].

We have personally studied the influence of the surrounding medium on the configuration of amine molecules in various environments and reported recently the synthesis of a series of urea, thiourea and cyclodextrin inclusion compounds. ^{13}C -CP-MAS-NMR and ^1H -NMR spectroscopy, and powder-X-Ray diffraction analysis confirmed the inclusion process [8–11].

We describe the visual phenomenon of decomposition of a crystal of urea-dialkylamine (dibutyl-, dipentyl-, dihexyl-, dioctyl-) and thiourea-quinuclidine inclusion compounds by dissolution into a solvent such as water or dimethylsulfoxide, with phenolphthalein as indicator.

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Demonstration

A quite peculiar phenomenon illustrates the presence of amine/urea and amine/thiourea inclusion compounds: the dissolution of the crystals in water or dimethylsulfoxide brings about a cleavage of the urea or thiourea matrix H-bonded structures. Amine moving from the van der Waals cavities has a visible influence on the surface of the crystals during the dissolution process (lasting about 10 sec. for a crystal of dimension $2 \times 1 \times 1$ mm). The exit of the amine produces a quick motion of the crystals and sometime the crystals jump out of the solution. In a phenolphthalein solution dissolution is accompanied by formation of a beautiful red track resulting from the basic character of the amine. This can be shown by directly projecting the experiment on a screen and using a transparency projector supporting a crystallization or a Petri dish containing a phenolphthalein solution in water and dropping a crystal of the inclusion compound into the solution. These kinds of compounds are particularly appropriate for such an experiment as they are more stable than the inclusion compounds of urea with hydrocarbons. Breaking down of the matrix makes easier also the exit of the amine due to its sensitivity to an acid-base indicator. Experiments with pure urea or thiourea induce indeed neither motion nor color.

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