

Poster Sessions

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Human MutT homolog-1 (hMTH1) hydrolyzes a variety of oxidized nucleoside triphosphates such as 8-oxo-dGTP, 2-oxo-dATP and 2-oxo-ATP to their corresponding monophosphates and prevents replicational and transcriptional errors caused by their misincorporations into DNA and RNA. We have determined crystal structures of hMTH1 complexed with 8-oxo-dGTP and 2-oxo-dATP and found that hMTH1 recognizes the two different oxidized nucleotides, 8-oxo-dGTP and 2-oxo-dATP, by the exchange of the protonation site between the neighboring Asp residues (Asp119 and Asp120) in the active site pocket. To our knowledge, this is a very novel mechanism for expression of broad substrate specificity by enzymes. In this study, we investigated the pH dependence of substrate-active site interactions in the crystal structures of the hMTH1-8-oxo-dGTP and hMTH1-2-oxo-dATP complexes. Under the crystallization condition with ammonium sulfate as precipitate, the hMTH1-8-oxo-dGTP crystals over pH 7.0 reveal that the substrate binding mode is altered toward an inactive form, in which the triphosphate group is located far from the catalytic residues in the Nudix motif. In the hMTH1-2-oxo-dATP crystals, electron densities for 2-oxo-dATP disappear at pH8.0. These are suggested that the deprotonation of Asp119 in the hMTH1-8-oxo-dGTP crystals and Asp120 in the hMTH1-2-oxo-dATP crystals occurs at these pHs.

Keywords: genome stability, broad substrate specificity, pH-dependence

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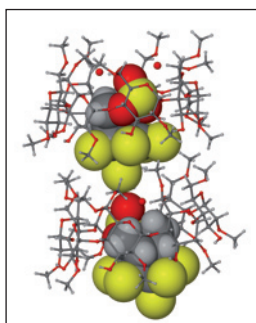
Inclusion of the insecticide endosulfan in cyclodextrins

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Most agrochemicals are highly insoluble in water, highly toxic and have reduced stability against chemical and photolytic degradation which makes them environmentally hazardous [1]. Endosulfan is an organochlorine insecticide and acaricide with a combination of these poor physical properties. Improving these physical properties has been attempted by complexing endosulfan with native and derivatised cyclodextrins (CDs).

Solid state inclusion complexes have been formed with β -CD, γ -CD and a derivatised CD known as DIMEB (heptakis(2,6-di-O-methyl)- β -CD). The single crystal X-ray structures of both the β -CD complex and the DIMEB complex of the symmetrical β -endosulfan isomer have been elucidated. The asymmetric unit of the DIMEB- β -endosulfan complex contains two DIMEB molecules with a disordered guest molecule situated in each (Figure). This complex shows a novel packing arrangement as the DIMEB molecules pack head-to-tail in infinite columns with adjacent columns parallel to one another rather than anti-parallel.

An amorphous CD, randomly methylated β -CD (RAMEB), was also investigated for inclusion with endosulfan using PXRD. Kneading experiments between RAMEB and endosulfan resulted in a semi-crystalline material with distinct peaks at low 2θ values. The peaks do not match those of the pure crystalline guest material but do show



The asymmetric unit showing only the major disordered guest component

some similarity to the DIMEB- β -endosulfan complex PXRD pattern.

An understanding of the host-guest interactions forms an essential part of complex characterisation needed for developing new agrochemical formulations.

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180° Domain detection by surface phase sensitive second harmonic generation microscopy of polar materials

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Phase Sensitive Second Harmonic Generation Microscopy (PS-SHM) technique [1], [2] was developed to map 180° domains of polarization. Domain contrast is achieved by using the interference effect between SHG responses of a sample and a homogeneous reference material. Previously it was shown [1] that interpretation of domain mapping is simple if the crystal thickness is homogeneous and in the range of or below the coherence length l_c . Our objective is to demonstrate experimentally, that PS-SHM technique can be performed using a sufficiently flat surface of samples irrespective of their thickness. This is offering most feasible conditions to investigate various as grown materials, and especially those which could not be obtained in μm thick layers.

Using the PS-SHM technique in transmission mode, we have demonstrated [3] either a mono- or bi-polar state for different nonlinear optical crystals such as *N,N*-dimethyl-2-acetamido-4-nitroaniline (DAN), 2-cyclo-octylamino-5-nitropyridine (COANP), a channel-type inclusion compound of perhydrotriphenylene (PHTP) / *N,N*-dimethyl-3-nitroaniline (DMNA), potassium dihydrogen phosphate (KH_2PO_4) crystals stained by dyes and the zeolite $\text{AlPO}_4\text{-5}$ loaded by 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (DCM). For all these cases a phase contrast was found irrespective of thickness and surface quality.

In this work, we have demonstrated that the application of PS-SHM can be realized under non phase matching conditions of samples much thicker than the coherence length. Further development is exploring the possibility to perform PS-SHM under reflection.

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Keywords: microscopy, phase contrast, polarity

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Molecular recognition and cluster size in supersaturated solutions of NaClO_3

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The classical nucleation theory is applied to the modelling of the cluster size distribution in supersaturated boiling sodium chlorate solutions. It was recently reported by the authors that under these conditions a strong bias of enantiomorphic crystals of the same chiral sign is obtained [1]. Given the catastrophic nature of the crystal nucleation process in boiling highly concentrated solutions, it was reasonable to hypothesize that the chiral selection was a result of molecular recognition among the clusters by collisions in the metastable period. Experimental support of this assumption was obtained recently by us in a series of experiments where the supersaturated solution carefully extracted, before the appearance of the first crystals, was also able to develop nearly homochiral samples [2]. Nevertheless, this mechanism only could be operative if the subcritical clusters have enough size to have a definite chiral sign.

In this contribution we evaluated the cluster size distribution in equilibrium with isolated molecules of sodium chlorate using the classical approach applied to cubic clusters using the formalism of K. Sangwal [3] and the value of 0.012 J/m² for the solid-solution surface energy for the sodium chlorate [4]. The critical cluster obtained by the degree of supersaturation attained at the onset of the nucleation contained 61 chlorate units, a cluster of such size clearly has a definite chirality as supposed, i.e. it cannot racemize. The metastability of the system was evaluated assuming that the nucleation appears when the first critical nucleus is formed giving a result comparable with the experimental. Finally the wall effect, (high temperature gradients are always presents in boiling systems near the heating wall), was also simulated showing a shift towards smaller cluster sizes in hotter zones. This phenomenon is important because it drives the partial dissolution of the clusters (recycling), an effect of importance in all the theoretical symmetry breaking scenarios. What is more, the calculations showed that this recycling increases with the supersaturation. As a result the degree of the homochirality of the population of crystals obtained should increase with the supersaturation and this is what effectively was observed.

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Keywords: nucleation theory, symmetry breaking, boiling crystallization

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The effect of solvents on the dissociation and association of decavanadates

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Tetra-*n*-amylammonium decavanadates show both the dimeric and monomeric hydrogen-bonded molecular complexes in the crystalline state, depending upon the protophobic or protophilic nature of the solvent. On the one hand, protonated decavanadate anions self-assemble into self-complementarily hydrogen-bonded dimers, $\{[H_3V_{10}O_{28}]_2\}^{6-}$, when crystallized with acetone. On the other hand, they form hydrogen bonds with solvent molecules and remained monomers, $[H_4V_{10}O_{28}]^{2-}$, when crystallized with 1,4-

dioxane.^[1] By using SAXS and ¹H- and ⁵¹V-NMR, we revealed that the behavior of the protonated decavanadate anions between the dimers and monomers depends on the protophobic and protophilic nature of acetone and 1,4-dioxane, respectively, also in the solution state.^[2]

Herein, in order to compare the effect of other solvents on the dissociation or association between the dimers and monomers, we measured SAXS, ¹H-NMR and ⁵¹V-NMR spectra of $[(n-C_5H_{11})_4N]_3[H_3V_{10}O_{28}]$ in acetone, acetonitrile, tetrahydrofuran, 1,4-dioxane and the mixtures of these solvents. Radius of gyration, R_g , estimated from the observed SAXS data was employed as a measure of the dimer formation. In order to determine the average R_g , we used three fitting methods (Guinier, form factor, and pair-distribution analyses) on the SAXS data that were collected at 12ID-B and 12ID-C beamlines in APS. R_g for the solution in 100% acetone and 100% acetonitrile were 5.9(1) Å and 5.8(1) Å, respectively. These values agree with those calculated from the crystal structure 5.1 Å for the dimer, $\{[H_3V_{10}O_{28}]_2\}^{6-}$, indicating that the decavanadate anions associate to the dimer. On the other hand, R_g for the solution in the tetrahydrofuran was 4.3(3) Å. This value is between those for the dimer (5.1-6.6 Å) and monomer (3.5 Å), indicating that a certain amount of decavanadate anions dissociate into the monomers. In case of the system of acetone and 1,4-dioxane, the dissociation into the monomers was completed in the mixed solvent consisting of 20% acetone and 80% 1,4-dioxane. Therefore, tetrahydrofuran has a weaker effect on the dissociation of the dimer into the monomers than 1,4-dioxane. These results are also confirmed by ¹H-NMR and ⁵¹V-NMR spectra.

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Keywords: SAXS, solvent, assembly

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Spontaneous mirror symmetry breaking in the crystallization of NaClO₃

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A transition towards chirality in the crystallization of NaClO₃ in supersaturated boiling solutions is reported [1]. The results agree with previous one obtained by wet grinding and point to a different mechanism than those of previous reports originated by secondary nucleation growth of a single chiral Adam crystal.

The phenomenon is discussed here on the basis of a thermodynamic scenario of non-uniform temperature distribution in the metastable supersaturated state. During this period, the evolution of the population of sub-critical nuclei takes place without any other noticeable crystal growth process. The fast evolution of supercritical nuclei and the experimental iprocedure of immediate separation of the crystals formed reasonable excludes secondary nucleation and Ostwald ripening as the cause of the transition towards chirality in these experimental conditions. Therefore, the evolution towards homochirality should be attributed to the primary nucleation process when maintained in a stationary state. The bifurcation towards a stationary homochiral state is a consequence of the instability of the system due to the chiral