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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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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, {[H₃V₁₀O₂₈]₂}⁶⁻, when crystallized with acetone. On the other hand, they form hydrogen bonds with solvent molecules and remained monomers, [H₄V₁₀O₂₈]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*-C₂H₁₁)₄N]₃[H₃V₁₀O₂₈] 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, {[H₃V₁₀O₂₈]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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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