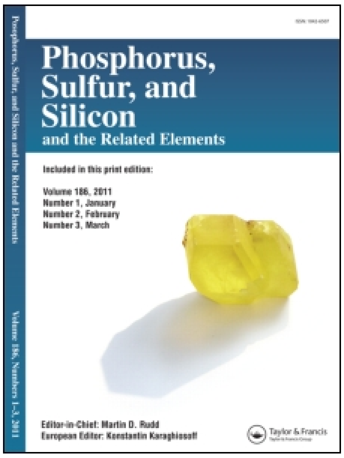

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# The Solution Properties of Supersaturated Sodium Triphosphate Forms I and II

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# THE SOLUTION PROPERTIES OF SUPERSATURATED SODIUM TRIPHOSPHATE FORMS I AND II

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Abstract Sodium triphosphate Form II is easily supersaturated while Form I is difficult to supersaturate. Stability of these supersaturated solutions can be expressed kinetically.

## Introduction

The behavior of sodium triphosphate during hydration and dissolution is extremely important in the application of the salt in processes and products. The formation and behavior of the supersaturated solutions and hydrates is but poorly understood.

## FORMS OF SODIUM TRIPHOSPHATE

Two forms of anhydrous sodium triphosphate, $Na_5P_3O_{10}$ I (Hi Temp) and $Na_5P_3O_{10}$ II (Low Temp), behave differently in aqueous supersaturated solutions. Both crystalize to $Na_5P_3O_{10}\cdot 6H_2O$. No differences have been reported for crystal structures of $Na_5P_3O_{10}\cdot 6H_2O$ derived from either anhydrous salt, but differences have been noted for crystal habits[1]. Solutions of $Na_5P_3O_{10}$ II can remain supersaturated for many hours under conditions Form I will crystallize toward $Na_5P_3O_{10}\cdot 6H_2O$ "equilibrium" rapidly.

This work had two objectives. 1. Determine conditions leading to supersaturation. 2. Study variables controlling metastability of supersaturated solutions. Considered variables were: ratios of $Na_5P_3O_{10}$ I to $Na_5P_3O_{10}$ II in a sample, degrees of supersaturation, temperature of solutions,

7. The maximum concentration of a supersaturated, 25°C solution of sodium triphosphate was approximately 50% solids. $Na_5P_3O_{10} \cdot 6H_2O$ has a metastable equilibrium solubility of about 13.0% solids at 25°C[2].

8. Powdered seed crystals of $Na_5P_3O_{10} \cdot 6H_2O$ greatly reduce the stability of supersaturated solutions, while larger, well-formed crystals had no measurable influence.

9. Two reactions compete when anhydrous sodium triphosphate is mixed with water. 1. is hydration of crystalline phosphate[3]. 2. is dissolution of the phosphate. Condition 1. dominates in the case of $Na_5P_3O_{10}$ I, while reaction 2 dominates in the case of $Na_5P_3O_{10}$ II.

10. Differences between Form I and Form II are evident in the dissolved state. Mixtures of Form I and Form II sodium triphosphate act almost independently of each other. This suggests there is a configurational difference between the $P_3O_{10}^{-5}$ ions in solution when derived from Form I or Form II sodium triphosphate. [4,5,6]

11. Rates of crystallization of $Na_5P_3O_{10} \cdot 6H_2O$ from supersaturated solutions can be expressed semiquantatively by the rate expression $\ln C_{xs} = kt$, where $C_{xs}$ is the instantaneous concentration of $Na_5P_3O_{10}$ greater than the equilibrium concentration $C_{eq}$. k is the crystallization constant and t is elapsed time after nucleation. There is an induction time $t_I$ that may range from seconds to many hours.

## Data

Table I: Rates of Crystallization of $Na_5P_3O_{10} \cdot 6H_2O$ From $Na_5P_3O_{10}$ II Solutions

| °C | %Solids | $t_I$ hr. | $C_{max}$ m/l | k $min^{-1}$ | Eq. Solub. |
|---|---|---|---|---|---|
| 25 | 28.0 | 2.2 | 0.90 | 9.67 $10^2$ | 13.0% |
| 25 | 31.5 | 0.3 | 0.98 | 11.2 $10^2$ | " |
| 50 | 25.0 | 0.5 | 0.80 | 24.3 $10^2$ | 14.3% |
| 50 | 25.0 | 0.5 | 0.77 | 25.0 $10^2$ | " |
| 50 | 28.0 | 0.14 | 0.86 | 30.0 $10^2$ | 14.3% |
| 50 | 31.5 | 0.03 | 0.84 | 34.5 $10^2$ | " |
| 75 | 25.0 | 0.2 | 0.80 | 26.7 $10^2$ | (16.6%) |
| 75 | 28.0 | 0.06 | 0.91 | 49.5 $10^2$ | " |
| 75 | 31.5 | 0.02 | 0.92 | 78.2 $10^2$ | " |

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particle size, order of addition, purity of samples, influence of seed crystals of $Na_5P_3O_{10}\cdot 6H_2O$ on stability of supersaturated solutions, and added foreign impurities to these systems.

## Conclusions

The conclusions were:

1. High purity $Na_5P_3O_{10}$ I did not form supersaturated solutions in these experiments.
2. Commercial samples of $Na_5P_3O_{10}$ with a high temperature rise (Hi TR) do form supersaturated solutions because more than one-half of the product is usually Form II.
3. $Na_5P_3O_{10}$ II readily forms supersaturated solutions under most conditions studied.
4. Increased temperature decreases stability of supersaturation, but increases metastable solubility of $Na_5P_3O_{10}\cdot 6H_2O$. (Condensed phosphates have no true equilibrium solubility in aqueous solutions.)
5. Increased concentrations decrease stability of supersaturated solutions. Rates of crystallization to $Na_5P_3O_{10}\cdot 6H_2O$ are approximately proportional to the degree of supersaturation.
6. Supersaturated solutions of purer samples are less stable than similar solutions containing other phosphates as in commercial products. Long chain polyphosphates, such as Kurrol's and Graham's salts, greatly increase the stability of supersaturated solutions.