DECOMPOSITION OF TETRAPHENYLBORATE*

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ABSTRACT

The chemical decomposition of aqueous alkaline solutions of sodium tetraphenylborate, NaTPB, has been investigated. The focus of the investigation is on the determination of components which influence NaTPB decomposition. Copper(II) ions, solution temperature, and solution pH (hydroxide ion concentration) have all been demonstrated to affect NaTPB stability. Their relationship with each other and the stability of NaTPB has been determined. Based upon this knowledge, a method for stabilizing NaTPB was determined. Decomposition of a NaTPB solution was delayed with the addition of sodium hydroxide. In additional work, the elimination of oxygen from the reaction environment did not prevent NaTPB decomposition in the presence of copper(II) ions but did, however, affect the course of decomposition.

INTRODUCTION

In-Tank Precipitation (ITP) is a process intended for decontamination of high level radioactive waste solutions at the Savannah River Site (SRS).(1,2) The two principal radionuclides to be removed by this process are cesium-137 and strontium-90. Two specialty chemicals required to conduct this procedure are sodium tetraphenylborate and sodium titanate. Sodium tetraphenylborate, NaTPB, will be obtained as an aqueous solution having a composition of 0.55± 0.05 M NaTPB and 0.10 M NaOH. The tendency of NaTPB to decompose prior to use was of serious concern. Strongly basic solutions of NaTPB are generally considered quite stable.(3) However, certain components (copper(II), light, and heat) were identified to be capable of decomposing NaTPB under basic conditions. This observed instability led to a more thorough investigation into the causes and prevention of NaTPB decomposition.

The work presented in this paper provides for: 1) identifying NaTPB solutions susceptible to decomposition, 2) predicting how long these solutions may remain stable and useable, 3) charting a solution's stability with monitoring procedures, and 4) stabilizing a decomposing solution for an extended period of time. The identification of components which initiate decomposition was necessary to achieve these objectives. Three principal factors were identified to affect the stability of NaTPB. These were 1) the presence of copper(II) ions, 2) temperature, and 3) solution pH (hydroxide ion concentration). Although all three were previously demonstrated to affect stability, their relationship was unclear. The experiments described herein were undertaken to gain an understanding of this relationship.

DISCUSSION

Experimental Method

The method employed for decomposition testing of NaTPB solutions was incubation under controlled conditions. This was achieved by introducing additives into aqueous alkaline solutions of NaTPB and subjecting the NaTPB solutions to controlled environmental conditions (e.g. elevated temperature and/or nitrogen atmosphere). Solutions were prepared from solid A.C.S. reagent grade NaTPB (purchased from the Aldrich Chemical Company) with a purity greater than 99.5%. Typical test solutions studied were 25 mL, in volume, with compositions of approximately 0.5 M NaTPB and 0.10 M NaOH. Components were added to the test solutions using microliter pipettes and prepared stock solutions. All test solutions, unless otherwise stated, were stored in capped polyethylene bottles at a temperature of 65°C in a laboratory oven in the presence of oxygen. Inert atmosphere studies were conducted by preparing and capping the test solutions in serum glass vials inside a nitrogen filled glove bag.

Three methods were utilized to monitor TPB- decomposition. These were silver-ion titration, pH, and visual observation. Solution pH was found to be a useful method of monitoring NaTPB-solution stability. A drop in the pH was observed immediately prior to decomposition. Solution appearance was also indicative of the stability status of the solutions. Stable aqueous NaTPB solutions are a transparent, flesh-toned color. During the initial stages of decomposition (or instability), the solution turns a golden color. As the quantity of TPB- that has decomposed increases, the solution turns dark red, then brown, and eventually black. Thus, the relative stability of a solution could be easily determined.

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Effect of Copper

Usually NaTPB solutions (0.5 M NaTPB and 0.1 M OH-), at 65°C, are relatively stable over a long period of time. However, the addition of 10 ppm Cu(II) ions to this solution resulted in the decomposition of the NaTPB in less than three weeks. Experiments have shown that under these reaction conditions, Cu(II) concentrations of 0.05 to 100 ppm initiate decomposition. Solutions containing high concentrations (≥1 ppm) of Cu(II) ions have an increased rate of decomposition. This is shown graphically in Fig. 1.

Solution pH Dependence

Solution pH proved to be a useful way of monitoring TPB- stability. Careful monitoring of Cu(II)-containing test solutions at 65°C revealed that the solution pH decreased from approximately 13.0 to 11.0 prior to TPB- decomposition whereas non-Cu(II)-containing solutions remained stable and their pH was relatively constant. Data demonstrating this phenomena is presented graphically in Fig. 2 and shows how rapid the rate of pH change is at 65°C. Follow-up work indicated that NaTPB solutions may be stabilized with larger concentrations of OH-.

NaTPB test solutions (0.5 M) containing OH- concentrations ranging from 0 to 0.5 M were tested at 65°C with Cu(II) (10.0 ppm) to examine the significance of the solution pH. Stability data obtained on these test solutions are plotted in Fig. 3. Solutions containing Cu(II) in conjunction with OH- concentrations of 0.01 M or less decomposed completely and rapidly (< 7 days). The NaTPB test solution containing Cu(II) and 0.5 molar OH- remained stable for over 4 weeks. The observation of delayed *decomposition in*

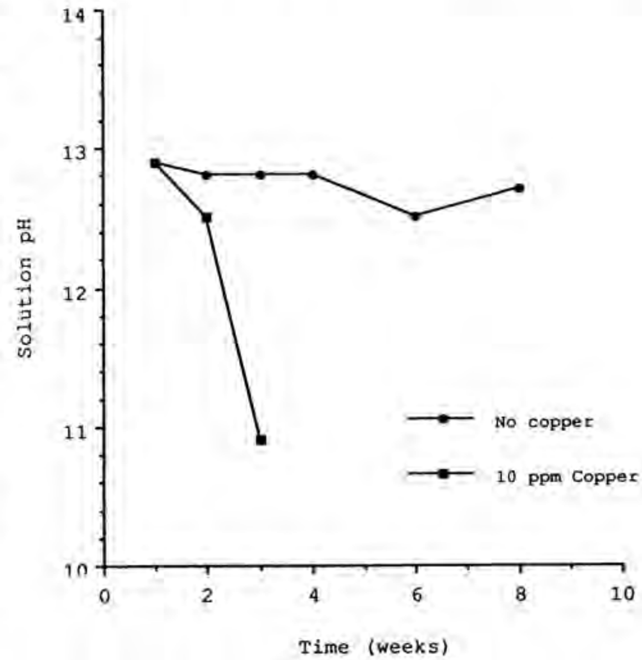

Fig. 2. Solution pH vs. time for NaTPB solutions with and without Copper (II) at 65°C.

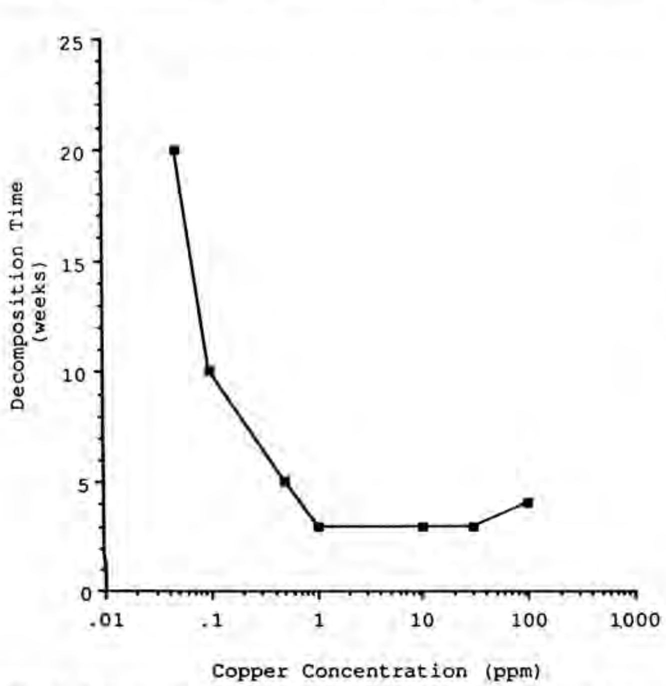

Fig. 1. Effect of copper concentration on NaTPB-solution stability at 65°C.

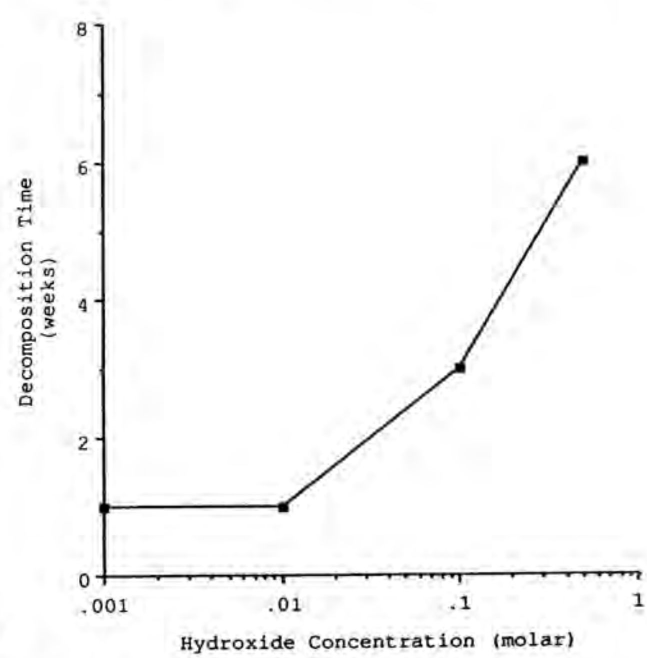

Fig. 3. Decomposition time of Cu-containing NaTPB solutions with varying hydroxide ion concentrations at 65°C.

solutions containing elevated OH- concentrations prompted further testing.

The addition of excess OH- to a Cu(II)-induced decomposing solution produced some stabilization. In the experiment, a Cu(II)-containing NaTPB solution was determined to be on the verge of decomposition three days after its preparation. An aliquot of the solution was withdrawn at that time and placed in a separate container. Concentrated NaOH(aq) was then added to the original decomposing solution to raise its pH back to 13.0. The unadjusted aliquot proceeded to decompose over the next four days. The original solution, which had been pH adjusted, remained relatively stable for an additional six weeks. Data representing the latter experiment is contained in Table I.

TABLE I

A Comparison of Two Aliquots of a 10 ppm Cu(II)-Containing NaTPB Solution. One Aliquot was Unaltered, the Other was pH Adjusted

Time (weeks)		Unaltered NaTPB (M)	Unaltered pH	Excess NaOH added on day 3 NaTPB (M)	Excess NaOH added on day 3 pH
1	day 1	0.48	12.7		
1	day 3	--	12.3	--->	13.0
1	day 7	<0.01	10.8	--	12.9
2				--	12.8
4				0.46	12.5
6				0.49	12.6
7				<0.01	12.5

Temperature Dependence

The rate of copper-induced decomposition is temperature dependent. NaTPB solutions containing initial concentrations of Cu(II) ions of 0.1 to 100 ppm, remained stable for more than a year at room temperature (23 ± 2°C). The 10 ppm Cu(II)-containing solution did show signs of instability. The solution pH dropped below 10 and it turned an opaque brown-black color. A slight decrease was observed in the NaTPB concentration after 46 weeks.

Similar copper-containing solutions show signs of instability after four weeks and begin to decompose in five to six weeks or longer at 40°C. The decomposition process is slowed considerably. Once initiated, complete decomposition of TPB- occurs in about two days at 65°C. At 40°C, complete decomposition requires about two weeks or longer after onset. Comparative temperature dependence data is contained in Table II. Figure 4 compares the rate of pH change for 10 ppm Cu(II)-containing solutions at the three different temperatures.

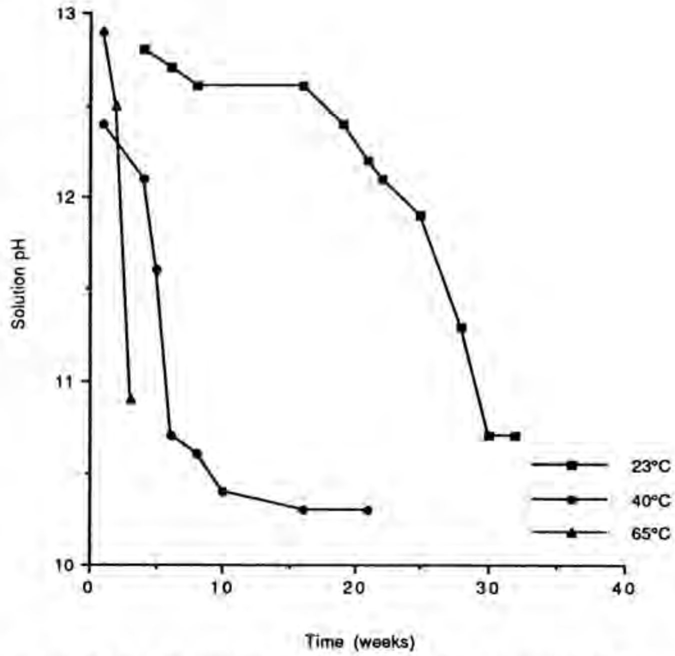

Fig. 4. Solution pH vs. time for 10 ppm copper-containing NaTPB solutions at 23°C, 40°C, and 65°C.

Effect of Oxygen

The role of oxygen in the decomposition mechanism was examined. Eliminating oxygen did not prevent the decomposition of NaTPB in the presence of Cu(II) ions. However, it did affect the course of the decomposition. This was observed in an experiment in which Cu(II)-containing NaTPB solutions were prepared in the absence of oxygen. Several properties associated with the decomposition process were different from what was observed when decomposition occurred in the presence of oxygen.

The most noticeable difference observed when comparing the two decomposition routes was that no change in the solution color occurred during decomposition in the absence of oxygen. An organic layer formed on the surface of the aqueous solution along with the formation of a white crystalline precipitate in the aqueous phase. The pH of the aqueous portion was determined to be approximately 12. Analysis of the organic layer by liquid chromatography identified benzene as the primary component along with smaller amounts of biphenyl, terphenyl, and a few unidentified compounds. No phenol or phenylboronic acid was observed in the organic layer.

Comparatively, decomposition of NaTPB in the presence of oxygen results in the solution turning a dark brown-black color. No organic layer or precipitate is observed. The

TABLE II
A Comparison of the Time Required Before a Noticeable Change is Observed in NaTPB Solutions with Three Different Copper (II) Concentrations at Three Different Temperatures.

	0.5 ppm Cu(II)		1.0 ppm Cu (II)		10. ppm Cu(II)	
Temperature (°C)	pH Change (weeks)	NaTPB Decomp. (weeks)	pH Change (weeks)	NaTPB Decomp. (weeks)	pH Change (weeks)	NaTPB Decomp. (weeks)
23	39	NC[a]	32	65	19	46
40	22	NC	8	10	4	5
65	3	5	3	3	3	3

[a] No change in NaTPB concentration was observed.

solution pH normally drops below 11. Finally, phenol and phenylboronic acid are produced as well as benzene, biphenyl, and other benzene ring derivatives.

CONCLUSIONS

Three principal factors were identified to affect the stability of NaTPB. These were: 1) the presence of copper(II) ions, 2) temperature, and 3) solution pH (hydroxide ion concentration). Copper (II) ion concentrations of 0.1 ppm or greater led to NaTPB decomposition. Elevated temperatures were demonstrated to increase the rate of NaTPB decomposition. Finally, the pH of NaTPB solutions was shown to be related to the solution's stability. The identification of these three main factors allows for: 1) identifying NaTPB solutions susceptible to decomposition, 2) predicting how long these solutions may remain stable and useable, 3) charting a solution's stability with monitoring procedures, and 4) stabilizing a decomposing solution for an extended period time.

The use of an inert atmosphere for storage of NaTPB was investigated. Results showed that decomposition occurred in both air and nitrogen. No noticeable change in the rate of decomposition was observed between the two environments. The course of decomposition was affected in the inert atmosphere. Different decomposition product distributions were observed. This verifies that oxygen does not play an initiator role in the NaTPB decomposition. However, oxygen is involved in a secondary reaction with the intermediate complexes produced during the initial stages of decomposition.

SUMMARY

The ITP process to be used at SRS will allow for the removal of soluble radionuclides from high level radioactive waste solutions. Success of the process depends on the ability to obtain the necessary cold feed chemicals. Therefore, it is mandatory that NaTPB solutions remain stable prior to their use. A thorough understanding of all factors which influence NaTPB stability is necessary to achieve this goal.

The results obtained from this project have resulted in an increased understanding of the NaTPB decomposition process. Potentially unstable NaTPB solutions can now be identified in advance of any decomposition symptoms. The expected shelflife of any potentially unstable NaTPB solutions can be predicted based on their copper concentration and storage temperature. Copper concentrations as low as 0.05 ppm produced decomposition of NaTPB solutions at 65°C. To ensure complete stability, copper must not be present in any quantity or form. However, under more moderate temperatures (25°C to 40°C) copper concentrations below 0.1 ppm may permit NaTPB solutions to remain stable for extended periods of time. The pH of NaTPB solutions can be periodically monitored to identify unstable solutions. Once an unstable NaTPB solution is identified, the addition of OH- to the solution will delay the decomposition process.

The NaTPB solution obtained for use at SRS will be stored under nitrogen. Decomposition properties of NaTPB in the absence of oxygen is therefore of interest. Research has shown that the elimination of oxygen from the NaTPB solution environment does not prevent NaTPB decomposition but does result in a different decomposition mechanism.

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