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SODIUM TETRAPHENYLBORATE SOLUTION STABILITY - A LONG TERM STUDY (U)

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SODIUM TETRAPHENYLBORATE SOLUTION STABILITY - A LONG TERM STUDY (U)

SUMMARY

Long term stability of aqueous alkaline solutions of sodium tetraphenylborate (NaTPB) has been investigated. The focus of the investigation is on the relative stabilities of NaTPB solutions exposed to varying temperatures and copper concentrations over an extended period of time. Additionally, vendor-supplied samples, incubated at 40°C, were stored for more than a year without decomposing. Collected data demonstrates that in the absence of elevated copper concentrations, NaTPB solutions will remain stable for periods of 1 to 2 years (at a minimum) at maximum expected operating conditions (<40°C). Additionally, biuret, $(H_2NCO)_2NH$, was tested as an additive to prevent copper-induced decomposition without success.

INTRODUCTION

NaTPB is a specialty chemical required for the In Tank Precipitation Process (ITP).[1,2] It precipitates cesium, aiding in the decontamination of high level radioactive waste solutions. Initially, it was obtained and stored in an aqueous solution having a composition of 0.55 ± 0.05 M NaTPB and 0.10 M NaOH.[3] Presently, all produced NaTPB solutions have been spray-dried and are being stored as a powder until needed. Of serious concern, however, was the observation that upon production, the NaTPB, in solution, showed varying degrees of stability.[4,5,6] This led to an initial investigation into the causes and prevention of NaTPB decomposition.[7] Copper ions, Cu(II), were identified as being a decomposition-inducing additive (impurity). During the initial testing, temperature was demonstrated to affect the rate of copper-induced, NaTPB decomposition. Additionally, the solution pH was shown to be both an indicator of impending decomposition as well as being a variable capable of affecting the rate of decomposition in copper-containing solutions. This document describes work aimed at providing a better understanding of NaTPB solution stability over extended periods of time.

DISCUSSION

Experimental Method and Details

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 (i.e. temperature). Long-term exposures (up to 2 years in some cases) were conducted to adequately determine the effect of the variables on the NaTPB solution's stability. Solutions were prepared from solid NaTPB. A.C.S. reagent grade NaTPB solid was purchased from the Aldrich Chemical Company with a purity greater than 99.5%.

Typical test solutions studied were 50 mL in volume with compositions of approximately 0.5 M NaTPB and 0.10 M NaOH. Copper (II) nitrate was added to the test solutions using microliter pipettes and prepared stock solutions. All test solutions were stored at temperatures of 75°C, 65°C, 40°C, or 23°C in the presence of oxygen. A laboratory oven was used to incubate the solutions at the elevated temperatures. All test solutions were stored in capped polyethylene bottles in the dark.

Four methods were utilized to monitor TPB^- decomposition. These were silver ion titration, pH, precipitation with potassium, and visual observation. Samples were analyzed for TPB^- concentration periodically using a TPB^--silver ion titration method.[8] Complete decomposition of TPB^- was typically verified by spot testing the NaTPB solutions with potassium chloride. When potassium ions, K^+, are exposed to TPB^- ions, a white precipitate (KTPB) forms. This spot test provides a simple and accurate way of determining if any TPB^- is present in the test solutions. Solution pH was found to be a useful method of monitoring NaTPB-solution stability. A drop in the pH was observed, in all solutions, prior to their decomposition. NaTPB-solution pH was measured using a pH meter equipped with a gel-filled combination pH electrode. 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 stability-status of a solution could be easily estimated. As an exception, there were a few cases in which the solution appearance indicated that decomposition had occurred, yet the TPB^- titration results and the other analyses proved otherwise.

Results

Temperature Dependence

Three principal factors which affect the stability of NaTPB were previously identified. These are 1) copper(II) ions, 2) temperature, and 3) solution pH. The focus of this investigation is on the relative stabilities of NaTPB solutions exposed to varying temperatures and copper concentrations over extended periods of time. Normal NaTPB solutions (0.5 M NaTPB and 0.1 M OH^-), at 65°C or less, are relatively stable over a long period of time. However, the addition of Cu(II) ions to the solution can render the solution unstable and, under certain conditions, result in the complete decomposition of the NaTPB in less than a few weeks. Experiments have shown that at elevated temperatures (65°C), Cu(II) concentrations of 0.1 ppm will initiate decomposition.[7] There are indications that even lower Cu(II) concentrations may result in decomposition given enough time. However, at more moderate temperatures, 40°C or less, these same solutions are relatively more stable. In some cases, solutions which would decompose in less than three weeks at 65°C remain stable for more than two years at room temperature (23°C). The two temperatures, 23°C and 40°C, represent what will most likely be the average and maximum expected temperatures which NaTPB feed solutions are likely to be exposed to in the ITP Cold Feeds Tank. Experiments were conducted to monitor the stability of NaTPB solutions at both 23°C and 40°C to better establish guidelines for predicting the shelf life of suspect copper-containing solutions. Test solutions containing copper (0.00 ppm to 100. ppm concentrations) were monitored for 18 to 23 months to observe the relative stabilities of the solutions under normal, or expected, temperatures. Data from these experiments at 23°C and 40°C are contained in Tables I and II respectively.

TABLE I. Effect of Copper(II) Concentration on NaTPB Stability at Room Temperature (23°C)

	NaTPB-Solution Molarity and pH							
	0.00 ppm Cu(II)		0.00 ppm Cu(II)		0.10 ppm Cu(II)		0.50 ppm Cu(II)	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	0.48	--	0.46	--	0.48	--	0.45	--
4	0.48	12.9	0.48	12.8	0.48	12.9	0.47	12.8
8	0.48	12.6	0.48	12.6	0.49	12.7	0.48	12.6
16	0.51	12.9	0.47	12.9	0.53	12.9	0.48	12.9
25	0.49	12.9	0.49	12.9	0.49	12.8	0.46	12.8
28	--	--	--	--	--	--	--	--
32	--	12.7	--	12.8	--	12.8	--	12.6
39	0.43	12.4	--	12.4	0.49	12.4	0.46	12.2
46	0.52	12.6	0.56	12.6	0.53	12.6	--	12.3
53	0.47	12.7	0.46	12.6	0.47	12.6	0.47	12.2
65	0.47	12.7	0.48	12.7	0.46	12.6	0.44	11.9
78	0.48	12.6	0.46	12.6	0.45	12.6	0.43	11.2
91	0.44	12.9	0.45	12.9	0.44	13.0	0.41	11.0
97	0.48	--	0.40	--	0.48	--	0.44	--

TABLE I. (continued from above)

	NaTPB-Solution Molarity and pH							
	1.00 ppm Cu(II)		10.0 ppm Cu(II)[a]		30.0 ppm Cu(II)		100. ppm Cu(II)	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1	0.44	--	0.48	--	0.48	--	0.44	--
4	0.46	12.8	0.48	12.8	0.48	12.8	0.47	12.8
8	0.47	12.6	0.48	12.6	0.47	12.6	0.46	12.6
16	0.47	12.8	0.48	12.6	0.51	12.8	0.45	12.8
25	0.45	12.6	0.46	11.9	0.47	12.7	0.47	12.7
28	--	12.6	0.52	11.3	--	12.7	--	12.7
32	--	12.3	0.51	10.7	--	12.5	--	12.6
39	0.46	11.8	0.49	9.9	0.52	12.0	--	12.1
46	0.54	11.8	0.37	9.9	0.45	12.1	0.51	12.2
53	0.46	11.0	0.29	10.2	0.47	12.1	0.46	12.5
65	0.42	10.7	0.24	--	0.43	10.7	0.44	12.4
78	0.40	10.5			0.40	10.5	0.43	--
[illegible]	0.38	10.7			0.32	10.5	0.42	--
97	0.41	--			0.32	--	0.45	--

[a]The 10.0 ppm Cu(II)-containing solution did not decompose completely after 65 weeks, but, rather, was exhausted by the periodic analyses.

TABLE II. Effect of Copper(II) Concentration on NaTPB Stability at 40°C

	NaTPB-Solution Molarity and pH							
	0.00 ppm Cu(II)		0.00 ppm Cu(II)		0.10 ppm Cu(II)		0.50 ppm Cu(II)	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
2	0.54	12.6	0.52	12.6	0.53	12.6	0.52	12.5
6	0.49	12.6	0.52	12.7	0.47	12.5	0.50	12.5
8	0.52	12.7	0.49	12.7	0.50	12.4	0.47	12.4
9	0.50	12.9	0.50	12.8	0.47	12.6	0.46	12.5
10	0.51	12.5	0.47	12.6	0.48	12.6	0.48	12.5
14	0.52	12.7	0.50	12.7	0.50	12.6	0.51	12.5
15	0.49	12.6	0.50	12.6	0.51	12.8	0.47	12.5
18	0.49	12.8	0.47	12.7	0.51	12.8	0.46	12.5
21	0.49	13.0	0.48	12.8	0.49	12.8	0.47	12.2
22	--	--	--	--	--	--	0.47	12.1
24	0.49	12.9	0.49	12.8	0.48	12.8	0.45	11.6
25	--	--	--	--	--	--	0.45	10.9
26	--	--	--	--	--	--	0.45	11.1
32	0.48	12.7	0.48	12.7	0.48	12.6	0.42	10.4
39	0.48	13.0	0.47	12.9	0.48	12.9	0.39	10.6
45	0.48	12.8	0.48	12.8	0.48	12.8	0.39	10.5
48	0.48	--	0.48	--	0.48	--	0.40	--
54	0.47	--	0.46	--	0.46	--	0.38	--
65	0.50	13.1	0.50	13.1	0.50	13.0	0.37	10.7
78	0.56	12.9	0.55	12.9	0.55	10.7	0.48	10.7

TABLE II. (continued from above)

	NaTPB-Solution Molarity and pH							
	1.00 ppm Cu(II)		10.0 ppm Cu(II)		30.0 ppm Cu(II)		100. ppm Cu(II)	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
2	0.50	12.5	0.49	12.5	0.50	12.5	0.53	12.5
6	0.46	12.3	--	10.7	0.50	12.5	0.50	12.6
8	0.45	12.1	--	10.6	0.48	12.4	0.46	12.6
9	0.47	12.0	--	10.4	0.46	12.5	0.49	12.6
10	0.19	10.9	--	10.4	0.49	12.5	0.47	12.6
14	0.04	10.4	--	10.3	0.55	12.4	0.49	12.5
15	0.04	10.4	--	10.3	0.47	12.4	0.47	12.6
18	0.04	10.4	0.03	10.3	0.46	12.0	0.46	12.5
21	0.03	10.4	0.02	10.3	0.47	11.9	0.47	12.8
22	0.03	10.4	0.02	10.3	0.46	11.3	0.46	12.6
24	0.03	10.5	0.02	10.4	0.43	10.7	0.45	12.6
25	DECOMPOSED		DECOMPOSED		0.22	10.5	0.45	12.5
26					0.01	10.6	--	--
32					DECOMPOSED		0.45	12.3
39							0.45	12.5
45							0.45	11.9
48							0.45	--
54							0.18	--
65							0.03	10.7
78							DECOMPOSED	

The data clearly indicate that copper-induced decomposition is temperature dependent. At 23°C, the 0.50, 1.00, 10.0 and 30.0 ppm Cu(II) samples were observed to have a significant decrease in pH over 97 weeks. Only the 10.0 and 30.0 ppm Cu(II) samples had a significant decrease in TPB^- concentration during that time and no sample was completely decomposed. At 40°C, all samples containing 0.1 ppm Cu(II) or more were observed to have a significant decrease in pH. At this temperature, all samples containing ≥1.00 ppm Cu(II) decomposed completely within 6 to 18 months of the start of the experiment. The rate of decomposition of TPB^- and the rate of change in pH are substantially increased at elevated temperatures. At 23°C, once decomposition begins, it is slow and drawn out over several weeks. At 40°C, decomposition, once started, occurs over a 2 to 3 week period. At 65°C, complete decomposition occurs in a few days.[7] A comparison of 0.10, 0.50, 1.00, and 10.0 ppm Cu(II)-containing NaTPB solution stability temperature data is shown in Table III. The data represents the length of exposure time accrued before an initial decrease in either the respective solution's pH or TPB^- concentration was observed.

TABLE III. Comparison of pH and Tetraphenylborate Stability of Copper(II)-Containing NaTPB Solutions at 23, 40, and 65°C (Number of weeks of exposure required to produce a significant decrease in pH and TPB^-)

	NaTPB-Solution Copper Concentration (Number of weeks required to observe a decrease in pH or TPB^-)							
	0.10 ppm Cu(II)		0.50 ppm Cu(II)		1.00 ppm Cu(II)		10.0 ppm Cu(II)	
Temperature	NaTPB	pH	NaTPB	pH	NaTPB	pH	NaTPB	pH
23°C	NC[a]	NC	NC	53	NC	32	46	25
40°C	NC	78	32	21	10	8	2	2 - 6
65°C[b]	9	6	5	1 - 3	1 - 3	1 - 3	1 - 3	3

[a]No significant change in value was observed during the test solution's lifetime

[b]Data previously reported in reference 7

Vendor-Produced NaTPB Stability

Table IV contains data collected from the incubation of vendor-produced NaTPB solution at both 40°C and 75°C. Three samples were monitored at 40°C and two others at 75°C. No substances were added to the samples and all were identical at the start of the experiment. The NaTPB solution was comprised of the first three batches of NaTPB produced by AFF for SRS. The solution contained 0.12 ppm residual copper. The samples were incubated at the two temperatures for 18 months. The data for the vendor-supplied sample is similar to that of 0.10 ppm Cu(II)-containing test samples reported in Table II and in earlier work.[7] The data clearly show the vendor-produced NaTPB solution is stable at 40°C for 18 months.

Effect of Biuret

In another experiment focused on NaTPB, an additive potentially capable of rendering copper inert in NaTPB solutions was tested in an effort to stabilize these solutions. The additive tested was biuret, $(H_2NCO)_2NH$. The NaTPB test solutions contained 10.0 ppm Cu(II). Biuret was added to these in concentrations ranging from 1.25 ppm to 100 ppm. Additionally, three blank NaTPB samples were tested for comparative purposes. One blank contained no Cu(II) and no biuret. A second blank contained 10.0 ppm Cu(II) and no biuret. The last contained no Cu(II) and 100 ppm biuret. The data shows that all Cu(II)-containing samples decomposed rapidly in 1 to 3 weeks. Both blanks without Cu(II) remained stable. The data is shown in Table V and indicates that biuret does not impede Cu(II)-induced decomposition. In fact, the data indicates that samples containing both biuret and Cu(II) may have decomposed at a slightly faster rate than the Cu(II)-containing sample without biuret. The TPB^- concentration in the two stable test solutions increases throughout the experiment. This is due to evaporation of water resulting in a concentrating effect.

TABLE IV. Vendor-Produced[a] NaTPB Stability at 40°C and 75°C

	NaTPB-Solution Molarity and pH									
	40°C		40°C		40°C		75°C[b]		75°C[b]	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
2	0.51	12.6	0.54	12.7	0.56	12.6	0.53	12.6	0.53	12.5
3	0.52	12.8	0.55	12.8	0.52	12.7	0.56	12.7	--	12.7
4	0.54	12.7	0.52	12.8	0.53	12.7	0.62	12.7	0.57	12.6
8	0.56	12.7	0.58	12.7	0.58	12.7	0.69	12.4	0.62	12.4
10	0.54	12.8	0.54	12.8	--	12.8	0.70	11.3	0.67	11.2
12	0.53	12.8	0.52	12.8	--	12.8	0.70	10.9	0.66	10.8
15	0.50	13.0	0.51	13.0	0.52	13.0	0.70	11.1	0.69	11.0
16	--	--	--	--	--	--	0.68	10.9	0.70	10.8
17	--	--	--	--	--	--	0.71	11.1	0.61	10.8
18	0.52	12.9	0.52	12.9	0.52	12.9	0.59	11.0	0.59	10.9
19	--	--	--	--	--	--	0.32	11.0		
21	0.52	13.1	0.52	13.0	0.52	13.0	0.30	--		
24	0.50	13.0	0.50	12.9	0.50	12.9				
28	0.50	12.7	0.49	12.7	0.50	12.7				
39	0.50	12.9	0.50	12.9	0.50	12.9				
58	0.51	13.3	0.52	13.2	0.51	13.2				
72	0.54	13.0	0.54	13.0	0.55	13.1				
78	0.57	13.1	0.59	13.1	0.58	13.1				

[a]All test solutions were taken from a 1 liter sample of NaTPB solution comprised of the first three batches of NaTPB produced (May 1990) for SRS. The AFF solutions tested contained 0.12 ppm residual copper.

[b]The 75°C test solutions did not decompose completely, but, rather, were exhausted by the periodic analyses.

CONCLUSION

Data demonstrates that in the absence of elevated copper concentrations, NaTPB solutions will remain stable for periods of 1 to 2 years (at a minimum) at maximum expected operating conditions (<40°C). NaTPB solutions containing a 0.10 to 100. ppm Cu(II) were incubated at both 23°C and 65°C. These were monitored for 18 to 23 months. At 23°C, the 0.50, 1.00, 10.0 and 30.0 ppm Cu(II) samples were observed to have a significant decrease in pH over 97 weeks. Only the 10.0 and 30.0 ppm Cu(II) samples had a significant decrease in TPB^- concentration during that time and none of the samples were completely decomposed. At 40°C, all samples containing 0.1 ppm Cu(II) or more were observed to have a significant decrease in pH. At this temperature, all samples containing ≥1.00 ppm Cu(II) decomposed completely. The rate of decomposition of TPB^- and the rate of change in pH were substantially increased at elevated temperatures. At 23°C, once decomposition began, it was slow and drawn out over several weeks. At 40°C, decomposition, once started, occurred over a 2 to 3 week period. In comparison, at 65°C, complete decomposition occurs in a few days.[7] In a separate experiment, vendor-supplied samples of NaTPB solution were incubated at 40°C for more than a year without decomposing. Additionally, biuret was tested as an additive to prevent copper-induced decomposition without success.

TABLE V. Effect of Biuret on the Stability of Copper(II)-Containing NaTPB at 65°C

	NaTPB-Solution Molarity and pH							
	0.00 ppm Cu(II) 0.00 ppm biuret		10.0 ppm Cu(II) 0.00 ppm biuret		0.00 ppm Cu(II)[a] 100. ppm biuret		10.0 ppm Cu(II) 1.25 ppm biuret	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1 (day 2)	0.44	13.1	0.24	13.0	0.43	13.1	0.26	13.0
1 (day 5)	0.45	13.1	0.06	12.4	0.43	13.1	0.06	12.4
2 (day 9)	0.45	13.1	0.04	11.8	0.43	13.2	0.04	11.7
2 (day 12)	0.45	13.2	0.04	11.4	0.43	13.2	0.04	11.4
3 (day 16)	0.44	13.2	0.02	11.2	0.43	13.1	0.02	11.2
3 (day 20)	0.48	13.0	0.01	11.0	0.46	13.1	DECOMPOSED	
4	0.49	13.0	DECOMPOSED		0.47	13.0		
8	0.49	13.2			0.47	13.2		
12	0.50	13.0			0.49	13.0		
16	0.53	13.4			0.53	13.3		
20	0.57	13.4			0.55	13.4		
24	0.56	13.0			0.56	12.9		
28	0.60	13.1						
32	0.63	12.9						
39	0.72	12.4						

TABLE V. (continued from above)

	NaTPB-Solution Molarity and pH							
	10.0 ppm Cu(II) 5.00 ppm biuret		10.0 ppm Cu(II) 10.0 ppm biuret		10.0 ppm Cu(II) 50.0 ppm biuret		10.0 ppm Cu(II) 100. ppm biuret	
Time (weeks)	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH	NaTPB (M)	pH
1 (day 2)	0.23	13.0	0.21	12.9	0.17	12.9	0.14	12.9
1 (day 5)	0.06	12.3	0.05	12.3	0.05	12.2	0.03	12.1
2 (day 9)	0.04	11.7	0.04	11.7	0.03	11.6	0.02	11.6
2 (day 12)	0.03	11.4	0.03	11.4	0.02	11.3	0.01	11.3
3 (day 16)	0.02	11.2	0.02	11.2	0.01	11.2	DECOMPOSED	
	DECOMPOSED		DECOMPOSED		DECOMPOSED			

[a]The 100 ppm Biuret-0.00 ppm Cu(II)-containing solution did not decompose after 24 weeks, but, rather, was exhausted by the periodic analyses.

QUALITY ASSURANCE

All work was conducted in accordance with the SRL Quality Assurance Program. Data are recorded in Laboratory Notebooks WSRC-NB-89-11, pp. 3-158 and WSRC-NB-90-161, pp. 7-62. Salt solutions were prepared from reagent grade chemicals. TPB^- titration analyses were performed by the DWPT Analytical Laboratory at TNX. A sloped calibration of the pH meter was conducted prior to its use each day.

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