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The Solubilities of Significant Organic Compounds in HLW Tank Supernate Solutions -- FY1995 Progress Report

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THE SOLUBILITIES OF SIGNIFICANT ORGANIC COMPOUNDS IN HLW TANK SUPERNATE SOLUTIONS – FY1995 PROGRESS REPORT

G. S. Barney

ABSTRACT

The solubilities of six metal salts of organic acids that are thought to exist in high-level waste at the Hanford Site were measured in tank supernate simulant solutions during FY1995. This solubility information will be used to determine if these organic salts could exist in solid phases (saltcake or sludges) in the waste where they might react violently with the nitrate or nitrite salts present in the tanks. Solubilities of sodium glycolate, succinate, and caproate salts; iron and aluminum dibutylphosphate salts; and aluminum oxalate were measured in simulated waste supernate solutions at 25 °C, 30 °C, 40 °C, and 50 °C. The organic compounds were selected because they are expected to exist in relatively high concentrations in the tanks. The tank supernate simulant was a 4.0 M sodium nitrate - 0.97 M sodium nitrite solution with sodium hydroxide concentrations ranging from 0.00003 M to 2.0 M. The solubilities of sodium glycolate, succinate, caproate, and dibutylphosphate in HLW tank supernate solutions were high over the temperature and sodium hydroxide concentration ranges expected in the tanks. The solubilities of these compounds are similar (in terms of total organic carbon) to sodium citrate, formate, ethylenediaminetetraacetate, and nitrilotriacetate which were measured previously. High solubilities will prevent solid sodium salts of these organic acids from precipitating from tank supernate solutions. The total organic carbon concentrations (TOC) of actual tank supernates are generally much lower than the TOC ranges for the simulated supernate solutions saturated (at the solubility limit) with the organic salts. This is true even if all the dissolved carbon in a given tank supernate is due to only one of these eight soluble compounds (an unlikely situation). Metal ion complexes of dibutyl phosphate and oxalate in supernate solutions were not stable in the *presence of free hydroxide concentrations expected in most tanks. Iron and aluminum dibutyl phosphate compounds reacted with hydroxide to form soluble sodium dibutyl phosphate and precipitated iron and aluminum hydroxides. Aluminum oxalate complexes were also not stable in the basic simulated supernate solutions. Solubilities of all the organic salts decrease with increasing sodium hydroxide concentration because of the common ion effect of* Na^+*. Increasing temperatures raised the solubilities of the organic salts, especially the succinate and caproate salts.*

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ACRONYMS AND TERMS

DBP	dibutyl phosphate
DSS	double-shell slurry
EDTA	ethylenediaminetetraacetate
ED3A	ethylenediaminetriacetate
HDBP	dibutyl phosphoric acid
HEDTA	N-(hydroxyethyl)ethylenediaminetriacetate
HLW	high-level waste
IDA	iminodiacetate
NTA	nitrilotriacetate
TBP	tributyl phosphate
TOC	total organic carbon
NPH	normal parrafin hydrocarbon
NCRW	neutralized cladding removal waste

THE SOLUBILITIES OF SIGNIFICANT ORGANIC COMPOUNDS IN HLW TANK SUPERNATE SOLUTIONS – FY1995 PROGRESS REPORT

G. S. Barney

1.0 INTRODUCTION

This report is a summary of work completed in FY1995 on the measurement of solubilities of organic compounds found in high-level waste (HLW) supernate solutions at Hanford. An earlier report (Barney 1994) presented the solubilities of five organic compounds known to exist in the wastes [sodium oxalate, formate, citrate, ethylenediaminetetraacetate (EDTA), and nitrilotriacetate (NTA)]. The present document reports laboratory solubility measurements for additional compounds known or thought to exist in the wastes. These compounds are sodium glycolate, sodium succinate, sodium caproate (hexanoate), aluminum dibutylphosphate, iron dibutylphosphate, and aluminum oxalate.

The overall objective for these solubility measurements is to obtain solubility data that will allow prediction of whether or not significant quantities of organics exist as solids in the HLW tanks. Knowledge of which phase (liquid or solid) the organic compounds are in is important to safety analyses of the waste tanks and also to operations where the phases are separated (salt well pumping, evaporation-crystallization, etc.). These data will also allow better estimates of how organic compounds in the wastes were distributed to different tanks after transfer operations.

The safety concern for tanks containing high concentrations of organic compounds is that the organics might react violently with nitrate or nitrite salts, which are also present in the tanks, to produce heat and gaseous compounds. The organic compounds and oxidizing salts must be present mainly in a solid form and the organic compounds must be present in a minimum concentration for a hazardous, self-propagating reaction to occur. The preliminary safety criteria (Webb et al. 1995) indicate that any waste organic-nitrite/nitrate mixture containing water concentrations greater than 20% by weight is safe and will not propagate. At or below this water concentration, the organic compounds in the waste must be present mainly as solids at the minimum total organic carbon (TOC) concentration range (4.5% to 7.9% by weight, depending on water content) that allows propagating reactions. The solubilities of the organic compounds in the waste supernate solutions must therefore be exceeded to have a propagating mixture present in the waste. If the organic solubilities are known and are compared with concentrations found in the waste supernate solutions, the presence of solid organic compounds can be predicted.

Prior measurements of the solubilities of sodium salts of formic acid, citric acid, EDTA, and NTA (Barney 1994) show that they are quite soluble in simulated supernate solutions. Their solubilities are much higher than any known TOC measurements of actual waste tank supernate solutions. This observation leads to the conclusion that none of these salts exist as solids in the tanks and that they will not form a propagating mixture. This, of course, assumes that the tank supernates analyzed are in equilibrium with the solid waste mixtures. Sodium oxalate solubilities were found to be relatively low and this compound could precipitate from some tank supernate solutions. The energy content of sodium oxalate is small, however.

Analyses of the organic components of several high-level wastes from different Hanford Site tanks have identified significant compounds. Campbell et al. (1994, 1995) analyzed core segments from tanks 241-SY-101 and 241-SY-103 and found the major organic components to be salts of chelating agents and low molecular weight carboxylic acids. The major chelating compounds were EDTA, NTA, citric acid, iminodiacetic acid (IDA), succinic acid, and ethylenediaminetriacetic acid (ED3A). The major low molecular weight carboxylic acids were oxalic, formic, glycolic, and acetic acids. Toste et al. (1988) identified organic compounds in a neutralized cladding removal waste (NCRW) and a double-shell slurry waste (DSS). They found citric acid, EDTA, tributyl phosphate, long chain hydrocarbons, and long chain carboxylic acids to be the major compounds present.

Two of the compounds found by analysis of the wastes and not previously studied were chosen for the present solubility studies. They are sodium salts of glycolic acid and succinic acid. The sodium salt of caproic acid (or hexanoic acid) was chosen because it is a likely degradation product (Babad et al. 1993) of the normal paraffin hydrocarbon (NPH) solvent used in the PUREX Process. Dibutyl phosphate (DBP) salts of aluminum and iron were chosen for study because DBP may be present in the wastes as a hydrolysis product of the large amounts of tributyl phosphate (TBP) that were added to the waste tanks. Aluminum oxalate solubility was measured to determine if soluble metal complexes could affect organic solubilities. The solubilities of these compounds were measured in simulated HLW supernate solutions containing sodium nitrate, sodium nitrite, and sodium hydroxide, which are major components of the HLW. Initially, the simulant contained 4.0 $\underline{M}$ sodium nitrate, 0.97 $\underline{M}$ sodium nitrite, and sodium hydroxide concentrations that ranged from 0.00003 $\underline{M}$ to 2.0 $\underline{M}$. Temperatures during solubility measurements were controlled to ± 0.1 °C over the range of 25 °C to 50 °C. These values approximate conditions expected in the tanks so that the solubility data can be used to estimate solubilities in the actual wastes.

The solubilities of some of the salts of relevant organic compounds have been measured in pure water. These solubility data were used as starting points for designing the solubility measurements. The available literature data are summarized in Table 1-1.

2.0 EXPERIMENTAL

2.1 Materials And Equipment

All starting chemicals used in these measurements were reagent grade except for the dibutylphosphoric acid, which was technical grade (Baker Chemical Company) and was purified before using by extracting the monobutylphosphoric acid impurity from it with water washes. All solutions were prepared using purified, deionized water. Mixtures of solid sodium salts of the organic acids and solutions of sodium nitrate, sodium nitrite, and sodium hydroxide were continuously equilibrated in a water shaker bath (Precision Scientific Model 50) with a constant temperature accuracy of ± 0.1 °C. The mixtures were contained in 50 mL polypropylene

Table 1-1. Solubilities of organic salts found in the literature.

Compound Formula	Compound Name	Solution Composition	Observations	References
$NaC_2H_3O_3$	Sodium Glycolate	No data was found	No data was found	No data was found
$Na_2C_4H_4O_4 \cdot 6H_2O$	Sodium Succinate	Water	In water solubility ranges from 25.87 to 36.02 Wt.% at 25 to 50 °C, respectively.	Marshall and Bain (1910)
$NaC_6H_{11}O_2$	Sodium Caproate (Hexanoate)	No data was found	No data was found	No data was found
$AlC_{24}H_{54}O_{12}P_3$	Aluminum Tri-dibutylphosphate	No data was found	No data was found	No data was found
$FeC_{24}H_{54}O_{12}P_3$	Iron Tri-dibutylphosphate	No data was found	No data was found	No data was found
$Al_2C_6O_{12} \cdot xH_2O$	Aluminum Oxalate	Water	Almost insoluble.	The Merck Index, (1968)

centrifuge tubes with screw caps so that an airtight seal could be maintained during equilibrium. Mechanical shaking of the mixtures shortened the equilibration times. The initial concentrations of sodium nitrate and sodium nitrite in the simulated HLW tank liquor were 4.0 M and 0.97 M, respectively. Initial sodium hydroxide concentrations varied from 0.0003 M to 2.0 M.

Aluminum and iron dibutylphosphate compounds were prepared by precipitating these insoluble compounds from aqueous solution. First, dibutylphosphoric acid (HDBP)was purified by washing the technical grade material with about four parts deionized water in a separatory funnel. This was repeated four additional times to remove the much more soluble monobutylphosphoric acid. The HDBP was weighed out and dissolved in a volume of deionized water by slowly adding a solution of sodium hydroxide. A solution of either $Al(NO_3)_3$ or $Fe(NO_3)_3$ was then added dropwise, forming the insoluble $Al(DBP)_3$ or $Fe(DBP)_3$, until a mole ratio of 3:1 DBP:Al or Fe was reached. The precipitate was washed thoroughly and air-dried for several days. About 91 % of the theoretical yield was obtained for $Al(DBP)_3$ and 116 % for $Fe(DBP)_3$.

2.2 Analyses

Measurements of concentrations of sodium salts of nitrate, nitrite, glycolate, succinate, dibutyl phosphate, and oxalate were performed using liquid chromatography. A Dionex* Model DX-500 liquid chromatograph with either a conductivity detector or a UV absorption detector was used for all these analyses. Standard solutions for calibration of the chromatograph were prepared from reagent chemicals except for DBP. A DBP standard solution was prepared from the recrystallized barium salt of DBP which was made according to a procedure reported by Higgins and Baldwin (1965). Standards were run before and after each set of analyses. The observed errors in the analyses of the standards were generally less than 5% relative error.

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* Dionex is a registered trademark of Dionex Corporation, Sunnyvale California.

Sodium caproate concentrations were determined by measuring the dissolved TOC using a Dohrmann DC-180 total organic carbon analyzer (Dohrmann, Santa Clara, California). This analyzer was used in the NPOC or non-purgeable organic carbon mode in which inorganic carbon was removed by adding acid and the resulting solution was sparged with oxygen gas before analysis of the caproate. The caproate TOC was analyzed by oxidizing it to carbon dioxide and then measuring the amount of carbon dioxide produced. The instrument was calibrated with 99.5+ % hexanoic acid (Aldrich Chemical Co., Inc.). Each calibration standard and sample was analyzed four times and the relative standard deviations ranged from about 4 % at 4 ppmC to 1 % at 56 ppmC.

2.3 Methods

Solubilities were determined by measuring concentrations of organics in the aqueous phase of simulated HLW waste mixtures equilibrated at a constant temperature. Solubilities were measured at 25 °C, 30 °C, 40 °C, and 50 °C. The sodium salt of the organic compound being tested was always present as a crystalline solid during the measurements to ensure saturation of the aqueous solution. The procedure used for conducting the solubility measurements addressed the following four requirements for solubility determination:

1. The temperature of the equilibrating mixtures must be maintained at a constant value.
2. The attainment of equilibrium in the mixtures before sampling the phases must be proven.
3. Sampling the liquid and solid phases must be accomplished without affecting the composition of the phases.
4. The liquid and solid phases must be analyzed to determine their composition and the crystalline identity of the solids.

To determine whether equilibrium had been reached at a given temperature, equilibrium was approached from undersaturation and supersaturation. Also, changes in organic concentrations in the aqueous phases were monitored over time. Solubility equilibrium was achieved if the organic concentrations remained constant over time and the solubilities from undersaturation and supersaturation were the same. Measurements from undersaturation were performed by equilibrating mixtures at the lowest temperature (25 °C), measuring organic concentrations over time, and then repeating the equilibration at increasing temperature steps of 30 °C, 40 °C, and 50 °C. Equilibration from supersaturated solutions was accomplished by heating the mixtures at 60 °C for two days, cooling and equilibrating at 50 °C, and then repeating the equilibrations at decreasing temperature steps of 40 °C, 30 °C, and 25 °C.

Required equilibration times were determined by sampling a given solution periodically until a constant concentration of dissolved organic was observed. Samples of the equilibrated mixtures were removed from the centrifuge tubes and placed in 5-mL syringes fitted with syringe filters (0.45 µm, polytetrafluoroethylene). The syringe, filter, and a vial used to receive the filtrate were pre-equilibrated at the sample temperature to prevent crystallization or dissolution during filtration. Approximately 2 mLs of the mixture were filtered through the syringe filter. Exactly 1.000 mL of the filtrate was diluted with 10.00 mLs of deionized water to prevent crystallization. These diluted samples were then analyzed by ion chromatography or by TOC analysis.

To simplify the analyses of the liquid and solid phases, only one organic compound was used in each mixture. This prevented interferences and eliminated the need for separations before analysis.

3.0 RESULTS AND DISCUSSION

3.1 Solution Densities

The densities of solutions saturated with the organic salts were measured at 25 °C so that concentrations in molalities or weight percent could be calculated from the molar concentrations given in this study. Densities of glycolate and succinate solutions were also measured at 30 °C, 40 °C and 50 °C, but were not measurably different from the 25 °C densities. The solution densities are also an indication of the concentrations of the sodium salts in solution because the salts are more dense than water. Table 3-1 compares densities of the simulant solution with saturated solutions of organic salts at 25 °C. Densities of the sodium glycolate saturated solutions are the highest and reflect the high solubility of this salt in the simulated supernate solutions. Solutions saturated with sodium succinate and caproate are more dense than the starting simulant solution and suggest appreciable solubilities for these salts.

Table 3-1. Densities of the simulated supernate solutions and supernate solutions saturated with organic salts at 25 °C.

Initial	Densities of Saturated Solutions at 25 °C, g/mL			
[NaOH], M	Simulant	Glycolate	Succinate	Caproate
0.00003	1.250	1.399	1.289	1.281
0.001	1.255	1.398	1.299	1.277
0.01	1.244	1.402	1.299	1.277
0.1	1.253	1.363	1.299	1.278
0.5	1.258	1.404	1.304	1.283
1.0	1.286	1.404	1.316	1.292
2.0	1.320	1.421	1.333	

3.2 Evidence For Equilibrium

Evidence for attainment of dissolution/crystallization equilibrium was obtained at each of the four temperatures studied. As described in the Methods section, solubilities were measured from undersaturation and supersaturation. The temperature was held constant over a period of time to allow equilibration. Because the time required for equilibration was unknown, samples of the aqueous phases were taken periodically to monitor changes in organic concentrations. An example of the data obtained at 40 °C is shown in Table 3-2. Each organic concentration shown in the table is an average for

Table 3-2. Average concentrations of organics versus time at 40 °C over all sodium hydroxide concentrations.

Equilibration Time, Days	Average [Glycolate], M	Average [Succinate], M	Equilibration Time, Days	Average [Caproate], M
From Undersaturation			From Undersaturation	
7	4.35	1.02	2	1.48
13	4.50	1.38	4	1.45
25	4.49	1.47	11	1.56
From Supersaturation			From Supersaturation	
7	5.18	1.71	6	ND*
15	5.18	1.69	9	1.43
22	5.18	1.61	23	1.50

*ND = not determined.

seven solutions having different initial sodium hydroxide concentrations (see Table 3-1) so that an overall trend of dissolution or crystallization could be observed. The data from undersaturation measurements clearly show that glycolate and succinate concentrations increased over the 25-day period and did not reach equilibrium after this time. In contrast, sodium caproate appeared to reach equilibrium after only two days. From supersaturation, equilibrium was attained more rapidly for glycolate and succinate. The equilibrium solubility values reported here for glycolate and succinate are those obtained from supersaturation and those reported for caproate, aluminum and iron dibutyl phosphate are those obtained from undersaturation.

3.3 Solution Volume Increases

Because of their high solubilities, dissolution of sodium glycolate, succinate, caproate, aluminum dibutylphosphate, and iron dibutylphosphate in the simulant solutions resulted in significant volume increases in these solutions. This volume increase caused a corresponding dilution of the initial concentrations of sodium nitrate, nitrite, and hydroxide. The volume increases shown in Table 3-3 (for sodium hydroxide concentrations less than 0.1 M) were calculated from the change in concentration of nitrate after dissolution of the organics, according to the equation,

% Volume Increase = 100(1 - Final Nitrate Concentration/Initial Nitrate Concentration).

3.4 Sodium Glycolate Solubility

Sodium glycolate is very soluble in simulated HLW supernate solutions. At low sodium hydroxide concentrations, glycolate solubilities as high as 5.8 M were observed. Solubilities increased as the temperature was raised, and the temperature effect on solubility was relatively large compared to the other compounds studied thus far. Figure 3-1A shows that the solubility decreased as sodium hydroxide concentration increased, probably because of the common ion effect of Na^+. No solubility data for sodium glycolate could be found in the chemical literature to compare with the results presented here. The effect of diluting the original simulant solution by

Table 3-3. Volume increases due to dissolution of organic salts.

	% Volume Increase			
Organic Salt	50 °C	40 °C	30 °C	25 °C
Glycolate	36	32	31	25
Succinate	43	32	22	19
Caproate	18	17	15	15
Aluminum Dibutylphosphate	ND*	ND	22	16
Iron Dibutylphosphate	ND	ND	26	23

*ND = not determined.

sodium glycolate dissolution can be seen in Figure 3-1B. The original nitrate and nitrite concentrations (4.0 M and 0.97 M, respectively) have been diluted by 25 to 36%. At higher hydroxide concentrations, nitrate and nitrite concentrations increase due to the decreasing solubility of the glycolate. Detailed solubility measurement data for all organic salts studied thus far are given in the Appendix. Sodium glycolate does not appear to form crystalline hydrates, but exists as $NaOOCCH_2OH$ at equilibrium with the simulated waste solutions.

3.5 Sodium Succinate Solubility

Sodium succinate was quite soluble in the simulated HLW supernate solutions. At low sodium hydroxide concentrations, succinate solubilities as high as 2.3 M were observed. Solubilities increased as the temperature was raised, and the temperature effect on solubility was very large compared to the other compounds studied thus far. Solubilities were lowered significantly by increasing the sodium hydroxide concentration, as shown in Figure 3-2A. This is due to the common ion effect of Na^+ and the effects of high ionic strength in the simulant solutions. The 16 % and 29% (by mass) solubility at 25 °C and 50 °C measured in this study at the lowest hydroxide concentrations are significantly lower than that reported by Marshall and Bain (1910) for solubility in pure water (26 and 36 Wt. %, respectively). This is due to the common ion effect of Na^+ and the effects of high ionic strength in the simulant solutions. The effect of diluting the simulant by sodium succinate dissolution on nitrate and nitrite concentrations can be seen in Figure 3-2B. The original nitrate and nitrite concentrations (4.0 M and 0.97 M, respectively) have been diluted by 19% to 43%. At higher hydroxide concentrations, nitrate and nitrite concentrations increase due to the decreasing solubility of the succinate. The solid phase compound observed by Marshall and Bain over the 25 °C to 50 °C temperature range was $(CH_2COONa)_2 \cdot 6H_2O$. This compound is also expected to be present in the present equilibrium solubility mixtures.

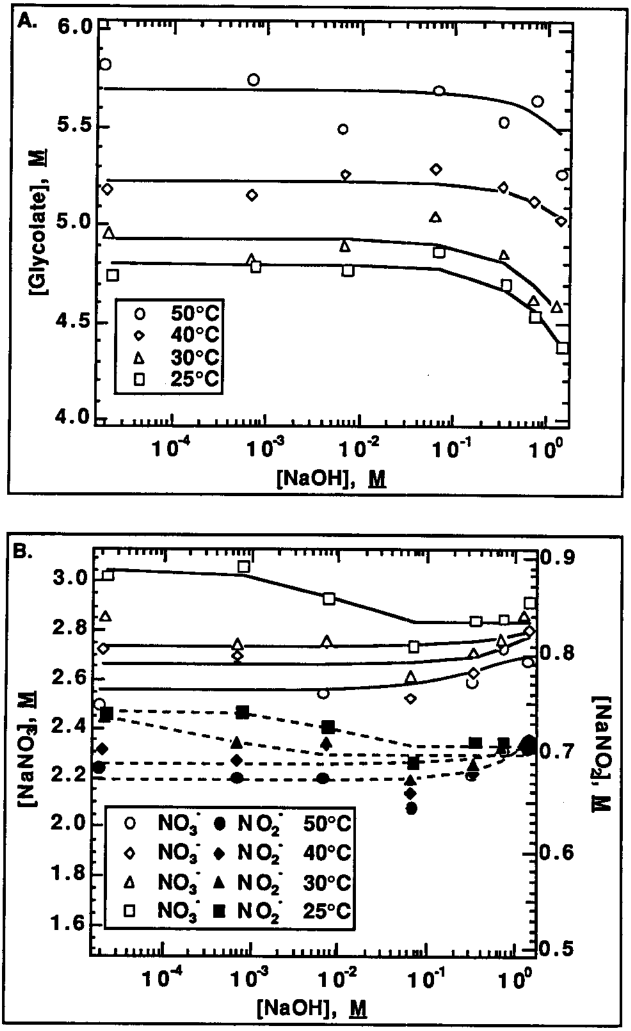

Figure 3-1. Solubility of sodium glycolate in $NaNO_3$ - $NaNO_2$ solutions at 25 °C, 30 °C, 40 °C, and 50 °C for various sodium hydroxide concentrations (A), and measured sodium nitrate and nitrite concentrations in the same solutions (B).

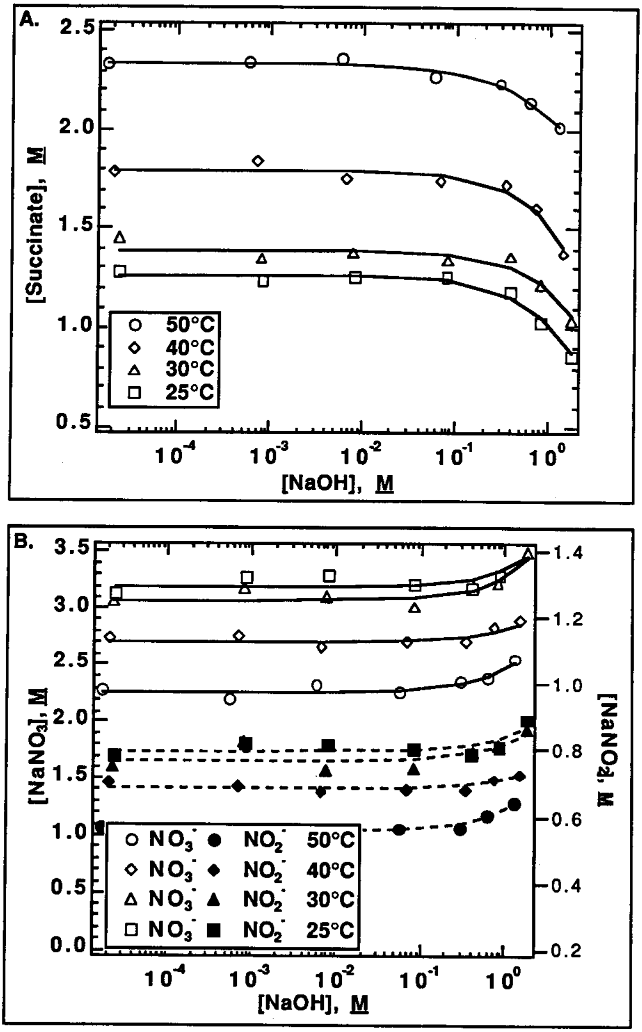

Figure 3-2. Solubility of sodium succinate in $NaNO_3$ - $NaNO_2$ solutions at 25 °C, 30 °C, 40 °C, and 50 °C for various sodium hydroxide concentrations (A), and measured sodium nitrate and nitrite concentrations in the same solutions (B).

3-6 Sodium Caproate Solubility

Sodium caproate (hexanoate) was quite soluble in the simulated HLW supernate solutions as long as sodium hydroxide concentrations were kept low. At low sodium hydroxide concentrations, caproate solubilities as high as 1.8 M were observed. Solubilities increased as the temperature was raised, and the temperature effect on solubility was relatively small compared to the other compounds studied thus far. Solubilities were lowered significantly by increasing the sodium hydroxide concentration, as shown in Figure 3-3. This is because of the common ion effect of Na^+ and the effects of high ionic strength in the simulant solutions. No solubility data for sodium caproate could be found in the literature to compare with the results presented here.

3-7 Aluminum and Iron Dibutyl Phosphate Solubilities

Attempts to prepare pure sodium dibutyl phosphate for solubility measurements were not successful. Because of its high solubility in water, the pure sodium compound could not be crystallized from solution. Aluminum and iron salts of DBP are known to be quite insoluble in water and might exist as solids in the high-level wastes. These compounds were prepared as described in the Experimental Section and used in solubility measurements. The HLW simulant solutions were used as in the previous solubility measurements.

It was found that the solubility of both aluminum and iron dibutyl phosphate was directly proportional to the original sodium hydroxide concentrations. This is explained by the following hydrolysis reactions:

$$Al(DBP)_3 + 3OH^- = Al(OH)_3\downarrow + 3DBP^-$$

$$Al(DBP)_3 + 4OH^- = Al(OH)_4^- + 3DBP^-$$

$$Fe(DBP)_3 + 3OH^- = Fe(OH)_3\downarrow + 3DBP^-.$$

Figures 3-4A and 3-5A show DBP concentrations in solutions equilibrated with excess aluminum and iron dibutyl phosphate for various initial sodium hydroxide concentrations. Above 0.01 M initial hydroxide, the slopes of these curves are nearly one. This suggests that each mole of hyroxide in the original solution reacts with $Al(DBP)_3$ and $Fe(DBP)_3$ to yield one mole of DBP in solution. Precipitates of aluminum hydroxide and iron hydroxide were observed, as expected.

As much as 0.94 M dibutyl phosphate was measured in these solubility experiments. This is not the maximum solubility for sodium dibutyl phosphate since the concentration in solution was limited by the initial sodium hydroxide concentration (1.0 M). The solubility of sodium dibutyl phosphate is greater than 0.94 M. No dibutyl phosphate compounds should be expected in the solid phases in the high-level waste tanks at Hanford as long as free hydroxide is present in the supernate.

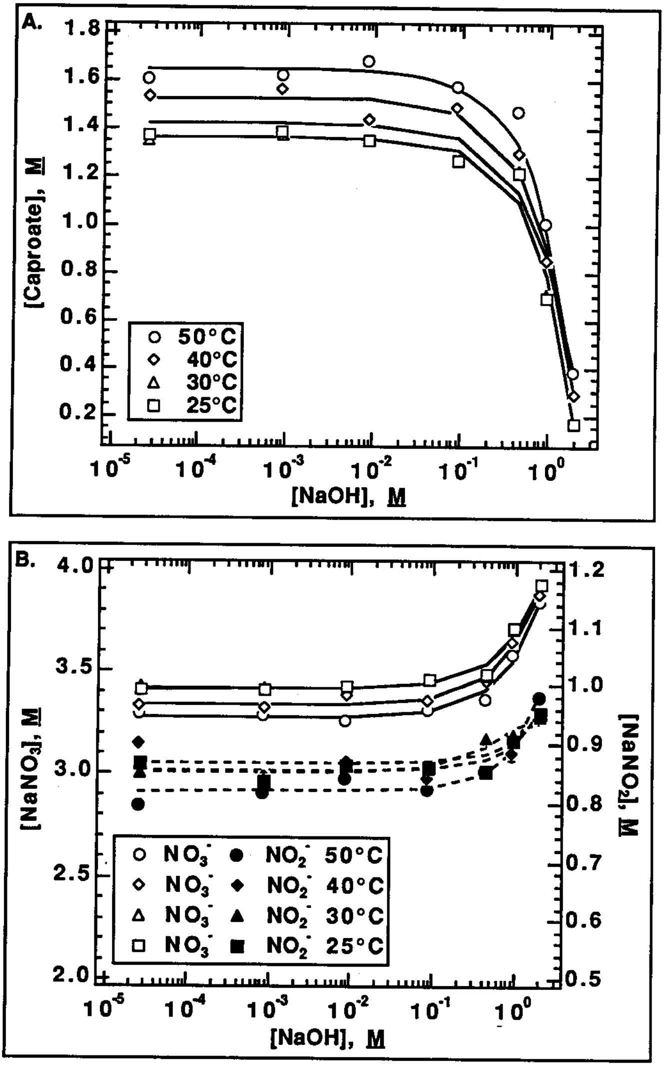

Figure 3-3. Solubility of sodium caproate in $NaNO_3$ - $NaNO_2$ solutions at 25 °C, 30 °C, 40 °C, and 50 °C for various sodium hydroxide concentrations (A), and measured sodium nitrate and nitrite concentrations in the same solutions (B).

The upper, linear portion of the curves in Figures 3-4A and 3-5A show no temperature effect. The curves at low initial hydroxide concentration flatten out and show a significant temperature effect. At low hydroxide concentrations, dissolution of the unreacted $Al(DBP)_3$ and $Fe(DBP)_3$ controls the concentration of total DBP in solution. The solubilities of these compounds are higher at 30 °C than at 25 °C.

The concentrations of sodium nitrate and sodium nitrite in the DBP solution, shown in Figures 3-4B and 3-5B, are significantly lowered as more DBP dissolves. The solution volume increases due to DBP dissolution range from 16 to 26 percent. Both nitrate and nitrite concentrations are higher at 25 °C than 30 °C due to lower DBP solubility at 25 °C.

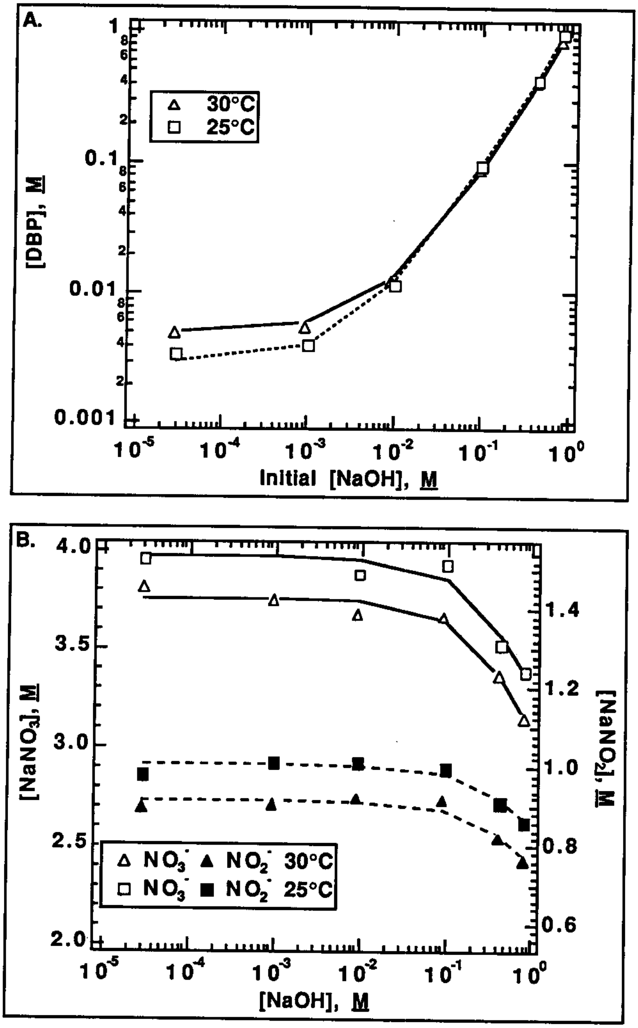

Figure 3-4. Solubility of aluminum dibutylphosphate in $NaNO_3$ - $NaNO_2$ solutions at 25 °C and 30 °C for various initial sodium hydroxide concentrations (A), and measured sodium nitrate and nitrite concentrations in the same solutions (B).

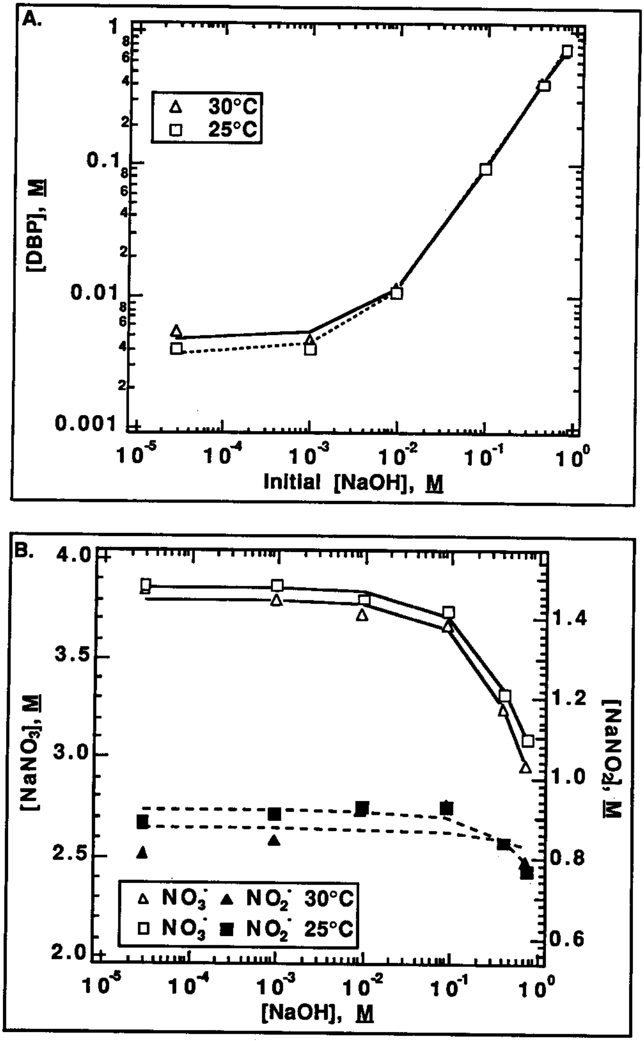

Figure 3-5. Solubility of iron dibutylphosphate in $NaNO_3$ - $NaNO_2$ solutions at 25 °C and 30 °C for various initial sodium hydroxide concentrations (A), and measured sodium nitrate and nitrite concentrations in the same solutions (B).

3.8 Effects of Aluminum on Oxalate Solubility

The presence of metal ions in the high-level waste could affect the solubility of organic anions by forming soluble complexes or by forming insoluble precipitates. Since aluminum is one of the most abundant components of the waste, experiments were performed to determine the effects of the presence of aluminum hydroxide on oxalate solubility over a range of sodium hydroxide concentrations. Five different mixtures of HLW simulant containing precipitated aluminum hydroxide were prepared for testing. Each 50 mL solution contained 4.0 M $NaNO_3$ and 1.0 M $NaNO_2$. Sodium hydroxide concentrations were 0.01, 0.1, 1.0, 2.0, and 3.0 M. The amounts of aluminum hydroxide (0.33 M) and sodium oxalate (1.0 M) were the same in each mixture. The solutions were equilibrated at 25 °C, 30 °C, 40 °C, and 50 °C and concentrations of total oxalate were measured at each temperature. The concentrations are compared with the solubility curves for pure sodium oxalate in Figure 3-6.

The oxalate concentrations are not significantly affected by the presence of aluminum hydroxide. Aluminum is known to form a strong complex with oxalate in acid solutions. The formation constants for successive addition of oxalate ligands are $K_1 = 10^{7.26}$, $K_2 = 10^{4.85}$, and $K_3 = 10^{1.31}$ (Sillen and Martell, 1964). Formation constants for successive addition of hydroxide ligands are $K_1 = 10^{8.98}$, $K_2 = 10^{9.72}$, $K_3 = 10^{8.31}$, and $K_4 = 10^{5.66}$ (Lindsay 1979). The higher formation constants for aluminum hydroxide complexes indicates that oxalate complexes are

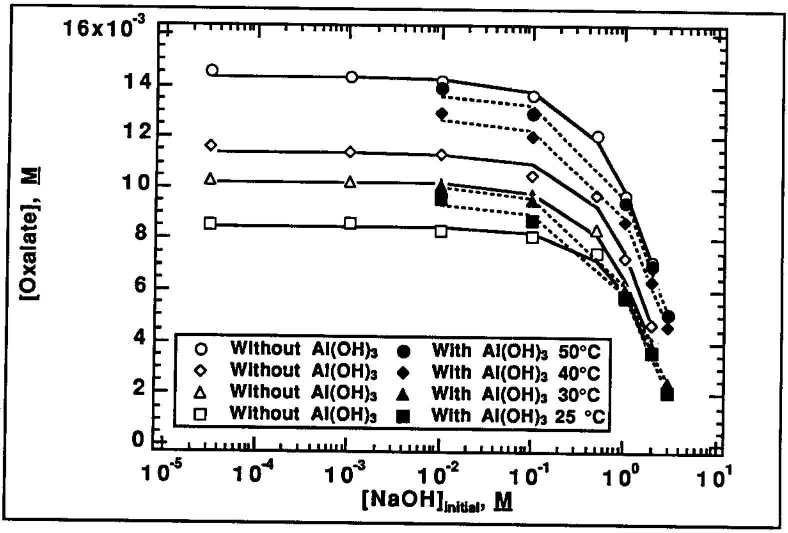

Figure 3-6. Solubility of sodium oxalate in $NaNO_3$ - $NaNO_2$ solutions at 25 °C, 30 °C, 40 °C, and 50 °C for various sodium hydroxide concentrations in the presence and absence of aluminum hydroxide.

important only at low pH values. As long as the hydroxide concentrations in tank supernates is greater than about 0.01 M, aluminum oxalate complexes will not form in significant amounts.

3.9 HLW Tank Total Organic Carbon Values

The solubility data presented above can be used to determine if solid sodium salts of organic compounds can exist in the HLW tanks at the Hanford Site. If concentrations of these salts measured in the supernate solutions are near the solubility limits measured in this study, then solid organic salts can be presumed to be present in the waste (assuming, of course, that the supernate is in equilibrium with the salts). Ideally, concentrations of the individual salts in actual supernate solutions should be obtained. Unfortunately, only TOC concentrations have been measured in supernate solutions for most of the waste tanks. The TOC values in grams of organic carbon per liter of solution have been collected for supernate solutions in 61 HLW tanks at the Hanford Site. These include values from single-shell tanks (Van Vleet 1993a) and double-shell tanks (Van Vleet 1993b). The frequency distribution for these 61 values is shown in Figure 3-7. The bulk of the TOC values are less than 14 g/L of organic carbon. For single-shell tanks, Toth et al. (1995) have calculated a mean value of 5.2 ± 1.1 g/L organic carbon (at the 95% confidence level) for the tank supernate solutions. This mean was calculated from analyses of 143 samples from 78 different single-shell tanks.

If the tank TOC values are compared with solubilities for the nine organic salts studied, only oxalate has a low enough solubility to be present as a solid in the tanks. This can be seen by comparing the TOC values in Table 3-4, which gives the ranges of measured solubilities of the

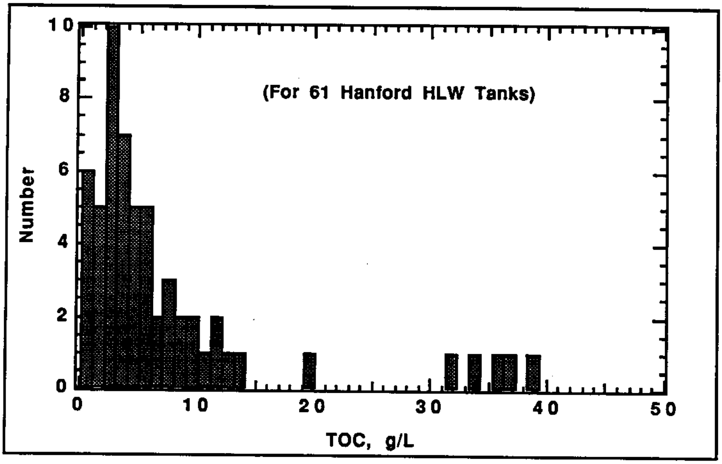

Figure 3-7. Frequency distribution of total organic carbon (TOC) concentrations measured in supernate solutions in 61 different Hanford Site HLW tanks.

Table 3-4. Comparison of measured organic sodium salt solubility ranges in units of molarity and total organic carbon concentrations (TOC).

Organic salt	Solubility Range*, M	TOC Range, gC/L
Glycolate	4.4 - 5.8	106 - 140
Succinate	0.9 - 2.3	43 - 110
Caproate	0.2 - 1.7	14 - 122
Dibutyphosphate	>0.9	>86
Oxalate	0.004 - .015	0.1 - 0.36
Citrate	0.6 - 1.2	43 - 86
Formate	6.8 - 9.8	82 - 118
EDTA	0.7 - 1.4	84 - 168
NTA	1.3 - 1.7	94 - 122

*Over all sodium hydroxide concentrations and temperatures.

individual organic salts in terms of TOC, with the tank values. Even if all the dissolved organic carbon in the tank supernates is pure glycolate, succinate, caproate, dibutyl phosphate, citrate, formate , EDTA, or NTA, there is not enough in solution to reach saturation and precipitate these organics.

4.0 CONCLUSIONS

The solubilities of sodium glycolate, succinate, caproate, and dibutylphosphate in HLW tank supernate solutions measured in the present work are high over the temperature and sodium hydroxide concentration ranges expected in the tanks. The solubilities of these compounds are similar (in terms of TOC) to sodium citrate, formate, EDTA, and NTA which were previously reported (Barney 1994). The high solubilities will prevent solid sodium salts of these eight organic acids from precipitating from tank supernate solutions. The TOC analyses of actual tank supernates are generally much lower than the TOC ranges for the simulated supernate solutions saturated (at the solubility limit) with the organic salts. This is true even if all the dissolved carbon in a given tank supernate is due to only one of the eight compounds (a very unlikely situation). Sodium caproate solubility at low temperatures and high hydroxide concentrations is below the TOC for several tanks, but is not expected to be present in high concentrations since it is only one of many possible degradation products of the normal paraffin hydrocarbon (NPH) solvent used in the PUREX process at Hanford (Babad et al. 1993). This compound has not yet been identified in actual waste. Because these eight organic compounds are not likely to exist as solids in the saltcake or sludge layers of the tanks, but only as aqueous solutions, self-propagating reactions with nitrates or nitrites are unlikely.

Metal ion complexes of DBP and oxalate in supernate solution are not stable in the presence of the free hydroxide concentrations expected in most tanks. Iron and aluminum DBP compounds reacted with hydroxide to form soluble sodium DBP and precipitated iron and aluminum hydroxides. If no hydroxide is present, the solubilities of $Al(DBP)_3$ and $Fe(DBP)_3$ in the simulant are small (0.010 M and 0.012 M, respectively at 25 °C).

The solubility of sodium oxalate is not significantly affected by the presence of aluminum hydroxide. Aluminum oxalate complexes are not significantly present in the supernate simulant solutions. Oxalate cannot compete with hydroxide as a ligand for aluminum in these solutions. The low solubility of sodium oxalate (far below most measured tank supernate TOC values) will allow it to precipitate in some tanks with nitrate and nitrite salts. The energy content of oxalate is quite low and mixtures with sodium nitrate/nitrite will not propagate Webb et al. 1994).

5.0 FUTURE WORK

Solubilities of additional organic compounds known to exist in the HLW tanks will be measured. These include three compounds that have been found in actual tank waste recently by Campbell et al., 1994 and 1995. They are sodium acetate, sodium HEDTA [N-(2-hydroxyethyl)ethylenediaminetriacetate], and sodium iminodiacetate, $NH(CH_2COONa)_2$. In addition to these compounds, solubility measurements are underway on the long-chain carboxylic acid salts, sodium laurate, $CH_3(CH_2)_{10}COONa$, and sodium palmitate, $CH_3(CH_2)_{14}COONa$. These compounds are possible degradation products of NPH. Sodium butyrate, $CH_3(CH_2)_2COONa$, is a possible degradation product of TBP and is also being studied.

Additional work remains to be done on determining whether or not organic complexes or compounds with metal ions can form and precipitate under waste conditions. Based on the observations described in this report on aluminum oxalate, iron DBP, and aluminum DBP, organic complexes/compounds are not stable as long as significant concentrations of free hydroxide are present. Metal-organic complexes that have high stability, such as EDTA complexes with thorium, bismuth, or zirconium, will be examined to determine their stabilities and solubilities under tank supernate conditions.

The effects of dissolved organics in supernate solutions on the solubility of other organic compounds needs to be determined. It seems likely that the presence of organic sodium salts in solution will lower the solubility of other organic sodium salts because of the common ion effect of sodium. There will be other factors involved, however, that could influence organic salt solubility such as organic anion-anion interactions. Several pairs of organic salts will be studied including acetate-citrate and EDTA-NTA.

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APPENDIX

SOLUBILITIES OF ORGANIC SALTS AND SOLUTION COMPOSITIONS

Oxalate Solubilities
(Molar Concentrations)

Initial	*EQUILIBRIUM SOLUBILITIES*			
[NaOH]	*[Oxalate], 50 °C*	*[Oxalate], 40 °C*	*[Oxalate], 30 °C*	*[Oxalate], 25 °C*
0.00003	0.0145	0.0116	0.0103	0.0085
0.001	0.0143	0.0114	0.0102	0.0086
0.01	0.0142	0.0113	0.0101	0.0083
0.1	0.0136	0.0105	0.0097	0.0081
0.5	0.0121	0.0097	0.0084	0.0075
1	0.0097	0.0073	0.0063	0.0057
2	0.0071	0.0047	0.0040	0.0036
	[$NaNO_3$], 50 °C	*[$NaNO_3$], 40 °C*	*[$NaNO_3$], 30 °C*	*[$NaNO_3$], 25 °C*
All	4.00	4.00	4.00	4.00
	[$NaNO_2$], 50 °C	*[$NaNO_2$], 40 °C*	*[$NaNO_2$], 30 °C*	*[$NaNO_2$], 25 °C*
All	1.00	1.00	1.00	1.00

Oxalate Solubilities in the Presence of Excess Aluminum Hydroxide
(Molar Concentrations)

Initial	*EQUILIBRIUM SOLUBILITIES*			
[NaOH]	*[Oxalate], 50 °C*	*[Oxalate], 40 °C*	*[Oxalate], 30 °C*	*[Oxalate], 25 °C*
0.01	0.0139	0.0129	0.0101	0.00956
0.1	0.0129	0.0120	0.00952	0.00875
1	0.00944	0.00864	0.00603	0.00581
2	0.00698	0.00637	0.00386	0.00361
3	0.00510	0.00459	0.00243	0.00213
	[$NaNO_3$], 50 °C	*[$NaNO_3$], 40 °C*	*[$NaNO_3$], 30 °C*	*[$NaNO_3$], 25 °C*
All	4.00	4.00	4.00	4.00
	[$NaNO_2$], 50 °C	*[$NaNO_2$], 40 °C*	*[$NaNO_2$], 30 °C*	*[$NaNO_2$], 25 °C*
All	1.00	1.00	1.00	1.00

Formate Solubilities
(Molar Concentrations)

Initial	*EQUILIBRIUM SOLUBILITIES*			
[NaOH]	*[Formate], 50 °C*	*[Formate], 40 °C*	*[Formate], 30 °C*	*[Formate], 25 °C*
0.00003	9.775	9.033	8.830	8.520
0.001	9.538	9.227	8.810	8.540
0.01	9.413	9.250	8.850	8.470
0.1	9.388	9.040	8.540	8.250
0.5	9.043	8.883	8.160	8.005
1	8.795	8.370	7.960	7.705
2	8.335	7.913	7.325	6.800
	[$NaNO_3$], 50 °C	*[$NaNO_3$], 40 °C*	*[$NaNO_3$], 30 °C*	*[$NaNO_3$], 25 °C*
0.00003	2.940	2.737	2.695	2.490
0.001	2.933	2.863	2.720	2.655
0.01	2.843	2.777	2.815	2.680
0.1	2.858	2.740	2.655	2.680
0.5	2.765	2.707	2.585	2.670
1	2.913	2.817	2.675	2.805
2	2.963	2.930	2.825	2.620
	[$NaNO_2$], 50 °C	*[$NaNO_2$], 40 °C*	*[$NaNO_2$], 30 °C*	*[$NaNO_2$], 25 °C*
0.00003	0.672	0.637	0.667	0.657
0.001	0.673	0.657	0.724	0.717
0.01	0.655	0.646	0.673	0.721
0.1	0.649	0.640	0.688	0.651
0.5	0.645	0.633	0.635	0.663
1	0.677	0.648	0.747	0.720
2	0.699	0.695	0.757	0.719
	[NaOH], 50 °C	*[NaOH], 40 °C*	*[NaOH], 30 °C*	*[NaOH], 25 °C*
0.00003	2.21E-05	2.05E-05	2.02E-05	1.87E-05
0.001	7.33E-04	7.16E-04	6.80E-04	6.64E-04
0.01	7.11E-03	6.94E-03	7.04E-03	6.70E-03
0.1	7.14E-02	6.85E-02	6.64E-02	6.70E-02
0.5	3.46E-01	3.38E-01	3.23E-01	3.34E-01
1	7.28E-01	7.04E-01	6.69E-01	7.01E-01
2	1.48E+00	1.47E+00	1.41E+00	1.31E+00

Citrate Solubilities
(Molar Concentrations)

Initial	*EQUILIBRIUM SOLUBILITIES*			
[NaOH]	*[Citrate], 50 °C*	*[Citrate], 40 °C*	*[Citrate], 30 °C*	*[Citrate], 25 °C*
0.00003	1.220	1.203	1.197	1.180
0.001	1.213	1.190	1.187	1.145
0.01	1.137	1.197	1.187	1.145
0.1	1.127	1.163	1.000	0.946
0.5	1.009	1.107	1.107	1.060
1	0.868	0.881	0.703	0.638
2	0.685	0.683	0.670	0.648
	[NaNO$_3$], 50 °C	*[NaNO$_3$], 40 °C*	*[NaNO$_3$], 30 °C*	*[NaNO$_3$], 25 °C*
0.00003	3.293	3.297	3.273	3.275
0.001	3.230	3.287	3.207	3.115
0.01	3.300	3.300	3.213	3.150
0.1	3.238	3.197	3.047	2.995
0.5	3.183	3.237	3.117	3.045
1	3.400	3.360	3.177	3.145
2	3.523	3.603	3.510	3.405
	[NaNO$_2$], 50 °C	*[NaNO$_2$], 40 °C*	*[NaNO$_2$], 30 °C*	*[NaNO$_2$], 25 °C*
0.00003	0.831	0.827	0.810	0.794
0.001	0.812	0.832	0.795	0.769
0.01	0.829	0.831	0.799	0.765
0.1	0.815	0.836	0.815	0.800
0.5	0.802	0.819	0.769	0.737
1	0.853	0.882	0.854	0.835
2	0.895	0.908	0.873	0.839
	[NaOH], 50 °C	*[NaOH], 40 °C*	*[NaOH], 30 °C*	*[NaOH], 25 °C*
0.00003	2.47E-05	2.47E-05	2.46E-05	2.46E-05
0.001	8.08E-04	8.22E-04	8.02E-04	7.79E-04
0.01	8.25E-03	8.25E-03	8.03E-03	7.88E-03
0.1	8.09E-02	7.99E-02	7.62E-02	7.49E-02
0.5	3.98E-01	4.05E-01	3.90E-01	3.81E-01
1	8.50E-01	8.40E-01	7.94E-01	7.86E-01
2	1.76E+00	1.80E+00	1.76E+00	1.70E+00

EDTA Solubilities (from supersaturation)
(Molar Concentrations)

Initial		***EQUILIBRIUM SOLUBILITIES***		
[NaOH]	***[EDTA], 50 °C***	***[EDTA], 40 °C***	***[EDTA], 30 °C***	***[EDTA], 25 °C***
0.00003	1.370	1.170	1.060	1.040
0.001	1.290	1.180	1.060	1.030
0.01	1.320	1.160	1.060	1.040
0.1	1.280	1.150	1.060	1.050
0.5	1.190	1.080	0.950	0.960
1	1.110	0.970	0.860	0.840
2	0.940	0.790	0.700	0.650
	[NaNO$_3$], 50 °C	***[NaNO$_3$], 40 °C***	***[NaNO$_3$], 30 °C***	***[NaNO$_3$], 25 °C***
0.00003	3.313	3.523	3.497	3.680
0.001	3.407	3.590	3.457	3.565
0.01	3.433	3.573	3.445	3.555
0.1	3.453	3.525	3.483	3.585
0.5	3.473	3.420	3.470	3.495
1	3.620	3.837	3.830	3.650
2	3.967	4.060	4.050	3.830
	[NaNO$_2$], 50 °C	***[NaNO$_2$], 40 °C***	***[NaNO$_2$], 30 °C***	***[NaNO$_2$], 25 °C***
0.00003	0.798	0.851	0.846	0.895
0.001	0.822	0.864	0.836	0.870
0.01	0.826	0.861	0.834	0.866
0.1	0.831	0.849	0.843	0.870
0.5	0.835	0.822	0.839	0.849
1	0.871	0.921	0.924	0.887
2	0.960	0.982	0.984	0.890
	[NaOH], 50 °C	***[NaOH], 40 °C***	***[NaOH], 30 °C***	***[NaOH], 25 °C***
0.00003	2.49E-05	2.64E-05	2.62E-05	2.76E-05
0.001	8.52E-04	8.98E-04	8.64E-04	8.91E-04
0.01	8.58E-03	8.93E-03	8.61E-03	8.89E-03
0.1	8.63E-02	8.81E-02	8.71E-02	8.96E-02
0.5	4.34E-01	4.28E-01	4.34E-01	4.37E-01
1	9.05E-01	9.59E-01	9.58E-01	9.13E-01
2	1.98E+00	2.03E+00	2.03E+00	1.92E+00

NTA Solubilities
(Molar Concentrations)

Initial	*EQUILIBRIUM SOLUBILITIES*			
[NaOH]	*[NTA], 50 °C*	*[NTA], 40 °C*	*[NTA], 30 °C*	*[NTA], 25 °C*
0.00003	1.730	1.743	1.813	1.830
0.001	1.713	1.733	1.827	1.823
0.01	1.757	1.777	1.813	1.757
0.1	1.723	1.770	1.777	1.820
0.5	1.630	1.673	1.723	1.667
1	1.440	1.490	1.613	1.460
2	1.193	1.227	1.250	1.270
	[$NaNO_3$], 50 °C	*[$NaNO_3$], 40 °C*	*[$NaNO_3$], 30 °C*	*[$NaNO_3$], 25 °C*
0.00003	3.143	3.237	3.213	3.143
0.001	3.127	3.220	3.277	3.187
0.01	3.137	3.270	3.197	3.157
0.1	3.140	3.200	3.210	3.270
0.5	3.097	3.177	3.183	3.200
1	3.237	3.237	3.540	3.463
2	3.295	3.393	3.673	3.607
	[$NaNO_2$], 50 °C	*[$NaNO_2$], 40 °C*	*[$NaNO_2$], 30 °C*	*[$NaNO_2$], 25 °C*
0.00003	0.733	0.739	0.750	0.739
0.001	0.725	0.743	0.751	0.735
0.01	0.725	0.753	0.754	0.736
0.1	0.727	0.745	0.759	0.766
0.5	0.719	0.731	0.741	0.740
1	0.746	0.764	0.803	0.790
2	0.798	0.820	0.849	0.832
	[NaOH], 50 °C	*[NaOH], 40 °C*	*[NaOH], 30 °C*	*[NaOH], 25 °C*
0.00003	2.36E-05	2.43E-05	2.41E-05	2.36E-05
0.001	7.82E-04	8.05E-04	8.19E-04	7.97E-04
0.01	7.84E-03	8.18E-03	7.99E-03	7.89E-03
0.1	7.85E-02	8.00E-02	8.03E-02	8.18E-02
0.5	3.87E-01	3.97E-01	3.98E-01	4.00E-01
1	8.09E-01	8.09E-01	8.85E-01	8.66E-01
2	1.65E+00	1.70E+00	1.84E+00	1.80E+00

Glycolate Solubilities
(Molar Concentrations)

Initial	*EQUILIBRIUM SOLUBILITIES*			
[NaOH]	*[GLY], 50 °C*	*[GLY], 40 °C*	*[GLY], 30 °C*	*[GLY], 25 °C*
0.00003	5.820	5.177	4.960	4.745
0.001	5.750	5.150	4.825	4.790
0.01	5.490	5.260	4.897	4.770
0.1	5.697	5.290	5.047	4.863
0.5	5.533	5.200	4.857	4.700
1	5.645	5.130	4.623	4.533
2	5.270	5.030	4.587	4.373
	[$NaNO_3$], 50 °C	*[$NaNO_3$], 40 °C*	*[$NaNO_3$], 30 °C*	*[$NaNO_3$], 25 °C*
0.00003	2.490	2.720	2.853	3.020
0.001	2.690	2.697	2.743	3.067
0.01	2.543	2.747	2.760	2.933
0.1	2.520	2.520	2.610	2.737
0.5	2.593	2.627	2.707	2.843
1	2.730	2.747	2.763	2.847
2	2.673	2.800	2.860	2.920
	[$NaNO_2$], 50 °C	*[$NaNO_2$], 40 °C*	*[$NaNO_2$], 30 °C*	*[$NaNO_2$], 25 °C*
0.00003	0.686	0.702	0.735	0.739
0.001	0.675	0.692	0.709	0.741
0.01	0.675	0.707	0.711	0.727
0.1	0.645	0.659	0.673	0.690
0.5	0.678	0.680	0.689	0.712
1	0.702	0.705	0.706	0.712
2	0.705	0.714	0.712	0.709
	[NaOH], 50 °C	*[NaOH], 40 °C*	*[NaOH], 30 °C*	*[NaOH], 25 °C*
0.00003	1.87E-05	2.04E-05	2.14E-05	2.27E-05
0.001	6.89E-04	6.74E-04	6.86E-04	7.67E-04
0.01	6.36E-03	6.87E-03	6.90E-03	7.33E-03
0.1	6.66E-02	6.30E-02	6.44E-02	6.84E-02
0.5	3.24E-01	3.28E-01	3.38E-01	3.55E-01
1	7.04E-01	6.87E-01	6.91E-01	7.12E-01
2	1.34E+00	1.37E+00	1.24E+00	1.40E+00

Succinate Solubilities
(Molar Concentrations)

Initial [NaOH]	*EQUILIBRIUM SOLUBILITIES*			
	[SUC], 50 °C	*[SUC], 40 °C*	*[SUC], 30 °C*	*[SUC], 25 °C*
0.00003	2.325	1.780	1.453	1.280
0.001	2.340	1.843	1.350	1.227
0.01	2.363	1.745	1.367	1.253
0.1	2.273	1.737	1.340	1.247
0.5	2.243	1.720	1.360	1.180
1	2.143	1.603	1.220	1.017
2	2.017	1.370	1.029	0.861
	[$NaNO_3$], 50 °C	*[$NaNO_3$], 40 °C*	*[$NaNO_3$], 30 °C*	*[$NaNO_3$], 25 °C*
0.00003	2.280	2.737	3.060	3.133
0.001	2.200	2.747	3.173	3.273
0.01	2.317	2.663	3.097	3.287
0.1	2.263	2.700	3.015	3.217
0.5	2.350	2.710	3.190	3.177
1	2.387	2.827	3.220	3.283
2	2.547	2.893	3.487	3.537
	[$NaNO_2$], 50 °C	*[$NaNO_2$], 40 °C*	*[$NaNO_2$], 30 °C*	*[$NaNO_2$], 25 °C*
0.00003	0.568	0.695	0.749	0.781
0.001	0.551	0.688	0.825	0.818
0.01	0.560	0.671	0.742	0.811
0.1	0.563	0.677	0.747	0.801
0.5	0.568	0.677	0.792	0.788
1	0.605	0.710	0.811	0.810
2	0.641	0.725	0.860	0.890
	[NaOH], 50 °C	*[NaOH], 40 °C*	*[NaOH], 30 °C*	*[NaOH], 25 °C*
0.00003	1.71E-05	2.05E-05	2.30E-05	2.35E-05
0.001	5.50E-04	6.87E-04	7.93E-04	8.18E-04
0.01	5.79E-03	6.66E-03	7.74E-03	8.22E-03
0.1	5.66E-02	6.75E-02	7.54E-02	8.04E-02
0.5	2.94E-01	3.39E-01	3.99E-01	3.97E-01
1	5.97E-01	7.07E-01	8.05E-01	8.21E-01
2	1.27E+00	1.45E+00	1.74E+00	1.77E+00

Caproate Solubilities
(Molar Concentrations)

Initial	*EQUILIBRIUM SOLUBILITIES*			
[NaOH]	*[CAP], 50 °C*	*[CAP], 40 °C*	*[CAP], 30 °C*	*[CAP], 25 °C*
0.00003	1.608	1.535	1.347	1.372
0.001	1.621	1.563	1.368	1.381
0.01	1.685	1.435	1.348	1.348
0.1	1.581	1.485	1.263	1.263
0.5	1.470	1.296	1.224	1.213
1	1.008	0.852	0.709	0.691
2	0.384	0.287	0.165	0.164
	$[NaNO_3]$, 50 °C	*$[NaNO_3]$, 40 °C*	*$[NaNO_3]$, 30 °C*	*$[NaNO_3]$, 25 °C*
0.00003	3.295	3.331	3.422	3.410
0.001	3.288	3.317	3.412	3.406
0.01	3.256	3.380	3.421	3.421
0.1	3.309	3.356	3.461	3.461
0.5	3.363	3.446	3.479	3.484
1	3.577	3.645	3.707	3.714
2	3.841	3.880	3.928	3.928
	$[NaNO_2]$, 50 °C	*$[NaNO_2]$, 40 °C*	*$[NaNO_2]$, 30 °C*	*$[NaNO_2]$, 25 °C*
0.00003	0.797	0.902	0.851	0.867
0.001	0.819	0.845	0.840	0.835
0.01	0.843	0.870	0.863	0.865
0.1	0.823	0.843	0.857	0.860
0.5	0.854	0.908	0.911	0.855
1	0.883	0.886	0.915	0.907
2	0.980	0.942	0.946	0.953
	[NaOH], 50 °C	*[NaOH], 40 °C*	*[NaOH], 30 °C*	*[NaOH], 25 °C*
0.00003	2.47E-05	2.50E-05	2.57E-05	2.56E-05
0.001	8.22E-04	8.29E-04	8.53E-04	8.51E-04
0.01	8.14E-03	8.45E-03	8.55E-03	8.55E-03
0.1	8.27E-02	8.39E-02	8.65E-02	8.65E-02
0.5	4.20E-01	4.31E-01	4.35E-01	4.36E-01
1	8.94E-01	9.11E-01	9.27E-01	9.29E-01
2	1.92E+00	1.94E+00	1.96E+00	1.96E+00

Aluminum Dibutylphosphate Solubilities
(Molar Concentrations)

Initial	***EQUILIBRIUM SOLUBILITIES***			
[NaOH]	***[DBP], 50 °C***	***[DBP], 40 °C***	***[DBP], 30 °C***	***[DBP], 25 °C***
0.00003	ND	ND	0.00478	0.00329
0.001	ND	ND	0.00528	0.00392
0.01	ND	ND	0.0122	0.0113
0.1	ND	ND	0.0870	0.0927
0.5	ND	ND	0.410	0.419
1	ND	ND	0.838	0.937
	[$NaNO_3$], 50 °C	***[$NaNO_3$], 40 °C***	***[$NaNO_3$], 30 °C***	***[$NaNO_3$], 25 °C***
0.00003	ND	ND	3.81	3.96
0.001	ND	ND	3.75	4.01
0.01	ND	ND	3.68	3.88
0.1	ND	ND	3.66	3.93
0.5	ND	ND	3.36	3.52
1	ND	ND	3.14	3.38
	[$NaNO_2$], 50 °C	***[$NaNO_2$], 40 °C***	***[$NaNO_2$], 30 °C***	***[$NaNO_2$], 25 °C***
0.00003	ND	ND	0.893	0.977
0.001	ND	ND	0.902	1.01
0.01	ND	ND	0.919	1.01
0.1	ND	ND	0.918	0.995
0.5	ND	ND	0.819	0.910
1	ND	ND	0.764	0.859
	[NaOH], 50 °C	***[NaOH], 40 °C***	***[$NaOH]_i$, 30 °C***	***[$NaOH]_i$, 25 °C***
0.00003	ND	ND	0.0000286	0.0000297
0.001	ND	ND	0.000938	0.00100
0.01	ND	ND	0.00920	0.00971
0.1	ND	ND	0.0915	0.0983
0.5	ND	ND	0.420	0.440
1	ND	ND	0.785	0.845

Iron Dibutylphosphate Solubilities (Molar Concentrations)

Initial		***EQUILIBRIUM SOLUBILITIES***		
[NaOH]	***[DBP], 50 °C***	***[DBP], 40 °C***	***[DBP], 30 °C***	***[DBP], 25 °C***
0.00003	ND	ND	0.00520	0.00388
0.001	ND	ND	0.00456	0.00389
0.01	ND	ND	0.0113	0.0105
0.1	ND	ND	0.0914	0.0915
0.5	ND	ND	0.418	0.411
1	ND	ND	0.716	0.745
	[NaNO$_3$], 50 °C	***[NaNO$_3$], 40 °C***	***[NaNO$_3$], 30 °C***	***[NaNO$_3$], 25 °C***
0.00003	ND	ND	3.85	3.87
0.001	ND	ND	3.80	3.87
0.01	ND	ND	3.72	3.80
0.1	ND	ND	3.67	3.74
0.5	ND	ND	3.25	3.32
1	ND	ND	2.96	3.09
	[NaNO$_2$], 50 °C	***[NaNO$_2$], 40 °C***	***[NaNO$_2$], 30 °C***	***[NaNO$_2$], 25 °C***
0.00003	ND	ND	0.808	0.887
0.001	ND	ND	0.842	0.908
0.01	ND	ND	0.918	0.924
0.1	ND	ND	0.931	0.926
0.5	ND	ND	0.836	0.836
1	ND	ND	0.789	0.770
	[NaOH], 50 °C	***[NaOH], 40 °C***	***[NaOH]$_i$, 30 °C***	***[NaOH]$_i$, 25 °C***
0.00003	ND	ND	0.0000289	0.0000291
0.001	ND	ND	0.000950	0.000968
0.01	ND	ND	0.00930	0.00949
0.1	ND	ND	0.0918	0.0935
0.5	ND	ND	0.406	0.415
1	ND	ND	0.740	0.772

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