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The Solubilities of Significant Organic Compounds in HLW Tank Supernate Solutions

G. S. Barney

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ABSTRACT

Large quantities of organic chemicals used in reprocessing spent nuclear fuels at the Hanford Site have accumulated in underground high-level radioactive waste tanks. The organic content of these tanks must be known so that the potential for hazardous reactions between organic components and sodium nitrate/nitrite salts in the waste can be evaluated. The solubilities of organic compounds described in this report will help determine if they are present in the solid phases (salt cake and sludges) as well as the liquid phase (interstitial liquor/supernate) in the tanks. The solubilities of five significant sodium salts of carboxylic acids and aminocarboxylic acids [sodium oxalate, formate, citrate, nitrilotriacetate (NTA) and ethylendiaminetetraacetate (EDTA)] were measured in a simulated supernate solution 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. Sodium oxalate solubilities were found to be relatively low and this compound could be expected to precipitate from some tank supernate solutions. The energy content of oxalate salts is, however, relatively small. Sodium formate, citrate, EDTA, and NTA solubilities are high and these salts are unlikely to precipitate under waste tank conditions. This conclusion is based on a comparison of measured total organic carbon (TOC) concentrations in actual tank supernates with the organic salt solubilities determined in this study. Because these organic compounds will only exist in aqueous supernate solutions, self-propagating reactions with nitrate or nitrite salts in the waste are unlikely. Also, draining the supernate from the waste tanks will lower the quantity of these organics left in the tanks. Solubilities of all the organic salts decrease with increasing sodium hydroxide concentration due to the common ion effect of Na^+. In general, increasing temperatures raised the solubilities, although for sodium citrate and NTA the temperature effect was small.

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ACRONYMS AND TERMS

DSS	double-shell slurry
EDTA	ethylenediaminetetraacetate
ED3A	ethylenediaminetriacetate
HEDTA	N-(hydroxyethyl)ethylenediaminetriacetate
HLW	high-level waste
NTA	nitrilotriacetate
TBP	tributyl phosphate
TOC	total organic carbon

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G. S. Barney

Process Laboratories and Technology
Westinghouse Hanford Company
Richland, Washington 99352

INTRODUCTION

Large quantities of organic chemicals used in reprocessing spent nuclear fuel at the Hanford Site have accumulated in underground tanks that contain high-level radioactive waste (HLW). These organic compounds can potentially react with nitrate or nitrite components of the wastes to produce heat and gaseous products. Preliminary laboratory tests (Beitel 1976a, 1976b, 1976c, and 1977) show that organic materials react violently if the organic content is in the range of 10 to 30 weight percent in mixtures with sodium nitrate. The ignition temperatures for these reactions are >400°C. Similar results (Fisher 1990) were obtained for mixtures of sodium acetate, sodium nitrite, and sodium nitrate. The mixtures deflagrate when strongly heated as long as they contain more than 10 weight percent sodium acetate and about 20 weight percent sodium nitrate/nitrite.

Because of the potential for these self-propagating reactions to occur in high-level waste, the organic content of the waste tanks must be known. Very little is known about the organic content of the solids in the waste tanks. Some measurements of total organic carbon (TOC) have been performed on solids, but the identity of the specific organic compounds present are unknown, except in a few cases. The measurements described in this study will help determine if major organic components in the waste have precipitated and settled in the solid phases (saltcake and sludges) or if they remain in the liquid phase (interstitial liquor/supernate) in the tanks. If most of the organic content is in the liquid phase, a gravity drained saltcake may not contain enough organic material to allow a propagating organic-nitrate/nitrite reaction to occur. The solubilities of many significant organic compounds may be high enough in the interstitial liquor/supernate to prevent precipitation in the solid phase. Solubilities of relevant organic compounds are unknown for the conditions expected in Hanford Site high level wastes.

It is known that large quantities of N-(2-hydroxethyl)ethylenediaminetriacetate (HEDTA), ethylenediaminetetraacetate (EDTA), glycolate, and citric acid were added to the tanks as a result of chemical processing at B-Plant (Allen 1976). Smaller quantities of tributyl phosphate (TBP), normal paraffin hydrocarbons (NPH), oxalate, di-2-ethylhexylphosphate, and dibutylbutylphosphonate were also added, as well as small quantities of many other organic compounds. Chemical and radiolytic degradation of some of these compounds has occurred over the years to produce a complex mixture of organic degradation products (Delegard 1987 and Babad et al. 1993). Some of these products are known, but many are unknown and need to be identified. The organic compounds to be examined in this report were chosen because they were added to the tanks in large quantities, they are likely degradation products of major organic compounds added to the tanks, or they have been found in significant quantities in the waste.

Analyses of the organic components of several high-level wastes from different Hanford tanks have been performed. Campbell et al. (1994) analyzed core segments from Tank 241-SY-101 and found the major organic components to be salts of chelating agents and low molecular weight carboxylic acids. These compounds accounted for 74 to 93 % of the TOC in these samples. The major chelating compounds were EDTA, nitrilotriacetic acid (NTA), citric 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.

Based on the available information on organic composition of HLW, five compounds were chosen for the solubility studies. They are the sodium salts of oxalic acid, formic acid, citric acid, EDTA, and NTA. The solubilities of these compounds were measured in a simulated HLW supernate solution containing sodium nitrate, sodium nitrite, and sodium hydroxide, which are major components of the HLW. Initially, the simulant contained 4.0 M sodium nitrate, 0.97 M sodium nitrite, and sodium hydroxide concentrations that ranged from 0.00003 M to 2.0 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 sodium salts of relevant organic compounds have been measured in pure water and/or in other aqueous solutions. These solubility data were used as starting points for designing the solubility measurements. The available literature data are summarized in Table 1. The known solubility data for sodium formate and sodium oxalate indicate that the presence of sodium salts ($NaNO_3$ and NaOH) in the HLW will significantly lower the solubilities of organic salts. This might be expected because of the common ion effect of Na^+.

EXPERIMENTAL

Materials and Equipment

All chemicals used in these measurements were reagent grade except for the tetrasodium ethylenediaminetetraacetate which was 98% pure (Aldrich Chemical Company). All solutions

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

Compound Formula	Compound Name	Solution Composition	Observations	References
$NaCHO_2$	Formate	Water and various NaOH concs.	In water solubility was 30.47 Wt. % at 0°C and 55.5 Wt. % at 60°C. Solubility decreases as NaOH concs. increase.	Elod and Tremmel, 1927 and Centola et al., 1980
$Na_2C_2O_4$	Oxalate	Various $NaNO_3$ concs.	At 20, 50, and 75°C solubility decreases with increasing $NaNO_3$ concentrations.	Zhikharev et al., 1979 and Kol'ba et al., 1980
$NaC_6H_5O_7 \cdot 2H_2O$	Citrate	Water	Solubility was 44 Wt. % at 25°C and 63 Wt. % at 100°C.	Merck Index, 1968
$Na_3NC_6H_6O_6 \cdot H_2O$	Nitrilotriacetate	Water	About 48.4 Wt. % at 25 °C	MDL Information Systems, Inc., 1993
$Na_4N_2C_{10}H_{12}O_8 \cdot 2H_2O$	Ethylenediaminetetraacetate	Water	About 51 Wt. % at room temperature	Merck Index, 1968

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 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.

Analyses

Measurements of concentrations of sodium salts of nitrate, nitrite, formate, oxalate, citrate, ethylenediaminetetraacetate, and nitrilotriacetate were performed using liquid chromatography. A Dionex Model DX-500 liquid chromatograph (Dionex Corporation, Sunnyvale California) 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. 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.

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 list of requirements for solubility determinations:

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, PTFE). 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.

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.

RESULTS AND DISCUSSION

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. 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 2 compares densities of the simulant solution with saturated solutions of organic salts at 25°C. Densities of the sodium oxalate saturated solutions are almost identical to the corresponding simulant solutions because oxalate solubilities are relatively low. Solutions saturated with sodium citrate, formate, EDTA, and NTA are significantly more dense than the starting simulant solution and suggest high solubilities for these salts.

Table 2. 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	Oxalate	Formate	Citrate	EDTA	NTA
0.00003	1.250	1.251	1.425	1.315	1.394	1.420
0.001	1.255	1.246	1.426	1.285	1.396	1.422
0.01	1.244	1.242	1.413	1.273	1.396	1.417
0.1	1.253	1.250	1.402	1.280	1.388	1.437
0.5	1.258	1.260	1.397	1.280	1.392	1.436
1.0	1.286	1.285	1.415	1.293	1.410	1.420
2.0	1.320	1.314	1.439	1.324	1.415	1.420

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. Each organic concentration shown in the table is an average for seven solutions having different initial sodium hydroxide concentrations (see Table 2) so that an overall trend of dissolution or crystallization could be observed. The data from undersaturation measurements clearly show that formate and citrate concentrations increased over the eleven-day period and did not reach equilibrium after this time. In contrast, sodium oxalate, EDTA, and NTA appeared to reach equilibrium after only two days. From

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

Equilibration Time, Days	Average [Oxalate], M	Average [Formate], M	Average [Citrate], M	Average [EDTA], M	Average [NTA], M
From Undersaturation					
2	0.0101	6.70	0.393	1.15	1.63
4	0.0088	8.03	0.477	1.09	1.62
11	0.0096	8.42	0.695	1.05	1.63
From Supersaturation					
6	0.0105	8.90	1.05	ND*	ND
9	0.0106	8.79	1.08	ND	ND
23	0.0108	8.75	1.05	ND	ND

*ND = not determined.

supersaturation, equilibrium was attained more rapidly for formate and citrate. The solubility values reported here for formate and citrate are those obtained from supersaturation and those reported for oxalate, EDTA and NTA are those obtained from undersaturation. Results from supersaturation measurements for oxalate, EDTA, and NTA were the same as undersaturation results, which proves equilibrium was achieved.

Solution Volume Increases

Because of their high solubilities, dissolution of sodium formate, citrate, EDTA, and NTA 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 4 (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).

Table 4. Volume increases due to dissolution of organic salts.

	% Volume Increase			
Organic Salt	50°C	40°C	30°C	25°C
Formate	28	30	27	30
Citrate	19	19	19	20
EDTA	15	12	13	10
NTA	22	19	19	20

Sodium Oxalate Solubility

Measured solubilities of sodium oxalate in 4.0 M $NaNO_3$ - 0.97 M $NaNO_2$ HLW supernate simulant solutions are shown in Figure 1A. Solubilities are low but increase as the temperature increases from 25°C to 50°C. Measured solubilities are in reasonable agreement with those reported by Zhikharev et al. (1979 and 1980) and Kol'ba et al. (1980). For example, Zhikharev measured sodium oxalate solubility at 50°C to be 0.18 % (by mass) in a sodium nitrate solution having a density of 1.251. At the same temperature and solution density, a solubility of 0.16 % (by mass) was measured in the mixed sodium nitrate/nitrite solutions (0.00003 M NaOH) used in the present study. Solubilities decrease rapidly as sodium hydroxide concentrations are raised from 0.0003 M to 2.0 M. This effect is mostly due to the common ion effect of total Na^+ concentration. Figure 1B shows a linear dependence of oxalate solubility on total sodium concentration. The slopes of these linear regression curves do not follow the theoretical stoichiometry, but range from -2.1 to -2.7. This is because concentrations were used rather than activities. Since the solutions have high ionic strengths, activities of oxalate and sodium ions must be used to calculate thermodynamic solubility products.

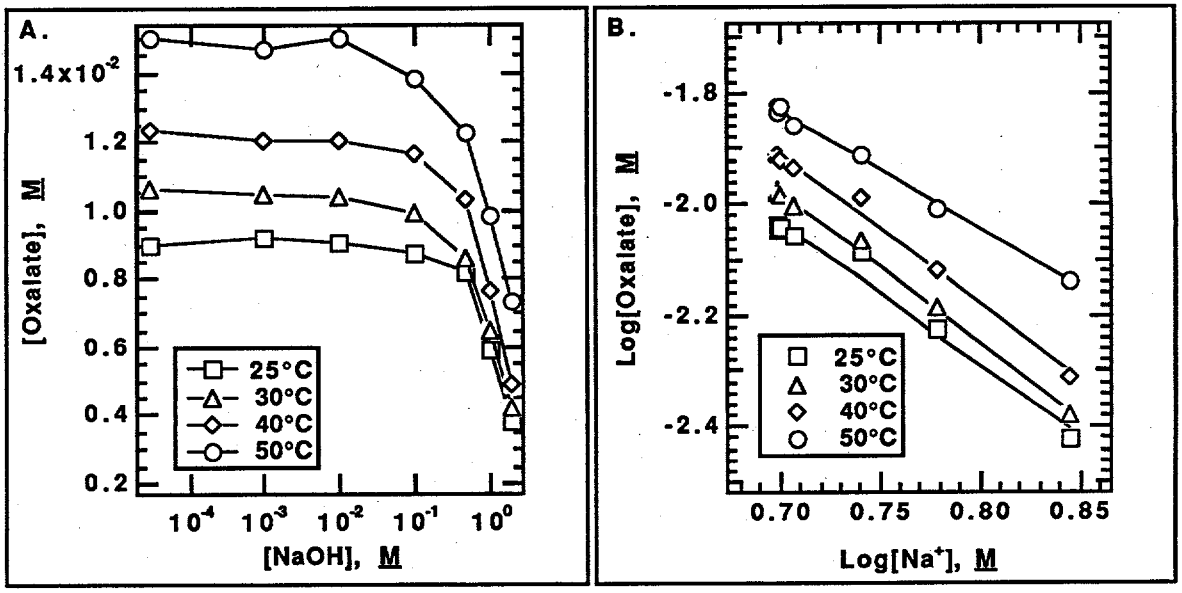

Figure 1. Solubility of sodium oxalate in 4.0 M $NaNO_3$ - 0.97 M $NaNO_2$ solutions at 25°C, 30°C, 40°C, and 50°C for various sodium hydroxide concentrations (A), and sodium oxalate solubility versus total sodium concentration at these temperatures showing linear regression lines (B).

Sodium Formate Solubility

Sodium formate is very soluble in simulated HLW supernate solutions. At low sodium hydroxide concentrations, formate solubilities as high as 9.7 M were observed. Solubilities increased as the temperature was raised, but the temperature effect was relatively small compared to oxalate solubility. Figure 2A shows that the solubility decreased as sodium hydroxide concentration increased, probably due to the common ion effect of Na^+. The measured solubilities obtained in this study are somewhat higher than those of Centola et al. (1980), probably because they studied sodium formate solubilities in a pure NaOH-H_2O system. A similar dependence on sodium hydroxide concentration was observed. The effect of diluting the original simulant solution by formate dissolution can be seen in Figure 2B. The original nitrate and nitrite concentrations (4.0 M and 0.97 M, respectively) have been diluted by about 30%. At higher hydroxide concentrations, nitrate and nitrite concentrations increase due to the decreasing solubility of the formate.

A very gradual loss of nitrite concentration in the formate solutions was observed over the time required for these measurements. Figure 3 shows the ratios (averaged over all sodium hydroxide concentrations) of nitrite/nitrate at 50°C over 41 days. This small loss of nitrite was not observed in any of the other organic solutions. Nitrite ion is slowly reduced by formate to NO or N_2O in these basic solutions (Smith et al. 1993).

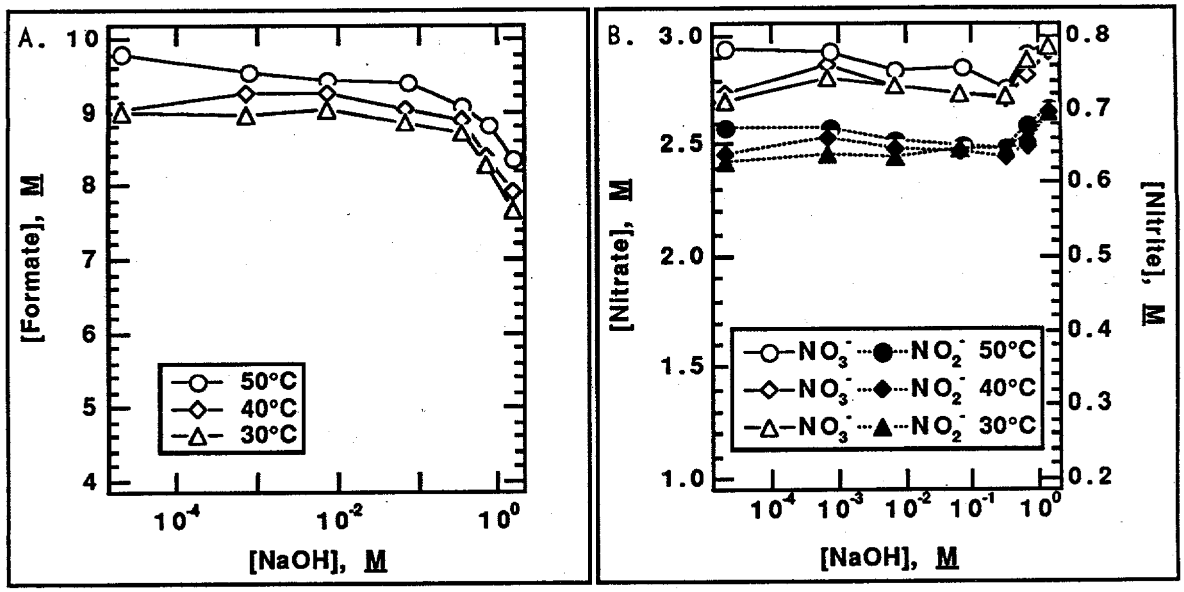

Figure 2. Solubility of sodium formate in $NaNO_3$ - $NaNO_2$ solutions at 30°C, 40°C, and 50°C for various sodium hydroxide concentrations (A), and measured sodium nitrate and nitrite concentrations in the same solutions (B).

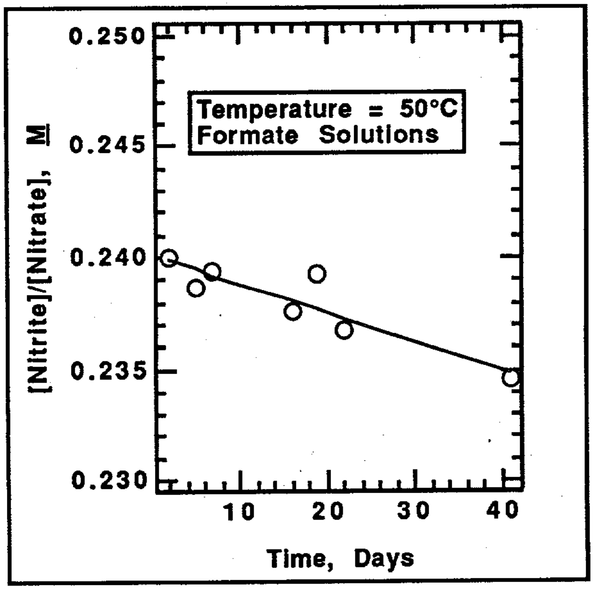

Figure 3. Ratios of nitrite/nitrate concentrations over 41 days averaged over all sodium hydroxide concentrations used in the formate solubility measurements at 50°C.

Sodium Citrate Solubility

Sodium citrate was quite soluble in the simulated HLW supernate solutions. At low sodium hydroxide concentrations, citrate solubilities as high as 1.22 M were observed. Solubilities were not significantly affected by temperature at 40°C and 50°C. Solubilities were lowered significantly by increasing the sodium hydroxide concentration, as shown in Figure 4A. The 27 % (by mass) solubility at 50°C measured in this study is about half that reported for sodium citrate solubility in pure water. 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 citrate dissolution on nitrate and nitrite concentrations can be seen in Figure 4B. The original nitrate and nitrite concentrations (4.0 M and 0.97 M, respectively) have been diluted by about 20%. At higher hydroxide concentrations, nitrate and nitrite concentrations increase due to the decreasing solubility of the citrate.

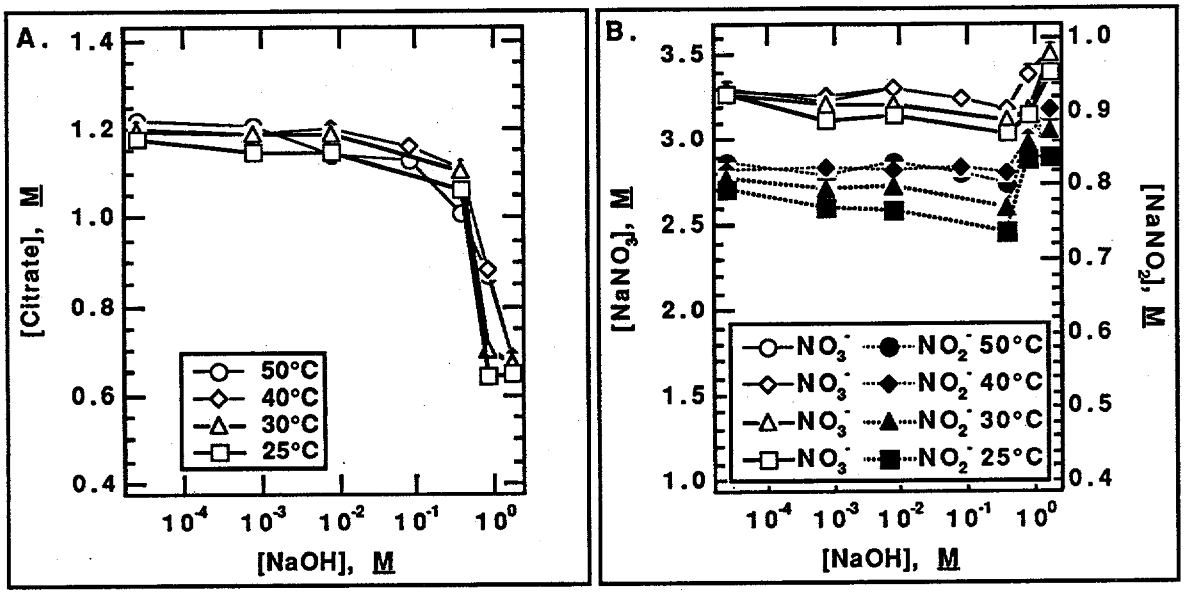

Figure 4. Solubility of sodium citrate in NaNO3 - NaNO2 solutions at 25°C, 30°C, 40°C, and 50°C for various sodium hydroxide concentrations (A), and measured sodium nitrate and nitrite concentrations in the same solutions (B).

Sodium EDTA Solubility

Sodium EDTA is quite soluble in simulated HLW supernate solutions. At low sodium hydroxide concentrations, EDTA solubilities as high as 1.4 M were observed. Solubilities increased as the temperature was raised and the temperature effect was relatively large. Figure 5A shows that the solubility decreased as sodium hydroxide concentration increased, probably due to the common ion effect of Na^+. The measured solubilities obtained in this study at 25°C (about 31 % by mass at the lowest sodium hydroxide concentration) are significantly lower than sodium EDTA solubilities in water reported in the Merck Index. This is mostly due to the common ion effect of Na^+. The effect of diluting the original simulant solution by EDTA dissolution can be seen in Figure 5B. The original nitrate and nitrite concentrations (4.0 M and 0.97 M, respectively) have been diluted by about 12%. At higher hydroxide concentrations, nitrate and nitrite concentrations increase due to the decreasing solubility of the EDTA.

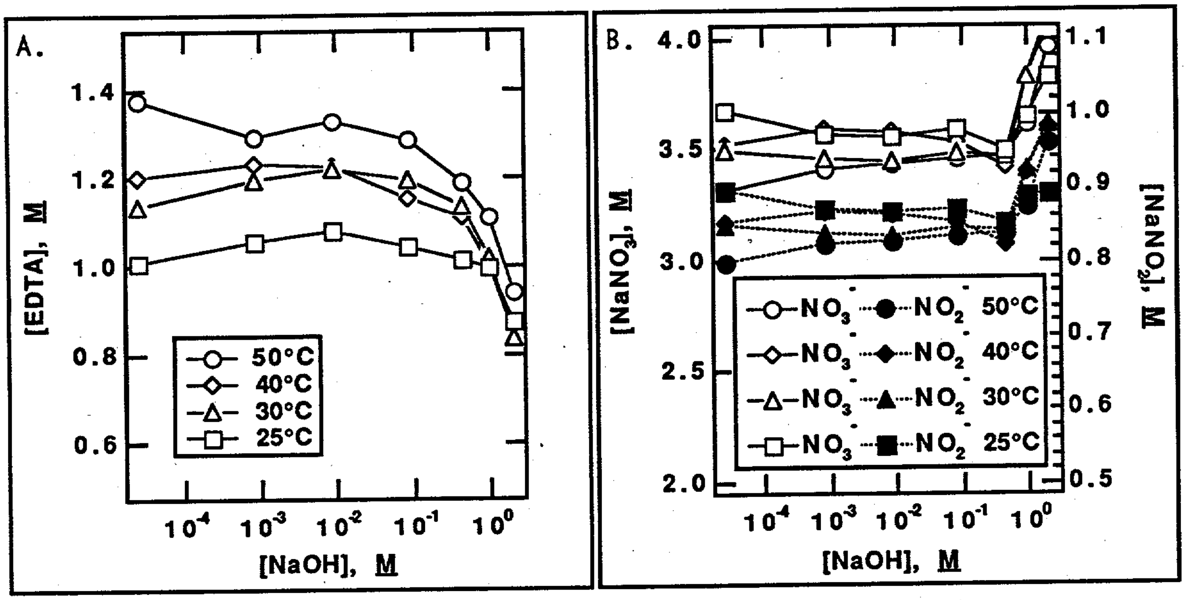

Figure 5. Solubility of sodium EDTA in $NaNO_3$ - $NaNO_2$ solutions at 25°C, 30°C, 40°C, and 50°C for various sodium hydroxide concentrations (A), and measured sodium nitrate and nitrite concentrations in the same solutions (B).

Sodium NTA Solubility

Sodium NTA is quite soluble in simulated HLW supernate solutions. At low sodium hydroxide concentrations, NTA solubilities as high as 1.8 M were observed. No measurable effect of temperature was observed. Figure 6A shows that the solubility decreased as sodium hydroxide concentration increased, probably due to the common ion effect of Na^+. The measured solubilities obtained in this study at 25°C (about 35 % by mass at the lowest sodium hydroxide concentration) are somewhat lower than sodium NTA solubilities in water reported by MDL Information Systems, Inc. (1993). This is mostly due to the common ion effect of Na^+. The effect of diluting the original simulant solution by NTA dissolution can be seen in Figure 6B. The original nitrate and nitrite concentrations (4.0 M and 0.97 M, respectively) have been diluted by about 20%. At higher hydroxide concentrations, nitrate and nitrite concentrations increase due to the decreasing solubility of the NTA.

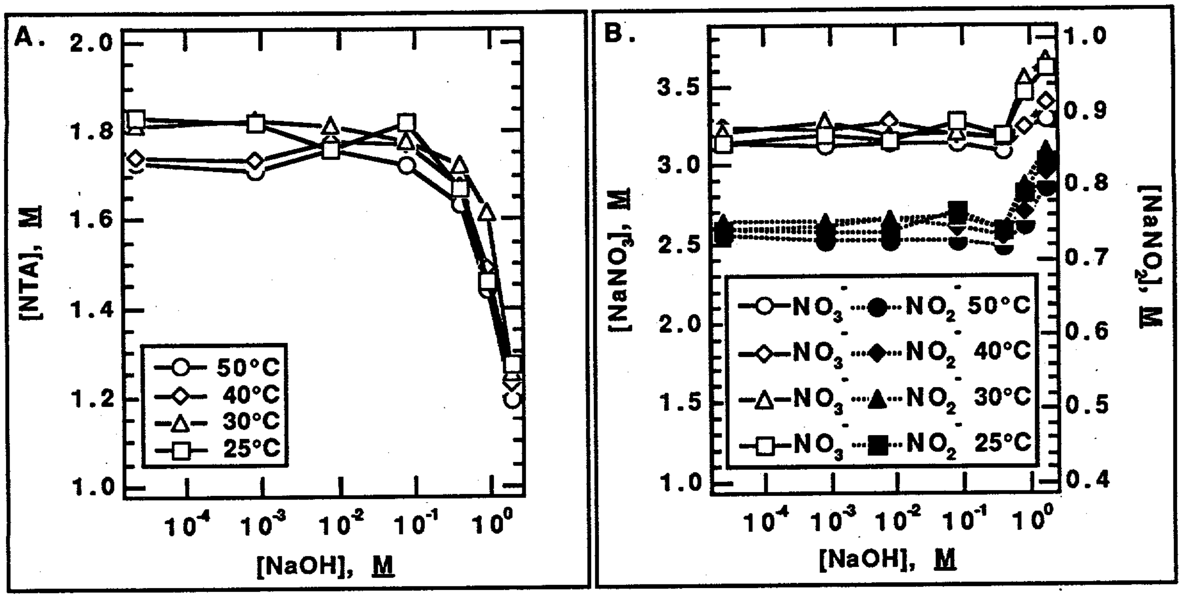

Figure 6. Solubility of sodium NTA in $NaNO_3$ - $NaNO_2$ solutions at 25°C, 30°C, 40°C, and 50°C for various sodium hydroxide concentrations (A), and measured sodium nitrate and nitrite concentrations in the same solutions (B).

HLW Tank TOC Values

The solubility data presented above can be used to determine if solid sodium salts of oxalate, formate, citrate, EDTA or NTA 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 assumed to be present in the waste. Ideally, concentrations of the individual salts in actual supernate solutions should be obtained. Unfortunately, only total organic carbon (TOC) concentrations have been measured in supernate solutions in 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 7. The bulk of the TOC values are less than 14 g/L of organic carbon. If the tank TOC values are compared with solubilities for the five 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 5, which represent solubilities of the individual organic salts in terms of TOC, with the tank values. Even if all the dissolved organic carbon in the tank supernates is pure citrate, formate , EDTA, or NTA, there is not enough in solution to reach saturation and precipitate these organics.

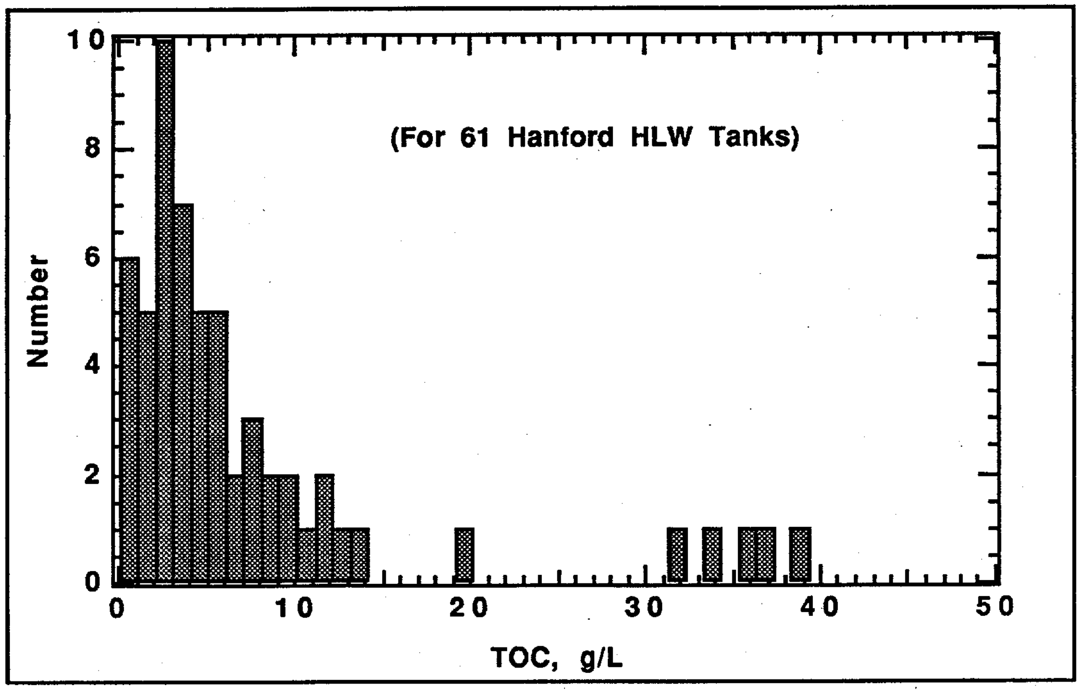

Figure 7. Frequency distribution of total organic carbon (TOC) concentrations measured in supernate solutions in 61 different Hanford Site HLW tanks.

Table 5. Comparison of measured organic salt solubilities in units of molarity and total organic carbon concentrations.

Organic salt	Solubility*, M at 25°C	TOC, g/L
Oxalate	0.004	0.01
Citrate	0.5	36
Formate	6.0	72
EDTA	0.8	96
NTA	1.3	94

*At the highest sodium hydroxide concentration studied.

CONCLUSIONS

The solubilities of sodium formate, citrate, EDTA, and NTA in Hanford Site HLW tank supernate solutions are high over the temperature and sodium hydroxide concentration ranges expected in the tanks. The high solubilities will prevent solid sodium salts of these organic acids from precipitating from supernate solutions. This conclusion is based on comparison of the measured solubilities with TOC analyses of supernates from 61 different tanks. Because these four organic compounds will not exist as solids in the saltcake or sludge layers of the tanks, but can exist only as aqueous solutions, self-propagating reactions with nitrates or nitrites are unlikely.

Measured values of sodium oxalate solubility were quite low. Precipitation of solid sodium oxalate is possible in many of the tanks, although the actual concentration of oxalate in the supernate solutions has not been determined. TOC values for some of the tanks exceed the sodium oxalate solubility in terms of TOC. The fraction of the tank supernate TOC attributable to oxalate is not known. If solid sodium oxalate exists in salt cake or sludge, it can be oxidized with nitrates or nitrites at high temperatures. The energy content of oxalate is, however, relatively low.

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