ENICO-1026

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# PURIFICATION OF DIHEXYL N,N-DIETHYLCARBAMYLMETHYLENEPHOSPHONATE BY MERCURY (II) PRECIPITATION

by

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January 1980

Prepared for the
Department of Energy
Idaho Operations Office
Under Contract DE-AC07-79ID01675

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# ABSTRACT

Dihexyl N,N-diethylcarbamylmethylenephosphonate (DHDECMP) is an important extractant for partitioning actinides from acidic nuclear waste solutions. A new technique for purifying DHDECMP is presented. Reaction of 20% crude DHDECMP in hexane with 1M mercuric nitrate at 40°C precipitates $Hg(DHDECMP)NO_3$. DHDECMP, liberated from the precipitate by treatment with caustic cyanide, is >95% pure. The procedure is fast, inexpensive and has a high yield (~85%) compared to previous methods.

# SUMMARY

A new method to purify DHDECMP by precipitation with mercury (II) is presented which is fast and inexpensive compared to previous methods. Efforts to optimize the procedure with respect to acidity, temperature, solvent, and stoichiometry are described in this report.

Initial precipitations of $Hg(DHDECMP)NO_3$ were performed by contacting acidic mercuric nitrate solutions with 20% DHDECMP in a mixed solvent composed of 2 parts decalin, 1 part diisopropylbenzene. Major product losses occur due to solubility of the precipitate in the resultant organic phase. Using 20% DHDECMP in hexane has maximized yields at about 85%.

Time required to perform the purification depends on the rate of the Hg-DHDECMP reaction. Reactions at 40°C are essentially complete after 1 hour.

Formation of $Hg(DHDECMP)NO_3$ causes DHDECMP to lose a methylene proton. Although acid is produced, there seems to be no acid dependence on the reaction as the initial aqueous phase acidity is varied from $0.05\underline{M}$ to $1.0\underline{M}$ $HNO_3$.

Stoichiometrically, a 1:1 mole ratio of Hg:DHDECMP is sufficient for precipitation. However, to insure complete precipitation and to account for side reactions, a ratio of 1.5:1, Hg:DHDECMP, is recommended.

These experimental results were used to optimize the purification procedure which is briefly described as follows: react 20% crude DHDECMP in hexane with an equal volume of $1\underline{M}$ $Hg(NO_3)$ - $1\underline{M}$ $HNO_3$ for 1 hour at 40°C. After washing the precipitate several times with hexane and water, DHDECMP is regenerated by treatment with caustic cyanide.

This procedure has produced >97% pure DHDECMP with yields of ~85%.

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# I. INTRODUCTION

Dihexyl N,N-diethylcarbamylmethylenephosphonate (DHDECMP) has shown desirable extractant properties for partitioning actinides from acidic nuclear waste solutions (1,2,3). A major problem associated with the work has been obtaining sufficiently pure extractant material. Commercially available DHDECMP is ~65% pure and contains numerous impurities, including acidic species which cause deleterious extraction characteristics. Actinides are irreversibly extracted from acidic waste solutions using crude DHDECMP as extractant. Actinides are readily stripped from purified DHDECMP using dilute nitric acid which contains hydroxylamine nitrate to reduce plutonium to valence (III). Previous purification procedures used in our laboratory have been centrifugal molecular distillation and preparative liquid chromatography (4). The former method yields bulk quantities of ~88% pure DHDECMP while the latter method has given several grams of >99% material. Both methods are expensive, require elaborate equipment, have poor yields, and are time consuming. A mercury precipitation method for purifying DHDECMP which is rapid, has a high recovery factor, results in a product of high purity and is inexpensive is reported in this paper.

Chemical means of purifying DHDECMP such as the copper precipitation method used to purify di(2-ethylhexyl) phosphoric acid (5) were explored. Attempts to form precipitates of DHDECMP with rare earth elements and with uranium as well were unsuccessful. Further efforts along this line were thus abandoned.

In a peripheral study to better understand the behavior of mercury (which is present in much of our nuclear waste) with the DHDECMP extractant, mercury loading studies were performed. The extractant was 20% DHDECMP* in a mixed solvent composed of two parts decalin and one part diisopropylbenzene (DIPB). At high mercury loading a white precipitate formed. After washing the precipitate twice with mixed solvent and water and contacting it with

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* This extractant was purified by centrifugal molecular distillation and was 88% pure.

caustic cyanide, the resultant organic liquid was found to be >97% pure DHDECMP. This paper describes our subsequent experimental work to optimize the use of mercury precipitation for the purification of DHDECMP.

## II. EXPERIMENTAL

### 1. General Procedures

All DHDECMP solutions used in this work are reported as volume percents. Crude DHDECMP (65%) was obtained from Wateree Chemical Company, Lugoff, South Carolina. Other chemicals used were reagent grade or better.

Purity of DHDECMP samples, as weight percents, were determined by gas chromatography using an internal spike of tributyl phosphate (TBP). The chromatograph, column and chromatographic parameters have been discussed previously (1). Purified DHDECMP (>99%), used for measuring the response function of TBP:DHDECMP, was obtained from previous work (4).

Elemental analysis for C, H, N, P were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Mercury determinations were made by neutron activation.

Acidity of organic and aqueous solutions were determined using procedures developed at ICPP (6).

Distribution coefficients for plutonium and mercury were performed using procedures established earlier (1).

$Hg(DHDECMP)NO_3$ (mp 120-122) was recrystalized from 20% benzene - 80% hexane solution.

Mercury - DHDECMP reactions and solubility studies at $\geq$ 25°C were carried out in a thermostated temperature bath while being agitated with a mechanical wrist shaker. Solubility studies below 25°C were maintained at the required temperature with a magnetic stirrer-cold plate. $^{203}Hg$ was used to tag $Hg(NO_3)_2$ solutions. Tagged precipitate, $*Hg(DHDECMP)NO_3$, was prepared by reacting DHDECMP with tagged $Hg(NO_3)_2$. Gamma-ray spectometry, using NaI(Tl) or Ge(Li) detectors, was used to determine mercury concentrations in aqueous and organic phases.

Overall yields for recovery of DHDECMP were determined by gas chromatography. A weighed sample of crude DHDECMP solution was spiked with a known weight of pure TBP before purification. After purification of a known weight of crude DHDECMP the resultant organic was spiked with TBP. The spiked crude and purified DHDECMP solutions were analyzed by gas chromatography. A comparison of TBP and DHDECMP peak areas in both solutions leads directly to a determination of yield.

Yield for the recovery of DHDECMP from $Hg(DHDECMP)NO_3$ was determined by weighing the recovered DHDECMP obtained after treating a known weight of precipitate with caustic cyanide.

### 2. Elemental Analysis of the Mercury Precipitate

Analysis of the recystalized organomercury compound for C, H, N, P and Hg gave 34.66%, 6.25%, 4.56%, 5.04% and 32.07%, respectively. This is consistent with a composition of $Hg(DHDECMP)NO_3$ where the corresponding theoretical values are 34.59%, 5.97%, 4.48%, 4.96% and 32.57%. Acid produced when purified DHDECMP is reacted with mercuric nitrate is equivalent to the amount of DHDECMP available. This suggests that DHDECMP deprotonates at the methylene carbon on forming the precipitate. Whether or not mercury attaches at this carbon or to an oxygen of an enolate form of DHDECMP subsequent to deprotonation is speculative at this point.

### 3. Solubility Studies

The purification procedure removes aqueous and organic soluble impurities from the mercury precipitate. However, major product losses occur due to the solubility of $Hg(DHDECMP)NO_3$ in the mixed solvent system decalin/DIPB. In addition, rotary evaporation of these solvents from the precipitate and purified DHDECMP is difficult. Results of solvent scoping studies to find a more suitable solvent, showed the mercury compound to be soluble in benzene, carbon tetrachloride, dichloromethane, acetone and crude DHDECMP with limited solubility in diisopropylbenzene and alcohols of $C_5$ or less. It is insoluble in decalin, hexane and other aliphatic solvents. The study indicates that hexane would be an ideal solvent for the purification procedure.

A more quantitative estimate of the solubility of Hg(DHDECMP)$NO_3$ in hexane and 1M $HNO_3$ is shown in Table 1. These values were determined by equilibrating traced precipitate with these solutions at the various temperatures. Centrifuged aliquots were then taken for gamma-ray spectrometry and their concentration determined by comparison to known standards.

TABLE 1

Solubility of Hg(DHDECMP)$NO_3$ in Hexane and 1M $HNO_3$

| Hexane (g/L) | Temp(°C) | 1M $HNO_3$(g/L) |
|---|---|---|
| 3.13 ± 0.05 | 40 | 0.17 ± 0.02 |
| 1.02 ± 0.02 | 25 | --- |
| 0.53 ± 0.03 | 15 | --- |
| 0.321 ± 0.003 | 0 | --- |

Aqueous samples were difficult to obtain free of suspended Hg(DHDECMP)$NO_3$. The only value obtainable for this solution was at 40°C.

As solvent scoping studies showed, Hg(DHDECMP)$NO_3$ is soluble in crude DHDECMP. To limit the solubility of the mercury compound during the precipitation reaction, starting crude DHDECMP was made 20% in hexane. As Table 2 shows, this concentration also produces the best yield for a one-hour reaction at 40°C.

## TABLE 2

### Overall Yields of DHDECMP vs % Crude DHDECMP in Hexane[a]

| % Crude DHDECMP | Yield (%) |
|---|---|
| 10 | 74 |
| 20 | 81 (85,86,86)[b] |
| 30 | 74 |

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a) Precipitation reaction at 40°C for 1 hour with 1M $Hg(NO_3)_2$ - 0.1M $HNO_3$

b) Precipitation reaction at 40°C for 1 hour with 1M $Hg(NO_3)_2$ - 1.0M $HNO_3$

Since recovery of DHDECMP is ~98% for the caustic cyanide step, the overall yields in Table 2 indicate that major product losses are due to solubility in the organic phase after precipitation. This it is not surprising since impurities present after precipitation are organophosphates, phosphonates and phosphites (1).

### 4. Temperature Dependence of the Hg-DHDECMP Reaction

Initial precipitation reactions, conducted at room temperature, generally took several hours to form a precipitate. In order to reduce the time necessary to perform the purification procedure, the effect of temperature on the precipitation reaction was studied at 25° and 40°C. The rate of these reactions were monitored by observing the decrease in mercury in the aqueous phase with time. For each run, eight sample tubes containing equal volumes of the reactants (0.61M DHDECMP and $^{203}Hg$ traced 1M $Hg(NO_3)_2$ - 1M $HNO_3$) were reacted. Tubes were removed periodically, centrifuged, and one ml aliquots of the aqueous phases analyzed for $^{203}Hg$ at a standardized geometry. The results (Figure 1) show that the reaction is essentially complete after one

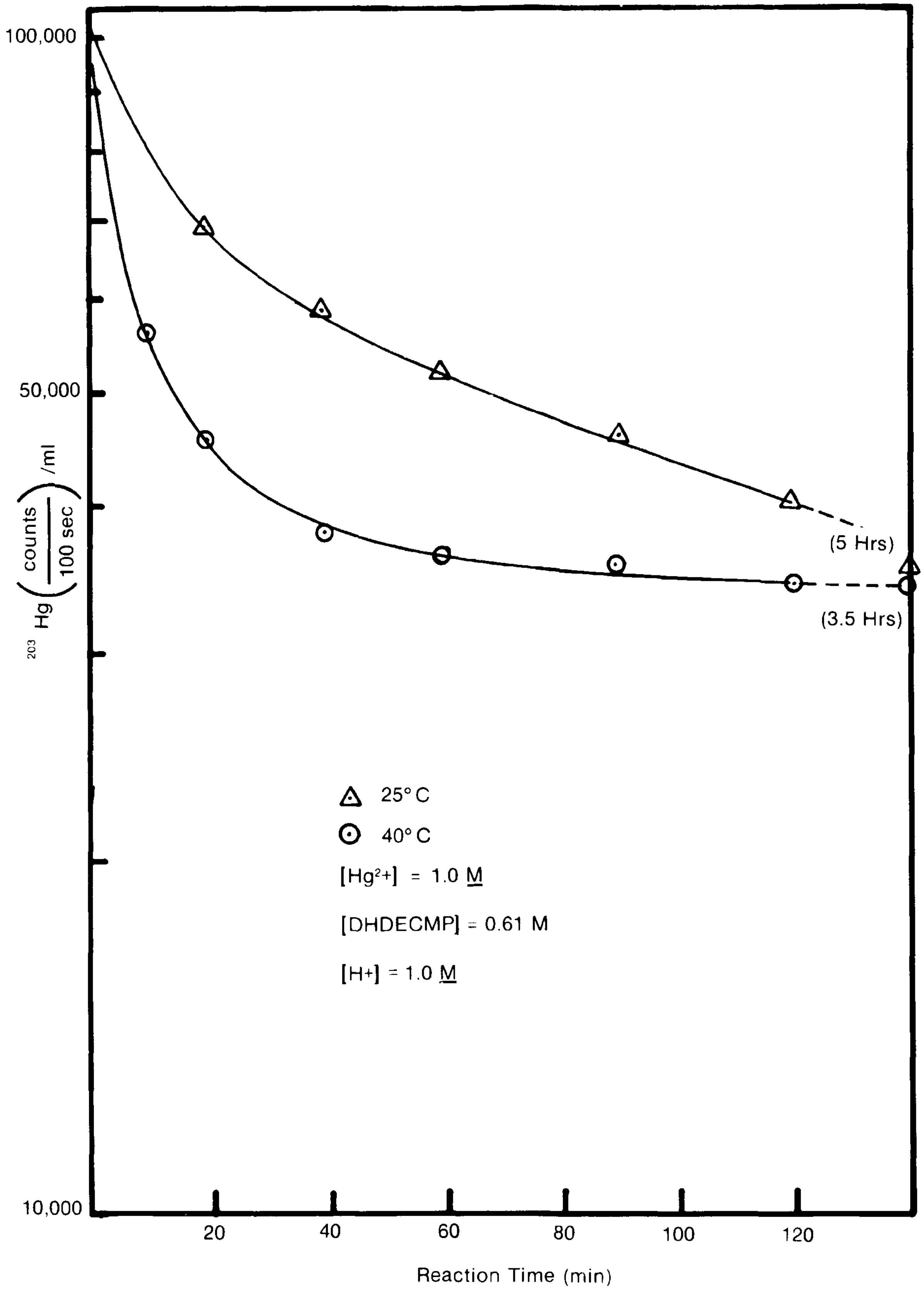

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FIGURE 1. Temperature Dependence of the Hg - DHDECMP Reaction

hour at 40°C. Under these conditions, a precipitate forms in about 30 minutes. Higher temperatures are not advised due to possible degradation of DHDECMP in the presence of acid.

## 5. Stoichiometry

Stoichemetrically, a 1:1 mole ratio of Hg:DHDECMP should be sufficient to precipitate Hg(DHDECMP)$NO_3$. However, best yields are obtained under excess mercury conditions. This not only insures complete precipitation but also makes up for mercury that may be consumed by impurities. In contrast to purified DHDECMP, crude material generates ~5-10% more acid than available DHDECMP, indicating that other mercury reactions may be occurring. For these reasons, a mole ratio of at least 1.5:1, Hg:DHDECMP, is recommended.

## 6. Acid Dependence

Precipitation of Hg(DHDECMP)$NO_3$ produces an equivalent amount of acid. Initial acidity of the mercury nitrate solution may have substantial effects on the Hg-DHDECMP reaction. To study this, mercury distribution coefficients were measured as a function of initial aqueous phase acidity. Non-equilibrium effects caused by Hg(DHDECMP)$NO_3$ precipitation were avoided by using dilute (0.0027$\underline{M}$) solutions of traced mercuric nitrate. Nitrate concentration was held constant throughout the acid range by adjusting with $NaNO_3$. A 0.5$\underline{M}$ solution of purified DHDECMP in hexane was used as the extractant. Equal volumes of each phase were contacted for 1 hour at 40°C. Distribution coefficient measurements showed no difference over the acid range 0.05$\underline{M}$ to 1.0$\underline{M}$ $HNO_3$. This is in contrast to the results in Table 2 where yields were slightly better at higher acid. Explanation of this is not obvious. It should be noted that the acid dependence was studied under dilute mercury conditions as compared to the precipitation reaction. There are indications that two separate reactions may occur depending on whether micro or macroscopic amounts of mercury are present. Since the purpose of this paper is to report on a purification process of a potentially important extractant, the theoretical aspects of this reaction will be pursued at a later date.

## 7. Optimized Purification Procedure

The previous studies have established optimum conditions for purifying DHDECMP by mercury precipitation. The complete procedure for purifying 10 grams of DHDECMP is given below.

Take 18.1 ml of crude DHDECMP (~65% pure) and make into a 20% solution with hexane. React with an equal volume of 1M $Hg(NO_3)$ - 1M $HNO_3$ for 1 hour at 40°C. After cooling, centrifuge and discard the organic and aqueous phases. The white amorphous precipitate is vigorously washed twice with 90 ml of hexane and water (45 ml of each); centrifuging after each wash. If centrifuging is not possible, the precipitate can be collected by vacuum filtration and washed with the same volumes of hexane and water. If washings are inefficient, recrystalization from 17 ml of 20% benzene - 80% hexane solution will free the precipitate from entrained impurities. DHDECMP is regenerated by contacting the precipitate with 55 ml of 0.5 M $Na_2CO_3$ - 2M KCN solution for 30 minutes; 25 ml of hexane being added to dissolve the liberated DHDECMP. The hexane-DHDECMP phase is then contacted with 15 ml of fresh cyanide solution for 15 minutes. This is followed by equivalent volume water washes until neutral. (Complete removal of mercury is checked by acidifying a portion of the organic phase with 1M $HNO_3$. A copper bead is then added to the acidified organic phase to see if any mercury plates out. If positive, more cyanide washings are necessary.) After centrifuging, the organic phase is filtered and the hexane removed under slight vacuum using a rotory evaporator. The recovered product is clear and colorless with a purity >95%, generally about 97%. Impurities present are approximately equal amount of dihexyl hexylphosphonate and the octyl, hexyl homologue of DHDECMP.

## III. CONCLUSIONS

In practice, this method has produced 100 ml quantities of >95% pure DHDECMP within one day using simple laboratory equipment. This is in marked contrast with previous methods, especially when higher purities were sought (i.e., liquid chromatography).

The precipitation reaction between DHDECMP and mercuric ion is the slowest step in the procedure. Carrying out the precipitation at 40°C will essentially complete the reaction in one hour.

Overall yields are eventually dependent on the quality of starting crude DHDECMP. Impurities present after precipitation dissolve $Hg(DHDECMP)NO_3$. Lower crude DHDECMP purities having more residual impurities will therefore dissolve more precipitate with a concomitant reduction in overall yields. Even so, 65% crude DHDECMP, which has been the commercially available product, will give 85% yields.

Of course the real proof of the method lies in the extraction characteristics of the recovered material. In our actinide partitioning studies with DHDECMP, extraction has always been successful. Reversing this process, or stripping is acutely influenced by impurities which form organic soluble complexes under dilute acid conditions (3). Plutonium (IV), which is the most difficult actinide to strip when impurities are present, is readily stripped from DHDECMP extractant purified by this method.

Finally, the possibility exists for extending this procedure to other similar extractants. Initial experiments show that other homologues of DHDECMP will also precipitate. Experiments to expand the method to these and other compounds will be reported on at a later date.

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