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Extracting Acetic Acid from Acidic Solutions

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Abstract: In the UREX + process, acetic acid must be removed from the raffinate stream to avoid interference with the recovery and recycle of nitric acid solutions. Solvent extraction was selected to be the most promising approach to accomplish this cleanup. Acetic acid partitioning into pure diluents used in the UREX + process were found to be too low for an effective separation. Of the solvents tested, the most promising solvents for the extraction of acetic acid were found to be TBP in dodecane and TBP in FS-13.

Keywords: Acetic acid, distribution coefficient, dodecane, dichloroethane, nitric acid, phenyltrifluoromethyl sulfone, solvent extraction, tributyl phosphate

INTRODUCTION/BACKGROUND

The UREX + process is a proposed new approach to separating the components of spent nuclear fuels. It has 5 steps all utilizing solvents to extract various components of the spent fuel. The current steps considered for the UREX + process are shown in Fig. 1. The first step is called the UREX step and uses tributylphosphate (TBP) with dodecane and acetohydroxamic acid to selectively extract uranium and technetium. The purpose of the acetohydroxamic acid is to prevent the extraction of plutonium in the UREX step. The next step uses polyethylene glycol (PEG) with phenyltrifluoromethyl sulfone, FS-13, and cobalt

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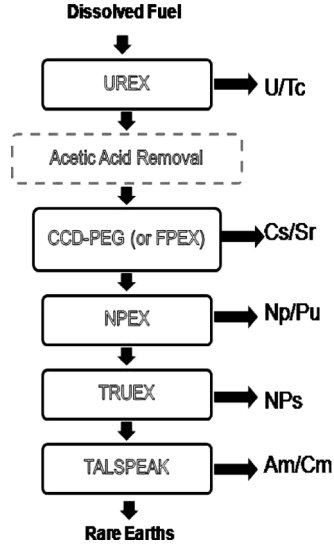

Figure 1. UREX+ flowsheet with proposed acetic acid removal step.

dicarbollide to extract both strontium and cesium. An alternative to CCD-PEG step is the FPEX step uses a BOB Calix solvent system in order to extract Sr and Cs. The NPEX step is next and uses the same TBP-dodecane solvent system as UREX without the acetohydroxamic acid so that plutonium and neptunium are co-extracted with any remaining uranium. During the TRUEX segment of the process, americium, curium, the rare earth elements (lanthanides), and any remaining plutonium and neptunium are extracted by a solvent containing octyl(phenyl)-N, N-diisobutyl carbamoylmethyl phosphine oxide (CMPO) and TBP with *n*-dodecane. The final step is the TALSPEAK step that extracts the lanthanides from the TRUEX product using diethylene triamine pentaacetic acid (DTPA) and a complexing agent (e.g. citric or lactic acid) to hold the actinides (e.g. americium and curium) in the aqueous solution (1,2).

In the first step of the UREX+ process, acetohydroxamic acid is added to suppress extraction of plutonium when TBP-dodecane extracts uranium and technetium. Plutonium forms a complex with acetohydroxamic acid so that TBP is unable to extract it from aqueous solution. After uranium and technetium are extracted, this complexing agent hydrolyzes to form acetic acid and hydroxylamine nitrate. While the hydroxylamine nitrate will break down in strong acid solutions and/or at elevated temperatures, the acetic acid degradation product needs to be removed or destroyed so it will not interfere in the recycling of nitric acid (2). The acetic acid removal is shown in Fig. 1 occurring just after the UREX step. The optimum location of the acetic acid

removal step is not established, but it should be used after the acetohydroxamic acid has decomposed. The extraction of acetic acid is also needed for many non-nuclear manufacturing processes, and the results from this study could also be useful to those processes.

Alternate Separation Methods Considered

Many technologies were examined as possible acetate removal and/or destruction methods, but some proved more favorable than others for the UREX+ process. Technologies such as membrane separation and ion exchange were eliminated early in the literature review. No membrane was found that was sufficiently selective to remove acetic acid effectively in a single pass, and multistage membrane operations did not appear attractive. Ion exchange was eliminated because no ion exchange material was identified with sufficient selectivity for acetate ions over higher concentrations of nitrate ions in a mixed stream. Crystallization is a simple process but requires a preliminary concentration step to create conditions where the acetic acid could crystallize from solution (5–7). Distillation does not seem to offer any advantage for acetic acid removal unless coupled with crystallization or another unit operation (6). Adsorption was considered, but no adsorbent was found with sufficient selectivity for acetic acid (3,4). Destruction methods could completely destroy the acetic acid. However, the extreme conditions required to destroy acetic acid are likely to destroy all or most of the nitric acid as well (8–10). It was decided that solvent extraction would be the most promising method to pursue further. Solvent extraction appears to be technically feasible and is a similar technology to that used elsewhere in the UREX+ system. A few solvent mixtures (diluent and extractant) have been shown to remove acetic acid from nitric acid (11,12), however, these mixtures are also capable of extracting some of the radioactive components in spent fuel solutions and add unwanted complexity to the process being developed. In addition, there appeared to be further opportunities for considering alternative solvents. The focus of this study is to identify an agent capable of extracting acetic acid without co-extraction of other radioactive components, or with minimal extraction of radioactive components. Ideally, the solvent selected would be commonly used in the UREX+ process.

Solvent Selection

The three solvents/diluents discussed, dodecane, dichloroethane, and FS-13 were chosen because dodecane is already present in the UREX+

process and dichloroethane is comparable in some ways to phenyltrifluoromethyl sulfone, also known as FS-13 solvent, utilized in the PEG-CCD step (13). Dodecane is used in the UREX, NPEX, and TRUEX steps of the process, and FS-13 solvent is used during the PEG/CCD step. It was decided that the most probable place to extract the excess acetic acid was after the UREX step and before the PEG/CCD step (Fig. 1). At this point, the acetohydroxamic acid is hydrolyzed into acetic acid and hydroxylamine nitrate (HAN). Since FS-13 was not readily available early in this study, dichloroethane was used initially as an analogue for FS-13 solvent [13]. Dichloroethane is not a suitable solvent for the UREX + process due to its flammability. A limited quantity of FS-13 became available during the experimental trials and was also tested. These solvents were also run through the experiment with tributyl phosphate (TBP) at a 2.5 M concentration.

EXPERIMENT

The distribution coefficients for a number of solvents and conditions were measured to determine the amount of acid transferred into the organic phase from solutions similar to those found in the UREX + process. Solutions of various acidic concentrations were prepared ranging from 0.01 M to 1 M of both nitric and acetic acids to serve as the reference aqueous solutions for this study. Organic solvents (diluents) dichloroethane, dodecane, and FS-13 were the first solvents tested. Dodecane 99% was obtained from ACROS Chemicals, ACS grade dichloroethane was obtained from Fisher Scientific, and FS-13 was obtained from Marshallton Reasearch Laboratories. Using a 250 mL separatory funnel, 10 mL of aqueous and 10 mL of organic solvent were added. The funnel was hand-shaken for approximately one minute and settling was allowed for full separation of the layers. The aqueous layer was drawn off into a small beaker and analyzed using a Mettler-Toledo SevenEasy pH meter and a Brinkmann 765 Dosimat set on dose mode containing 1 M caustic solution. Using the amount of caustic required to obtain the equivalence point of the aqueous solution, the concentration of acid in the aqueous phase was determined by equation 1.

$$[AQ] = \frac{[Base] \times V_{Base}}{(V_{Sample})} \quad (1)$$

[Base] represents the standardized concentration of the solution used to titrate, V_{Base} is the amount of base needed to reach the equivalence point

(Fig. 2), V_{Sample} is the sample size, and [AQ] is the calculated concentration of the aqueous phase after mixing with the organic phase. The amount of acid in the organic phase is then found by mass balance.

$$[AQ_{Original}]V_{Original} - [AQ]V_{sample} = [ORG]V_{ORG} \tag{2}$$

$[AQ_{Original}]$ represents the initial concentration of the aqueous phase when put into the separatory funnel. $V_{Original}$ is the volume of aqueous put into the separatory funnel. [ORG] is the concentration of acid in the organic phase calculated by the difference of the initial aqueous acid concentration and aqueous concentration after equilibration, and V_{ORG} is the volume of organic initially in the separatory funnel. The distribution coefficient was then calculated using equation 3.

$$K_D = \frac{[ORG]}{[AQ]} \tag{3}$$

When using a mixture of nitric and acetic acids with equal volumes, the amount of caustic required to reach equivalence must be read from the titration plot with two equivalence points and calculated as shown in equations 4 and 5 and Fig. 3.

$$V_2 - V_1 = V_{Base-Acetic} \tag{4}$$

$$V_1 = V_{Base-Nitric} \tag{5}$$

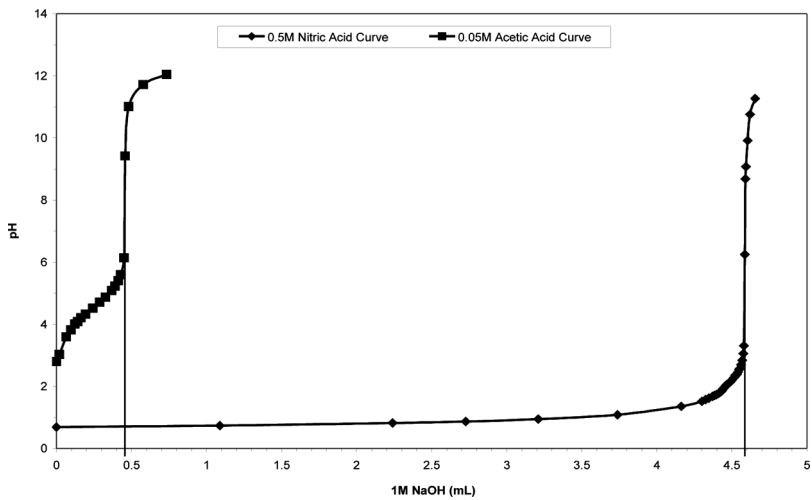

Figure 2. Single acid titration curves (nitric acid and acetic acid).

V_2 is the second equivalence point and V_1 is the first equivalence point. The calculations result in the volume of base required to reach the end point for equal volume acetic and nitric acids, respectively.

RESULTS AND DISCUSSION

Titration Curve Analysis

For the single acid case, the procedure is simple. The steepest point of the curve where the concavity changes is the equivalence point reading (Fig. 2). The volume of base required is then simply read from the x-axis. Using this value, the above calculations can be completed. For the mixed acid case, the procedure becomes slightly more complicated. The titration curve is similar to that of a diprotic acid analysis with two equivalence points. In the case of nitric and acetic acids, the first curve is completion of nitric acid neutralization while the difference between the endpoints of the first curve and the second curve is the completion of acetic acid neutralization (Fig. 3) (14,15). Using equations 4 and 5, the volume of base needed to neutralize each acid can be found and then inserted into equations 1–3 to obtain a distribution coefficient for each acid.

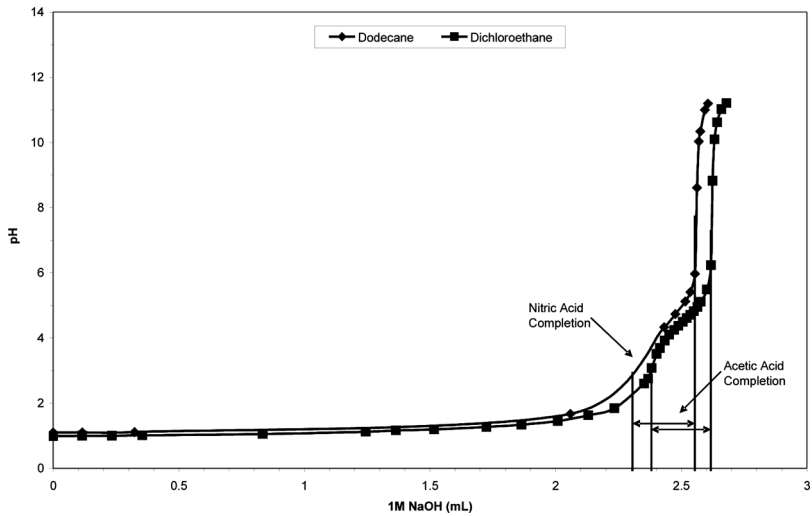

Figure 3. Mixed acid titration curves (both nitric and acetic acid together).

Table 1. Extraction of acetic acid in experimental organic diluents

Acetic acid concentration	K_D	Standard deviation
Dodecane		
0.01M	−0.00397	0.022258
0.05M	0.006039	0.003788
0.5M	0.050085	0.01119
1M	0.010973	0.034771
Dichloroethane		
0.01M	0.041742	0.020909
0.05M	0.01898	0.008563
0.5M	0.030064	0.024639
1M	0.050004	0.01795
FS-13		
0.01M	−0.83036	0.00089
0.05M	−0.25364	0.2257
0.5M	−0.0696	0.04424
1M	−0.00995	0.023845

Acetic Acid Extraction from Water-Acetic Acid Solutions

Tests were run to determine the distribution coefficient for acetic acid between aqueous and diluent phases (Table 1). The distribution coefficients found in this study for dodecane was small, but generally comparable to those reported by Judd King using several diluents with acetic acid (Table 2). The distribution for the other two solvents, dichloroethane and FS-13 were also small. A plausible explanation of the significant negative numbers for FS-13 is that there may have been some transfer of an acidic contaminant from the organic phase to the aqueous phase.

Table 2. Extraction of acetic acid in pure organic diluents.

Diluent	K_D	Reference
Chevron Solvent 25	0.009	[3]
n-Hexanol	0.88	[3]
Nitrobenzene	0.06	[3]
Chloroform	0.028	[3]
n-Heptane	0.02	[3]

Table 3. Extraction of nitric acid in pure organic diluents

Nitric acid concentration	K_D	Standard deviation
Dodecane		
0.01M	0.050017	0.022206
0.05M	0.061638	0.050059
0.5M	0.027958	0.00172
1M	−0.00474	0.009551
Dichloroethane		
0.01M	0.020709	0.032938
0.05M	0.020515	0.016487
0.5M	−0.02579	0.030955
1M	0.015247	0.002282
FS-13		
0.01M	−0.83136	0.00016
0.05M	−0.51616	0.021645
0.5M	−0.10366	0.018025
1M	−0.03877	0.048026

Nitric Acid Extraction from Water-Nitric Acid Solutions

The next tests involved determining the distribution coefficient for nitric acid between aqueous and diluent phases. When contacting aqueous nitric acid with the three diluents tested, a low distribution coefficient was obtained similar to those measured with acetic acid solutions (Table 3). This was expected since nitric acid almost completely dissociates in water.

Nitric and Acetic Acid Extraction from Water-Acetic Acid-Nitric Acid Solutions

A two equivalence point titration curve was produced using both nitric and acetic acids in the aqueous layer (Fig. 3). The distribution coefficients of acetic acid and nitric acid separately both yield little extraction. When combined, the distribution coefficients of acetic and nitric acid are still very small (See Table 4).

As shown Table 4, n-dodecane extracts nitric acid at a higher ratio than acetic acid. With dichloroethane, acetic extracts more strongly than nitric acid. The negative extraction values probably mean the very small extent of extraction is within the experimental error. This case is represented by the larger negative values in the FS-13 results. In either case, all the distribution coefficients

Table 4. Extraction of acetic and nitric acids in organic diluents

Ratio of concentrations (Acetic:nitric)	Nitric acid		Acetic acid	
	K_D	Standard deviation	K_D	Standard deviation
Dodecane				
1:0.05	0.030	0.012	−0.015	0.003
1:0.5	0.026	0.024	−0.001	0.001
1:1	0.008	0.010	−0.022	0.003
0.5:1	−0.003	0.001	−0.014	0.005
0.05:1	−0.011	0.000	−0.081	0.004
Dichloroethane				
1:0.05	0.058	0.098	0.096	0.036
1:0.5	0.024	0.017	0.048	0.012
1:1	0.021	0.002	0.096	0.029
0.5:1	0.013	0.012	0.078	0.029
0.05:1	0.037	0.007	0.061	0.006
FS-13				
1:0.05	−0.588	0.010	−0.010	0.002
1:0.5	−0.200	0.079	0.048	0.047
1:1	−0.048	0.022	−0.038	0.016
0.5:1	−0.065	0.024	−0.014	0.001
0.05:1	0.060	0.010	−0.306	0.006

show that there is a need for another approach to the extraction of acetic acid.

2.5 M Tributyl Phosphate Mixed with Organic Diluents

The addition of tributyl phosphate (TBP) to the system can be used to enhance the extraction of either acid when using Chevron Solvent 25 (11). Addition of tributyl phosphate to these diluents also improves the extraction of both acetic and nitric acids as shown in Table 5. Tests were made with aqueous solutions of 0.05 M acetic acid only and 0.5 M nitric acid only. Then an equal-volume mixture of 0.05 M acetic acid and 0.5 M nitric acid was tested.

While the TBP in dodecane has the largest distribution coefficient for acetic acid out of the three diluents, the solvent with dichloroethane has the largest separation factor. The separation factor is the ratio of acetic acid to nitric acid distribution coefficients in the mixtures. FS-13 also shows a high separation factor and might be suitable in the UREX + process since, as noted earlier, dichloroethane is unsuitable. FS-13 also

Table 5. Extraction of acids in 2.5 M TBP mixtures

	Nitric acid		Acetic acid	
Concentration of acid	K	Standard deviation	K	Standard deviation
Dodecane				
0.05M Acetic acid	–	–	1.408	0.021
0.5M Nitric acid	0.404	0.073	–	–
0.05M:0.5M mixture	0.308	0.081	1.481	0.161
Dichloroethane				
0.05M acetic acid	–	–	1.255	0.010
0.5M nitric acid	0.193	0.021	–	–
0.05M:0.5M Mixture	0.134	0.012	1.350	0.124
FS-13				
0.05M acetic acid	–	–	0.530	0.063
0.5M nitric acid	0.259	0.014	–	–
0.05M:0.5M mixture	0.133	0.012	1.083	0.044

shows the highest jump between the distribution coefficients of the single acids and the mixture. This is favorable for the UREX + process and will be explored in further research as a method to extract acetic acid from the waste stream.

CONCLUSIONS

The diluent results confirm the results by King and coworkers (3) that neither acetic acid nor nitric acid is extracted effectively by simple hydrocarbon solvents. All of the solvents and extractants used by King were partially soluble in water or able to extract salts, including radioactive compounds present in the UREX + process. FS-13 is not soluble in water and is already used in one proposed step of the UREX + process. The most promising solvents for the extraction of acetic acid are TBP in dodecane and TBP in FS-13. Each solvent system exhibits a distribution coefficient greater than one with a sufficiently large separation factor.

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