

Chemical Technology Division

**CITRATE BASED "TALSPEAK" LANTHANIDE-ACTINIDE
SEPARATION PROCESS**

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TABLE OF CONTENTS

LIST OF FIGURES	v
ABSTRACT	vii
1. INTRODUCTION	1
2. THE TALSPEAK ACTINIDE-LANTHANIDE SEPARATION PROCESS	3
3. OUTSTANDING ISSUES AND OBJECTIVES	5
4. EXPERIMENTAL RESULTS	9
4.1 EFFECTS PRODUCED BY THE PRESENCE OF ZIRCONIUM : THIRD PHASE FORMATION	9
4.2 GLYCOLIC ACID SYSTEMS	9
4.3 CITRIC ACID SYSTEMS	14
4.4 DIFFERENCES BETWEEN THE GLYCOLIC AND THE CITRIC ACID SYSTEM	17
4.5 CITRATE-BASED-TALSPEAK SCOPING EXTRACTION TESTS	25
4.6 EXTRACTION AND STRIPPING FROM NITRIC ACID SOLUTION.	28
4.7 PURIFICATION OF THE ORGANIC EXTRACTANT	31
4.8 MULTISTAGE TESTING	32
4.9 MECHANISTIC EFFECTS THAT INFLUENCE THE TALSPEAK SEPARATION PROCESS	37
5. SUMMARY AND CONCLUSIONS	39
6. FUTURE RESEARCH AND DEVELOPMENT ACTIVITIES	40
7. REFERENCES	41

LIST OF FIGURES

1.	Schematic diagram for a typical TALSPEAK process	6
2.	"Third Phase" formation due to the presence of Zr(IV) ions	7
3.	"Third Phase" after treatment with sodium fluoride [1:1 F/Zr(IV) ratio]	12
4.	"Third-phase" formation due to the presence of Zr(IV) ions and in absence of DTPA ...	13
5.	Distribution coefficients for Citrate TALSPEAK lanthanide extraction at different loadings	16
6.	Distribution coefficients for Citrate TALSPEAK lanthanide extraction at different loadings in the presence of 10^{-3} M Zr(IV) and Mo(VI)	18
7.	Absorption spectrum of 0.8 <u>M</u> HDEHP in DIPB contacted with glycolic acid showing band responsible for the yellow color	19
8.	Viscosities of typical aqueous TALSPEAK solutions	21
9.	Viscosities of typical organic TALSPEAK solutions	22
10.	Interfacial tensions for the system 1.0 <u>M</u> citrate, 0.1 <u>M</u> DTPA / 0.8 <u>M</u> HDEHP in DIPB at pH=3.0 and room temperature	23

11.	Interfacial tensions for the system 1.0 <u>M</u> citrate, 0.1 <u>M</u> DTPA / 0.8 <u>M</u> HDEHP in DIPB at pH = 3.0 at 31°C, 41°C, and 52°C	24
12.	UV-VIS absorption spectra for the lanthanide mix of neodymium, praseodymium, europium, and erbium, in the 340 to 900 nm region	26
13.	Citrate-based TALSPEAK extraction using 0.8 <u>M</u> HDEHP in DIPB	29
14.	Reverse TALSPEAK extraction from 0.1 <u>M</u> HNO ₃ solutions using 0.8 <u>M</u> HDEHP in DIPB	30
15.	Neutralization curve of a 0.8 <u>M</u> solution of HDEHP in DIPB containing about 5% of MEHPA	33
16.	Neutralization curve of a 0.8 <u>M</u> solution of HDEHP in DIPB initially containing about 5% of MEHPA after washing with 0.5 <u>M</u> ammonium carbonate solution (1:1 volume ratio)	34
17.	Three-stages glass mixer-settler apparatus	35

ABSTRACT

The potential hazard posed to future generations by long-lived radionuclides such as the transuranic elements (TRU) is perceived as a major problem associated with the use of nuclear power. TRU wastes have to remain isolated from the environment for "geological" periods of time. The costs of building, maintaining, and operating a "geological TRU repository" can be very high. Therefore, there are significant economical advantages in segregating the relatively low volume of TRU wastes from other nuclear wastes.

Lanthanide elements are produced in relatively high yield by fission of ^{235}U . Almost all the lanthanide isotopes decay to stable nonradioactive lanthanide-isotopes in a relatively short time. Consequently, it is highly advantageous to separate the relatively small actinide fraction from the relatively large quantities of mainly stable lanthanide-isotopes.

The chemical behavior of lanthanides and actinides, 4f and 5f elements respectively, is rather similar. As a consequence, the separation of these two groups is difficult. The "TALSPEAK" process (Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes) is one of the few means available to separate the trivalent actinides from the lanthanides. The method is based on the preferential complexation of the trivalent actinides by an aminopolyacetic acid. At the same time, the lanthanides are more strongly extracted by a monoacidic organophosphate or phosphonate. Single-stage separation factors between neodymium (the least extractable lanthanide) and americium or curium are about 50.

Previous work based on the use of lactic or glycolic acid has shown deleterious effects of some impurity ions such as Zr(IV) even at concentrations as low as of 10^{-4} M . Other perceived problems were the need to maintain the pH and reagent concentrations within a narrow range along with a significant solubility of the organic phase at high carboxylic acid concentrations.

Our cold experiments showed that replacing the glycolic or lactic acid by citric acid eliminates or greatly reduces the deleterious effects produced by impurities such as zirconium.

An extensive series of batch tests was done using a wide range of reagent concentrations at different acidities, temperatures, and contact times. The results demonstrated that the citrate based TALSPEAK can tolerate appreciable changes in pH and reagent concentrations while maintaining an adequate lanthanide extraction. Visual observation of relative volumes did not show any significant loss of organic phase under a wide variety of conditions.

Experiments using a three-stage glass mixer-settler showed a good lanthanide extraction, appropriate phase disengagement, no appreciable deleterious effects due to the presence of impurities such as zirconium [Zr(IV)], excellent pH buffering, and no significant loss of organic phase.

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1. INTRODUCTION

One of the major problems in utilizing nuclear materials is the generation of radioactive wastes such as those present in the Hanford-site waste tanks. These wastes contain a large number of different radioactive isotopes that can be categorized in four different groups.

The first group is composed of very short lived isotopes (e.g. ^{89}Sr , ^{95}Nb , ^{134}Cs) that will decay after a few years of storage, usually accomplished in the water pool at or near the reactor. The second group is composed of short lived fission products, predominantly $^{90}\text{Sr}/^{90}\text{Y}$ and $^{137}\text{Cs}/^{137}\text{Ba}$ with a half-life of about 30 years. The radioactive contribution of these short lived fission products disappears in about 500 years. A third group is represented by the long lived fission products ^{99}Tc ($T=2.1 \cdot 10^5$ y), ^{129}I ($1.6 \cdot 10^7$ y), ^{135}Cs ($1.6 \cdot 10^7$ y), ^{107}Pd ($6.5 \cdot 10^6$ y), ^{93}Zr ($1.5 \cdot 10^6$ y), and ^{126}Sn (10^5 y), which along with the fourth group of long-lived actinides (Th, Pa, U, Np, Pu, Am, Cm), will decay in geological periods of time.

The potential hazard posed to future generations over periods of thousands of years by long lived radionuclides, such as the last mentioned two groups, constitutes a major problem in the responsible management of this nuclear legacy. However, some of the actinides can be recycled and reused as fissile material; the remaining ones can be transmuted into fissile materials. Similarly the long-lived fission products can be transmuted into stable or short-lived isotopes.

If the long-lived isotopes are recycled, reused, and or destroyed, the only remaining potential hazard due to very short and short-lived fission products will disappear after a few hundred years of storage. Under such a scheme, there is no significant "legacy" of radioactive wastes; and, in fact, it can be shown¹ that after a relatively short period, the radioactive hazard of the waste falls below that of the original uranium ore. Due to an increased political and economic discussion on nuclear waste responsibility, there is an increased interest in such partitioning, recycling, and destruction of long-lived radionuclides.

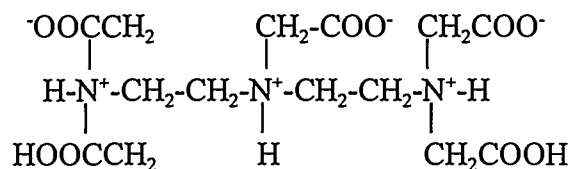
The partitioning of the different groups of radionuclides can be accomplished using a variety of methods. One crucial aspect of the partitioning is the separation of the long-lived, highly radioactive actinides from the rather similar, short-lived or nonradioactive, lanthanides. The longest-lived lanthanides are ^{147}Pm (beta decaying to stable ^{147}Sm with a half-life $T = 2.62$ y), ^{154}Eu (beta decaying to stable ^{154}Gd with a $T = 8.5$ y), ^{155}Eu (beta decaying to stable ^{155}Gd with a $T = 4.96$ y), and ^{151}Sm (beta decaying to stable ^{151}Eu with a $T=93$ y).

Because of their almost identical chemical behavior, the separation between actinide and lanthanide elements is very difficult. A treatment that can successfully and efficiently accomplish this difficult separation in aqueous systems is the so-called "TALSPEAK"² separative process (Trivalent Actinide-Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes).

Besides TALSPEAK, there are two other main processes that can separate the lanthanides from the actinides. One process uses a tertiary-amine extraction from concentrated lithium chloride solutions.^{3,4} This process is adequate for a small-scale operation but becomes impractical to full-scale operations because it generates large volumes of concentrated LiCl waste-brines that pose very difficult problems in waste disposal. The other process uses organic ion-exchange resins^{5,7} that are prone to severe radiolytic damage. This results in the consumption of large quantities of resin and necessitates the development of a suitable technology for treating the spent organic resins.

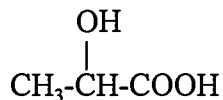
2. THE TALSPEAK ACTINIDE-LANTHANIDE SEPARATION PROCESS

In the TALSPEAK solvent-extraction process, the separation of lanthanides from actinides is accomplished using a combination of buffers and complexants in the aqueous phase, such as carboxylic and aminopolycarboxylic acids, and organophosphorus extractant diluted in an organic solvent. The resulting high level of separation is achieved through subtle chemical interactions in the complicated extraction system where many factors can alter the efficiency and speed of the separation. The essential separative mechanism is the preferential complexation of the trivalent actinides by an aminopolyacetic acid to form unextractable species, while the lanthanides are extracted using a monoacidic organophosphate or phosphate. The most common "TALSPEAK" aqueous complexant used is diethylenetriaminepentaacetic acid (DTPA).

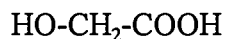


Diethylenetriaminepentaacetic acid (DTPA)

The typical carboxylic acids previously used as buffer complexants are lactic and glycolic acids.

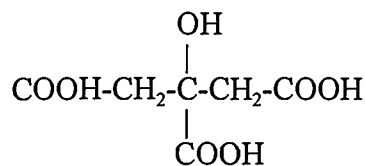


Lactic Acid (2-hydroxy-propanoic acid)



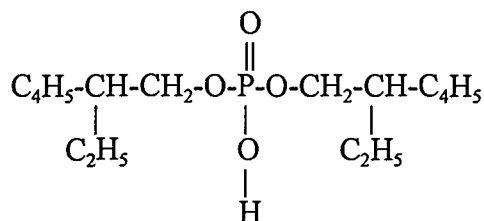
Glycolic Acid (hydroxy-acetic acid)

Although the use of citric acid as the buffer complexant was considered previously,² extensive testing was not documented. However, because of its known complexing power, it shows potential in limiting the negative effects of impurities such as Zr(IV). Also, since the citric acid is a tricarboxylic acid, its buffering capacity should be higher relative to the lactic or glycolic acids.



Citric Acid (2-hydroxy-1,2,3-propanetricarboxylic acid)

The most often used organic extractant is di(2-ethyl-hexyl)phosphoric acid (HDEHP) dissolved in an aromatic or aliphatic solvent, in order to reduce its viscosity.



HDEHP [DEHPA] (di-(2-ethylhexyl)phosphoric acid)

Some extensive lab-scale testing^{2,8-16} has shown that excellent separation can be achieved using glycolic or lactic acid, as the complexant buffer, in combination with DTPA, as the main complexant, in the aqueous phase, and HDEHP or 2-ethylhexyl phenylphosphonic acid (HEH[φP]) dissolved in diisopropylbenzene (DIPB) or diethylbenzene (DEB) as the organic extractant. Single-stage separation factors between neodymium, the least favorable lanthanide, and americium are about 50;² the separation factor for other lanthanides is even better.

In the **normal** TALSPEAK process, the aqueous phase containing the complexing reagents plus the lanthanides and actinides is contacted with the organic phase to extract the lanthanides. In the **reverse** TALSPEAK process,¹⁷ the organic phase is first loaded with the actinides and lanthanides, usually from a dilute acid solution (0.05-0.1 M HNO₃), and then contacted with the complexing aqueous phase to strip the actinides.

This **reverse** process can be a very convenient way of connecting the TALSPEAK partitioning process with other separative schemes. On the other hand, the **normal** TALSPEAK (See Fig. 1) has some advantages over the **reverse** mode related to the extraction kinetics of heavy lanthanides and actinides.

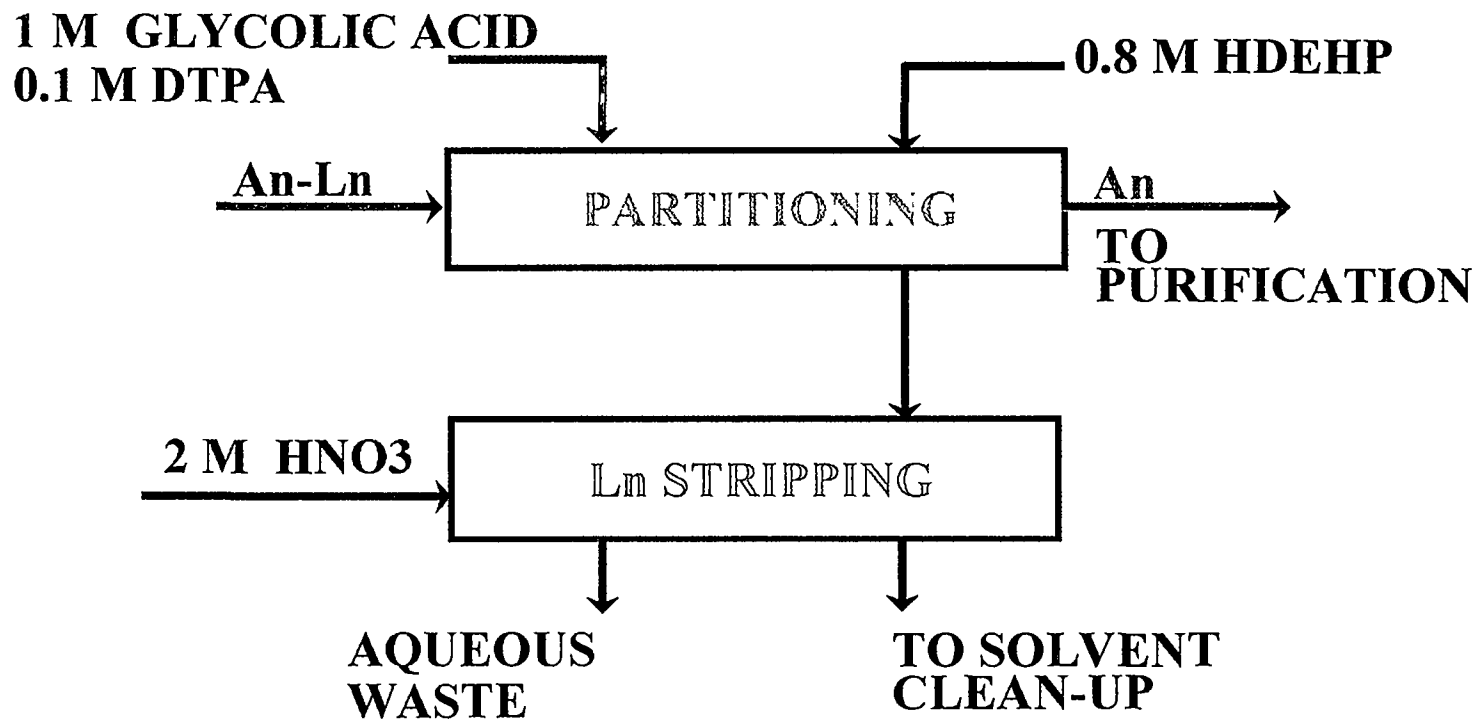
The heavy lanthanides and actinides can display slow partitioning kinetics. In the **normal** extraction, the actinides and lanthanides are dissolved in the aqueous phase and the lanthanides extracted into the organic phase. The slower extraction kinetics for the heavy lanthanides is compensated by their much larger extractability. As a consequence, even at short times, a significant fraction of the heavy lanthanides is transferred into the organic phase. Since the actinides remain in the aqueous phase, good separation between the lanthanides and actinides can be achieved even at short contacting times. Another advantage relates to the processing of wastes that were not stored long enough to allow for the substantial decay of the lanthanides into stable isotopes (see Section 1). For the processing of these "aged" wastes, the radiolytic damage of the organic phase is reduced using the **normal** process since the radioactive actinides are never dissolved in the organic phase.

3. OUTSTANDING ISSUES AND OBJECTIVES

As mentioned in the introduction, extensive laboratory-scale research and development on the TALSPEAK process have already been done. Some limited, closed-loop, tests using high-level wastes generated from low-burnt spent fuel were also completed.^{18,19} However, significant research and development are still needed before the method could be adequately implemented at pilot and full industrial scale.

One of the topics that needs to be evaluated is the effect of impurity ions on the lanthanide extraction and loading. Small amounts of Zr(IV) reduced the Ln-Ac separation, while higher concentrations can generate a "third phase" (see Fig. 2) .

TALSPEAK PROCESS



6

Fig. 1. Schematic diagram for a typical TALSPEAK process.

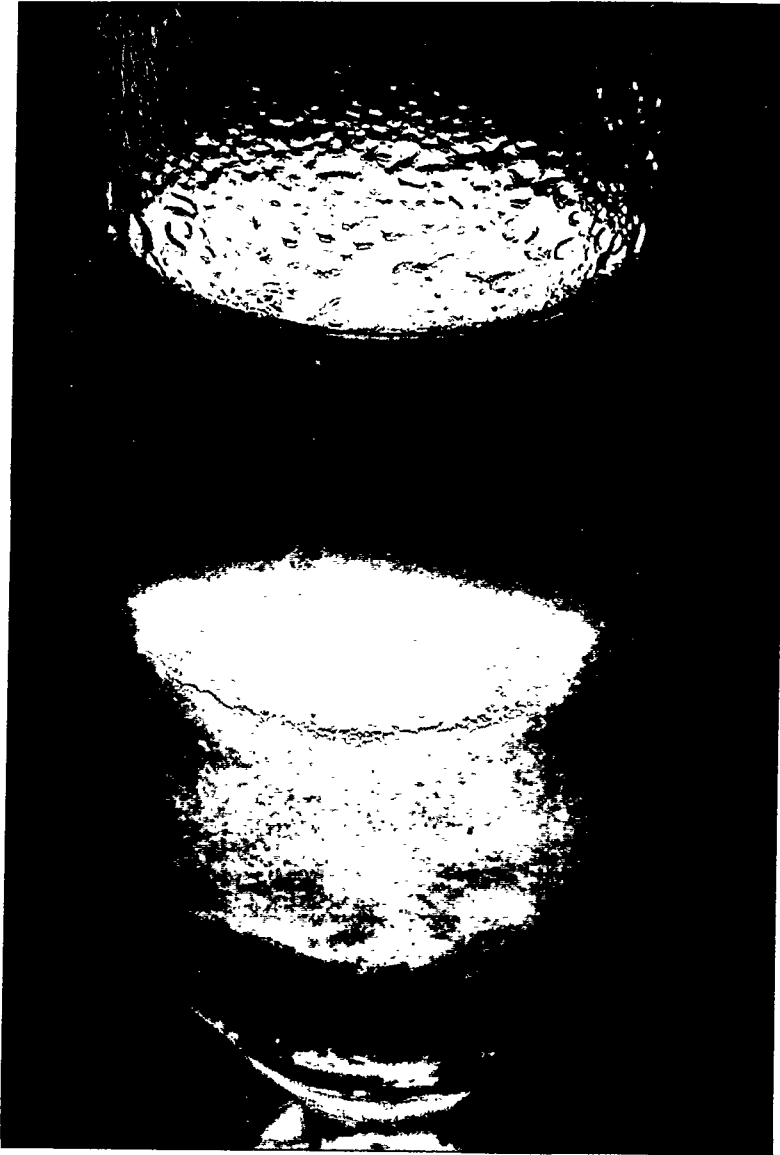


Fig. 2. "Third Phase" formation due to the presence of Zr(IV) ions.

It was previously reported¹⁶ that a Zr(IV) concentration of 10^{-4} M produced severe losses of neodymium into the actinide stream during a mixer-settler experiment. Besides zirconium, molybdenum is another impurity of concern because of its possible interference with the Ln-Ac separation. For such reasons, the concentration levels and conditions at which Zr(IV) and Mo(VI) can be tolerated in the process stream need to be determined.

There is also a perception from previous experiments that the pH and reagent concentrations have to be controlled within a narrow range to maintain an adequate separation. Another potential problem is a significant solubility of the organic phase at high buffer (i.e., carboxylic acid) concentrations.^{2,18} Using 2-ethylhexyl phenylphosphoric acid and 6 M lactic acid concentration, Weaver² reported a 20 vol% loss of the organic phase at pH 2.5. However, a high carboxylic acid concentration has several advantages which include a highly buffered aqueous phase with increased DTPA solubility (DTPA precipitation particularly at low pH can be a problem), faster extraction kinetics, and better phase disengagement. A 0.8-1.5 M carboxylic acid concentration appears to be a good compromise between good separation and low organic extractant loss.^{2,11,18,19}

The primary emphasis of this work is to determine the best set of conditions for TALSPEAK processing particularly with respect to the reduction or elimination of the deleterious effects of impurity ions such as Zr and Mo. "Cold" batch tests were conducted to find the range of conditions for acceptable separations and adequate rates of extraction. Reagent concentrations were varied, and rates of extraction and distribution factors were determined. Also, methods of purifying the extractants, from the radiolytic degradation products, for recycling and reuse were examined.

Considerable concern for radiolytic changes in the pH warranted closer examination of the organic/aqueous phase behavior and solvent/extractant degradation. Also, the solubility of the organic phase under different conditions, such as carboxylic acid concentration, pH, etc., was studied to determine the best conditions for a good separation and a low loss of extractant. As batch tests reached their completion, the initiation of mixer-settler tests was pursued on laboratory-scale quantities of solutions in order to optimize conditions for multistage operations.

4. EXPERIMENTAL RESULTS

4.1 EFFECTS PRODUCED BY THE PRESENCE OF ZIRCONIUM : THIRD-PHASE FORMATION

Third-phase formation is a well-known phenomenon that sometimes occurs during the reprocessing of nuclear fuel using tri-n-butylphosphate (TBP) in the PUREX process. This "third phase" appears as an emulsion at the interface between the aqueous and the organic phases, leading to significant separative problems. Several reports²⁰⁻²⁶ have shown that this third phase is produced by a reaction between zirconium and by-products produced by radiolytic degradation of TBP such as mono- and dibutylphosphate. The third phase appears to be a three-dimensional layered structure with two or more phosphate groups per zirconium ion.

In the TALSPEAK process, zirconium will also generate a third phase under certain conditions (see Fig. 2). The nature of this third phase has not been studied yet. However, it can be assumed to be a layered structure similar to the third phase generated during the PUREX process. Nevertheless, the presence of a strong complexant such as DTPA could also play an important role.

Since, as reported and probably due to an incipient third-phase formation,¹⁶ Zr(IV) can seriously affect the separation process, even at concentrations as low as 10^{-4} M, experiments were conducted to establish the conditions at which Zr(IV) will interfere with the actinide-lanthanide separation.

4.2 GLYCOLIC ACID SYSTEMS

Previous work done by B. S. Weaver²⁷ indicated that the extraction kinetics and phase disengagement were improved by the use of glycolic acid instead of lactic acid. For this reason, our initial work was conducted using glycolic acid for comparative purposes.

Preliminary tests were conducted to determine the levels of zirconium that can be tolerated without third-phase formation. One liter of 0.80 M HDEHP solution in DIPB was contacted with 1 L of aqueous solution of 1.0 M glycolic acid and 0.1 M DTPA. The pH was adjusted to 3.0 using NaOH. These reagent concentrations and pH were chosen because previous work showed these conditions to be satisfactory.

Ten-milliliter aliquants from each phase were drawn and transferred to a separatory funnel. The appropriate volumes of zirconyl nitrate and neodymium nitrate solutions were added to the aqueous phase in each funnel, using micropipettes. The initial zirconium concentration ranged from 0.01 to 0.1 mg/mL while the initial neodymium concentration ranged from 0.01 to 2 mg/mL (the reported initial concentrations correspond to the concentration in the aqueous phase before partitioning). Each funnel was agitated for 3min. and allowed to settle.

The visual observation indicated the formation of a third phase at Zr concentrations ≥ 0.05 mg/mL (aq.) and no apparent third phase for ≤ 0.01 mg/mL (aq.). For the samples containing zirconium >0.01 mg/mL, there is an initial stage where a globular phase occupies a significant volume of the aqueous phase (see Figure 2). That globular phase breaks down slowly (from several hours to a day or two) if left undisturbed. Time or centrifugation transforms the globular phase into a relatively thin layer located between the organic and the aqueous phases. Higher neodymium concentrations seem to stabilize the globular phase.

Additional tests were performed using new batches of aqueous and organic phases. For that purpose, 1 L of 0.80 M solution of HDEHP in DIPB was contacted with 1 L of an aqueous solution 1.0 M in glycolic acid and 0.1 M in DTPA. The pH of both phases was equilibrated to 3.0 using NaOH.

From each phase, 30 mL aliquants were drawn and transferred to separatory funnels. The appropriate volume of zirconyl nitrate and neodymium nitrate solutions were added, using micropipettes, to the aqueous phase in each funnel.

The initial zirconium concentration ranged from 0.01 to 1.0 mg/mL (aq.), while the initial neodymium concentration ranged from 0.01 to 20 mg/mL (aq.). Each funnel was agitated for 3 min. and allowed to settle. Absorption spectra for the aqueous and organic phase were obtained from each sample in the visible range (830-400 nm).

Tests conducted with different levels of zirconium and neodymium, all at higher than trace level concentration, showed that there is no appreciable change in the neodymium distribution ratio due to the presence of zirconium. As it was observed before, higher neodymium concentrations seem to stabilize the third phase.

The addition of fluoride ions, as sodium fluoride, along with the Nd and Zr in a 1:1 F⁻/Zr(IV) ratio, largely prevented the formation of the third phase (see Fig. 3). Instead, a cloudy aqueous single phase was present. The neodymium distribution remained unchanged. The organic and aqueous phase disengaged in the presence of 1:1 fluoride as fast as in the absence of zirconium (about 2 min. by natural settling).

Using a lower fluoride/zirconium ratio, such as 0.5:1 F⁻/Zr(IV), helped only marginally in limiting the third-phase formation. The use of a higher fluoride/zirconium ratio such as 2:1 F⁻/Zr(IV), produced a different kind of third-phase (more like a reticular pattern, not the cotton-like structure as in the absence of fluoride). This third phase broke down and disappeared in about 30 min. of natural settling, leaving a clear aqueous phase. Again, the Nd distribution remained unchanged.

The addition of fluoride at a 1:1 F⁻/Zr(IV) ratio into a system with an already existent third phase was also studied. It was observed that the third phase slowly disappeared (about 15-20 minutes), leaving the aqueous phase cloudy in appearance.

It was also noted that the addition of zirconium into the same kind of system (0.80 M solution of HDEHP in DIPB and 1.0 M in glycolic acid) but without DTPA displayed an even more extended third phase (see Figure 4) that occupied almost the entire aqueous phase and that could not be eliminated even by prolonged centrifugation (about 20-30 min. at the maximum speed of our lab centrifuge, about 3400 rpm).

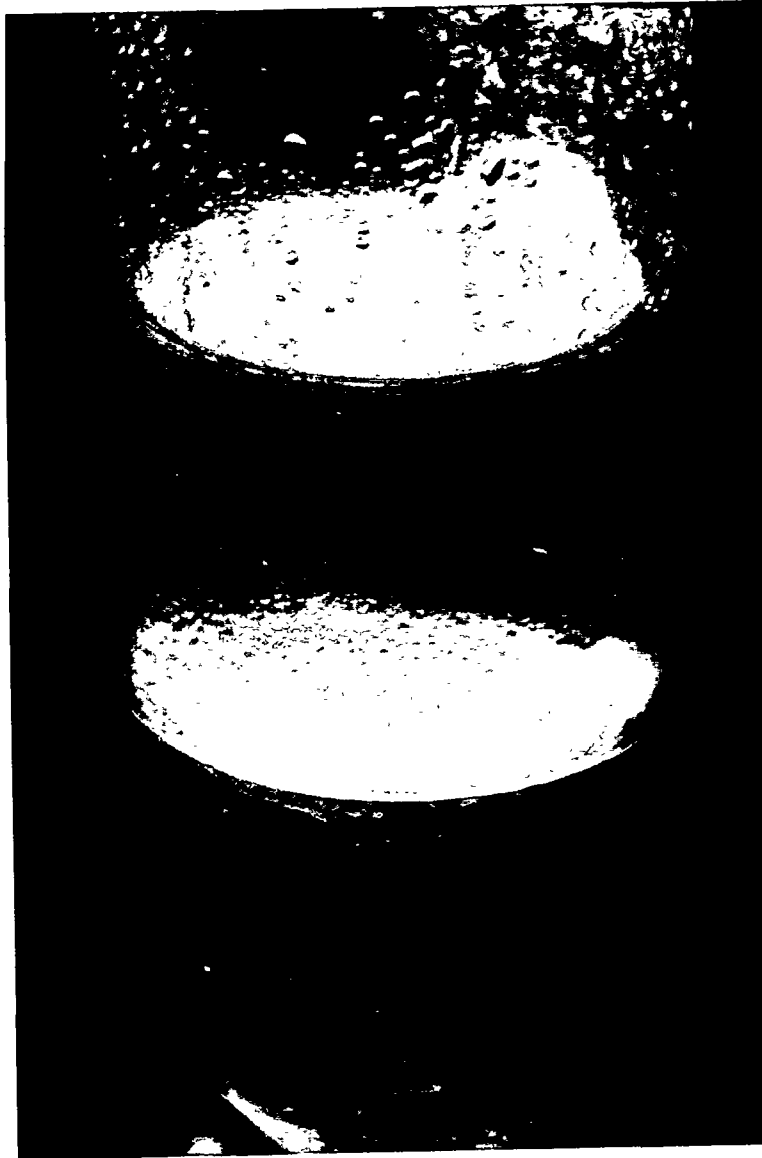


Fig. 3. "Third Phase" after treatment with sodium fluoride [1:1 $F^-/Zr(IV)$ ratio].

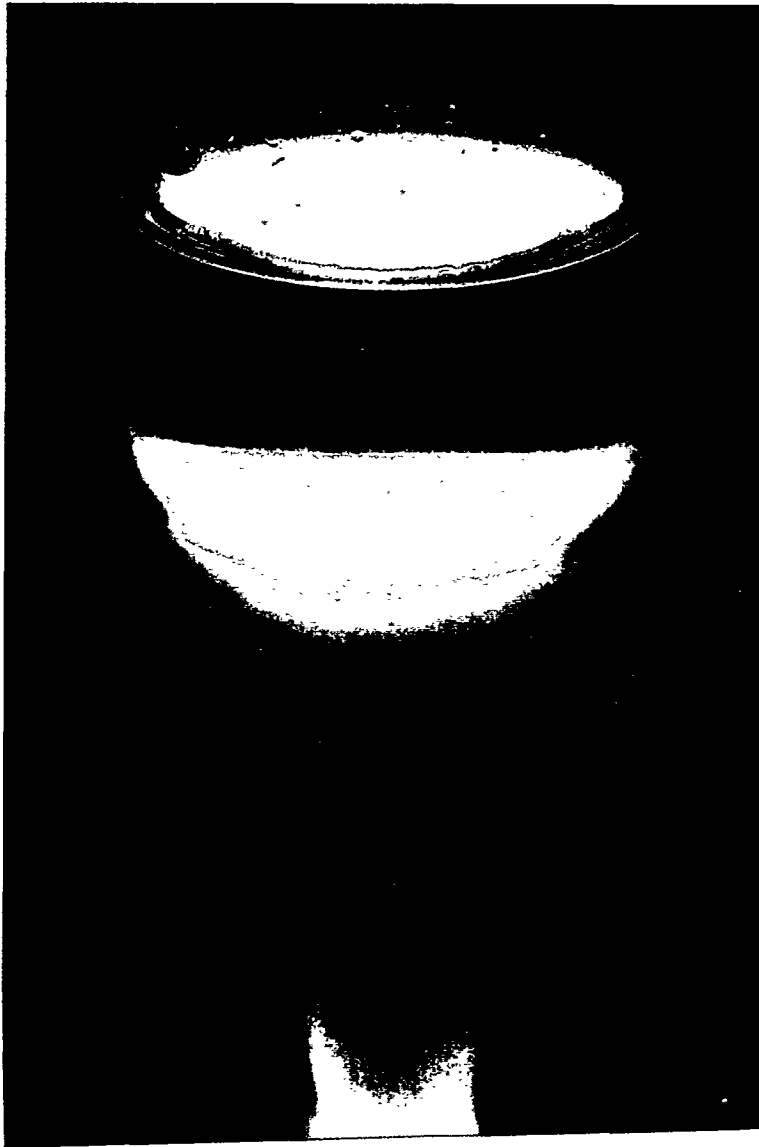


Fig. 4. "Third-Phase" formation due to the presence of Zr(IV) ions and in absence of DTPA.

The use of fluoride ions, however effective, has the drawback of requiring a knowledge of the zirconium concentration to adjust the fluoride doses. Additionally, the presence of fluoride even at very low concentrations ($\sim 10^{-4}$ M) is problematic because of the known corrosivity of fluoride solutions.

For these reasons, several other alternatives were tried including the addition of known Zr complexants such as hydrogen peroxide and citric acid. While hydrogen peroxide was not useful, citric acid proved to be very effective.

Similar tests using Mo(VI) (as sodium molybdate), Zr(IV), and Nd(III) showed that molybdenum causes no additional problems even at the highest concentration tested (1.0 mg/mL, initial aqueous).

4.3 CITRIC ACID SYSTEMS

Previous work² indicated that citric acid solutions containing DTPA also gave large separations between the lanthanides and the americium-curium pair. It was also reported² that citric acid increased the solubility of DTPA. Since our preliminary tests indicated that the addition of citric acid to the glycolic acid largely prevented the formation of the third phase in the presence of Zr(IV), a series of experiments were conducted using citric acid alone as the buffer/complexant additive.

One liter of 0.80 M solution of HDEHP in DIPB was contacted with 1 liter of an aqueous solution 1.0 M in citric acid and 0.1 M in DTPA. The pH was adjusted to 3.0 using NaOH. From each phase, 30 mL aliquants were drawn and transferred to separatory funnels. The appropriate volumes of zirconyl nitrate and neodymium nitrate solutions were added, using micropipettes, to the aqueous phase in each funnel.

The initial zirconium concentration ranged from 0.01 to 5mg/mL while the initial neodymium concentration ranged from 0.01 to 20 mg/mL (initial aq.). Each funnel was agitated for 3 min. and allowed to settle. Absorption spectra for the aqueous and organic phase were obtained from each sample in the visible range (400-830 nm).

Tests conducted with different levels of zirconium and neodymium, all at higher than trace level concentration, showed that there is no appreciable change in the neodymium distribution ratio due to the presence of zirconium. Only experiments at the highest zirconium concentration tested, 1.0 mg/mL (initial aq.), showed a third phase in the organic phase; this third phase was like a haze or emulsion with large bubbles. At 0.5 mg/mL the organic phase was hazy and had few bubbles. At zirconium concentrations of ≤ 0.25 mg/mL there were no visible effects. Similar tests using Mo, Zr, and Nd showed that molybdenum causes no additional problems even at the highest concentration tested (1.0 mg/mL, initial aqueous).

In order to measure the distribution of lanthanide (III) ions between the aqueous and organic phases at different lanthanide concentrations with and without Zr and Mo, several samples were prepared. Three samples were prepared containing all the lanthanides from lanthanum through lutetium, except promethium, and yttrium, at three different concentrations. The concentrations were determined using an inductively coupled plasma/mass spectrometer (ICP/MS).

One solution had a lanthanide total concentration of 0.001 M ($\sim 7 \times 10^{-5}$ M for each lanthanide, initial aq.); another was 0.01 M ($\sim 7 \times 10^{-4}$ M for each lanthanide, initial aq.); and the third was 0.04 M ($\sim 2.5 \times 10^{-3}$ M for each lanthanide, initial aq.). The results, displayed as the ratio between the concentration in the organic and the concentration in the aqueous phase, are shown in Fig. 5. The distribution coefficients for the first two solutions are almost identical; however, for the most concentrated solution, the values are somewhat lower for the early lanthanides (La to Gd). There was no visual difference between the three samples.

Another two similar samples were prepared with the addition of Zr and Mo. The first sample had a lanthanide total concentration of 0.01 M ($\sim 7 \times 10^{-4}$ M for each lanthanide, init. aq.), and 0.5 mg/mL ($\sim 5 \times 10^{-3}$ M) of Zr and Mo. The second sample had a lanthanide total concentration of 0.03 M ($\sim 2 \times 10^{-3}$ M for each lanthanide, init. aq.), and 1.0 mg/mL ($\sim 1 \times 10^{-2}$ M) of Zr and Mo.

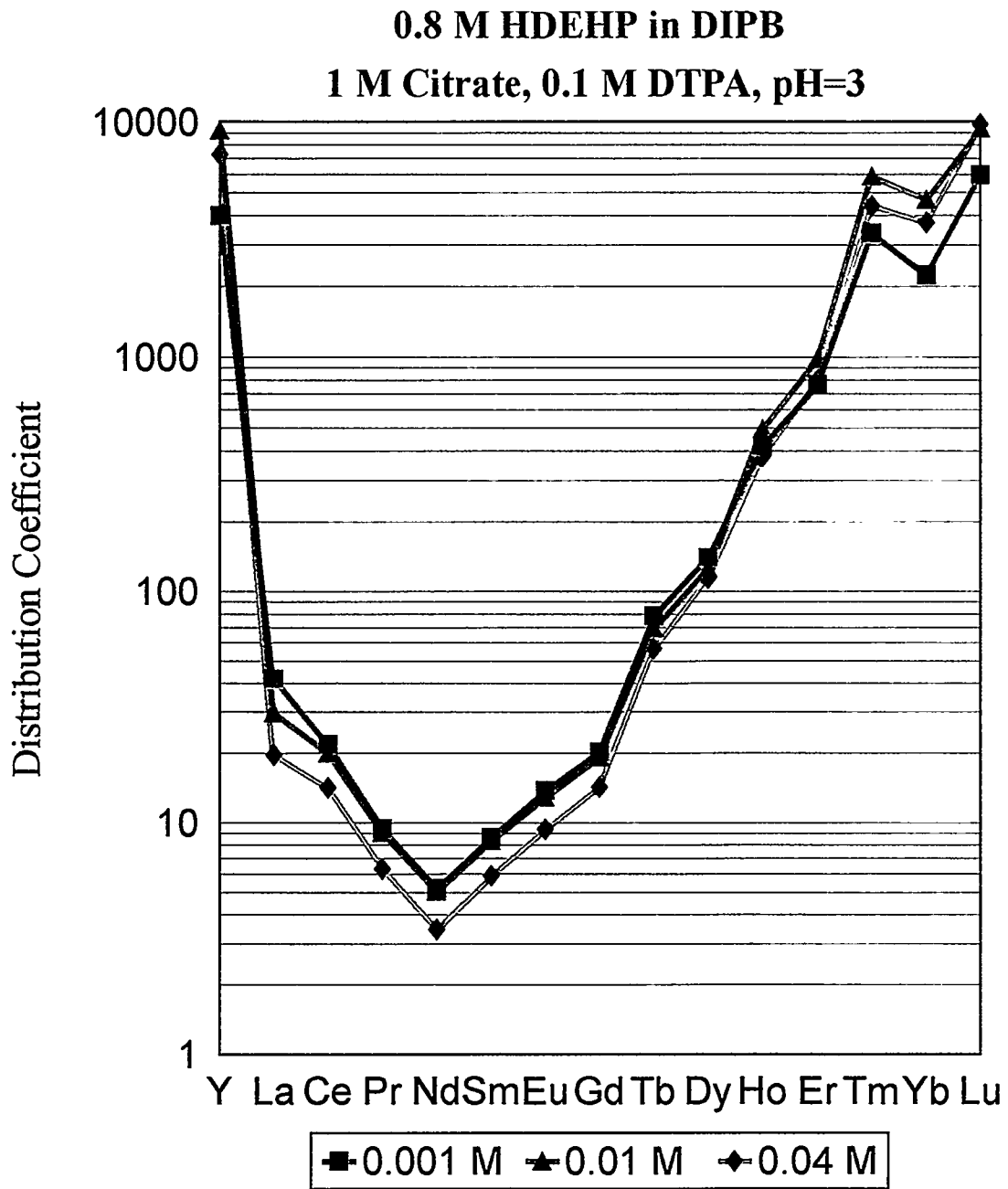


Fig. 5. Distribution coefficients for Citrate TALSPEAK lanthanide extraction at different loadings.

The results, along with the previously described 0.01 M sample prepared without Zr or Mo, are displayed in Fig. 6. The distribution coefficients for the first two solutions (0.01 M with and without Zr and Mo) are almost identical, however for the most concentrated solution the values are somewhat lower for all lanthanides. There was no visual difference between the samples. The analytical results also indicated that only traces of molybdenum were found in the organic phase. The distribution coefficient for zirconium was between 0.2 and 0.6. In contrast, previously reported experiments² using glycolic acid and zirconium showed that the zirconium activity remained almost completely in the aqueous phase.

4.4 DIFFERENCES BETWEEN THE GLYCOLIC AND THE CITRIC ACID SYSTEM

It was noted that the organic phase (0.80 M solution of HDEHP in DIPB) contacted with the glycolic/DTPA aqueous phase turns yellow with time. The color intensity increases with time. The same organic phase contacted with the citric/DTPA aqueous phase remains colorless. It was noted that the yellow color appears even when the ampoule containing the organic solution was covered with aluminum foil to eliminate any possible photoreaction. This yellow color is produced by the tail of a broad absorption band centered at about 400 nm (See Fig. 7). Since DIPB is known to form peroxides, it is possible that the yellow color is due to a DIPB peroxide, and that the citric acid is preventing the formation of peroxide precursors. There is no apparent effect on the extraction chemistry due to the yellowish coloration of the organic phase.

0.8 M HDEHP in DIPB
1 M Citrate, 0.1 M DTPA, pH=3

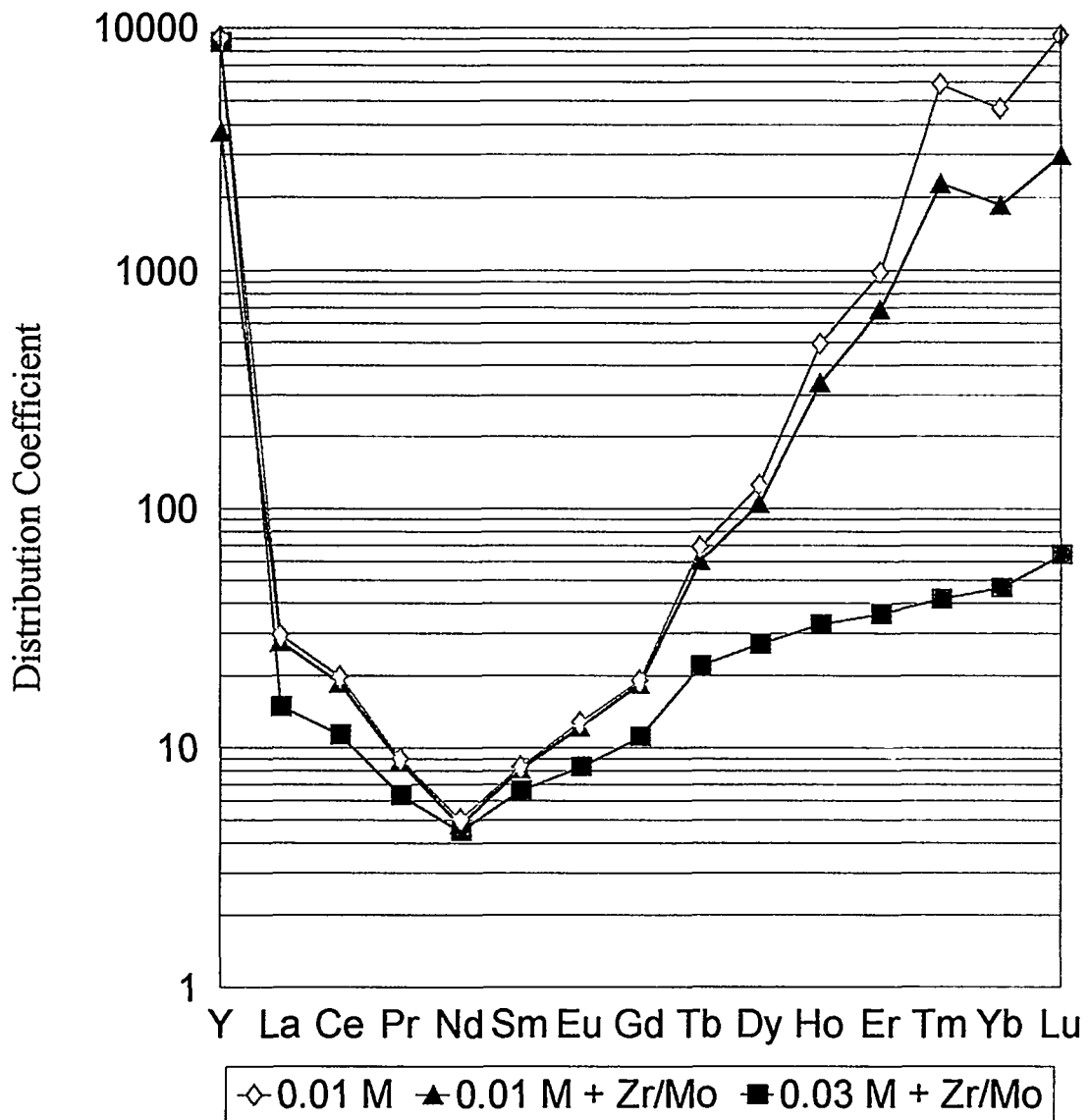


Fig. 6. Distribution coefficients for Citrate TAL₃SPEAK lanthanide extraction at different loadings in the presence of 10^{-3} M Zr(IV) and Mo(VI).

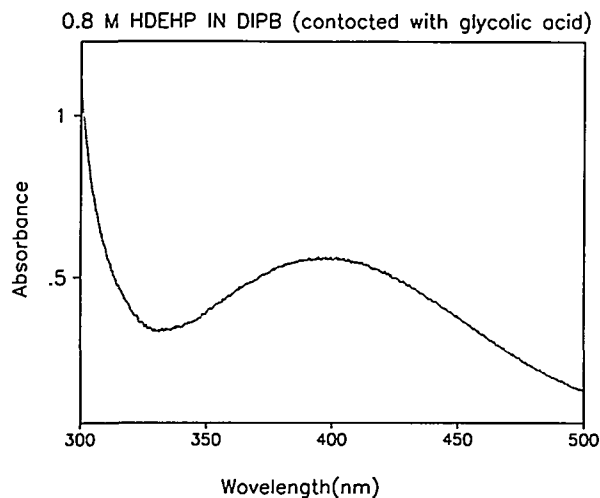


Fig. 7. Absorption spectrum of 0.8 M HDEHP in DIPB contacted with glycolic acid showing band responsible for the yellow color.

The densities, viscosities, and interfacial tensions were measured for the 1 M glycolic, 0.1 M DTPA/ 0.8 M HDEHP in DIPB and the 1 M citric, 0.1 M DTPA/ 0.8 M HDEHP in DIPB systems. Viscosities were measured using a low-viscosity, fixed-cup, rotating-cylinder Brookfield viscometer. Interfacial tensions were measured using a Fisher Autotensiomat "DuNoüy-detachment-type," surface tensiometer and a platinum ring 3 cm in diameter.

The densities for some TALSPEAK aqueous and organic solutions are given in Table 1 including information from ref. 12.

Table 1. Densities of TALSPEAK solutions (g/ cm³)

Solution	22 °C	50 °C
1 <u>M</u> lactic acid, 0.1 <u>M</u> DTPA ¹²	1.047	1.037
1 <u>M</u> glycolic acid, 0.1 <u>M</u> DTPA ¹²	1.047	1.035
1 <u>M</u> citric acid, 0.1 <u>M</u> DTPA	1.168	1.1012
1 <u>M</u> HDEHP in DIPB ¹²	0.903	0.887
0.8 <u>M</u> HDEHP in DIPB	0.883	0.862

A large difference in densities between the organic and aqueous phase, along with low viscosities and low interfacial tension, will accelerate the mass transfer and phase disengagement.

Figure 8 shows the viscosities for the citric and glycolic solutions as a function of temperature. The viscosity for the solution containing the glycolic acid unexpectedly levels off beyond 50 °C. This behavior is probably due to a change in chemical speciation.

Figure 9 displays the viscosities for the organic solution equilibrated with glycolic acid (yellowish color), citric acid, and citric/DTPA solution containing 2.5 mg/mL of Nd, 0.25 mg/mL Zr and 0.25 mg/mL Mo. As can be seen, there is no significant change in the viscosity due to the loading of the organic phase. The values¹² for a 1 M HDEHP solution in DIPB are also shown for comparison.

Figure 10 shows the interfacial tensions for the aqueous/organic and the organic/air interfaces, for the system 1.0M citric, 0.1M DTPA/ 0.8M HDEHP in DIPB at pH = 3 when measured by a tensiometer using a platinum ring 3 cm in diameter.

Figure 11 shows the interfacial tensions for the same system at three different temperatures. As can be seen, there are no significant changes in the values measured between room temperature and 52 °C. Similar measurements on systems containing 2.5 mg/mL of Nd, 0.25 mg/mL Zr, and 0.25 mg/mL Mo showed no appreciable differences with respect to the "unloaded" systems.

There was, however, a difference in the behavior of the organic phase/air interface for the laden organic. During the measurements, the ring will move further apart from the surface stretching a much more extended portion of interface before breaking it. However, the maximum surface tension value was approximately equal to the maximum value measured for the "unloaded" organic.

Viscosity of Aqueous Phase

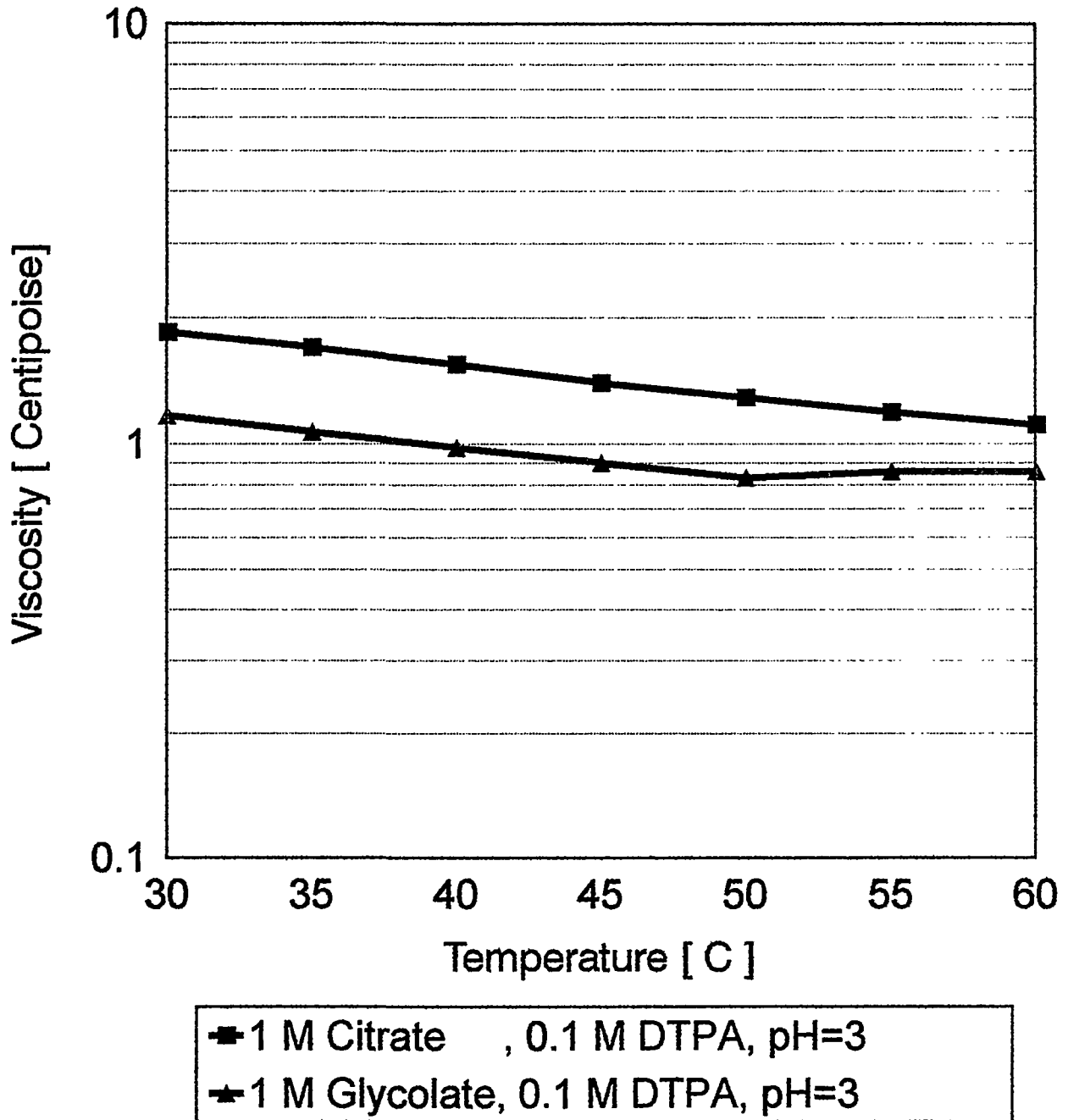


Fig. 8. Viscosities of typical aqueous TALSPEAK solutions.

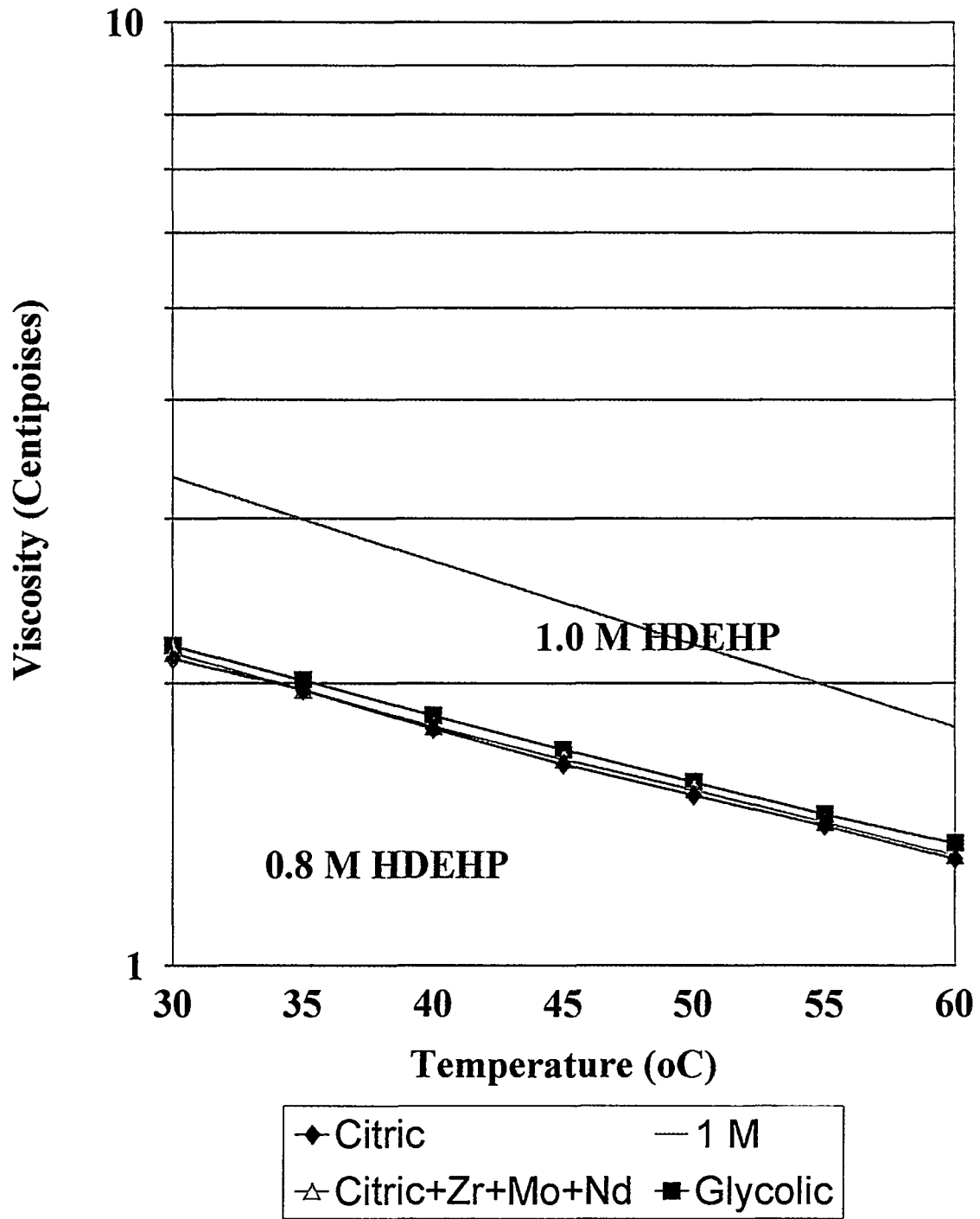


Fig. 9. Viscosities of typical organic TALSPEAK solutions.

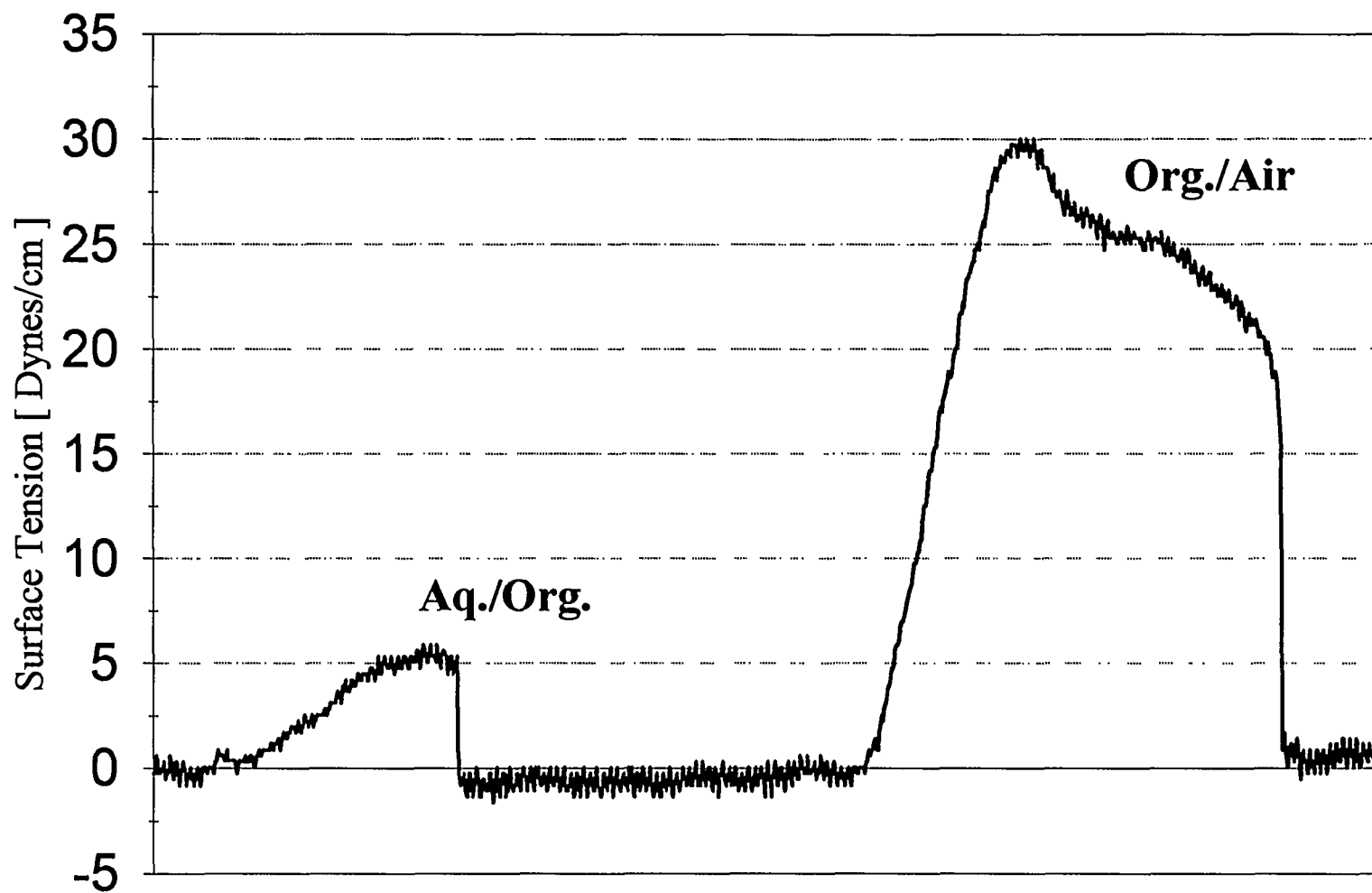


Fig. 10. Interfacial tensions for the system 1.0 M citrate, 0.1 M DTPA / 0.8 M HDEHP in DIPB at pH=3.0 and room temperature.

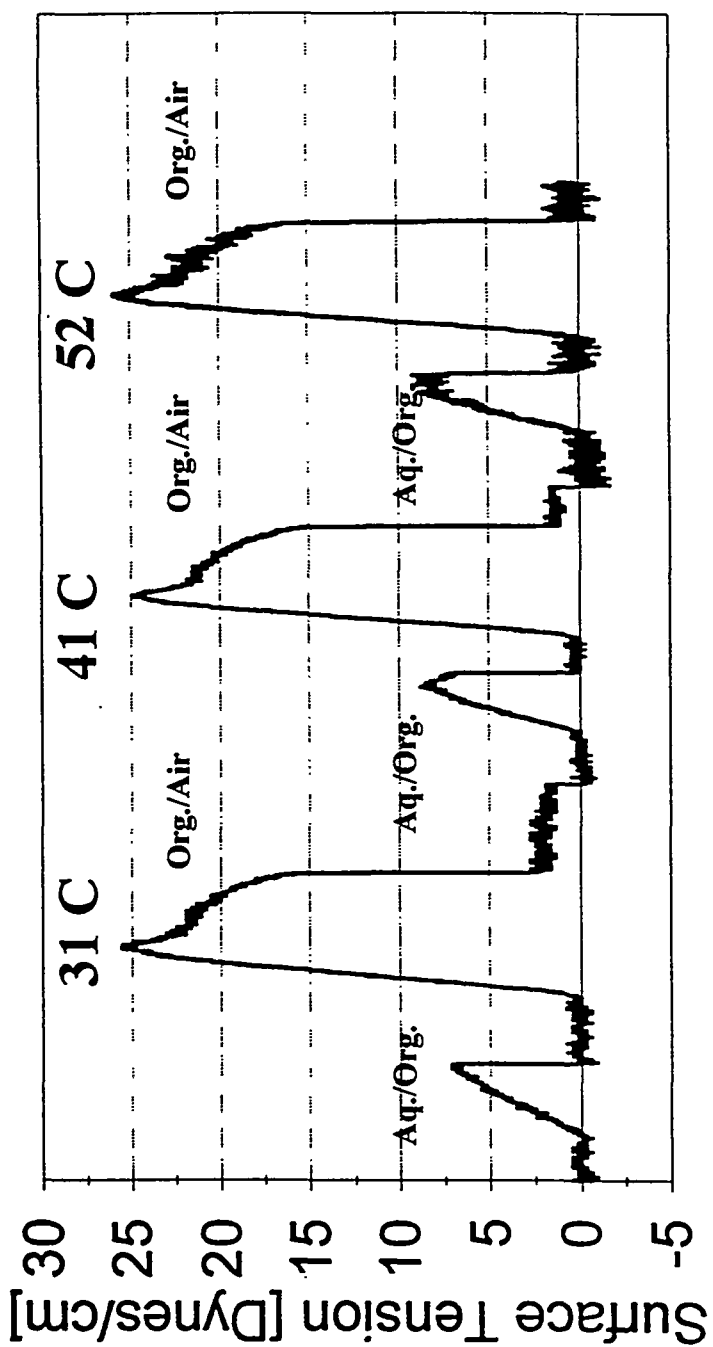


Fig. 11. Interfacial tensions for the system 1.0 M citrate, 0.1 M DTPA/0.8 M HDEHP in DIPB at pH = 3.0 at 31°C, 41°C, and 52°C.

4.5 CITRATE-BASED-TALSPEAK SCOPING EXTRACTION TESTS

The primary emphasis of this work was to determine the best set of conditions for TALSPEAK processing particularly with respect to the reduction or elimination of the deleterious effects of impurity ions such as Zr and Mo. Our preliminary tests indicated that the use of citric acid as the buffer/complexant was preferable to the usage of glycolic acid. For this reason, an extensive series of a small-volume batch extraction experiments (15-30 mL), using a wide range of reagent concentrations at different pH values, temperatures and contact times, was done to scope the Citrate-Based-TALSPEAK extraction process.

A mix of Nd, Pr, Eu and Er at ($\sim 10^{-3}\text{M}$ each), with and without Zr and Mo, was used as a cold surrogate. The mix of the lanthanides Nd, Pr, Eu and Er was chosen because their individual absorption spectra do not overlap significantly in the region 340-900 nm,^{28,29} as shown in Fig. 12; and so, the lanthanide concentrations were spectrophotometrically monitored in the near UV/visible/near-IR (340-900 nm) range. The appearance of interfacial precipitates and the phase disengagement process were visually followed.

The citrate concentration was varied between 0.5M and 2.0M, while the DTPA was added in the range 0-0.1M. The organic and aqueous phases were pre-equilibrated at a pH value between 2.5 and 4.4 using sodium hydroxide. Mo(VI) as and Zr(IV) were added as sodium molybdate and zirconyl nitrate at concentrations ranging from 0 to 1.0 mg of metal/mL. All experiments were done using the same type of separatory funnels with Teflon™ stopcocks, and, in all cases, they were stirred at the same speed using glass propellers.

The results indicate that relatively wide pH and concentration changes can be tolerated with good lanthanide extraction. The lanthanide extraction kinetics and phase disengagement were acceptable in the range 2.5-4.1. The phase disengagement was good under most conditions but was somewhat better at the higher pH values. All lanthanides are more extracted at the lower pH values tested; however, the distribution factors do not change significantly in the pH range between 3 and 4.

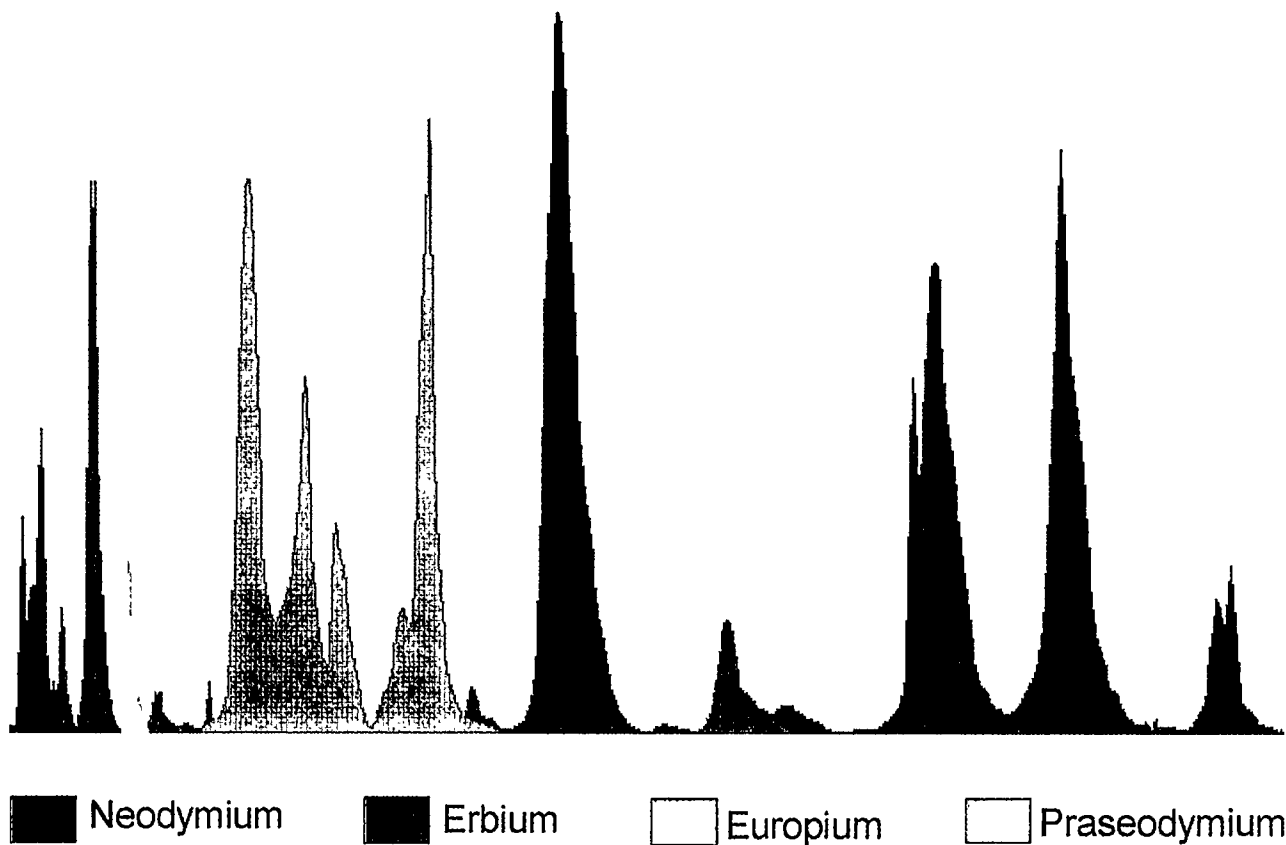


Fig. 12. UV-VIS absorption spectra for the lanthanide mix of neodymium, praseodymium, europium, and erbium, in the 340 to 900 nm region.

Higher concentrations of DTPA and citrate anions (higher concentration of the extractants or higher pH) somewhat diminish the lanthanide extraction because of the increased complexing power of both reagents. The solubility of DTPA decreases at lower pH's. Deposits of DTPA on glass surfaces were observed at the lower pH values when stored for prolonged periods (a few days).

At lower pH values (near pH 2), the lanthanide extraction by the organic phase increases. However, the actinide extraction by the organic phase, although very low, is also higher. As a consequence, a low-pH separation will produce an aqueous phase essentially free of lanthanides that contain most of the actinides. At the same time, the organic phase will contain all the lanthanides and a small fraction of the actinides. Because of the increased concentration of DTPA and citrate anions (higher complexing power in the aqueous phase) at higher pH values (near pH 4), the actinide extraction is expected to be extremely low. However, the lanthanide extraction by the organic phase, although still high, will also diminish. As a result, a high-pH separation will produce an organic phase essentially free of actinides that contain most of the lanthanides and an aqueous phase that contains all the actinides and a small residual concentration of lanthanides.

Similarly, the Zr(IV) concentrations that can be tolerated increase at higher pH values, probably due to the same increased complexing power of the free DTPA and citrate anions. No significant losses of organic extractant were observed. The lanthanide extraction kinetics in absence of DTPA was significantly slower.

In order to test the extraction of other impurity ions besides the lanthanides from TALSPEAK aqueous solutions, 200 mL of an aqueous solution was prepared containing 39 elements at concentrations in the range of 10^{-3} to 10^{-4} M. Citric acid and DTPA were added up to a concentration of 1.0 M for the citrate and 0.1 M for the DTPA. Four 15-mL aliquants of the aqueous phase were contacted with an equal volume of 0.8 M HDEHP in DIPB. The pH of the four aliquants was adjusted using NaOH at pH 2.6, 3.0, 3.6 and 3.9, respectively. They were energetically stirred for about 10 min. and then allowed to settle. The composition of both the organic phase and the aqueous phase were analyzed using ICP/MS.

The results are shown in Fig. 13 as a periodic table.³⁰ The black circles indicate elements that were extracted into the organic phase; the dotted-squares are assigned to elements that showed partial extraction into the organic phase; and the empty circles indicate elements that were not extracted by the organic phase and remained in the aqueous TALSPEAK solution. The partial extraction of Rb, Cs, Sr, and Ba increased with increased pH.

4.6 EXTRACTION AND STRIPPING FROM NITRIC ACID SOLUTION

As mentioned in Sect. 2, the reverse TALSPEAK process can be very convenient to connect the TALSPEAK process to other separative schemes. In this reverse TALSPEAK process,¹⁷ the organic phase is first loaded with the actinides and lanthanides, usually from a diluted acidic solution (0.05-0.1 M HNO₃), and then contacted with the aqueous phase to strip the actinides.

To test the loading and stripping of lanthanides and other impurity ions from diluted nitric acid, 200 mL of an aqueous solution was prepared containing 39 elements at concentrations in the range of 10⁻³ to 10⁻⁴ M. The solution was contacted with an equal volume of 0.8 M HDEHP in DIPB and stirred for about 10 minutes. Fifteen mL aliquants of the organic phase were contacted with an equal volume of nitric acid solutions of different concentrations and analyzed using ICP/MS.

The molar concentrations of HNO₃ tested were 0.1 , 0.3 , 0.6 , 1 , 2 , 4 , and 6. The results for the 0.1 M HNO₃ solutions are shown in Fig. 14 as a periodic table. The black circles indicate elements that were extracted into the organic phase; the dotted-squares are assigned to elements that showed partial extraction; and the empty circles indicate that those elements were not extracted and remained in the 0.1 M HNO₃ solution.

The results for more concentrated nitric acid solutions indicated that lanthanides are not significantly extracted at acid concentrations above 0.1 M. Acid concentrations as low as 0.3-0.6 M can be used to strip the lighter lanthanides from the organic extractant. The heavy lanthanides, which represent only a small fraction of the lanthanides produced as a consequence of fission, require more concentrated HNO₃ (2-4 M) and display a slower kinetics.

Organic: 0.8 M HDEHP in DIPB
 Aqueous: 1.0 M Citrate, 0.1 M DTPA

H												B	C	N	O	F
Li	Be															
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
Fr	Ra	Ac														
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf					

● EXTRACTED
 ○ UNEXTRACTED
 ◻ PARTIAL EXTRACTION

Figure 13. Citrate-based "TALSPEAK" extraction using 0.8 M HDEHP in DIPB.

Organic: 0.8 M HDEHP in DIPB
 Aqueous: 0.1 M HNO₃

H																
Li	Be											B	C	N	O	F
Na	Mg											Al	Si	P	S	Cl
K	Ca	Sc ●	Ti	V	Cr ○	Mn ●	Fe ◻	Co ○	Ni ○	Cu ○	Zn ○	Ga	Ge	As	Se	Br
Rb ◻	Sr ◻	Y ●	Zr ○	Nb	Mo ○	Tc	Ru ○	Rh ○	Pd ○	Ag ○	Cd ○	In ○	Sn ○	Sb ○	Te	I
Cs ◻	Ba ◻	La ●	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
Fr	Ra	Ac														
			Ce ●	Pr ●	Nd ●	Pm ●	Sm ●	Eu ●	Gd ●	Tb ●	Dy ●	Ho ●	Er ●	Tm ●	Yb ●	Lu ●
			Th	Pa	U	Np	Pu ●	Am ●	Cm ●	Bk ●	Cf ●					

● EXTRACTED
 ○ UNEXTRACTED
 ◻ PARTIAL EXTRACTION

Fig. 14. Reverse "TALSPEAK" extraction from 0.1 M HNO₃ solutions using 0.8 M HDEHP in DIPB.

4.7 PURIFICATION OF THE ORGANIC EXTRACTANT

One of the major by-products of the radiolytic damage of the monoacid HDEHP is the diacid mono-substituted 2-ethylhexyl-phosphoric acid (MEHPA).³¹⁻³⁴ The dibasic character of the 2-ethylhexyl-phosphate ion makes this species a very strong complexant. This strong complexation capacity interferes with the TALSPEAK separative process that otherwise succeeds as a result of subtle differences in complexation between lanthanides and actinides. The net result is the co-extraction of lanthanides and actinides and a less-than-satisfactory separation. For this reason, it is necessary to continuously remove the MEHPA as it is formed by radiolysis.

There are several methods described in the literature that could be used to purify the HDEHP.^{10,35-43} including the precipitation of the HDEHP copper salt, liquid-liquid partitioning of the HDEHP and MEHPA between ethylene glycol and petroleum ether, vacuum distillation, caustic washing, etc.

The need of a continuous purification of HDEHP dissolved in an organic solvent such as the DIPB precludes most of the methods but the caustic washing. The monobasic di-substituted di-2-ethyl-hexyl-phosphate is not water soluble; however, the mono-substituted di-basic 2-ethylhexyl-phosphate is highly soluble. This difference in solubilities can, in principle, be used to purify the organic extractant by caustic washing.

Our tests showed that the caustic washing using sodium carbonate solutions produced very-difficult-to-handle gel-type precipitates. The use of ammonium carbonate, however, proved to be effective and did not form any precipitates. The caustic washing has to be preceded by a stripping of the organic extractant. The caustic washing of partially laden organic extractant produced total gelation of the organic phase when sodium carbonate was used and partial gelation when ammonium carbonate solutions were used.

In our tests, a single-step washing of the organic extractant with an equal volume of 0.5 M ammonium carbonate solution almost completely removed the MEHPA, as determined by titration of the treated solution.

Fig. 15 shows the neutralization curve of a 0.8 M solution of the organic extractant in DIPB containing approximately 5 mol % of MEHPA. The first step corresponds to the neutralization of the HDEHP and the first proton from the MEHPA; the second step corresponds to the neutralization of the second proton from the MEHPA.

Fig. 16 displays the neutralization behavior after washing with 0.5 M $(\text{NH}_4)_2\text{CO}_3$ (1:1 volume ratio). As can be seen, there is no indication of the presence of MEHPA (the minimum observable concentration by neutralization is about 0.3%).

4.8 MULTISTAGE TESTING

A three-stage glass mixer-settler apparatus, as shown in Fig.17, was assembled to test the general behavior of the Citrate-Based-TALSPEAK separative process. The organic extractant and the lanthanide laden aqueous phase were fed countercurrently. Both phases were introduced at the bottom of the internal annular mixing chamber on each mixer-settler unit. A motor-driven glass propeller was used to maintain an intimate contact between the two phases. The contacted phases, overflowed to the external annular settling compartment, where the aqueous and organic phases disengaged. An adjustable lateral drain allowed for the adjustment of the interface level.

Calibrated valveless-FMI-metering-pumps were used to feed the laden aqueous phase into the first stage, and the clean organic phase into the third stage. Interstage flows of the aqueous phase occurred by gravity while interstage flows of the organic phase were done by pumping. Flow rates could be altered to regulate the contacting time from several seconds to minutes. Glass combination electrodes on each stage allowed for a continuous pH monitoring.

Initially, a trial run was conducted using an organic solution of 0.80 M HDEHP in DIPB and an aqueous solution 1.0 M in citric acid and 0.1 M in DTPA at pH = 3.0 containing Nd, Pr, Eu and Er. The organic phase was pre-equilibrated with 1.0 M in citric acid and 0.1 M in DTPA at pH = 3.0.

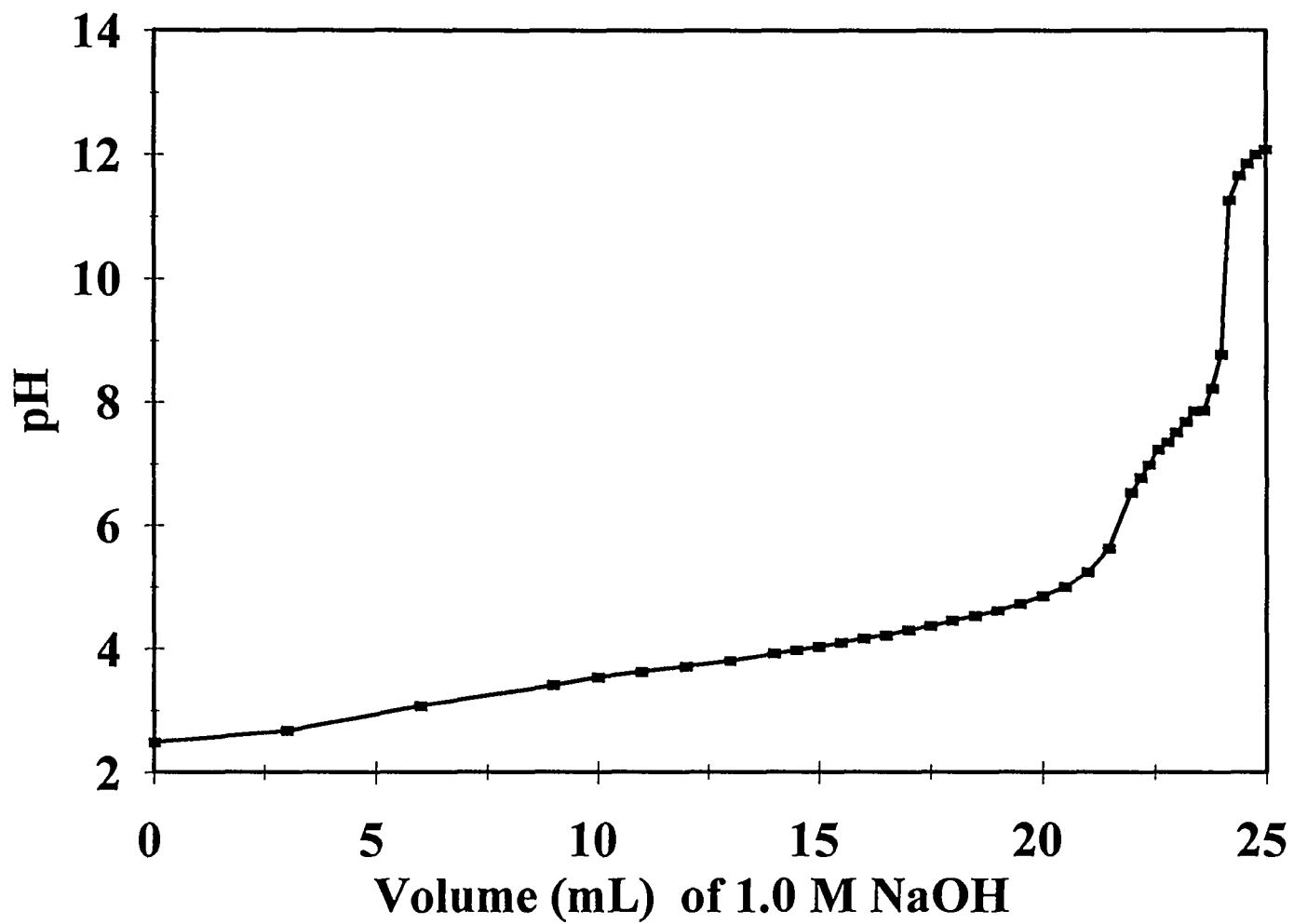


Fig. Neutralization curve of a 0.8 M solution of HDEHP in DIPB containing about 5% of MEHPA.

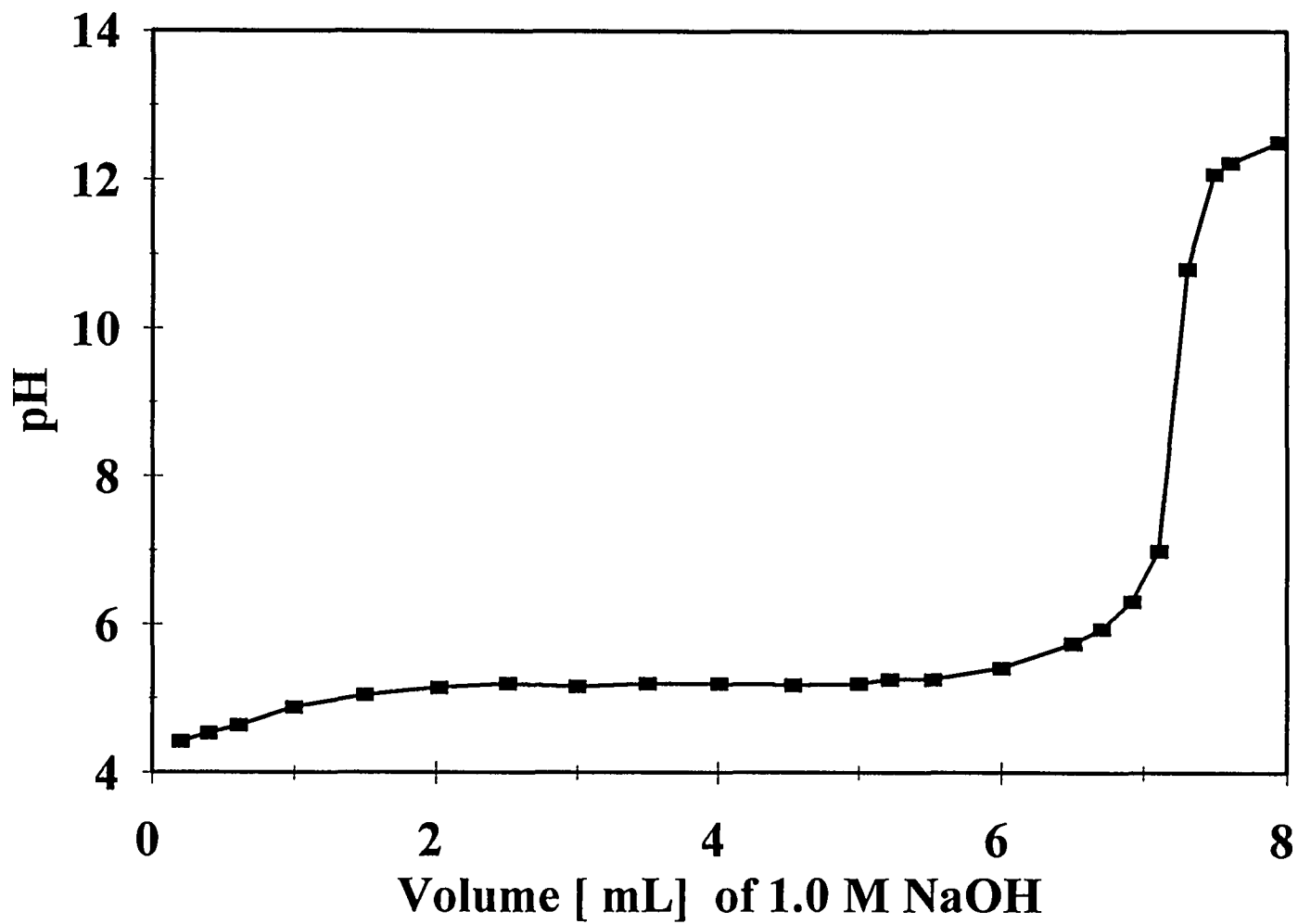


Fig. 16. Neutralization curve of a 0.8 M solution of HDEHP in DIPB initially containing about 5% of MEHPA after washing with 0.5 M ammonium carbonate solution (1:1 volume ratio).

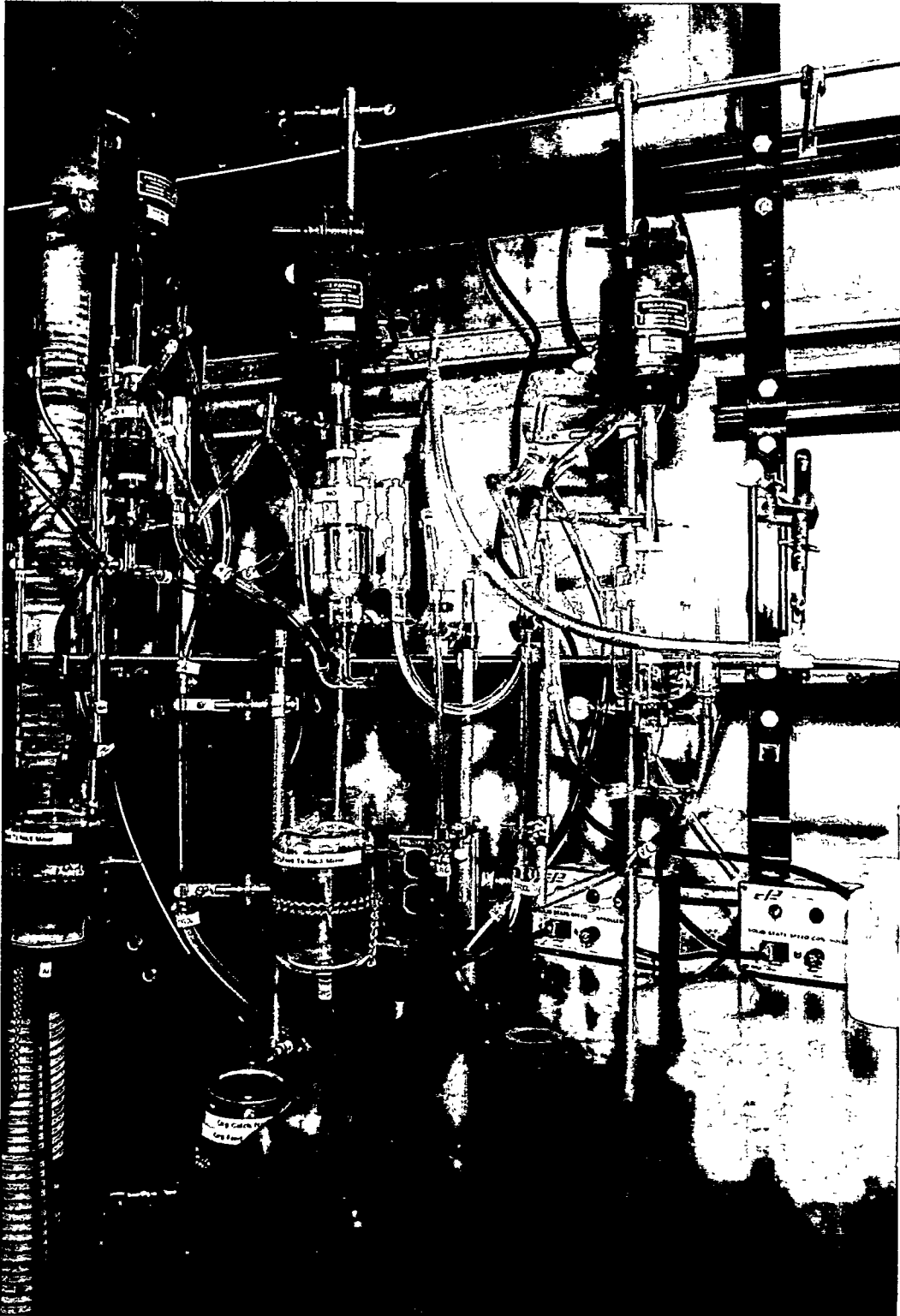


Fig. 17. Three-stages glass mixer-settler apparatus.

The phase separation was very good in all three stages. Extraction of Nd, Pr, Eu and Er was followed by absorption spectrometry on samples withdrawn for analysis. The extended first run indicated that some small changes in the equipment were needed and that the pumps had to be recalibrated in order to maintain the 1:1 organic/aqueous ratio in the three stages.

The initial testing was followed by several extensive extractive runs using the glass three-stage mixer-settler apparatus. Extraction of Nd, Pr, Eu and Er was followed by absorption spectrometry. The organic solution used was 0.80 M HDEHP in DIPB and an aqueous solution containing 1.0 M in citric acid and 0.1M DTPA. The pH for the different runs ranged from 2.5 to 4.0. The phase separation and lanthanide extraction in all three stages were very good in all cases. The results were very satisfactory, and no significant problems were encountered.

The experiments showed a high constancy of the pH even at significant loading of the organic phase. In fact, the pH was essentially constant before and after reaching the steady state in all three stages. The lanthanide extraction and phase disengagement were acceptable in the entire 2.5-4.0 pH range. No significant losses of organic extractant were observed and there were no appreciable effects due to impurities such as zirconium.

Extensive "cold" runs using a three-stage mixer-settler showed good lanthanide extraction, appropriate phase disengagement, and excellent pH buffering. In order to test the recycling of the extractant, stripping and washing runs were also performed with very good results. All the experimental information indicates that the citrate-based TALSPEAK can be fully deployed and implemented for the separation of lanthanides from the actinide elements.

4.9 MECHANISTIC FACTORS THAT INFLUENCE THE TALSPEAK SEPARATION PROCESS

Association in organophosphoric acids due to hydrogen bonding is stronger than in monocarboxylic acids.⁴⁴ The monobasic phosphoric acids, such as HDEHP, and the phosphinic acids form dimers through the formation of intermolecular bonds. Their hydrogen bonds are stronger than those present in monocarboxylic acids. The dimerization constant is large ($\sim 10^4$).

Polymerization increases at higher solute concentration and decreasing polarity of the solvent. Experimental information seems to indicate that the kinetics of extraction is slower at higher concentrations of solute and decreasing polarity of the solvent. It seems that a higher degree of dimerization-polymerization correlates with a slower extraction process. Also, it is reported^{2,45,46} that the extractive power of the phosphoric acids, such as HDEHP, is higher when dissolved in aliphatic solvents (less polar, higher degree of dimerization-polymerization) than when dissolved in aromatic solvents such as DIPB. However, it is also reported that the separation between lanthanides and actinides is better when aromatic solvents are used.²

The length and branching of the alkyl groups, along with the nature of the solvent used, have a significant influence on the extracting ability of the dialkylphosphoric acids.^{2,45,46} The length of the chain affects the extracting ability from moderately acidic solutions. Branching of the chain leads to a reduction in the extraction of impurity ions such as iron [Fe(III)], chromium [Cr(III)], and aluminum [Al(III)].⁴⁵ HDEHP is the most tested dialkylphosphoric acid used in TALSPEAK separations. Other potentially useful dialkylphosphoric acids are dibutylphosphoric acid (DBPA), dioctyl- and diisooctylphosphoric acids (DOPA, DIOPA), dinonylphosphoric acid (DNPA), and didecyl- and diisodecylphosphoric acids (DDPA, DIDPA). However, the availability, radiation stability, and better overall selectivity characteristics make HDEHP the best choice of extractant for most separation applications.

It was previously determined^{2,11,47} that when lactic acid is used as the buffer reagent, the lanthanide or actinide species extracted into the organic phase is the monolactate complex [(MeLact)²⁺,

where Me is Ln or Ac]. Our experimental evidence, as described in the following two paragraphs, suggests that the extraction mechanism is different when using glycolic or citric acid.

Three 15mL aqueous samples were prepared containing 1.0 M lactic, glycolic or citric acids. DTPA was added to the three samples at a 0.1 M concentration. The three aqueous samples were pre-equilibrated with an equal volume of 0.8 M HDEHP in DIPB, and the pH was adjusted to 3.0 using sodium hydroxide. Nd^{3+} was added to the three aqueous solutions at a 10^{-3} M concentration. They were then extracted with pre-equilibrated organic solutions under energetic stirring for 10 min. and then allowed to settle. The three organic samples were stripped using 1 M nitric acid. The stripped aqueous samples had the typical purplish color due to the presence of Nd(III).

The three stripped aqueous samples were analyzed using ^{13}C NMR to determine the presence of carboxylic acids. Only the sample stripped from the lactic acid extraction contained lactic acid as indicated by the NMR analysis. The ^{13}C NMR analysis is not adequate for trace analysis, but it is possible to conclude that when citric or glycolic acid is used they are not significantly co-extracted as in the lactic acid case.

5. SUMMARY AND CONCLUSIONS

A citrate-based TALSPEAK is preferable because the interference of impurity ions such as zirconium is eliminated or minimized. Because the citric acid is a tricarboxylic acid, its buffering capacity in the pH range between 2 and 4.5 is very high relative to the lactic or glycolic acids. In fact, all our batch and mixer-settler experiments showed a high constancy of the pH even when there was a significant loading of the organic phase. Relatively wide pH and concentrations changes can be tolerated with good lanthanide extraction. The lanthanide extraction kinetics and phase disengagement were acceptable. No significant losses of organic extractant were observed.

Extensive "cold" runs using a three-stages mixer-settler exhibited good lanthanide extraction, appropriate phase disengagement, no appreciable effects due to impurities such as zirconium, and excellent pH buffering.

Stripping of the lanthanides can be accomplished using diluted nitric acid 0.5 M-1.0 M. Stripping of Nd, Pr, and Eu was almost complete in the three-stage mixer-settler tested, while stripping of Er was only partial.

Purification of the organic extractant di-(2-ethylhexyl)phosphoric (HDEHP) acid diluted in diisopropylbenzene (DIPB) to remove the monosubstituted 2-ethylhexylphosphoric acid can be accomplished by washing with 1 M ammonium carbonate[$(\text{NH}_4)_2\text{CO}_3$]. After a three stage washing with the ammonium carbonate solution, titration curves of the organic extractant purposely spiked with 3-5 mol % mono 2-ethylhexyl-phosphoric acid (diprotonated) showed the neutralization of only one proton. In all cases. the organic extractant must be stripped before the washing treatment to avoid the formation of gel-like "third phases." Washing with sodium carbonate solutions is inconvenient because it causes gelation of the entire organic phase.

6. FUTURE RESEARCH AND DEVELOPMENT ACTIVITIES

Our cold test results using a citrate-based TALSPEAK, along with the previously accumulated knowledge, indicate that this technology can be effectively deployed after some further "hot" developmental work is concluded. Some of the proposed future activities include the use of americium and curium tracers (^{243}Am , ^{247}Cm or ^{248}Cm) first in batch tests followed by multistage processing to evaluate the actinide-lanthanide separation by a citrate-based TALSPEAK. The behavior of uranium and plutonium has to be determined. The interface of separative schemes, such as the TRUEX^{30,48-49} process, with TALSPEAK should also be analyzed. The combination TRUEX-TALSPEAK can potentially generate relatively pure lanthanide and actinide fractions with exclusion of almost any other impurity.

Radiation effects need to be completely evaluated. However, all available information indicates the process to be rather robust in respect to radiolytic damage. The "warm" tests using tracer levels of americium and curium should be followed by small-scale multistage treatment of real wastes.

It is also important to determine the effect of process variables on the actinide-lanthanide separation factors because those separation factors will determine the flow ratios to be used in actual processing.

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