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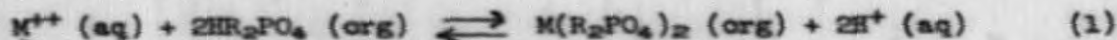
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EXTRACTION OF METAL IONS WITH DI-2-ETHYLHEXYL PHOSPHORIC ACID

W. J. Ross and J. C. White

Blake and his co-workers have shown that uranium and other elements can be extracted from acidic solutions by various types of organo-phosphorus compounds.^{1,2} Earlier investigations in this laboratory have demonstrated the applicability of tri-n-alkylphosphine oxides to the extraction of metal ions from acidic solutions for analytical purposes.^{3,4} This paper is concerned with a similar qualitative investigation of the extraction of metal ions with a di-alkyl phosphoric acid, di-2-ethylhexyl phosphoric acid (D2EHPA).

In their discussion of the extraction of uranium(VI) with di-2-ethylhexyl phosphoric acid,² Blake et al showed that this reagent was highly efficient for the extraction of uranium from weakly acidic solutions. The mechanism that they postulated for the extraction of a metallic ion, M^{++} , by di-2-ethylhexyl phosphoric acid:



involved the displacement of hydrogen ions by the metal ion. The formation of the organo-metallic complex is thus favored by the minimum concentration of acid that will prevent the precipitation of the metal hydroxide. They also reported that the rate with which equilibrium is attained between di-2-ethylhexyl phosphoric acid and various elements varies considerably.

As a result of this work, the survey of the use of this reagent as a possible analytical means for separating metal ions by solvent extraction was performed over a limited range of acidity, pH 0 to 1.9. In addition, a period of one hour was chosen to insure that equilibrium had been attained.

Experimental

The standard solutions of the elements were the same as used in previous studies,^{3,4} while the extractant consisted of 0.1 M di-2-ethylhexyl phosphoric acid in a diluent of cyclohexane. The di-2-ethylhexyl phosphoric acid was purified to greater than 99 per cent.

The ions to be investigated were divided into six groups similar to those described in extractions with alkyl phosphine oxides.^{3,4} These groups were:

- A. B^{+3} , Mg^{+2} , Ca^{+2} , Sr^{+2} , and Ba^{+2} .
- B. Ti^{+4} , Mo^{+6} , As^{+5} , V^{+4} , and Hf^{+4} .
- C. Co^{+2} , Al^{+3} , Y^{+3} , La^{+3} , Hg^{+2} , Ga^{+3} , In^{+3} .
- D. Pd^{+2} , Pt^{+2} , and Ru^{+2} .
- E. Cu^{+2} , Zn^{+2} , Cd^{+2} , Au^{+} , Sn^{+4} , Ge^{+4} , and Be^{+2} .
- F. Fe^{+3} , Ni^{+2} , Cr^{+6} , Zr^{+4} , U^{+6} .

The solutions of each group contained 1 to 2 mg of the individual ions. To each of the test solutions was added one ml of 5 M NaCl, $NaNO_3$, or $(NH_4)_2SO_4$, after which the pH was adjusted, in a volume of five ml, with NaOH. Each solution was extracted with five ml of 0.1 M di-2-ethylhexyl phosphoric acid in cyclohexane for one hour by means of a Kahn shaker; then the phases were allowed to separate. Portions of the organic and aqueous phases were removed and analyzed by qualitative spectrographic methods. The pH of the aqueous phase was measured as a check on the increase in hydrogen ion concentration due to displacement of hydrogen ions from di-2-ethylhexyl phosphoric acid by the metal ion. The results of these tests are reported in Tables I and II and Figures 1 and 2.

Table I

Extraction of Metal Ions from Acidic Solutions with 0.1 M
Di-2-Ethylhexyl Phosphoric Acid in Cyclohexane

Metal Ion	Sodium Chloride (1 M)			Ammonium Sulfate (1 M)	Sodium Nitrate (1 M)
	pH 0	pH 0.5	pH 1.5	pH 1.5	pH 1.5
Al ⁺³	-	-	N	N	N
As ⁺⁵	-	-	N	N	N
Ba ⁺²	-	-	N	-	N
Be ⁺²	P	P	P	P	P
B ⁺³	-	-	N	-	N
Cd ⁺²	-	-	N	N	N
Ca ⁺²	-	-	N	-	N
Cr ⁺⁶	P	P	P	P	P
Co ⁺²	-	-	N	N	N
Cu ⁺²	-	-	N	N	N
Ga ⁺³	-	-	N	N	N
Au ⁺	-	-	N	N	N
Hf ⁺⁴	E	E	E	E	E
In ⁺³	N	N	P	P	P
Fe ⁺³	P	P	P	P	P
La ⁺³	N	N	N	N	N
Mg ⁺²	-	-	N	-	N
Hg ⁺²	-	-	N	N	N
Mo ⁺⁶	E	E	E	E	E
Ni ⁺²	-	-	N	N	N
Pd ⁺²	-	-	N	N	N
Pt ⁺²	-	-	N	N	N
Ru ⁺²	-	-	N	N	N
Sr ⁺²	-	-	N	-	N
Tb ⁺³	E	E	E	E	E
Ta ⁺⁵	E	E	E	E	E
Ti ⁺⁴	E	E	E	E	E
U ⁺⁶	E	E	E	E	E
Y ⁺³	N	E	E	E	E
V ⁺⁴	N	N	P	E	P
Zn ⁺²	N	N	P	N	P
Zr ⁺⁴	E	E	E	E	E

E = complete extraction
P = partial extraction

N = no extraction
- = no test was conducted

Table II

Extraction of Metal Ions from Chloride Solutions with 0.1 M
Di-2-Ethylhexyl Phosphoric Acid in Cyclohexane

Unless indicated otherwise - Equilibration time - 1 hour
Aqueous phase - 1 M NaCl

Metal Ion	pH 0.5	pH 0	pH 0 ^a	pH 0 ^b	2 M HCl	2 M HCl ^a	2 M HCl ^b
Be ⁺²	P	P	P	P	P	P	P
Cr ⁺⁶	P	P	P	P	P	N	P
Hf ⁺⁴	E	E	E	E	E	E	E
Fe ⁺³	P	P	P	P	P	P	P
Mo ⁺⁶	E	E	E	E	P	P	E
Th ⁺⁴	E	E	E	E	E	E	E
Sn ⁺⁴	E	E	P	P	P	P	P
Ti ⁺⁴	E	E	E	E	E	E	E
U ⁺⁶	E	E	E	E	E	E	E
Zr ⁺⁴	E	E	E	E	E	E	E

^a Extracted 10 minutes

^b No NaCl

E = complete extraction

P = partial extraction

N = no extraction

Discussion

The results in Table I show which metal ions are extracted by di-2-ethylhexyl phosphoric acid at various acidities. The number of ions that are partially or completely extracted at the more favorable pH, 1.9, is considerably less than that found in phosphine oxide systems wherein the complex is the result of coordinate, rather than ionic, bonding. The degree to which the various ions combine with di-2-ethylhexyl phosphoric acid at a pH of 1.9 can be roughly correlated with the pH at which the hydroxide of the individual ions precipitates; i.e., those ions which precipitate at the lowest pH form the most stable complexes. This correlation is only approximate since all the ions tested do not attain equilibrium at the same rate.

The results of these qualitative tests are in agreement with the postulated reaction (equation 1) for the extraction of ions with di-2-ethylhexyl phosphoric acid in that the anion plays no controlling role in the extraction. The degree to which the ions are extracted lessens with increasing acidity. The apparently anomalous behavior of Sn(IV) can be explained by the fact that Sn(IV) precipitates as the hydroxide at a low pH and it cannot be extracted as completely from a solution of pH 1.9 as from more acidic media.

Only ten of the elements investigated were extracted from 1 M HCl, pH 0. Of these elements, seven were extracted completely, while the extraction of beryllium was sufficiently complete to afford a valuable means of isolating this element.

The data in Table II show the effects of extraction time, ionic strength, and concentration of acid on the extraction of these ten elements from chloride solutions. Chromium and tin are examples of the rather slow rate with which equilibrium is attained. In a solution at pH 0, Sn(IV) was only partially extracted after 10 minutes, but at the end of one hour, no tin was found in the aqueous phase, thereby showing complete extraction of tin had taken place. In 2 M HCl, chromium was not found in the organic phase after the 10-minute extraction period. Some chromium was extracted, however, after one hour. Molybdenum and tin also demonstrate the effect of high acid concentration. The extraction of these two ions is apparently vitiated at high acidities. Since the reliability of spectrographic determinations is adversely affected by the presence of a large concentration of sodium, more

refined experiments are necessary before valid conclusions can be drawn with respect to the effect of ionic strength on the extraction of metal ions from chloride solutions.

Extraction of Rare Earths

Yttrium was completely extracted from 1 M solutions of chloride, nitrate, and sulfate at a pH of 1.5 and partially from 1 M chloride solutions at pH 0.5 and zero. Under the same conditions, lanthanum was not extracted. Inasmuch as the rare earth elements exhibit chemical characteristics similar to yttrium or lanthanum, the different behavior of these two elements during equilibration with di-2-ethylhexyl phosphoric acid made it appear likely that selective extraction of individual or groups of rare earths might be feasible.

A standard solution of rare earth elements that contained 2 mg per ml of Ce^{+3} ; 1 mg per ml of Pr^{+3} , Nd^{+3} , Sm^{+3} , Dy^{+3} , and Ho^{+3} ; 0.5 mg per ml of Tb^{+3} ; 0.2 mg per ml of Y^{+3} , La^{+3} , Eu^{+3} , Gd^{+3} , Er^{+3} ; and 0.1 mg per ml of Yb^{+3} was used in all extraction tests. The aqueous solutions contained one ml of the standard solution of ions, one ml of 5 M NaCl and sufficient NaOH or HCl to yield 5 ml of aqueous solution of the desired pH. The organic extractant was 5 ml of 0.1 M di-2-ethylhexyl phosphoric acid in cyclohexane. The chloride solution was extracted for one hour and allowed to stand until both phases were clear. Aliquots of the organic and aqueous phases were removed and analyzed qualitatively by spectrographic methods. The results of these tests are presented in Table III and Figure 3.

Figure 3

EXTRACTION OF THE RARE EARTHS FROM CHLORIDE SOLUTIONS WITH DI 2-ETHYLHEXYL PHOSPHORIC ACID

CHLORIDE, 1M
D2EHPA, 0.1M IN CYCLOHEXANE

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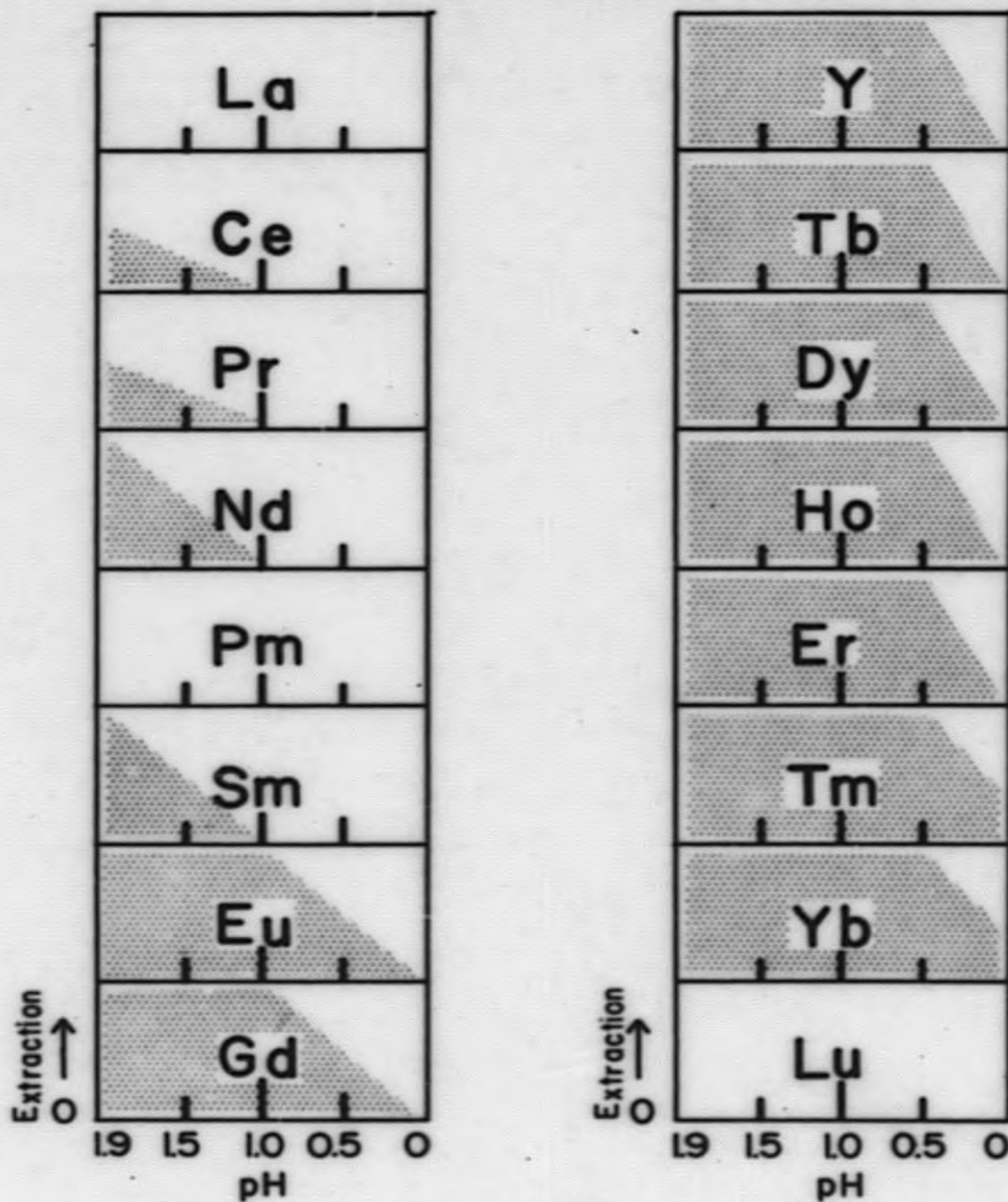


Table III

Extraction of Rare Earths from Chloride Solutions with
Di-2-Ethylhexyl Phosphoric Acid in Cyclohexane

<u>Ion</u>	<u>pH 1.9</u>	<u>pH 1.0</u>	<u>pH 1.0</u> (a)	<u>pH 0.5</u>	<u>pH 0.5</u> (a)	<u>pH 0</u>
Y ⁺³	E	E	E	E	P	N
La ⁺³	N	N	N	N	N	N
Ce ⁺³	P	N	N	N	N	N
Pr ⁺³	P	N	N	N	N	N
Nd ⁺³	E	N	P	N	N	N
Sm ⁺³	E	N	P	N	N	N
Eu ⁺³	E	E	E	P	N	N
Gd ⁺³	E	E	E	P	N	N
Tb ⁺³	E	E	E	E	E	N
Dy ⁺³	E	E	E	E	E	N
Ho ⁺³	E	E	E	E	E	N
Er ⁺³	E	E	E	E	E	N
Tm ⁺³	E	E	E	E	E	P
Yb ⁺³	E	E	E	E	E	P

^a Without NaCl

E = complete extraction
P = partial extraction
N = no extraction

The effect of hydrogen ion concentration on the extraction of ions by di-2-ethylhexyl phosphoric acid is clearly illustrated in Figure 2 and Table III. Although these data are qualitative in nature, they indicate that the selectivity of di-2-ethylhexyl phosphoric acid is enhanced by increasing the concentration of hydrogen ion. The similarity between the rare earth elements and lanthanum diminishes as the atomic number of the element increases, and, consequently, the similarity between these elements and those of yttrium becomes greater. This trend conforms with the relative basicity of the elements, i.e., lanthanum forms the strongest bases, while the yttrium forms a weak base that is similar to terbium, dysprosium,

holmium, and erbium, but stronger than thallium and ytterbium. This qualitative data is inconclusive and is dependent to a certain extent on the ionic strength of the systems; however, it does indicate possible methods for (1) separating lanthanum from all the rare earth elements and yttrium, (2) isolating cerium and praseodymium, (3) isolating cerium, praseodymium, neodymium and samarium from the other rare earth elements, or (4) isolating thulium and ytterbium. Schmitt⁵ has demonstrated that useable differences in extraction coefficients do exist between several of these elements in di-2-ethylhexyl phosphoric acid systems. This type of extraction offers a rapid method for preliminary separation of the rare earth elements into smaller groups.

Conclusion

On the basis of the screening tests reported herein, di-2-ethylhexyl phosphoric acid is a relatively specific extractant for metal ions and as such merits further quantitative study as to its potential uses in the separation of metal ions by solvent extraction.

Acknowledgement

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