Extraction of Thorium(IV), Yttrium(III), and Lanthanum(III) by Mesityl Oxide

E. C. Chen[1] **and Herbert Y. Lee**
Quebec Iron and Titanium Corp., Sorel, P.Q., Canada

Extraction of thorium(IV), yttrium(III), and lanthanum(III) by mesityl oxide was investigated. The aqueous phases were nitrate solutions with a nitric acid concentration varying from 3 to $12N$. In all cases, the extraction increased with the HNO_3 and mesityl oxide concentrations but decreased slightly as the initial metal concentration was increased. The largest separation factors obtained between thorium and yttrium and between yttrium and lanthanum were 84.4 and 1.2, respectively.

Mesityl oxide, 4-methyl-3-pentene-2-one, has been used recently as an extractant for transition metals (*4*–*7*). The extraction of thorium(IV) by this organic solvent was first reported in 1954 (*2*), and the literature has gradually accumulated (*1*). However, data available in the literature are still limited. The present work investigates the extraction of thorium(IV), yttrium(III), and lanthanum(III) by mesityl oxide from nitrate solutions as a function of the acid, solvent, and metal ion concentrations, as well as the organic to aqueous-phase ratio.

Experimental

All the experiments were carried out at room temperature. For a typical run, a known volume of the organic phase and an aliquot of the sample solution, prepared with desired acid and metal concentration, were introduced into a separatory funnel and shaken for 10 sec (a time of "10 sec" was mentioned in the literature for obtaining a maximum extraction). The phases were allowed to separate, and the aqueous raffinate was analyzed for its metal content by EDTA titration with xylenol orange indicator. The titration conditions for Th(IV) are an acetic acid buffer and pH 1.7–3.5, and the conditions for Y(III) and La(III) determination are the addition of hexamethylenetetraamine and pH 4.5–6.0.

Mesityl oxide (FW, 98.15; bp, 128–130°C; sp gr, 0.836) supplied by Eastmen Organic Chemicals, thorium nitrate tetrahydrate, lanthanum nitrate hexahydrate, yttrium nitrate hexahydrate, and nitric acid (69.0–71.0%) from Baker Chemicals were used without further purification. Deionized water was used to prepare the sample solutions, and kerosine was the diluent for the organic extractant.

Results and Discussion

The experimental results, expressed as the percentage of metal extracted E, are given in Table I. The extraction in all cases increases significantly with the nitric acid concentration, the organic to aqueous-phase ratio (O/A), and the solvent concentration. However, an increase in the initial metal concentration slightly decreases the extraction.

Since the extraction mechanisms for all oxygen-bearing organic solvents are generally considered to involve solvation, it is assumed that the extraction of Th(IV), Y(III), or La(III) by mesityl oxide (MO) is governed by a solvating reaction. The extraction reaction for Th(IV), for example, is:

$$\mathrm{Th}^{4+} + 4\mathrm{NO_3}^- + n\mathrm{MO} = \mathrm{Th(NO_3)_4}\cdot n\mathrm{MO} \qquad (1)$$

and

$$K = [\mathrm{Th(NO_3)_4}\cdot n\mathrm{MO}]/[\mathrm{Th}^{4+}][\mathrm{NO_3}^-]^4[\mathrm{MO}]^n \qquad (2)$$

where K is the equilibrium constant.

Thus,

$$\log D = \log K + 4 \log [\mathrm{NO_3}^-] + n \log [\mathrm{MO}] \qquad (3)$$

The distribution coefficient D may be calculated from the percentage extraction E by the following equation:

$$D = E/(100 - E)\ (\mathrm{O/A}) \qquad (4)$$

The plots of log D vs. log [MO] for a HNO_3 concentration of $9.46N$ and a metal concentration of $0.05M$ are shown in Figure 1. The distribution coefficients were based on an O/A of 2.50. The slopes of the best lines are 3.59 for thorium and 1.08 for both yttrium and lanthanum. However, equally acceptable lines varying in slope from about 3 to 4 could be drawn in the case of thorium and from about 1 to 2 in the case of yttrium and lanthanum. These indicate that the value of n in Equation 1 is between 3 and 4, whereas the values of n for yttrium and lanthanum are from 1 to 2. Throughout the experiments, water and nitric acid were both extracted into the mesityl oxide phase as the volume and acidity of the aqueous phase decreased appreciably after contacting with the solvent. Since ketones may extract nitric acid by solvation through a water-molecule bridge (*3*), a reaction between HNO_3 and mesityl oxide is assumed to be:

$$\mathrm{HNO_3} + \mathrm{H_2O} + n\mathrm{MO} = \mathrm{HNO_3}\cdot\mathrm{H_2O}\cdot n\mathrm{MO} \qquad (5)$$

Table I. Experimental Data

Acid concn, *N*	O/A phase ratio	Solvent concn, %	Initial metal concn, *M*	Metal extracted, %		
				Th	Y	La
3.15	1.25	100	0.05	13.8	0.48	0.60
6.31	1.25	100	0.05	43.8	1.21	1.28
9.46	1.25	100	0.05	65.8	2.23	2.44
12.62	1.25	100	0.05	75.7	6.02	5.30
3.15	2.50	100	0.05	14.2	1.06	1.01
6.31	2.50	100	0.05	47.1	2.72	2.66
9.46	2.50	100	0.05	82.3	5.37	5.02
12.62	2.50	100	0.05	94.3	16.50	13.90
9.46	0.5	100	0.05	36.2	1.30	1.17
9.46	5.0	100	0.05	88.9	8.31	8.27
9.46	2.50	100	0.10	80.1	4.88	4.79
9.46	2.50	100	0.25	79.0	4.68	4.47
9.46	2.50	100	0.50	69.8	3.72	3.03
9.46	2.50	75	0.50	32.8	1.92	2.14
9.46	2.50	50	0.50	13.2	1.99	1.80
9.46	2.50	25	0.50	2.17	0.87	0.90

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[1] Present address, Inland Waters Directorate, Department of the Environment, Ottawa, Ont., Canada. To whom correspondence should be addressed.

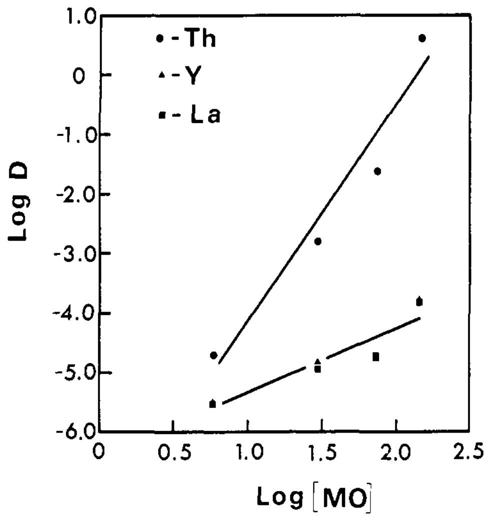

Figure 1. Log D vs. log [MO] for metal extraction (HNO_3 concn = 9.46N; O/A = 2.50; initial metal concn = 0.05M)

To obtain the value of n in the above equation, extractions of HNO_3 were carried out as a function of the solvent concentration with solutions containing no metal ions. The results are given as a log D vs. log [MO] plot shown in Figure 2, where the slope of the best line is 1.18. The species ($HNO_3 \cdot H_2O \cdot MO$) was either coextracted with the metal ions or could be formed first and then coordinated with the metal nitrates. In each of these experiments the acidity of the aqueous raffinate was practically the same as that of the corresponding experiment for the metal extraction.

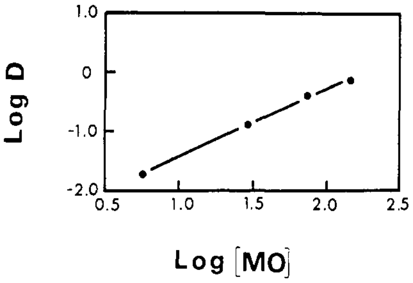

Figure 2. Log D vs. log [MO] for HNO_3 extraction (HNO_3 concn = 9.46N; O/A = 2.50; initial metal concn = 0.05M)

Although extraction of the metals is greater at higher HNO_3 concentration and O/A value, the largest separation factor between thorium and yttrium (D_{Th}/D_Y), 84.4, occurred at a HNO_3 concentration of 9.46N and an O/A value of 1.25. The separation factor between yttrium and lanthanum (D_Y/D_{La}) was less than 1.2 in all cases.

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Binary Diffusion Coefficients of *n*-Pentane in Gases

Minoru Nagasaka
Faculty of Engineering, Ibaraki University, Hitachi, Japan

The Stefan method was used to measure the binary gaseous diffusion coefficients of *n*-pentane (*n*Pe) in hydrogen, helium, nitrogen, air, and argon at 1 atm pressure and a temperature from −15° to 25°C at sec; *n*Pe-He, 0.3044 ± 0.0003 cm^2/sec; *n*Pe-N_2, 0.0885 ± 0.0001 cm^2/sec, *n*Pe-air, 0.0877 ± 0.0002 cm^2/sec; and *n*Pe-Ar, 0.0792 ± 0.0007 cm^2/sec. The 0.0885 ± 0.0001 cm^2/sec, 2*n*Pe-air, 0.0877 [illegible] 0.0002 cm^2/sec; and *n*Pe-Ar, 0.0792 ± 0.0007 cm^2/sec. The temperature exponent for each system lay between 1.778 and 1.971, in good agreement with the predicted values based upon the Lennard-Jones force constants in the Chapman-Enskog approximate kinetic theory.

Binary gaseous diffusion coefficients in hydrocarbon systems are important physical properties for chemical engineering. The temperature exponents of diffusion coefficients are also important for simplifying interpolation and (possibly) for extrapolation. There are relatively few such data in the literature, and those values differ in many cases. Therefore, we measured the diffusion coefficients by the Stefan method with hydrogen, helium, nitrogen, air, and argon as the carrier gases for *n*-pentane.

Experimental

The *n*-pentane was of pure grade (99 mol % minimum purity). The carrier gases—hydrogen, helium, nitrogen, air, and argon—were supplied by Hitachi Oxygen Co. (99.9 mol % minimum purity).

The Stefan method was used for the determination of the binary gaseous diffusion coefficients. Since the experimental method is well known, only a brief description will be given here. The apparatus consisted of the diffusion cell (Figure 1), which contained a capillary tube of 0.10-cm i.d., 0.60-cm o.d., and 10-cm length. The cell was immersed in a well-agitated water (or methanol solution) bath whose temperature was controlled to within 0.05°C. The temperature of the bath was measured to a precision of 0.01°C with a calibrated mercury thermometer with a magnifying glass. After steady state was reached, at certain time intervals the liquid level in the capillary tube was measured with a reading microscope which could be read to a precision of 0.001 cm.

The time duration of experimental runs varied between 1 and 25 hr, depending on the temperature level and carrier gases. Care was taken to ensure that the diffusion coefficients were not influenced by flow rates of carrier gases in the approximate range of 100-500 cm^3/min.