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RECEIVED for review September 15, 1971. Accepted December 21, 1971. The authors thank the Council of Scientific and Industrial Research, India, for financial assistance for the project and for a research fellowship to one of them (SKJ).

Characterization of Iron and Rare Earth Polymers of Di(2-ethylhexyl) Phosphoric Acid

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The characterization of the iron, yttrium, lanthanum, praseodymium, neodymium, dysprosium, holmium and ytterbium polymers of di(2-ethylhexyl) phosphoric acid by chemical and X-ray diffraction technique are reported.

The formation of a third phase or a white precipitate in the organic phase has been observed by several investigators (*2*, *8*, *10*, *11*) to limit the extraction of the lanthanides in the liquid cationic ion exchanger, di(2-ethylhexyl) phosphoric acid. The formation of chain polymers with uranium (*1*) and copper (*9*) when di(2-ethylhexyl) phosphoric acid is used as an extractant has also been reported. Harada et al. (*3*) have recently reported the experimental conditions under which this third phase becomes limiting during the extraction of rare earths. The formation of the polymers as a function of di-(2-ethylhexyl) phosphoric acid concentration acidity and aqueous metal concentration has been studied. In this note are presented additional results obtained in characterizing the polymers of iron and rare earths with di(2-ethylhexyl) phosphoric acid.

In this liquid-liquid extraction system, the extraction of the metal in aqueous solution involves the formation of a complex with di(2-ethylhexyl) phosphoric acid which is soluble in the organic phase. The di(2-ethylhexyl) phosphoric acid is diluted with an aliphatic naphtha with a boiling range from 177–99°C and is marketed by the American Mineral Spirits Co. as AMSCO Odorless Mineral Spirits. The extraction equilibrium can be represented by the reaction

$$M^{3+} + 3H_2G_2 = M(HG_2)_3 + 3H^+ \qquad (1)$$

where M^{3+} is the trivalent metal ion, H_2G_2 is the di(2-ethylhexyl) phosphoric acid dimer, and $M(HG_2)_3$ is the complex soluble in the organic phase.

The addition of more metal ions into the organic phase results in an irreversible polymerization reaction which can be represented by

$$nM^{3+} + nM(HG_2)_3 = (MG_3)_n + 3nH^+ \qquad (2)$$

where n is the number of moles and $(MG_3)_n$ is the metal polymers.

The degree of polymerization of the rare earth-D2EHPA was

Table I. Chemical Composition of Iron and Rare Earth–D2EHPA Polymers[a]

	YG_3		FeG_3	
	% Obsd	% Calcd	% Obsd	% Calcd
Metal	8.7	8.5	6.8	5.5
C	53.6	54.7	50.2	56.5
H	9.9	9.8	8.9	10.1
P	8.6	8.8	8.6	9.1
O	17.7	18.2	17.7	18.8
Sum	98.5	100.0	92.2	100.0

	LaG_3		PrG_3		NdG_3	
	% Obsd	% Calcd	% Obsd	% Calcd	% Obsd	% Calcd
Metal	12.6	12.6	12.8	12.7	12.8	13.0
C	49.6	52.3	50.9	52.2	51.4	52.0
H	9.0	9.3	9.1	9.3	9.2	9.3
P	8.3	8.4	8.4	8.4	8.4	8.4
O	17.1	17.4	17.4	17.4	17.3	17.3
Sum	96.6	100.0	98.6	100.0	99.1	100.0

	DyG_3		HoG_3		YbG_3	
	% Obsd	% Calcd	% Obsd	% Calcd	% Obsd	% Calcd
Metal	14.5	14.4	14.2	14.6	16.6	15.2
C	50.0	51.2	49.5	51.1	47.3	50.7
H	9.0	9.1	8.9	9.1	8.7	9.0
P	8.3	8.3	8.1	8.2	7.8	8.2
O	17.1	17.0	16.8	17.0	16.0	16.9
Sum	98.9	100.0	97.5	100.0	96.4	100.0

[a] $G = (C_8H_{17})_2PO_4^-$. Polymer: $P = P/PO_4$, $O = (1\text{-}P/PO_4)$.

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Table II. X-Ray Powder Diffraction Pattern of Iron and Rare Earths Polymers[a]

YG_3

Line	2θ	d	I_0
1	5.30	16.646	100
2	9.28	9.513	3.2
3	10.70	8.254	5.1
4	11.80	7.487	1.9
5	14.20	6.226	5.1
6	16.17	5.472	7.6
7	17.41	5.046	6.3
8	20.68	4.092	16.5
9	23.40	3.795	6.3

HoG_3

Line	2θ	d	I_0
1	5.60	15.755	100
2	9.37	9.422	6.1
3	10.90	8.103	9.8
4	14.38	6.149	9.8
5	16.30	5.429	8.5
6	18.60	4.762	6.1
7	19.60	4.521	8.5
8	20.70	4.284	17.0
9	22.13	4.009	7.3

DyG_3

Line	2θ	d	I_0
1	3.60	24.501	2
2	5.78	15.264	100
3	9.72	9.084	4.4
4	11.04	8.795	5.2
5	14.62	6.048	5.6
6	16.58	5.337	4.8
7	18.98	4.667	4.8
8	19.90	4.454	4.8
9	20.88	4.413	8.4
10	23.80	3.732	4.8

NdG_3

Line	2θ	d	I_0
1	5.48	16.099	100
2	9.40	9.392	7
3	10.95	8.066	9.5
4	14.40	6.140	9.0
5	16.45	5.379	9.5
6	19.75	4.487	7
7	20.40	4.346	12.5
8	20.90	4.243	9.5
9	21.80	4.070	6.5
10	23.85	3.724	7.0

PrG_3

Line	2θ	d	I_0
1	6.15	14.323	100
2	10.10	8.743	5.1
3	11.60	7.615	6.2
4	15.00	5.896	8.2
5	16.80	5.268	7.2
6	20.90	4.243	12.4
7	24.40	3.642	8.2

YbG_3

Line	2θ	d	I_0
1	5.30	16.646	100
2	9.30	9.493	7.9
3	10.75	8.216	10.0
4	11.90	7.424	1.4
5	14.25	6.205	11.4
6	16.20	5.462	8.6
7	18.60	4.762	8.6
8	19.40	4.568	7.8
9	20.70	4.283	18.6
10	22.15	4.006	7.1
11	23.50	3.779	7.8
12	24.10	3.686	7.1
13	24.60	3.612	7.1
14	25.80	3.447	5.0
15	26.90	3.309	5.0
16	27.90	3.192	4.3
17	28.70	3.105	5.7

FeG_3

Line	2θ	d	I_0
1	6.00	14.705	100
2	10.20	8.657	9.7
3	11.70	7.551	5.5
4	15.45	5.725	13.9

LaG_3

Line	2θ	d	I_0
1	5.70	15.478	100
2	9.73	9.074	10
3	11.10	7.957	5.8
4	14.70	6.016	17.4

[a] Cu $K_{\alpha\,\mathrm{Mean}} = 1.54178$. G = $(C_8H_{17})_2PO_4^-$.

determined by extrapolating to zero concentration the relationship between molecular weight and viscosity of the polymer solution as proposed by Mark (*7*) and Houwink (*4*). A range of values for the different polymers was obtained, indicative of the different molecular weight distributions obtainable for polymeric materials (*12*). The degree of polymerization for the rare earth–D2EHPA polymers is as follows: yttrium, 1000–6000; lanthanum, 200–800; praseodymium, ~7000; neodynium, ~6000; holmium, ~7000; dysprosium, 3000–6000, and ytterbium, 400–1400. The iron polymer degree of polymerization varied from 0.5 to 10.

The composition analyses of the iron and rare earth di(2-ethylhexyl) phosphoric acid polymers are given in Table I. The polymer samples were dissolved in chloroform, back-extracted with 6*M* HCl, the acid evaporated and titrated directly with the rare earths with EDTA using xylenol orange (*5*). The iron was determined by the addition of excess EDTA and back titration with zinc. The Schoniger flask method for determining phosphorus did not work due to complexing of the phosphates by the rare earths. The phosphorus was approximated by weighing the residue after evaporation of the chloroform phase used in dissolving the polymers.

The carbon and hydrogen were determined by the method described by Lysyj and Zarembo (*6*). This consists of burning the organic sample at 600–700°C in an atmosphere of oxygen. The carbon is converted to carbon dioxide and the hydrogen to water. The conversion is accelerated by the passage of the combustion product over decomposed silver permanganate. The sulfur and phosphorus oxides are combined directly with silver wool, and the silver permanganate is decomposed. The water is absorbed in Anhydrone and the carbon dioxide in Ascarite tubes. The inconsistency between the observed and calculated composition of the iron and ytterbium polymers could be due to the preparation of an impure sample.

X-ray powder diffraction of all the polymer samples was made using a Philips X-ray diffractometer. The results shown in Table II include the angle 2 θ as obtained from the scan and the relative intensities, with the strongest peak taken as 100% and all other peaks adjusted to it. The ytterbium polymer has 17 diffraction lines, the dysprosium and neodymium polymers have 10 each, the yttrium and holmium polymers have 9 each, praseodymium has 7, and the lanthanum and iron polymers have 4 each.

ACKNOWLEDGMENT

The authors thank the Ames Laboratory analytical service group for the chemical analysis of the samples, and the X-ray group in the Metallurgy Division for running the X-ray powder diffraction patterns of the samples.

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RECEIVED for review September 24, 1971. Accepted December 13, 1971. Work was done in the Ames Laboratory of the U. S. Atomic Energy Commission.