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Synthesis and Polarographic Reduction of Ytterbium(III) Anthranilate and Nicotinate Complexes in Aqueous—Non Aqueous Mixtures at D. M. E.

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The stoichiometry of the compounds formed by the interaction of Yb(III) perchlorate with anthranilate and nicotinate have been investigated by means of amperometric titrations. The titration curve provides evidence for the formation of 1 : 3 complexes. The reduction of Yb(III) and Yb(III) anthranilate and nicotinate ions are studied polarographically at constant ionic strength at 25 and 35 ± 1 °C in aqueous—non aqueous mixtures. The reduction was found to be diffusion controlled, but the electrode process is irreversible in all cases. The kinetic parameters have been determined by *Koutecky*'s method.

Introduction

Polarographic reduction of rare earths falls under two categories: group one (La, Ce—Lu) in which metal ions get reduced directly to the metallic state with a three electron reduction, while the others (Sm, Eu, and Yb) are characterised by a single electron reduction. Yb(III) complexes have drawn little attention as far as their polarographic studies are concerned[1–3]. Synthesised complexes of ytterbium and other rare earths have not been studied in detail polarographically.

Synthetic aspects of rare earth nicotinates in aqueous medium were investigated by *Chupathina* and *Serebrennikov*[4]. The present paper

Table 1. *Results of amperometric titrations.* Amperometric titration of Yb (0.02*M*) with (0.2*M*) Ligand in 5.0 ml of (0.2*M*) LiCl
Applied potential = — 1.65 V vs. *SCE*

S. No.	Ligand	Vol. of Yb metal solution	Vol. of ligand required	Ratio at end point
1	Sod. Anthranilate	5.0 ml	1.5 ml	1.3
2	Nicotinic Acid	5.0 ml	1.5 ml	1.3

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Table 2. *Polarographic characteristics and kinetic parameters of 0.5 mM* Yb(III)

Solvent Percentage	Yb(III) metal ion					Yb(III)	
	i_d, μA	$-E_{1/2}$, V vs. *SCE*	Slope, mV	$\alpha\, n_a$	$K°fh$	i_d, μA	$-E_{1/2}$, V vs. *SCE*
DMF (25 °C)							
20	1.0593	1.4720	57	0.940	1.259×10^{-19}	0.9850	1.4710
40	0.9106	1.5020	71	0.790	1.995×10^{-19}	0.8920	1.4095
60	0.3345	1.4600	50	0.940	1.000×10^{-23}	0.6133	1.4170
80	0.8363	1.4130	125	0.448	1.995×10^{-12}	1.0593	1.4535
DMF (35 °C)							
20	2.5647	1.4200	95	0.444	2.512×10^{-14}	0.8363	1.3875
40	2.7134	1.4180	121	0.510	4.467×10^{-13}	0.7805	1.3810
60	1.6912	1.3780	165	0.330	3.981×10^{-9}	0.7619	1.4020
80	2.0257	1.3400	72	0.810	6.310×10^{-17}	1.4310	1.4612
CH_3CN (25 °C)							
20	2.2673	1.4160	60	0.944	6.310×10^{-22}	0.8177	1.4495
40	2.4718	1.4060	66	0.800	1.259×10^{-19}	0.7805	1.4315
60	2.4718	1.3950	70	0.920	6.310×10^{-21}	0.3902	1.4640
80	2.7877	1.3825	80	0.778	3.981×10^{-18}	0.9106	1.5480
CH_3CN (35 °C)							
20	2.7319	1.4005	68	0.901	1.000×10^{-21}	1.2080	1.3901
40	2.9178	1.3890	72	0.690	3.982×10^{-16}	1.1151	1.4165
60	2.8063	1.3710	64	0.940	1.585×10^{-20}	0.7991	1.4390
80	3.2709	1.3565	56	0.980	1.259×10^{-22}	—	—
DMSO (25 °C)							
40	3.2468	1.4400	67	0.885	1.000×10^{-20}		
60	2.8912	1.4590	73	0.814	6.310×10^{-19}		
80	2.4160	1.4820	77	0.749	6.310×10^{-19}		
DMSO (35 °C)							
40	3.8658	1.4240	68	0.793	3.162×10^{-18}		
60	3.4939	1.4370	70	0.823	3.981×10^{-19}		
80	2.7505	1.4635	82	0.732	6.310×10^{-18}		

deals with the synthesis and polarographic behaviour of ytterbium anthranilate and ytterbium nicotinate complexes in aqueous—organic solvent media: the former in aqueous dimethyl formamide and aqueous acetonitrile mixtures, the nicotinate complex in aqueous dimethyl formamide and aqueous dimethyl sulfoxide mixtures.

Experimental

Analytical grade reagents were used for all experiments. The Yb_2O_3 (supplied by Dr. Theodor Schuchardt, München, Germany, 99.9% pure) was dissolved in a requisite amount of $HClO_4$. The solution was heated to *metal ion and* Yb(III) *complexes (*$LiClO_4$ *as a base electrolyte) at 25 and 35 ± 1 °C*

Anthranilate			Yb(III) Nicotinate				
Slope, mV	αn_a	$K^\circ fh$	i_d, μA	$-E_{1/2}$, V vs. *SCE*	Slope, mV	αn_a	$K^\circ fh$
145	0.436	1.413×10^{-12}	1.4126	1.3860	72	0.737	1.585×10^{-18}
134	0.454	3.162×10^{-12}	1.1151	1.4050	63	0.767	1.000×10^{-18}
94	0.520	3.548×10^{-14}	1.0036	1.4225	75	0.767	1.000×10^{-18}
120	0.477	3.162×10^{-13}	1.2723	1.4235	97	0.605	3.981×10^{-16}
75	0.760	1.122×10^{-17}	1.4309	1.3620	72	0.889	1.000×10^{-18}
98	0.630	1.413×10^{-15}	1.4868	1.3860	75	0.756	1.995×10^{-17}
83	0.670	1.259×10^{-16}	1.4497	1.4060	87	0.701	1.259×10^{-16}
109	0.515	5.120×10^{-14}	1.5239	1.4005	110	0.564	5.018×10^{-14}
78	0.720	1.585×10^{-18}					
71	0.830	2.512×10^{-22}					
105	0.590	2.818×10^{-16}					
142	0.413	7.943×10^{-13}					
59	0.967	6.310×10^{-22}					
88	0.643	6.310×10^{-16}					
105	0.757	1.885×10^{-18}					
—	—	—					
			0.7619	1.4080	62	0.944	2.512×10^{-22}
			0.6504	1.4460	70	0.852	5.012×10^{-21}
			0.8735	1.4575	127	0.501	3.981×10^{-13}
			1.0407	1.4015	68	0.762	6.310×10^{-18}
			1.0036	1.4260	92	0.696	5.012×10^{-17}
			0.9665	1.4365	82	0.744	3.162×10^{-18}

evaporate excess of $HClO_4$. Stock solution (0.1*M*) was then made up with doubly distilled water and was standardised[5]. The molar ratio (1 : 3) of the formation of the complexes was initially checked by amperometric titration.

1. Synthesis of the Complexes

a) Ytterbium Anthranilate

The following procedure was adopted: Anthranilic acid was dissolved in NaOH, maintaining the pH to 6.5 by using $HClO_4$. Sodium anthranilate 4.5 mMole was added slowly and gradually with constant stirring to the measured amount of $Yb(ClO_4)_3$ 1.5 mMole. A brown crystalline precipitate

slowly appeared which was allowed to settle for about two hours under ice. This was then filtered by decantation under vacuum. The compound was then washed first by water and then alcohol and finally by ether. The complex was dried at 100–110 °C and then put in a dessicator.
Yield 1,41 mMole.

$C_{21}H_{18}N_3O_6Yb$.	Calc.	N 7.22,	Yb 29.76.
	Found	N 7.17,	Yb 29.60.
		7.12,	29.72

The stable compound is insoluble in water and is soluble in solvents like acetonitrile, dimethyl formamide and formamide.

b) An aqueous solution of nicotinic acid (4.5 mMole) was added with constant stirring to the $Yb(ClO_4)_3$ (1.5 mMole) solution, pH 4.0 ± 0.05 was maintained to avoid hydrolysis. The mixture so obtained was digested for two hours on a water bath. White crystalline needles were kept over night before filtration, washed with water and absolute alcohol and finally with ether. They were then dried at 100–110 °C in an electric oven and put in dessicator. They are insoluble in water and methyl cyanide, soluble in dimethyl formamide and dimethyl sulfoxide.

$C_{18}H_{12}N_3O_6Yb$.	Calc.	N 7.77,	Yb 31.88.
	Found	N 7.68,	Yb 32.00.
		7.64,	31.84

2. Identification of the Complexes

a) The percentage of ytterbium was determined by *EDTA* titration as well as by ignition of the complex at 800 to 900 °C. Nitrogen was estimated by *Kjeldahl*'s method.

b) I.R. Spectra: The infrared spectra of the ligands as well as the metal chelates are recorded (using Perkin Elmer model 337 grating infra red spectrophotometer).

Some of the inportant assignments are given below:

1. Two strong bands are observed in anthranilic acid in the region 3340–3440 cm^{-1}. This may be due to O—H···N or O···H—N type of hydrogen bonding. However these bands are absent in the metal chelates.

2. The bands between 1650–1680 cm^{-1} are also observed in the ligands due to stretching C=O frequencies. These bands are shifted in the lower side in the region 1610–1630 cm^{-1}.

3. No bands observed in the range 1110 cm^{-1}. This indicates the absence of ClO_4^-.

4. The bands at about 1575 cm^{-1} are also observed due to ionised COO^- in the metal chelates and are absent in the ligands.

The above results indicate the coordination of metal ion with carboxylic group in nicotinate ion while in anthranilate ion the chelation is based on amino as well as carboxylic group.

3. Polarographic Analysis

A manual type of polarographic set up with Ajco galvanometer, was used to measure the current vs. voltage curves. The *d.m.e.* had the following characteristics $m = 1.745$ mg/sec and $t = 4.2$ sec in open circuit. Reductions were carried out in "H" type cell with agar-agar plug saturated with NaCl. Redistilled solvents were used for the experiments. Pure $LiClO_4$ was used as a base electrolyte. Oxygen was removed by bubbling purified N_2 which was presaturated with solvent mixtures. The measured half wave potential were corrected for IR drops.

Results and Discussion

Ytterbium gives a single well defined diffusion controlled wave in aqueous organic solvent mixtures (Table 2). The plots of log $i/(i_d - i)$ vs. E are linear in all cases. The value of slope of log plots indicates irreversible reduction of the complexes, Table 2.

The kinetic parameters (Table 2) for the irreversible reduction at *d.m.e.* have been calculated by *Koutecky*'s[6] method. The plots of — log Kf vs. E (*N.H.E.*) gave a straight line with slope equal to $\alpha\, nF/2.303RT$ from which the values of n_a and $K°_{fh}$ have been calculated. Extrapolation of this line to zero volts (at *N.H.E.*) gave the value of K°_{fh}.

It has been a general observation in ytterbium anthranilate and ytterbium nicotinate complexes the shift in $E_{1/2}$ is relatively more anodic as compared to simple Yb(III) ion. However at higher percentage of the solvent the shift in $E\ 1/2$ is in cathodic direction with respect to simple Yb(III). This indicates that the reduction of Yb(III) complexes is easier in lower percentage of the solvent. As the solvent percentage increases the solvent enters the coordination sphere and thus makes the reduction relatively difficult. However the behaviour of solvent also depends upon various factors as discussed by *Gaur* & *Goswami*[7]. No unified theory is available to explain solvent behaviour.

The reduction being diffusion controlled, thus it makes possible the estimation of Yb(III) in presence of anthranilate and nicotinate ion.

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