INVESTIGATION OF Yb (III) - ASPARTATE COMPLEXES AT D.M.E.

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The reduction of Yb'iii) asptarate in aq. methanoe. CH_3CN, and formamide media is diffusion controlled and irreversible. The reversible half wave potentials, calculated using Gelling's treatment, shift towards more cathodic direction with aspartate ion concentration, indicating complexation. The overall formation constants are : β_1 = 180; β_2 = 1500 & β_3 = 21500 in aqueous media : β_1 = 60, B_2 = 1100 and β_3 = 21000 in aq. methyl cyanide : β_1 = 50, β_2 = 5000 β_3 = 12500, β_4 = 1240000 in aq. dimethyl formamide ; and β_1 = 20, β_2 = 3200, β_3 = 48000. β_4 = 397000 in aq. methanol The stability of the complexes inereases linearly with donor number of the solvents used.

Much less information is available for the reduction of ytterbium since it exhibits fairly high negative potential at dropping mercury electrode ; the data on electrode kinetics of ytterbium complexes are also scanty. The reduction of ytterbium in aqueous and non-aqueous medium has been investigated by some workers[1—3]. Polarography of ytterbium complexes with some polycarboxylic acids have been studied by various authors[4—6]. Complexes of Eu(III) with asparate ion have also been reported[7—8].

The present paper deals with the polarographic studies of complexes formed by Yb(III) with aspartate ions in aqueous, and aqueous methyl cyanide, methanol and dimethyl formamide. Overall formation constants have been determined and distribution of various complex species present in solution have also been calculated.

EXPERIMENTAL

Reagent grade chemicals were used in all experiments. A manual polarographic set up with Ajco galvanometer was used to measure the current voltage curves. The d.m e. had the following characteristics : m = 1.745 mg/sec., t = 4.2 sec. (in open circuit). Reduction was carried out in a "H" type cell with agaragar plug, saturated with sodium chloride. The dissolved oxygen was removed by bubbling purified nitrogen, presaturated with solvent mixtures. Solution of Yb(III) perchlorate, was prepared from reagent grade Yb_2O_3 (99.9% pure) and was then standardized by EDTA titration[9]. Lithium perchlorate was used as base electrolyte. The ionic strength was maintained constant (μ = 0.5). The pH of all the experimental solutions was maintained as 6.5 ± 0.1. Solutions containing 0.5 mm of Yb(III) with varying amounts of ligand concentration (0.00 to 0.16M) were prepared in aqueous and aqueous organic solvent (20% by volume) media. All the polarograms were recorded at 30 ± 1°C. The measured half wave potential were corrected for i r. drops.

Results and Discussion

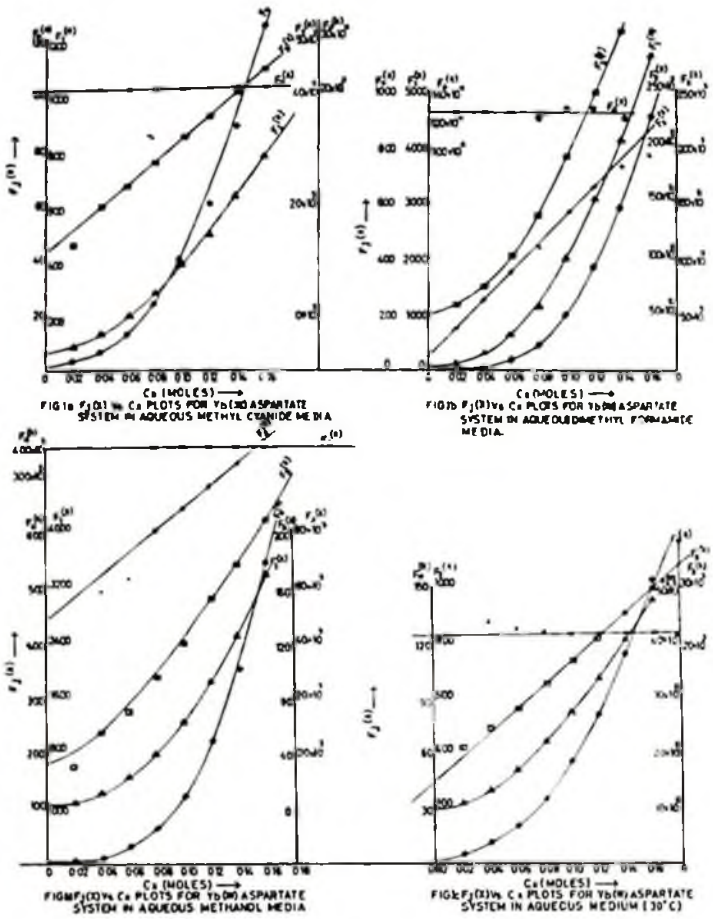
A single well defined diffusion controlled wave appeared in each case. The plots of $\log[i/(i_d - i)]$ vs-E(S.C.E) were observed to be linear in all cases. The slope showed the reduction to be irreversible. Hence the reversible half wave potential ($E^r_{\frac{1}{2}}$) has been determined using Gelling's treatment. The half wave potedtial shifted to a more cathodic direction ($\Delta E^r_{\frac{1}{2}}$ = 0.1250V) in aqueous media when the ligand concentration was 0.16M and diffusion current decreased with concentration of the glutamate ions. The plots of $-E^r_{\frac{1}{2}}$ vs-log Cx (Cx is the glutamate ion concentration in moles) were found to be smooth curves in all cases indicating the formation of two or more complex species in equilibrium.

Hence the method of Lingane[10] could not be applied for the determination of formation constants ; Debord and Hume's[11] treatment for the stepwise formation constants has also been applied. The stability constants of the various species are calculated and are tabulated in table 1. The percentage distribution of ytterbium present in various complex species has been plotted.

Table—1 values of stability constants of Yb(III)—aspartate complexes.

Solvent (30°C)	Stability constants			
	β_1	β_2	β_3	β_4
Aqueous	1.8×10^2	1.5×10^3	2.15×10^4	—
Aqueous methanol	20	3.2×10^3	4.8×10^4	39.7×10^4
Aqueous DMF	50	5×10^3	1.25×10^4	1.24×10^6
Aqueous methyl Cyanide	60	11×10^2	2.1×10^4	—

It has been observed that in aqueous and aqueous methyl cyanide media three complex species are formed in each case On the other hand, four complex species are being formed in aqueous methanol and dimethyl formamide media.



From the results it is inferred that the solvent plays an important role in the complex formation. The dielectric constant of the organic solvent is one of the important factors which is playing a major role. As the value of the dielectric constant increases the more species are revealed. Moreover the stability of the complexes also increased as the dielectric constant value is increased. In aqueous dimethyl formamide the stability is maximum while it is minimum in aqueous methyl cyanide media. The irreversible nature of the reduction is also affected with change in solvent composition The values of K_s and α_n indicate that by increase in the concentration generally decreases the irreversibility in beginning. However when aspartate ions are in larger concentrations, the irreversibility is further increased

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