AMPEROMETRIC TRACE DETERMINATION OF Tb^{3+} , Dy^{3+} AND Er^{3+} WITH ALIZARIN RED S

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Amperometric titration procedure has been successfully employed for the trace determination of Tb^{3+}, Dy^{3+} and Er^{3+} in aqueous and partially nonaqueous media. The titrations have been carried out at - 0.7 V vs. Hg pool; pH = 4.5, and μ = 0.1. The current-volume plots indicated a metal to ARS complexation ratio of 1:2 in each case. Absorptiometric studies made on the above complexation, also confirmed the said ratio. Interference to the titration by other ions is examined.

A survey of literature reveals that Alizarin Red-S (Abbr. as ARS) has been widely used as a complexometric spectrophotometric, and pH metric reagent [1-5]. In continuation of the work in our laboratory on trace determination of rare earths with reagents of modern analytical importance[6-11], the present paper describes the results of amperometric titration of Tb^{3+}, Dy^{3+} and $Er^{3+}$with ARS using a dme-Hg pool electrode system.

EXPERIMENTAL

All the chemicals used were of Analar/Extrapure quality. Tb^{3+}, Er^{3+} and Dy^{3+} solutions were prepared and standardised[9]. The solution of ARS was prepared by disolving a requisite quantity of the reagent in double distilled water and standardised by the procedure of Larson and Hirozawa[12]. A manually operated polarograph with a multiflex galvanometer (Sens. 8.1×10^{-9} amp/div) was used for amperometric titrations, using dme-Hg pool electrode system. An Elico-digital pH meter model LI-120 was used for measuring pH of the test solutions. The metal ligand complexation equilibrium was studied using a double beam sample chamber GCA/MCPHERSON Spectrophotometer model Eu 707-11.

Amperometric titrations were done by preparing sets of solutions containing different concentration of ARS in 0.1 mole dm^{-3} KCl as supporting electrolyte. The pH of these experimental sets was adjusted at 4.5 using acetate buffer.

RESULTS AND DISCUSSION

ARS gives a well defined cathodic reduction wave[13] in 0.1 mol. dm^{-3} KCl and acetate buffer at pH 4.5 (Fig.1). The diffusion current is proportional to the concentration of ARS. For amperometric titrations, test solution containing a known concentration of ARS in 0.1 mol dm^{-3} KCl and acetate buffer (pH = 4.5) was taken in a titration cell. The plateau potential of the polarogram for ARS, i.e. - 0.7 V vs Hg pool, was applied. At this potential the titrated metal ions are not reduced (Fig. 1). The standard solution of metal ion

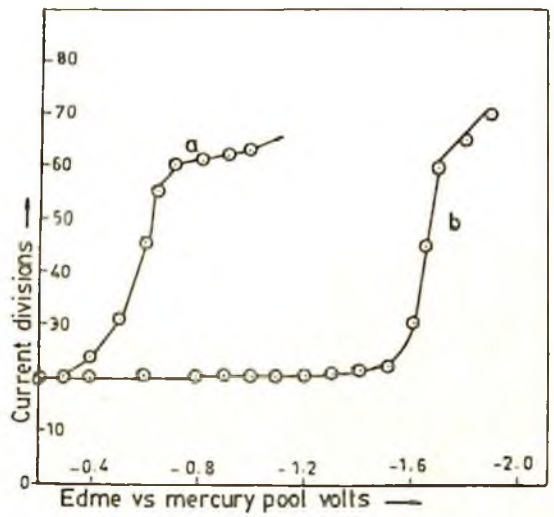


Fig. 1 (A) Polarogram of 1m M Alizarin Red s in 0.1 m KCl at pH = 4.5
(B) Polarogram of 2 m M metal (Tb^{3+}, Dy^{3+} or Er^{3+}) in 0.1 M KCl at pH = 4.5

(pH = 4.5) was added drop by drop from 1 cm^3 microburrette. A violet red precipitate was observed in the test solution. The current was noted on a multiflex galvanometer. The galvanometer deflection after making necessary volume correction was plotted against the volume of metal added when a L shaped curve was observed. Typical graph is given in Fig. 2. The end point indicated a metal to ligand ratio of 1:2 which is in excellent agreement with the results reported in the literature [10,11]. A reversed L shaped curve is obtained by taking rare earths as titrate and ARS as titrant under the above mentioned experimental conditions. It is also observed that the amperometric titration procedure holds good in 25% ethanol water medium as well.

Interference Study

For the study of the effect of diverse ions, known ammount of foreign ions were added to a definite

TABLE 1

AMPEROMETRIC DETERMINATION OF TERBIUM, DYSPROSEUM AND ERBIUM WITH ALIZARIN RED S AT - 0.7 V vs MERCURY POOL

μ = 0.1 pH = 4.5

Sl. No.	Approximate concentration m Molar	Terbium (mg) Taken	Found	% Error	Dysproseum (mg) Taken	Found	% Error	Erbium (mg) Taken	Found	% Error
1	0.25	0.7900	0.7880	- 0.25	0.8125	0.8098	- 0.33	0.4181	0.4156	- 0.59
2	0.50	1.5800	1.5750	- 0.31	1.6250	1.6212	- 0.23	0.8363	0.8320	- 0.51
3	0.75	2.3700	2.3754	+ 0.22	2.4375	2.4452	+ 0.31	1.2543	1.2490	- 0.42
4	1.0	3.1600	3.1670	+ 0.22	3.2500	3.2388	- 0.34	1.6726	1.6800	+ 0.44
5	1.25	3.9500	3.9612	+ 0.28	4.0625	4.0782	+ 0.38	2.0907	2.0830	- 0.36
6	1.5	4.7400	4.7250	- 0.30	4.8750	4.8608	- 0.29	2.5089	2.5184	+ 0.37
7	1.75	5.5300	5.5532	+ 0.42	5.6875	5.7124	+ 0.43	2.9270	2.9352	+ 0.28
	Standard Deviation	= 0.21%			Standard Deviation	= 0.18%		Standard Deviation		= 0.25%
	Coefficient of Variance	= 0.45			Coefficient of Variance	= 0.38		Coefficient of Variance		= 0.35

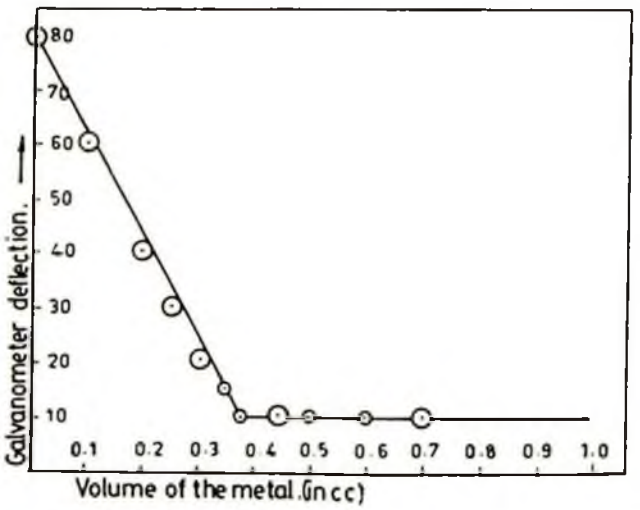


Fig. 2 Amperometric titration curve of Tb with ARS concentration of ARS solution taken in cell = 0.015 mM 10 ml(concentration of TB solution = 0.02 m M/ml)

ammount of ARS in test solution and then the titrations were performed following the procedure described above. It was observed that hundred fold concentration of the ions, NH_4^+, K^+, Na^+, Cl^-, ClO_4^-, SO_4^{2-}, NO_3^-, and CH_3COO^- do not interfere in the titration procedure (Table 2). However, small ammounts of Ag^+, Pb^{++}, Bi^{3+}, Al^{3+}, Fe^{3+} VO_3^- $Cr_2O_7^{2-}$ MoO_4^{2-} and CO_3^{2-} ions interfere in the titration appreciably.

Absorption Studies on Metal Ligand Equilibrium

Vosburgh & Cooper s[14] method was used to study the complex formed. The visible absorption spectra of 0.1 m Mol dm^{-3} of ARS at pH = 4.5 consists of a single maximum at 420 mμ and ARS complexes with each of the titled metals at 540 mμ. The shift in λ_{max} may be attributed to the formation of metal complex. To study the stoichiometry of the complex, job's method of continuous variation[5] has been successfully applied. The measurements were carried out at pH 4.5 and wave length 540 mu. Absorption studies were made within 1 hr of preparing the sets as it was observed that in nearly three hours gelatinous precipitation takes place. The metal ligand stoichiometric ratio with all the three titled metal ions with ARS is found to be 1:2 (Fig.3) which confirms the the ratio observed by authors in the amperometric titration procedure. To evaluate the equilibrium constant, the molar ratio method and non-linear

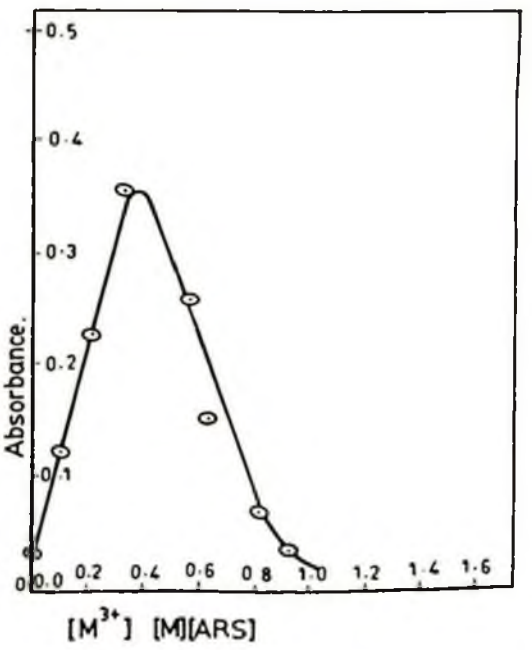


Fig. 3 Job's plot for composition at 54 μ.

TABLE 2

AMPEROMETRIC DETERMINATION OF TERBIUM, DYSPROSEUM AND ERBIUM WITH ARS IN PRESENCE OF DIVERSE IONS

Metal Taken	Terbium 1.5800 mg.		Dysproseum 1.6250 mg.		Erbium 0.8363 mg.	
Diverse ions added	Found	% Error	Found	% Error	Found	% Error
Na^{+} (115 mg)	1.5816	+ 0.10	1.6204	- 0.28	0.8392	+ 0.34
K^{+} (195 mg)	1.5834	+ 0.21	1.6196	- 0.33	0.8316	- 0.56
NH_4^{+} (42.5 mg)	1.5738	- 0.39	1.6276	+ 0.16	0.8384	+ 0.25
Mg^{++} (24.3 mg)	1.5708	- 0.58	1.6294	+ 0.27	0.8304	- 0.70
Zn^{++} (32.69 mg)	1.5818	+ 0.11	1.6105	- 0.89	0.8344	- 0.22
Sn^{++} (11.86 mg)	1.5698	- 0.65	1.6190	- 0.37	0.8348	- 0.17
Hg^{++} (10 mg)	1.5910	+ 0.69	1.6184	- 0.40	0.8310	- 0.63
Cd^{++} (11.24 mg)	1.5652	- 0.93	1.6209	- 0.25	0.8388	+ 0.29
Se^{++} (3.94 mg)	1.5704	- 0.60	1.6314	+ 0.39	0.8298	- 0.77
Te^{++} (3.19 mg)	1.5664	- 0.86	1.6410	+ 0.98	0.8412	+ 0.58
Tl^{+} (10.2 mg)	1.5652	- 0.93	1.6158	- 0.56	0.8296	- 0.80

method of Job was employed. The conditional formation constants are found to be 10.51, and 10.13, 9.81 respectively for 1:2, Er^{3+} : ARS, Tb^{3+} : ARS and Dy^{3+} : ARS complexes in solution.

Statistical Treatment of the Data

Ultramicro and microgram quantities of Er^{3+}, Tb^{3+} and Dy^{3+} have been determined by this amperometric procedure with ARS. The error in determination is found to be less than $\pm$ 0.8% and coefficient of variation never exceeded 0.45.

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