DME-Mercury Pool Electrode system for the estimation of Trace amount of Pr^{3+} and Nd^{3+} in Aquous and partially Nonaquous Media

S. C. LAVALE AND K. S. PITRE

Department of Chemistry, University of Saugar : Sagar (MP) 470 003.

DME—Mercury pool electrode system has been applied successfully for the precise determination of Pr^{3+} and Nd^{3+} in aquous and partially non-aquous media using Alizarin Red-S as an amperometric titrant. The titrations have been performed at pH = 4.5 in acetate buffer and $\mu = 0.3$. Titrations are not in any way hampered by the presence of different amounts of reported foreign metal ions. The experiments could be done with an error of less than ±0.51%. The relative mean deviation and standard deviations in case of Pr^{3+} vs. ARS to be 0.08% and 0.11% and in case of Nd^{3+} ARS to be 0.06% and 0.07% respectively. Experimental data reports the accuracy, precision and confidence of the procedure adopted.

A survey of existing literature reveals the application of Alizarin red-S (a sodium salt of 1, 2 dihydroxyanthraquinone 3-sulphonic acid) as a successful complexo-metric reagent. Many investigators have carried out spectrophotometric[1-4] studies of ARS complexes with Cu^{2+}, ZrO_2^{2+}, Th^{2+}, Al^{3+}, and a few rare earths metal ions with regards to their stoichiometries and possible use of the ligand in spectrophotometric estimation of the aforesaid metal ions. Larson and Hirozawa[5] have studied the reaction of ARS with Zr^{2+} and Hf^{2+} in aqueous or alcoholic medium using an amperometric technique. However, so far, the amperometric procedure has not bean developed for the estimation of trace quantitles of Pr^{3+} and Nd_3^{+} with ARS using DME-Mercury pool electrode system. The results obtained in our laboratory are quite satisfactory for estimating trace quantities of the said metal ions.

EXPERIMENTAL

The chemicals used were Analar or extrapure quality. Pr^{3+} and Nd^{3+} solutions were prepared by dissolving a calculated amount of each of the metal oxide in minimum quantity of hydrochloric acid and making up the solution to the required volume with distilled water. These solutions were standardised by EDTA method[6]. Stock solution of ARS was prepared by dissolving requisite quantity of the reagent (BDH) in double distilled water and it has been standardised by the analytical procedure developed by Larson and Hirozawa[5]. Acetic acid-sodium acetate buffer was used to keep the pH value of the test solution at 4.5 and the ionic strength (0.3) was adjusted with the requisite amount of KCl solution.

Amperometric titrations were made on manually operated polarograph with multiplex galvanometer (sens. 8.10×10^{-9} amp/div) using d m e as indicator electrode and mercury pool as reference. The capillary used for d m e had a m value of 2.3733 mg/sec at a drop time 3.0 sec in air free 1 M potassium chloride at 41 Cms effective height of the mercury column ($m^{2/3}\ t^{1/6} = 2.136\ mg^{2/3}\ sec^{-1/2}$). An Elico-digital pH meter (Model Li-120) was used for measuring pH of the test solutions.

For titrations a number of solutions containing calculated amounts of Pr^{3+} or Nd^{3+} (in specific volume) at $\mu = 0.3$ and pH = 4.5 were prepared. Titrations of those solutions were carried out at an applied voltage of −0.7 N vs. mercury pool.

RESULTS AND DISCUSSION

The current voltage behaviour of ARS has been studied in acetate buffer of pH 4.5 and $\mu = 0.3$, adjusted with requisite amount of KCl, ARS gives a well defined cathodic wave[7] under these conditions (fig. 1A). The height of the diffusion current is proportional to the concentration of ARS. An aliquot of the metal solution (Pr^{3+} or Nd^{3+}) was taken into a titration cell in which acetate buffer and Potassium chloride solution were added and the mixture made up to a volume (here 10 ml). A potential of −0.7 V vs. mercury pool was applied (plateau of the ARS wave but Pr^{3+} and Nd^{3+} are unaffected fig 1-B) and a standard solution of ARS

(pH = 4.5) was added drop by drop from 1 ml semi-micro burette and current was noted with a multiflex galvanometer. On plotting galvanometer reading after necessary volume correction[8] against the titrant volume, a reversed L shaped curve was

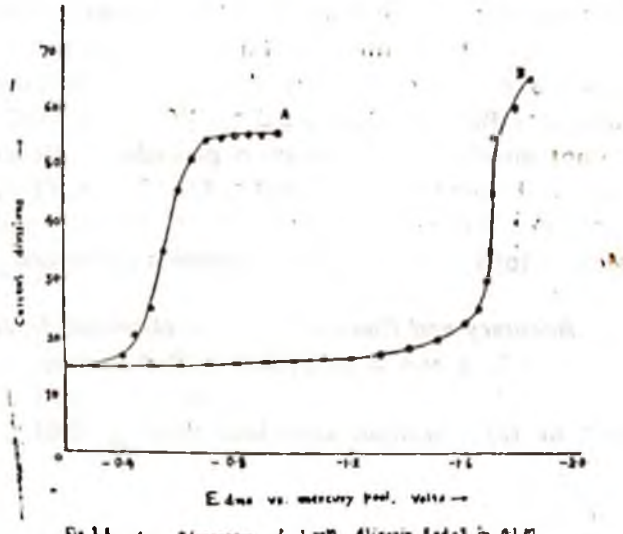


Fig 1 A - Polarogram of 1 mM Alizarin Red-S in 0.1 M KCl at pH = 4.5
B - Polarogram of 2 mM metal (Pr^{3+} or Nd^{3+}) in 0.1 M KCl at pH = 4.5

obtained (fig. 2 and Fig. 3). The end point indicated a metal to ARS ratio of 1:2 which is in good agreement with the spectrophotometric results observed by Soni and Viswanath[9]. Under the identical experimental conditions, similar results were

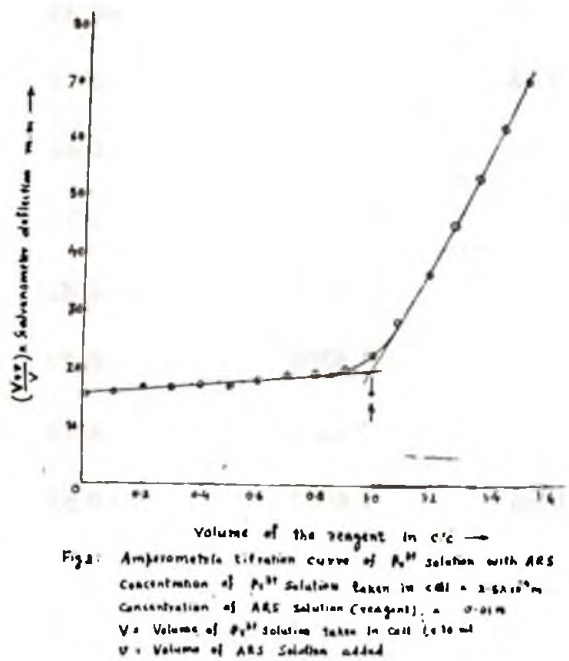


Fig 2 Amperometric titration curve of Pr^{3+} solution with ARS
Concentration of Pr^{3+} solution taken in cell = 2.5×10^{-3} M
Concentration of ARS solution (reagent) = 0.01 M
V = Volume of Pr^{3+} solution taken in cell (= 10 ml)
v = Volume of ARS solution added

observed by choosing ARS as titrate and Pr^{3+} or Nd^{3+} as titrant. In the latter case an L shaped curve was observed. Moreover, it is observed that each of these titration can be performed in 25% ethanol medium which may be useful for the estimation of Pr^{3+} and Nd^{3+} in a compound or ores soluble in partially ethanol medium.

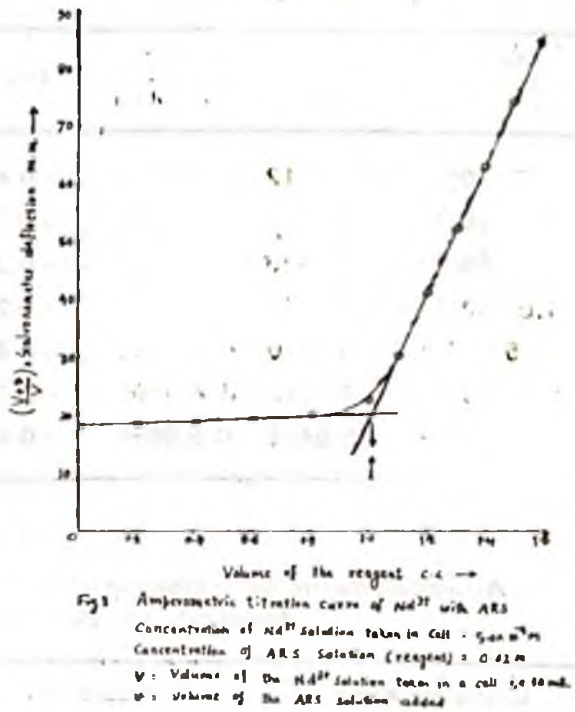


Fig 3 Amperometric titration curve of Nd^{3+} with ARS
Concentration of Nd^{3+} solution taken in cell = 5×10^{-3} M
Concentration of ARS solution (reagent) = 0.01 M
V = Volume of the Nd^{3+} solution taken in a cell (= 10 ml)
v = Volume of the ARS solution added

The data in table 1 and 2 clearly indicate that this method is successfully applicable for the estimation of trace amount of Pr^{3+} and Nd^{3+} with an error of less than ±0.51%.

TABLE 1

An amperometric determination of Pr^{3+} with Alizarin Red S at −0.7 V vs mercury pool
$\mu = 0.3$ pH = 4.5

Sl. No.	Approximate Concentration M	Amounts of Pr^{+}		% Error
		Taken mg	Found mg	
1.	2.5×10^{-4}	0.7046	0.7010	−0.51
2.	5.0×10^{-4}	1.4092	1.4040	−0.36
3.	7.5×10^{-4}	2.1143	2.1203	+0.28
4.	1.0×10^{-3}	2.8184	2.8132	−0.18
5.	1.25×10^{-3}	3.5230	3.5327	+0.27
6.	1.5×10^{-3}	4.2276	4.2406	+0.30
7.	1.75×10^{-3}	4.9322	4.9518	+0.39

TABLE 2

An amperometric determination of Nd^{3+} with Alizarin Red-S at −0.7 V vs mecury pool $\mu = 0.5$ pH = 4.5

Sl. No.	Approximate Concentration M	Amount of Nd^{3+} Taken mg	Amount of Nd^{3+} Found mg	Error
1.	2.5×10^{-4}	0.7212	0.7176	−0.49
2.	5.0×10^{-4}	1.4424	1.4472	+0.33
3.	7.5×10^{-4}	2.1636	2.1696	+0.27
4.	1.0×10^{-3}	2.8848	2.8763	−0.29
5.	1.25×10^{-3}	3.6060	3.6211	+0.41
6.	1.5×10^{-3}	4.2372	4.3102	−0.39
7.	1.75×10^{-3}	5.0484	5.0696	+0.41

Study of the effect of diverse ions : For interference studies, known amounts of the foreign ions were added to a definite amount of metal ion (Pr^{3+} or Nd^{3+}) and the metal was titrated following the procedure as described above. The titrations of Pr^{3+} or Nd^{3+} are not hampered by the presence of large amounts of different foreign ions as shown in table 3. Moreover, it is also observed that the ions Cl^-, Br^-, I^-, ClO_4^-, SO_4^{-2}, NO_3^-, CH_3COO^- do not interfere in the titration procedure. However it is observed that NO_2^-, CO_3^{-2}, Ag^+, Pb^{+2}, Bi^{+3}, Ca^{+2}, Ba^{+2} Al^{3+} Fe^{+3}, VO_3^{-2}, $Cr_2O_7^{-2}$ and MoO_4^{-2} ions interfere in this titrimetric procedure.

Accuracy and Precision : It is observed from the table 1, 2 and 3 that Alizarin Red-S may be successfully used for the trace determination of Pr^{3+} or Nd^{3+} with an error less than ± 0.51%.

TABLE 3

An amperometric determination of Pr^{3+} and Nd^{3+} with ARS in presence of diverse ions.
Metal taken : Pr^{3+} = 1.4092 mg and Nd^{3+} = 1.4424 mg

Diverse Ion Added	Pr^{3+} found (mg)	% error	Nd^{3+} found (mg)	error
Na^+ (115 mg)	1.4106	+0.11	1.4390	−0.21
K (195 mg)	1.4128	+0.24	1.4472	+0.33
NH_4^+ (42.5 mg)	1.4031	−0.43	1.4393	−0.21
Mg^{2+} (24.3 mg)	1.4002	−0.62	1.4496	−0.49
Zn^{+2} (32.69 mg)	1.4108	+0.11	1.4526	+0.70
Sn^{+2} (11.86 mg)	1.3991	−0.71	1.4305	−0.82
H_3^{+2} (10 mg)	1.4198	+0.75	1.4365	−0.40
Cd^{+2} (11.24 mg)	1.3950	−1.0	1.4401	−0.16
Se^{4+} (3.94 mg)	1.4009	−0.58	1.4507	+0.57
Te^{4+} (3.19 mg)	1.3987	−0.75	1.4280	−0.99
Tl^{+1} (10.2 mg)	1.3992	−0.70	1.4515	+0.63

N.B. The figure within parenthesis show the amount of foreign ion added.

However, in presence of a few diverse ions the metal can be estimated with an error less than ±1.0%. The relative mean deviation and standard deviation in case of Pr^{3+} vs. ARS is found to be 0.08% and 0.11% respectively and Nd^{3+} vs ARS is 0.06% and 0.071% respectively. Data in table 1, 2, 3 and calculated statistical data indicate high accuracy and precision of the procedure adopted.

Acknowledgement

One of the authors (S.C.L.) is greatful to the U.G.C. for awarding him teacher fellowship. Thanks are also due to the Head, Department of Chemistry, University of Saugar, Sagar, M.P. for providing Laboratory facilities.

REFERENCES

1. H. A. Liebhafsky and E. H. Winslow : *J. Amer chem. Soc.* 60, (1938) 1776.
2. A. K. Mukherji and A. K. Dey : *Bull. Chem. Soc.* Japan 31, (1958) 521.
3. I. S. Mustafin and E. A Koshkovskaya : *Zhur. Obshchei kim* 26, (1956) 2381.
4. Robert, W. Rinehant. *Anal. Chem.* 26, (1954) 1820-2.
5. E. M. Larson and S. T. Hirozawa . *J. Inorg. Nucl. Chem.* 3, (1656) pp. 198-205.
6. F. J. Welcher : *The Analytical uses of Ethylene diamine tetraacetic acid (D. Van Nostrand company Inc.)* (1957) pp. 174, 181.
7. N. H. Furman and K. G. Stone, *J. Am. Chem. Soc.* 71 (1949) 3055.
8. J. T. Stock, Amperometric Titrations, *R. E. Krieger, Pub. Co)* Huntington, New York, 1975 pp. 7-8.
9. L. L. Soni and G. Viswanath : *J. Ind. Chem. Soc.* 48 (9. (1971) 799.

THE METTUR CHEMICAL AND INDUSTRIAL CORPORATION LIMITED

The Mettur Chemical and Industrial Corporation Limited

METTUR DAM-636.402 (TAMIL NADU)

LARGE SCALE MANUFACTURERS OF

Caustic Soda
Stable Bleaching Powder
Methylene Chloride
Methyl Chloride
Carbon Tetrachloride
Chloroform
Ethyl Silicate
Silicon Tetrachloride
Liquid Chlorine
Chlorinated Paraffin Wax
Hydrochloric acid
Potassium Chlorate
Calcium Chloride
Sulphate of Alumina
Chemical Lime
Common Salt
Vanaspathi
Refined Vegetable Oils
and
Toilet & Washing Soaps