January, 1983] © 1983 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 56, 341—342 (1983) 341

Alizarin Red-S, an Amperometric Reagent for Ultramicro and Microgram Estimation of Sm^{3+} and Gd^{3+}

S. C. Lavale* and K. S. Pitre

Department of Chemistry, University of Saugar, Sagar (M. P.) 470003, India

(Received January 5, 1982)

Synopsis. Alizarin Red-S has been employed successfully as an amperometric reagent for the precise determination of Sm^{3+} and Gd^{3+} in aqueous and partially non aqueous media. Amperometric titrations have been performed at −0.7 V *vs.* Hg-pool, pH=4.5 and μ=0.1. The current-volume titration curves obtained were well defined, indicating 1:2 stoichiometric ratio of metal:ARS complexation in each case. The absorptiometric studies made on the equilibrium of above complexation also confirm the said ratio. Many ions do not interfere the titration procedure.

Alizarin Red-S (Abbr. as ARS) has been employed in analytical chemistry since Atack[1)] discovered that Al^{3+} could be detected with this reagent. The use of ARS as an complexometric, spectrophotometric and pH-metric reagent is described in the literature.[2–5)] Larson and Hirozawa[6)] have studied the complexation of Zr^{2+} and Hf^{2+} with ARS in aqueous and alcoholic media using amperometric titrations. In continuation of our work[7–10)] on trace estimation of rare earths, the present paper deals with the results of amperometric estimation of Sm^{3+} and Gd^{3+} with ARS using a d.m.e. -Hg pool electrode system. The amperometric estimations have been supplemented by absorption studies to establish the metal-ligand equilibria.

Experimental

The chemicals used were of AnalaR or Extra pure quality. Sm^{3+} and Gd^{3+} solutions were prepared and standardized.[10)] The solution of ARS was prepared by dissolving requisite quantity of this reagent in conductivity water and standardized by the analytical procedure developed by Larson and Hirozawa.[6)]

Amperometric titrations were done on mannually operated polarograph with multiflex galvanometer (sens. 8.10×10^{-9} A/div.) using d.m.e. as indicator and Hg-pool as reference electrode. An Elico digital pH meter (model LI.120) was used for measuring pH of the test solutions. A Beckman DU-2 spectrophotometer was used to study the equilibrium of metal-ligand complexation.

For titrations a number of solutions, containing calculated amounts of Sm^{3+} or Gd^{3+} in 0.1 mol/dm³ KCl as supporting electrolyte were prepared and pH of these test solutions was fixed at 4.5 using acetate buffer.

Results and Discussion

The current voltage behaviour of ARS has been studied in 0.1 M (1 M=1 mol dm⁻³) KCl and acetate buffer at pH 4.5. ARS gives a well defined cathodic wave[11)] (Fig. 1-A). The height of diffusion current is proportional to the concentration of ARS. The test solution of Sm^{3+} or Gd^{3+} was taken in a titration cell. The plateau potential of the polarogram for ARS *i.e.* −0.7 V *vs.* Hg pool (at which Sm^{3+} or Gd^{3+} do not give any diffusion current Fig. 1-M) was applied.

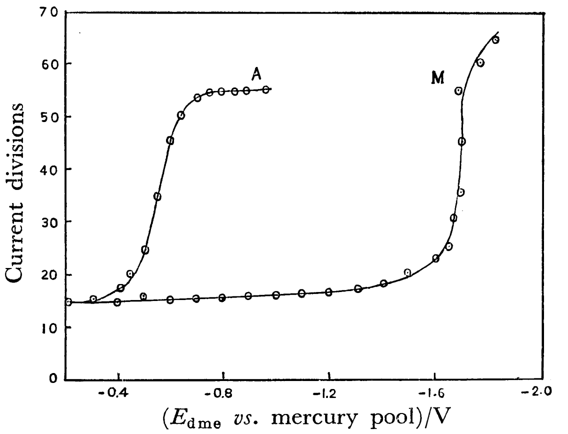

Fig. 1. A: Polarogram of 1 mM Alizarin Red-S in 0.1 M KCl at pH=4.5. M: Polarogram of 2 mM metal(Sm^{3+} or Gd^{3+}) in 0.1 M KCl at pH=4.5.

The standard solution of ARS (pH=4.5) was added drop by drop from 1 cm³ semi-micro burette, a pinkish red coloration was observed. The current was noted with multiflex galvanometer. On plotting galvanometer reading after necessary volume correction[12)] against titrant volume a reversed L shaped curve was obtained. The end point indicated a metal: ARS ratio of 1:2, which is in good agreement with the results reported in the literature[13,14)] and that observed by the authors with absorbtiometric studies discussed in this paper. Moreover, it is also observed that each of these titrations can be performed in 25% ethanol medium which may be fruitful for the estimation of Sm^{3+} and Gd^{3+} in a compound or ore soluble in partially ethanol medium.

Study of the Effect of Diverse Ions. For interference studies, known amout of foreign ions were added to a definite amount of metal ion (Sm^{3+} or Gd^{3+}) and the metal was titrated following the procedure described above. The maximum amount of diverse ions reported in Table 1. do not hamper the titrations. It is also observed that 100 folds of concentrations of the ions NH_4^+, Cl^-, ClO_4^-, SO_4^{2-}, NO_3^-, and CH_3COO^- do not interfere in this titrimetric procedure. However, small amounts of Ag^+, Pb^{2+}, Bi^{3+}, Ca^{2+}, Al^{3+}, Fe^{3+}, VO_3^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, and CO_3^{2-} ions interfere the titration procedure appreciably.

Absorbtion Studies on Complexation. Vosburgh and Cooper's[15)] method was used to study the nature of complex formed. The visible absorbtion spectra of 1×10^{-4} M ARS at pH 4.5 consists a single maximum at 420 nm and ARS complexes with Sm^{3+} or Gd^{3+} at 530 nm. The shift in λ_{max} is attributed to the formation of complex. Under varying ratio of mixing and varying pHs only one absorption maximum was obtained, supports to the formation of complex. To determine the stoichiometry of the complexes job's

Table 1. An amperometric determination of Sm^{3+} and Gd^{3+} with ARS in presence of diverse ions

Metal taken: $Sm^{3+} = 1.504$ mg (0.01 mM), $Gd^{3+} = 1.592$ mg (0.01 mM).

Diverse ion added	Sm^{+3} found (mg)	% error	Gd^{3+} found (mg)	% error
K^+ (195 mg)	1.49	−0.97	1.599	+0.43
Na (115 mg)	1.499	−0.32	1.587	−0.31
Mg^{2+} (48.6 mg)	1.51	+0.39	1.584	−0.50
Zn^{2+} (24.3 mg)	1.518	+0.93	1.60	+0.50
Tl^{+1} (15.3 mg)	1.501	−0.19	1.601	+0.56
Sn^{2+} (11.86 mg)	1.51	+0.39	1.588	−0.25
Cd^{2+} (11.24 mg)	1.495	−0.59	1.583	−0.56
Hg^{2+} (10 mg)	1.491	−0.86	1.607	+0.94
Se^{4+} (3.94 mg)	1.507	+0.19	1.59	−0.12
Te^{4+} (3.19 mg)	1.498	+0.39	1.583	−0.56

a) The figure within parenthesis shows the amount of foregn ion added under the prescribed experimental conditions.

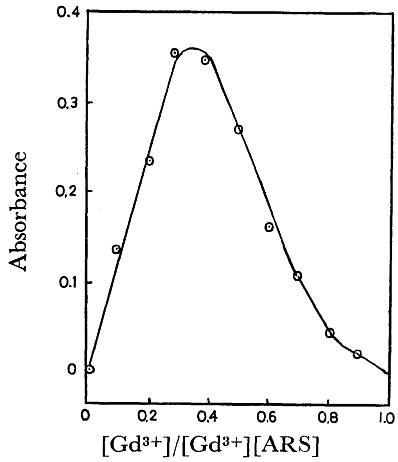

Fig. 2. Job's plot for composition at 530 nm.

method of continuous variations[16] (Fig. 2) has been successfully applied. The measurements were carried out at pH 4.5 and wavelength 530 nm. The fresh solution of ARS was prepared before use and the experimental sets were made. The color development of complex is instanteneous. Absorbtion studies were made within 1 h, as it is found that a gelatineous precipitation takes place on standing for nearly three hours. Stoichiometric ratio of Sm^{3+} and Gd^{3+} complexes with ARS were found to be 1:2 in both the cases, which confirms the ratio observed by authors in amperometric titration technique. The equilibrium constants were evaluated by mole ratio method and nonlinear method of job. The log conditional formation constants are found to be 10.94 and 11.51 for Sm^{3+}–ARS and Gd^{3+}–ARS complexes in solution. The molar ratio and numerical values of stability constants obtained using absorption studies supplemented the authors view on amperometric estimations of Sm^{3+} and Gd^{3+} with ARS.

Accuracy and Precision. The ultramicro and microgram quantities of Sm^{3+} and Gd^{3+} have been estimated amperometrically with an error of less than ±0.8%. For each set replicate titrations were done and statistical methods have been applied to interpret the data obtained. A more accurate measure of precision known as coefficient of variation never exceeded 0.55.

One of the authors (SCL) is grateful to the UGC, New Delhi, for awarding him Teacher Fellowship.

References

1) Atack, *J. Soc. Chem. Ind.*, **34**, 936 (1915).
2) H. A. Liebhafsky and E. H. Winslov, *J. Am. Chem. Soc.*, **60**, 1776 (1938).
3) A. K. Mukerji and A. K. Dey, *Bull. Chem. Soc. Jpn.*, **31**, 521 (1958).
4) R. W. Renehant, *Anal. Chem.*, **26**, 1820 (1954).
5) A. Varadarajulu and U. V. Seshaiah, *J. Indian Chem. Soc.*, **48**, 11 (1971).
6) E. M. Larson and S. T. Hirozawa, *J. Inorg. Nucl. Chem.*, **3**, 198 (1956).
7) S. C. Lavale and K. S. Pitre, *J. Electrochem. Soc. India.*, **30**, 328 (1981).
8) S. C. Lavale and K. S. Pitre, *Rev. Roum. Chim.*, in press.
9) K. S. Pitre and S. C. Lavale, *J. Inst. Chem. (India)*, **53**, 211 (1981).
10) S. C. Lavale and K. S. Pitre, *Proc. Natl. Acad. Sci. India*, in press.
11) N. H. Furman and K. G. Stone, *J. Am. Chem. Soc.*, **71**, 3055 (1948).
12) J. T. Stock, "Amperometric Titrations," R. E. Krieger Pub. Com. Huntington, New York (1975), p. 7.
13) A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, **74**, 4744 (1952).
14) L. L. Soni and G. Vishwanath, *J. Indian Chem. Soc.*, **48**, 799 (1971).
15) W. C. Vasburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941); **64**, 1630 (1942).
16) P. Job, *Ann. Chim.*, **9**, 113 (1928); **6**, 97 (1936).