

absorbance over the entire visible range decreased as the concentration of the added carboxylic acid increased. This indicates a progressive conversion of the Fe-SB complex to a Fe-carboxylate complex. It was, therefore, concluded that no mixed ligand complexes are formed in these systems.

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### Stabilities of Pr(III), Nd(III) & Sm(III) Complexes with Girard T Derivative of Resacetophenone

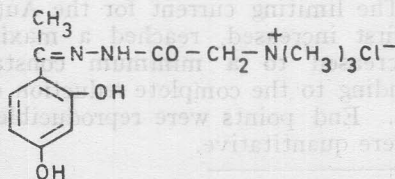
S. P. RAO & T. ADI SESA REDDY

Department of Chemistry, University of Jodhpur, Jodhpur

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The dissociation constant of the ligand and stability constants of complexes of Pr(III), Nd(III) and Sm(III) with Girard's T-derivative of resacetophenone have been determined potentiometrically using Calvin-Bjerrum pH-titration technique at  $27 \pm 0.1^\circ$  and  $\mu = 0.1M$  ( $\text{NaClO}_4$ ) in aqueous medium.  $\log K_1$ ,  $\log K_2$  and  $\log K_3$  values have been calculated for Pr(III), Nd(III) and Sm(III) complexes ( $\log \beta_3 = 11.31, 11.60$  and  $11.82$  respectively).

THE oxime of resacetophenone<sup>1</sup> was used for the determination of Cu(II) and Ni(II) in the presence of certain cations. The phenylhydrazone of resacetophenone<sup>2</sup> was used as a spot test reagent for Cu(II). The study of the stabilities of metal complexes in solution is facilitated by introducing a solubilizing group like quaternary ammonium group into the ligand. In the present investigations trimethylammoniumacetylhydrazine chloride (Girard T-reagent) derivative (I) of resacetophenone, containing azo methine group and solubilizing quaternary ammonium group has been prepared



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and the stability constants of its complexes with Pr(III), Nd(III) and Sm(III) have been determined in aqueous medium at  $\mu = 0.1M$  ( $\text{NaClO}_4$ ) and  $27^\circ \pm 0.1^\circ$  employing Calvin-Bjerrum pH titration technique.

Resacetophenone, Girard T-reagent, sodium perchlorate, etc., were of AR grade. Metal solutions were prepared from their respective nitrates (BDH, analar). Sodium perchlorate (BDH, analar, 1.0M) was used for maintaining the ionic medium constant at 0.1M. An aqueous solution of carbonate-free sodium hydroxide (analar) was prepared and standardized against potassium hydrogen phthalate.

A Cambridge bench type pH-meter (accuracy 0.02) with glass and calomel electrodes was used. The measurements were checked before and after the titration with standard buffers.

*Synthesis of the ligand (GTRP)*—Equimolecular proportions of resacetophenone and Girard T-reagent were taken in absolute ethyl alcohol. A small quantity of glacial acetic acid was added to it to dissolve Girard T-reagent. The reaction mixture was boiled under reflux for 2 hr. On cooling overnight, yellow crystals of the reagent (GTRP) appeared. The crystals were filtered and recrystallized from absolute ethanol. The yield was almost quantitative.

The substance does not have a sharp melting point but decomposed at  $245-48^\circ$ . It is fairly soluble in water but sparingly in alcohol [Found: C, 51.64; Cl, 11.80; N, 14.02; O, 15.87. Req'd: C, 51.74; Cl, 11.77; N, 13.93; O, 15.92%].

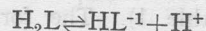
The molecular weight of the compound was found to be 300 which is very near to the theoretical value (301.5).

*pH-Titration procedure*—The following solutions (total volume 50 ml) were prepared and titrated against carbonate-free 0.1M NaOH (i) 1.0 ml of 0.1M perchloric acid+5.0 ml of 1M sodium perchlorate. (ii) 1.0 ml of 0.1M perchloric acid+5.0 ml of 1.0M sodium perchlorate+5.0 ml of 0.02M ligand solution. (iii) 1.0 ml of 0.1M perchloric acid+5.0 ml of 1.0M perchlorate+5.0 ml of 0.02M ligand solution+2.0 ml of 0.01M metal solution.

The metal and the ligand were taken in the ratio 1:5. The metal-ligand titration curves for the three metal ions under study are similar.

The acid dissociation constant of GTRP was calculated to be  $pK_1=6.1$  and  $pK_2=8.05$  by Irving and Rossotti method<sup>3</sup>. Formation curves for the metal-ligand systems (Fig. 1) were drawn between  $\bar{n}$  and  $pA$  where  $\bar{n}$  is the average number of ligands associated with each metal ion and  $pA$  is the free ligand exponent. The values of these terms were obtained from Bjerrum's method<sup>4</sup> as modified by Calvin and Wilson<sup>5</sup>.

In the complex formation there was no liberation of second proton and so the second phenolic proton has not taken part in complexation. Thus, GTRP acts as a biprotic bidentate ligand and neutralizes one equivalent of base to yield one buffer region in the potentiometric equilibrium curve.



Complex formation was evident from the drop in pH when metal solutions were added to ligand solution.

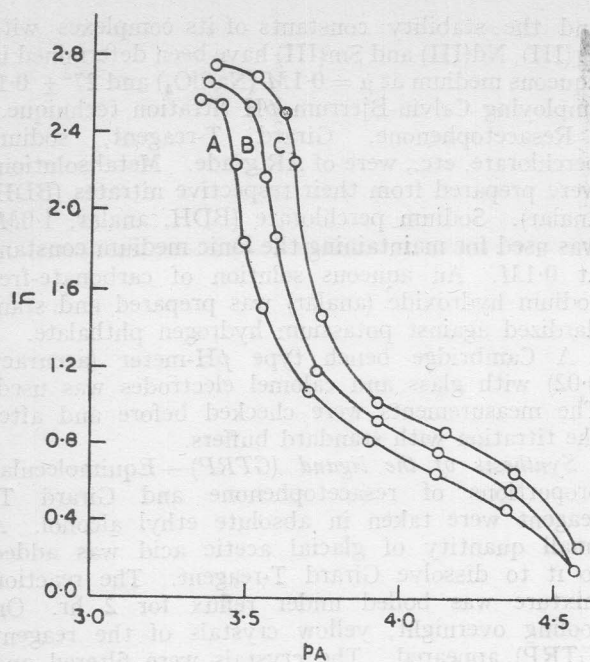


Fig. 1 — Formation curves of metal-GTRP systems [Curve A, Pr(III)-GTRP system; curve B, Nd(III)-GTRP system; and curve C, Sm(III)-GTRP system]

TABLE 1 — VALUES OF STEPWISE STABILITY CONSTANTS OF METAL CHELATES

log $K_1$	log $K_2$	log $K_3$	log $\beta_3$	$-\Delta F$ (kcal)
Pr(III)				
(a) 4.33	3.55	3.43	11.31	15.53
(b) 4.31	3.51	3.45	11.27	
4.32	3.53	3.44	11.29	
( $\pm 0.01$ )	( $\pm 0.02$ )	( $\pm 0.01$ )	( $\pm 0.02$ )	
Nd(III)				
(a) 4.41	3.65	3.54	11.60	15.94
(b) 4.38	3.63	3.52	11.53	
4.40	3.64	3.53	11.57	
( $\pm 0.01$ )	( $\pm 0.01$ )	( $\pm 0.01$ )	( $\pm 0.03$ )	
Sm(III)				
(a) 4.45	3.74	3.63	11.82	16.24
(b) 4.46	3.72	3.61	11.79	
4.46	3.73	3.62	11.81	
	( $\pm 0.01$ )	( $\pm 0.01$ )	( $\pm 0.01$ )	

(a) Extension of Bjerrum's method.  
(b) Graphical method.

Sm(III) forms stronger complexes than Nd(III) and Pr(III). This has been confirmed by the formation curves (Fig. 1). The  $\bar{n}$  values go beyond 2.50 thereby indicating metal:ligand ratio 1:3. The chelate stability constants have been calculated at  $pH < 6.0$  as the complexation was complete by that  $pH$  (Table 1). The formation constants increase regularly with decrease in ionic radius. This is in accordance with lanthanide contraction order. In general  $\log K_1 > \log K_2 > \log K_3$  for a

given metal. The values of overall change in free energies ( $\Delta F = -RT \ln K$ ) are also calculated at  $27^\circ \pm 0.1^\circ$ .

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#### Biamperometric Determination of Au(III) & of Au(III) & U(VI) in Their Binary Mixtures

P. N. PANDEY, M. M. SINGH\* & Y. D. UPADHYA

Chemical Engineering Department, Institute of Technology  
Banaras Hindu University, Varanasi 221005

Received 30 January 1975; accepted 13 June 1975

The differences in formal redox potentials of the couples  $Au^{3+}/Au^0$  and  $U^{6+}/U^{4+}$  enable the reducing agent sodium dithionite to react with Au(III) first, leaving U(VI) unaffected. After the completion of the reaction with Au(III), U(VI) is titrated with dithionite. The results obtained are good and the reaction is stoichiometric. The method is quick, simple, sensitive and precise.

VARIOUS methods<sup>1-6</sup> are available for the quantitative determination of Au(III). Sodium dithionite is a strong reducing agent and has been used for the estimation of various metal ions<sup>7</sup>. Uranium(VI) has been estimated amperometrically using sodium dithionite<sup>8</sup> as a reductant at an applied potential of 250 mV. In this note a simple biamperometric method is described for determining Au(III) in its pure salts and also for determining Au(III) and U(VI) in their binary mixture employing sodium dithionite as a reductant.

Sodium dithionite solution was prepared and standardized against ceric sulphate as described previously<sup>7</sup>. Au(III) chloride solutions were prepared and standardized as usual. Amperometric titrations were carried out using a modified circuit similar to those used by Foulk and Bawden<sup>9</sup> and Stone and Scholten<sup>10</sup>. Equivalence points were obtained graphically.

*Determination of Au(III)* — The normal redox potential of the system  $Au^{3+}/Au^0$  ( $E_0 = 1.42$  V) depends only to a very small extent on acidity of the medium, therefore, for the quantitative determination of Au(III) by dithionite the medium was 0.1N sulphuric acid. Sodium dithionite reacted with Au(III) which formed a reversible couple with Au(0). The limiting current for the Au(III)/Au(I) system first increased, reached a maximum and then decreased to a minimum constant value corresponding to the complete reduction of Au(III) to Au(0). End points were reproducible and the results were quantitative.

\*Applied Chemistry Section, Institute of Technology, Banaras Hindu University.