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Spectrophotometric Study of Ti(IV)-Gallic Acid/Sulphosalicylic Acid Systems in Presence of Lactic Acid, Glycerol & Glycol

P MURUGAIYAN, C K PILLAI & Ch VENKATESWARLU*
Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085

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A comparison of the influence of lactic acid, glycerol and glycol on Ti(IV)-gallic acid, sulphosalicylic acid systems at different acidities indicates that the first forms mixed complexes, while the other two do not.

It is reported that dicarboxylic acids like oxalic[1,2] and hydroxy acids like tartaric[1,2] form mixed complexes with Ti(IV) and gallic acid (GA)/sulphosalicylic acid (SSA) over a wide *p*H range, while simple alcohols like methanol[3] do not. This note describes similar studies with lactic acid (LA) and two polyalcohols, viz. glycol (GC) and glycerol (GR).

Hyperchromic effect was observed on the addition of the three reagents (around 1.0 *M*) to Ti-GA and Ti-SSA mixtures (Ti $= 5.0 \times 10^{-3}$ *M*, GA $= 2.0 \times 10^{-2}$ *M* and SSA $= 0.5$ *M*) at 1.87 *N* acidity as shown by the data in Fig. 1 (corrected for binary systems). Application of Job's method by varying Ti and GA/SSA continuously in the presence of constant excess of the reagents indicated a 1:1 composition with respect to the variants (Table 1). Similar application of modified Job's method[4] wherein the concentration of lactic acid was kept as a constant multiple of C_{Ti} indicated a 1:1:1 composition in these systems (Table 1). Bent and French method varying one[5], two[6] and three components[6] at a time gave slopes, indicating the same 1:1:1 species formation (Table 2).

Since formation of a probable 1:2 complex in Ti-SSA system at 1.87 *N* is reported[1] at high concentration of SSA, the effect of varying SSA concentration on Ti-LA/GC/GR mixtures was studied (Fig. 1). Data without any auxiliary ligand are reproduced for comparison (curve 1). From the absence of a second step in the curve in the presence of LA (curve 4), it is postulated that only LA forms a mixed ligand complex of 1:1:1 composition at this acidity and hinders the 1:2:1 formation, while the polyalcohols influence only the solvation of the

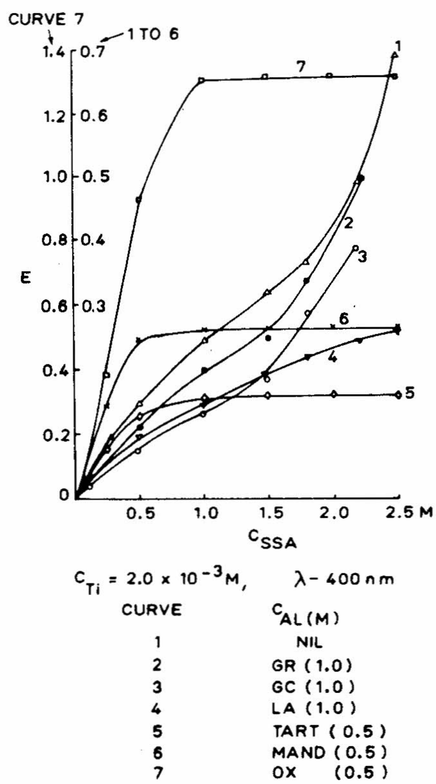

Fig. 1—Effect of SSA on Ti-LA/GR/GC/tart/mandelic/oxalic mixtures at 1.87 acidity

Table 1—Results of Continuous Variation Method in Equimolar Solutions*

Acidity/*p*H	$C_{Ti} + C_{GA}/C_{SSA}$ $\times 10^3$ *M*	C^*_{LA} *M*	X_{max}
	Ti-GA-LA		
1.87*N*	40	Nil	0.50
1.87*N*	40	0.40	0.50
1.87*N*	40	$10 \times C_{Ti}$	0.35(6)
	Ti-SSA-LA		
1.87*N*	40	Nil	0.50
1.87*N*	40	0.96	0.50
1.87*N*	40	$10 \times C_{Ti}$	0.33(6)
	Ti-GA-LA		
4.0	4.0	Nil	0.80
4.0	4.0	0.15	0.50
4.0	4.0	0.20	0.50
5.5	0.25	Nil	0.75
5.5	0.25	0.10	0.50
5.5	0.25	0.15	0.50
	Ti-SSA-LA		
5.0	4.0	Nil	0.66
5.0	4.0	0.08	0.50
5.0	4.0	0.15	0.50

* Though the hyperchromic effect is observed in presence of GR and GC also 1.87 *N* acidity, these data are not given, as it has been shown that these do not form the mixed ligand complexes.

Table 2—Bent and French Method at $1.87\,N$ Acidity: Variation of One, Two and Three Reactions at a Time

Sl. No.	$C_{Ti} \times 10^3 M$	$C_{GA}/C_{SSA} \times 10^2 M$	$C^*_{LA} \times 10M$	Slope
		Ti-GA-LA System		
1	5.0	2.5	2.0-10.0	1.1
2	5.0	2.0-6.0	$C_{GA} \times 10$	1.7
3	2.5-5.0	$C_{Ti} \times 100$	$C_{GA} \times 10$	2.7
		Ti-SSA-LA System		
4	5.0	5.0	5.0-14.0	1.2
5	5.0	2.0-5.0	$C_{SSA} \times 2$	1.8
6	2.0-10.0	$C_{Ti} \times 50$	$C_{Ti} \times 100$	2.9

* Though the hyperchromic effect is observed in presence of GR and GC also at $1.87N$ acidity, these data are not given, as it has been shown that these do not form mixed ligand complexes.

respective binary complexes. The stabilisation of the 1:1:1 complex is more pronounced in the presence of oxalate, tartrate and mandelate (curves 5-7).

When varying amounts of LA/GC/GR were added to Ti-GA/SSA mixtures at pH 4.0 (1:2 complex expected) and 5.5 (1:3 expected) with GA and at pH 5.0 (1:2 expected) with SSA, E-values of ternary mixtures decreased with increase in C_{LA}, while there was no significant change in the case of GC and GR (upto 1.0 M). This supports the earlier view that only LA is able to dissociate higher complexes with main ligands to form mixed complexes. The composition of the mixed complexes with respect to Ti and GA/SSA was studied by continuous variation method in equimolar solutions in the presence of constant concentration (which is varied in different sets) of LA. The X_{max} values shifted to 0.5 and remained constant with increase in C_{LA} (Table 1), revealing the composition to be 1:1. The composition with respect to LA could not be determined in the present conditions.

From these studies, it can be concluded that hydroxy acids and dicarboxylic acids form mixed complexes in these systems, while polyalcohols do not, and behave like simple alcohols as shown by Shnaiderman and Chernaya[3].

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