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Research Paper

Titanium carboxylate complexes stability constants estimated by four graphical methods

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Abstract

This investigation represents a comparative study of four graphical methods for overall stability constant estimation techniques, included point wise calculation method, half integral method, linear plot method and least squares method, in purpose to select the most sensitive and accurate method, the paper aiming also to determine the parameters that affect the precision of these methods under investigation.

Metal-ligand stability constant and stoichiometries of above systems are to be determined by Calvin and Bjerrum pH-metric titration technique as adopted by Irving and Rossotti. For this purpose titanium has been chosen as a central metal ion. Titanium element from first transition series of d-block and has four valence bond electrons 3d24s2.

Acetic acid, oxalic acid and oxalacetic acid have been selected as ligands. The obtained results seem in a good agreement with each other, with some restriction on least squares method for accumulation of error in Kn-1. These suggestions have been introduced in conclusion for treatment of data by least squares method and Henderson's Hasselbalch's equation and other modifications have been done.

Keywords: *Oxalacetic Acid, Titanium Caboxylates, Graphical Methods, Mat-Lab Program.*

1. Introduction

Many method of great diversity are now being used for determination of step-wise stability constants. However the most widely used and the most accurate and reliable method for determination of stability constant are based on potentiometric measurement of hydrogen ion concentration. The magnitude of the observed pH change may be employed to determine the stability constant of the metal complex by Bjerrum's is used by Calvin and Wilson’s method [1]. Some of these methods used to calculate the stability constants, have been reviewed recently by Sullivan and Hindman [2]. Fundamental assumption that the complex formation is stepwise process, if this true then the ratios of various stability constants could in theory is predicted by statistical considerations [3].

The study of metal-ligand complexes in a solution would be of interest which throw a light on the mode of storage and transport of metal ion in biological kingdom with a view to understand the bio-inorganic chemistry of the metal ions [4]. The proton-ligand and metal-ligand stability constants are strongly affected by ionic strength of the medium [5]. Dissociation of organic acid and their interactions with metal ions (complex formation) may be extremely sensitive to ionic strength of the medium. If charges in the reacting species are opposite then there is a decrease in the reaction rate with increasing ionic strength, whereas if the charges are identical, an increase in the reaction rate will occur, and if one of the reactants is charge less the reaction rate will not be affected by ionic strength of the medium. This could be related to the concentration of electrolytes and indicates how effective the charge on a particular ion is shielded or stabilized by other ions in an electrolyte [6].

2. Material and methods

2.1. Preparation of stock solution

All materials used in this investigation were chemically pure brand and hence were used without further purification. The solutions used throughout the experiments were prepared in doubly distilled water.

All measurements were carried out with pH-meter Denver instrument ultra-basic pH/mV meter with combine electrode at 29 ± 1^0C, the sensitivity of the pH-meter is 0.01 units, the instrument could read pH in range 0.00 to 14.00 in step 0.01. The pH-meter was switched on before half an hour for warm up before starting titration. The instrument was calibrated before each set of titration using two buffer solutions of pH 4 and 10. The electrode was washed with distilled water and dried with tissue paper. The readings were recorded only when the instrument registered a steady value for at least one minute.

2.2. Procedure

Three set of solutions total volume of each (V) 200cm^3 were prepared for titration against free carbonate sodium hydroxide solution. The change in pH of solution with each addition of alkali was recorded for each of the following mixtures to calculate values of formation functions n_A, n^-, pL (where n_A average number of proton associated with ligand, n^- the average number of ligand attached to metal ion and pL is the free ligand exponential function) [1].

A/ Free acid. (A)
C/ Free acid + ligand. (A+L)
D/ Free acid + ligand + metal ion. (A+L+M)

All solutions were completed with double distilled water to 200cm^3, after adding 1cm^3 of potassium nitrate solution to maintain ionic strength constant, the titrations were carried out in 250cm^3 beaker with magnet bar inside for stirring the solution.

On plotting the observed pH against the volume of alkali added, different trends have got, Acid curve (A), a ligand curve (A+L) lies below the acid curve indicating the dissociation of ligand in the reaction medium, and metal complex curve (A+L+M) lies below the ligand titration curve indicating the complex formation.

A matlab program have been created for plotting the graph for volume of alkali solution versus pH of each three set of solutions (acid, acid+ligand and acid+ligand+metal ion) and secondly to find the volume of alkali required for bring each of three set of solutions to the same pH. Calvin and Wilson have demonstrated pH measurement made during titration with alkali solution of ligand in presence and absence of metal ion could be employed to calculate the formation functions n_A, n^- and pL .

The values of formation functions were calculated by excel program on personal computer according to the expressions 1, 2 and 3 [7].

$$\bar{n}_A = y - \frac{(V_1 - V_2)(N^0 + E^0)}{(V^0 + V_1)T^0_{CL}} \tag{1}$$

Where y= the number of dissociable protons, N^0 is the concentration of the alkali, E^0 is the concentration of the free acid, T^0_{CL} is the total ligand concentration, V^0 is the total volume of titration solution,$V_1$and V_2 the volume of alkali add to acid and acid + ligand respectively bring each of them to same pH value.

The average number of the ligand to metal or metal-ligand formation number at various pH values determined according to Irving and Rossotti by the following equation:

$$\bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T^0_{cm}} \tag{2}$$

Where V_2 and V_3 the volume of alkali required to mixture of (acid + ligand) and (acid+ligand +metal) to bring them to same pH value, T_{cm} is the total concentration of the metal and other significances as in equation (1).

A free ligand exponent function (PL) was calculated using equation (3) [8].

$$PL = \log_{10}\{\frac{1 + \beta^H_n \frac{1}{[anti\ \log \mathrm{pH}]^n}}{\mathrm{T}^0_{\mathrm{CL}} - \bar{n}T^0_{cm}} \mathrm{X} \frac{(V^0 + V_3)}{V^0}\} \tag{3}$$

Where V_3 = volume of alkali required to bring the solution of the complex to same pH in titration curve.

3. Result and discussion

3.1 proton-ligand stability constant

3.1.1. Poinwise calculation method

The calculation of free ligand exponent function (pL) of metal complexes requires a prior knowledge of the practical proton-ligand stability constant [9] (equation 3). Using excel program on personal computer the values of n_A at various pH reading (B) were calculated from the acid and ligand titration curve. For acetic acid the ligand titration curve is well separated from the free acid titration curve at pH 2.5 ,oxalic acid at pH 2.3 and oxalacetic acid at pH=2.3 indicating the dissociation of the ligand in the titration medium [10].

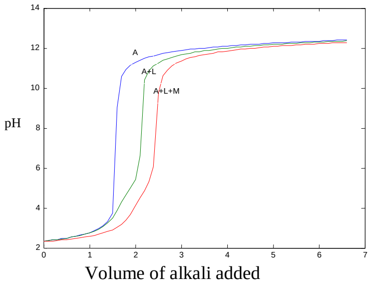

Fig. 1: Formation Curves of Three Set of Solutions. A-Free Acid (Hno3), L-Ligand (Acetic Acid), M-Metal Ion (Titanium Chloride)

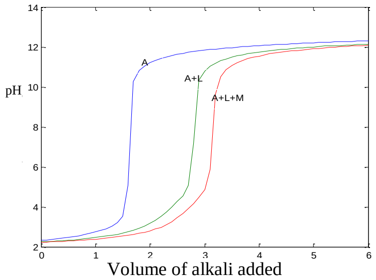

Fig. 2: Titration Curves of Three Set of Solutions. A-Free Acid (Hno3), L-Ligand (Oxalic Acid), M-Metal Ion (Titanium Chloride) (Titanium Chloride).

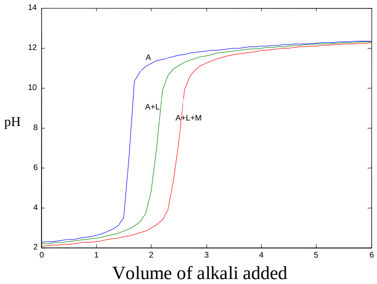

Fig. 3: Titration Curves of Three Set of Solutions. A-Free Acid(Hno3), L-Ligand (Oxalacetic Acid), M-Metal Ion (Titanium Chloride)

The formation number for the ligands extends $0<n_A<1$, $0<n_A<1.6$ and between 1.4267 and 0.6656 in n_A scale for acetic, oxalic and oxalacetic acid respectively. According to point-wise calculation method the dissociation constants were calculated for acetic acid, oxalic acid and oxalacetic acid on tables below. The values of pK_{a1} and pKa_2 were taken as an average on range of 0.2 to 0.8 and 1.2 to 1.8 on n_A scale respectively [11].

Table 1: Proton-Ligand Stability Constant (Pk_a) of Acetic Acid. Average Pk_a=4.669

B	V1	V2	n_A	$\log\left(\frac{n_A}{(1-n_A)}\right)$	pKa
3.6	1.4674	1.5308	0.8894	0.9055	4.5055
3.7	1.4907	1.5564	0.8854	0.8881	4.5881
3.8	1.5011	1.5821	0.8588	0.7839	4.5839
3.9	1.5030	1.6071	0.8185	0.6541	4.5541
4.0	1.5049	1.6310	0.7801	0.5500	4.5500
4.1	1.5068	1.6548	0.7420	0.4587	4.5587
4.2	1.5087	1.6786	0.7038	0.3758	4.5758
4.3	1.5106	1.7028	0.6649	0.2976	4.5976
4.4	1.5125	1.7306	0.6197	0.2121	4.6121
4.5	1.5143	1.7583	0.5746	0.1306	4.6306
4.6	1.5162	1.7861	0.5294	0.0512	4.6512
4.7	1.5181	1.8143	0.4836	-0.0285	4.6715
4.8	1.5200	1.8429	0.4371	-0.1099	4.6901
4.9	1.5219	1.8714	0.3907	-0.1930	4.7070
5.0	1.5238	1.9000	0.3441	-0.2801	4.7199
5.1	1.5257	1.9233	0.3068	-0.3539	4.7461
5.2	1.5275	1.9465	0.2695	-0.4330	4.7670
5.3	1.5294	1.9698	0.2322	-0.5193	4.7807

Table 2: Determination of Log Pka1 of Oxalic Acid (Average Logka1=1.4645)

pH	n_A	$logKa_1$
2.1	1.9735	0.5342
2.2	1.9473	0.9457
2.3	1.1958	2.9135
2.4	1.1884	3.0343
2.5	1.1675	3.1964
2.6	1.1552	3.3360
2.7	1.1362	3.5022
2.8	1.1206	3.6627
2.9	1.1011	3.8488
3	1.0869	4.0214
3.1	1.0654	4.2548
3.2	1.0445	4.5315
3.3	1.0157	5.0970
-	-	-

Table 3: Determination of Log Pk$_{a2}$ of Oxalic Acid (Average Pka$_2$=4.5869)

pH	n_A	logKa$_2$
3.7	0.8638	4.5022
3.8	0.8169	4.4494
3.9	0.7653	4.4134
4.0	0.7178	4.4056
4.1	0.6605	4.3890
4.2	0.6136	4.4008
4.3	0.5676	4.4182
4.4	0.5295	4.4514
4.5	0.4886	4.4801
4.6	0.4500	4.5129
4.7	0.4159	4.5525
4.8	0.3876	4.6014
4.9	0.3631	4.6560
5.0	0.3421	4.7159
5.1	0.3221	4.7768
5.2	0.3114	4.8553
5.3	0.3006	4.9333
5.4	0.2899	5.0108

Table 4: Determination of Log Pka$_1$ of Oxalacetic Acid (Average Pka$_2$= 2.8967)

B	V1	V2	n_A	$\log\left(\frac{n_A}{(1-n_A)}\right)$	pK$_{a2}$
2.4	0.3000	0.625	1.4267	-0.1283	2.2717
2.5	0.5750	0.875	1.4715	-0.0495	2.4505
2.6	0.7667	1.0667	1.4720	-0.0487	2.5514
2.7	0.9286	1.2167	1.4934	-0.0115	2.6885
2.8	1.0556	1.3556	1.4728	-0.0473	2.7527
2.9	1.1500	1.4900	1.4028	-0.1711	2.7289
3.0	1.2267	1.5500	1.4323	-0.1183	2.8817
3.1	1.2933	1.6267	1.4148	-0.1495	2.9504
3.2	1.3321	1.6933	1.3661	-0.2384	2.9616
3.3	1.3679	1.7391	1.3487	-0.2714	3.0286
3.4	1.4013	1.7826	1.3311	-0.3055	3.0945
3.5	1.4143	1.8177	1.2923	-0.3840	3.1160
3.6	1.4273	1.8471	1.2636	-0.4462	3.1539
3.7	1.4403	1.8765	1.2349	-0.5129	3.1871
3.8	1.4532	1.9035	1.2102	-0.5748	3.2251
3.9	1.4662	1.9211	1.2022	-0.5961	3.3039

Table 5: Determination of Log Pka$_2$ of Oxalacetic Acid (Average Pka$_1$=10.6056)

B	V1	V2	n_A	$\log\left(\frac{(n_A-1)}{(2-n_A)}\right)$	pK$_{a1}$
8	1.5658	2.2401	0.8180	0.6527	8.6527
8.3	1.5709	2.2511	0.8077	0.6232	8.9232
8.6	1.576	2.262	0.7975	0.5954	9.1954
8.9	1.5812	2.273	0.7874	0.5686	9.4686
9.2	1.5863	2.2839	0.7773	0.5428	9.7428
9.5	1.5914	2.2949	0.7670	0.5173	10.017
9.8	1.5966	2.3191	0.7340	0.4401	10.240
10.1	1.6137	2.3548	0.7012	0.3705	10.470
10.4	1.6548	2.3905	0.7109	0.3908	10.791
10.7	1.6959	2.4595	0.6623	0.2926	10.993
11.0	1.79	2.5653	0.6425	0.2545	11.255
11.3	1.9751	2.7501	0.6442	0.2579	11.558
11.6	2.3335	3.1144	0.6363	0.2430	11.843
11.9	3.0337	3.8005	0.6656	0.2989	12.199

3.2. Metal ligand stability constant: (Ti-acetate, Ti-oxalate and Ti-oxalacete)

3.2.1. Poinwise calculation method

Metal titration curve showed a displacement with respect to the ligand titration curve along the volume axis for acetic acid at pH 2.4, oxalic acid at pH 2.4, and oxalacetic acid at pH 2.3, figure (1), figure (2) and figure (3) indicating the affinity of ligand with metal ions which release a protons and produced the volume difference (V_3-V_2) [12], which utilized to calculate the values n^- and pL and further to evaluate the metal-ligand stability constants. Calculation of n^-'s values, showed that titanium-acetic acid system forms two complexes ML_2 and ML_3.

Table 6: Point Wise Calculation Method Logk (Average Logk$_2$=5.4153 (Titanium Acetate)

B	V2	V3	n^{-}	pL	Log K_2
2.5	0.5250	0.8000	1.4582	5.4532	5.3805
2.6	0.7600	1.0400	1.5421	5.3786	5.4518
2.7	0.9286	1.2286	1.6193	5.3032	5.5145
2.8	1.0625	1.3714	1.6933	5.2283	5.5825
2.9	1.1700	1.4889	1.7455	5.1473	5.6141
3.0	1.2539	1.5818	1.8029	5.0691	5.6790
3.1	1.3235	1.6533	1.8227	4.9781	5.6446
3.2	1.3824	1.7150	1.8623	4.8951	5.6919
3.3	1.4280	1.7650	1.8711	4.8012	5.6310

Table 7: Pointwise Calculation Method Log Average Logk$_3$= 4.2640 (Titanium Acetate)

B	V2	V3	n^{-}	pL	K_3
3.6	1.5308	1.8742	2.0192	4.5745	2.8667
3.7	1.5564	1.9047	2.0570	4.4978	3.2793
3.8	1.5821	1.9279	2.1054	4.4283	3.4995
3.9	1.6071	1.9512	2.1979	4.3851	3.7772
4.0	1.6310	1.9744	2.3010	4.3564	3.9904
4.1	1.6548	1.9977	2.4156	4.3483	4.2002
4.2	1.6786	2.0225	2.5537	4.3826	4.4763
4.3	1.7028	2.0475	2.7090	4.4889	4.8758
4.4	1.7306	2.0725	2.8824	4.8070	5.6823

Titanium-oxalic acid system forms two chelates ML_2 and ML_3.

Table 8: Logk$_2$ by Point Wise Method (Average Logk$_2$=5.081; Ti-Oxalate)

B	V2	V3	n^{-}	pL	Log K_2
2.5	1.1000	1.4000	1.5170	4.9825	5.0120
2.6	1.3400	1.6500	1.5909	4.9024	5.0620
2.7	1.5167	1.8500	1.7489	4.8530	5.3277
2.8	1.6625	2.0000	1.7778	4.7632	5.3072
2.9	1.7778	2.1200	1.8361	4.6856	5.3933

Table 9: Determination of Logk$_3$ by Point-Wise Method (Average Logk$_3$=4.1907; Ti-Oxalate)

B	V2	V3	n^{-}	pL	logK_3
3.3	2.0875	2.4211	2.0570	4.3957	3.1772
3.4	2.1400	2.4737	2.1460	4.3478	3.5807
3.5	2.1900	2.5227	2.2236	4.3006	3.7601
3.6	2.2348	2.5682	2.3911	4.3202	4.1281
3.7	2.2783	2.6125	2.6296	4.4535	4.6840
3.8	2.3200	2.6542	2.8983	4.9357	5.8816

Titanium-oxalacetic acid system forms only one chelate ML_2.

Table 10: Logk$_2$ of Titanium Oxalacelate by Point Wise Method. Average Logk$_2$=8.6384

B	V2	V3	n^{-}	pL	Log K_2
2.7	1.3714	1.7445	1.2653	11.1601	10.7178
2.9	1.575	1.9500	1.3132	10.8617	10.5207
3.1	1.7091	2.0824	1.3438	10.5817	10.3010
3.3	1.800	2.1708	1.3937	10.3286	10.1411
3.5	1.8513	2.2250	1.4059	10.0841	9.91856
3.7	1.9009	2.2635	1.4418	9.86084	9.75929
3.9	1.9191	2.3007	1.5409	9.66712	9.73838
4.1	1.9373	2.3152	1.5503	9.45522	9.54288
4.3	1.9555	2.3297	1.5600	9.24861	9.35326
4.5	1.9736	2.3442	1.5701	9.04559	9.16824
4.7	1.9918	2.3587	1.5805	8.84485	8.98585
4.9	2.0052	2.3732	1.6010	8.64871	8.82653
5.1	2.0147	2.3877	1.6297	8.45618	8.68677
5.3	2.0242	2.4016	1.6558	8.26357	8.54358
5.5	2.0337	2.4120	1.6670	8.06659	8.36824
5.7	2.0431	2.4225	1.6789	7.87011	8.19525
5.9	2.0526	2.4330	1.6907	7.67379	8.02268
6.1	2.0621	2.4435	1.7026	7.47763	7.85100
6.3	2.0716	2.4539	1.7142	7.28145	7.67915
6.5	2.081	2.4644	1.7265	7.08561	7.50986
6.7	2.0905	2.4749	1.7408	6.89054	7.34666
6.9	2.100	2.4853	1.7559	6.69584	7.18684
7.1	2.1067	2.4958	1.7767	6.50323	7.04456
7.3	2.1135	2.5044	1.7889	6.30773	6.88027
7.6	2.1236	2.5154	1.7987	6.01161	6.61002

What should be mentioned, during titration course of oxalacetic acid a precipitation occurred at low values of pH, and then disappear at high values of pH which indicates Henderson's or Hasselbalch's equation will be eligible for determination of stability constant of this chelate. [3]

Every two consecutive complex species having appreciable difference (≥1.8) i.e. $\log K_2$ and $\log K_3$ values, this difference indicate chelates or complexes were occurred in stepwise process, and not simultaneously.[13] that is not the case in this investigation. Titanium-oxalacetic acid system forms one chelate ML_2 if it compared with titanium oxalic acid which formed two chelates ML_2 and ML_3, one can say this may refer to the longer chain of oxalacetic acid relative to oxalic acid chain, that might leave no room for complex ML_2 (titanium oxalacetate) to accommodate extra ligand. These values obtained by this method were further verified by half integral method.

3.2.2. Half integral method: (Ti-acetates, Ti-oxalates and Ti-oxalacetate)

For estimation of metal-ligand stability constants, a formation curve was constructed by plotting n^- against pL. The values of pL at which $n^- = 1.5$ and $n^- = 2.5$ corresponds to values of $\log K_2$ and $\log K_3$ respectively. [11]

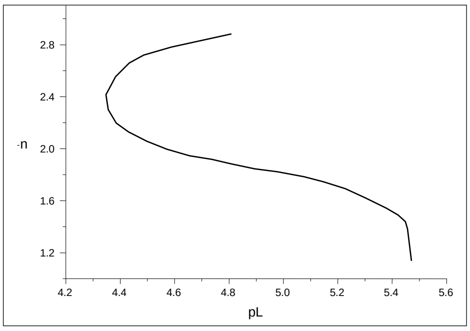

Fig. 4: Metal-Ligand Formation Curve (Titanium Acetate). Logk2=5.412, Logk3=4.352 –Half Integral Method

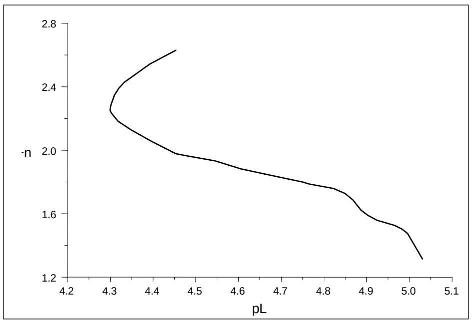

Fig. 5: Metal-Ligand Formation Curve (Titanium Oxalate). Logk2= 4.986 and Logk3= 4.376 -Half Integral Method.

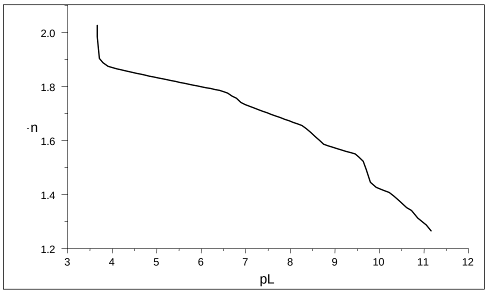

Fig. 6: Metal-Ligand Formation Curve (Titanium Oxalacetate). Logk2 =9.76 Half Integral Method

The values were in a good agreement with those obtained by point-wise method. These values were further verified by linear plot method.

3.2.3. Linear plot method: (Ti-acetates, Ti-oxalates and Ti-oxalacetate)

In this method $\log (n^- -1)/(2-n^-)$, $\log (n^- -2)/(3-n^-)$, etc. were plotted versus corresponding pL for determination of $\log K_2$, $\log K_3$… etc [14]. The values of stability constants obtained for titanium acetate complexes were estimated from figures (7) and (8).

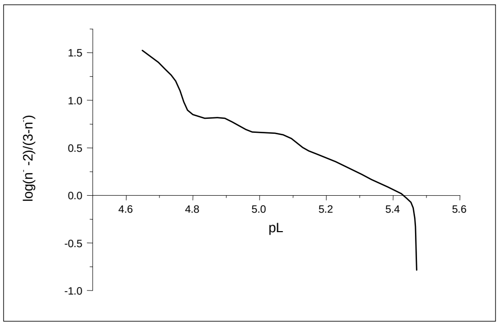

Fig. 7: Linear Plot Method Logk2 =5.427 (Titanium Acetate)

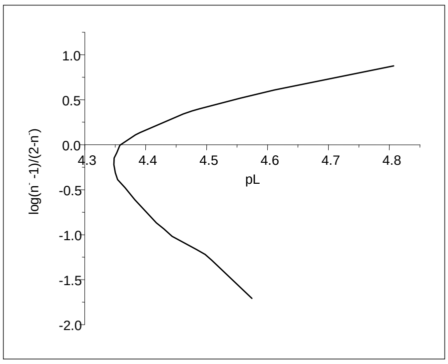

Fig. 8: Linear Plot Method Logk3=4.36 (Titanium Acetate)

The values of $\log K_2$ and $\log K_3$ for titanium oxalate chelates were estimated from figures (9) and (10).

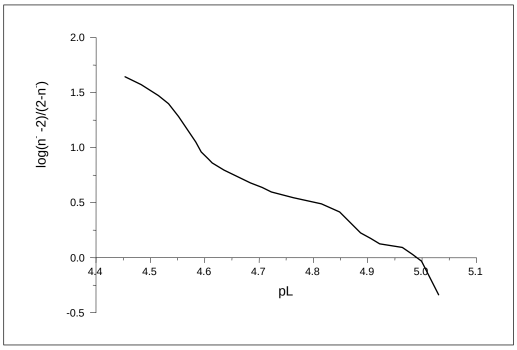

Fig. 9: Linear Plot Method $\mathrm{Logk}_2=4.991$(Titanium Oxalate)

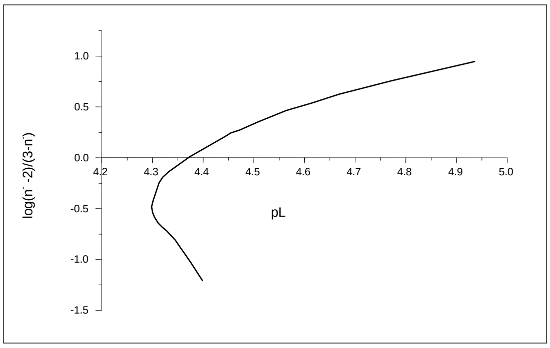

Fig. 10: Linear Plot Method $\mathrm{Logk}_3=4.375$ (Titanium Oxalate)

The stability constant of titanium oxalacetate chelate was found from figure (11).

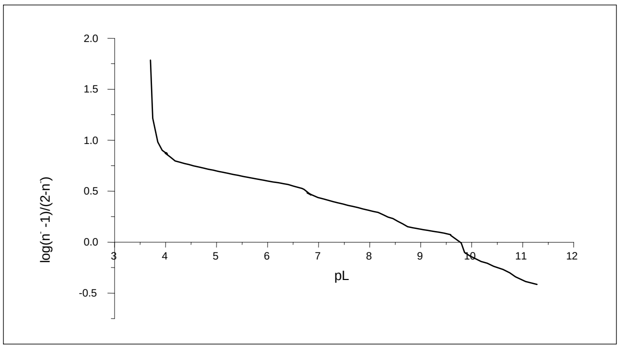

Fig. 11: Linear Plot Method $\mathrm{Logk}_2=9.821$. (Titanium Oxalacetat

The values obtained were in a good concordance with the other values of two previous methods, point wise calculation method and half integral one.

The neutral salt KNO_3 that used to maintain the ionic strength constant has very slight complexing tendency, and the competition between nitrate and the ligands under study are of minor importance [14]. These values were further verified by least squares method but the value of titanium oxalacetate was verified by equation familiar as Henderson's or Hasselbalch's equation.

3.2.4. Least squares method: (Ti-acetate and Ti-oxalate)

For estimation of K_2 and K_3 for titanium acetate and titanium oxalate by this method, linear equation of Rossotti and Rossotti as expressed below with some modification to meet our purpose has been employed:

$$\frac{(\bar{n}-1)}{(2-\bar{n})[L]} = \frac{(3-\bar{n})[L]}{(2-\bar{n})} \times K_2K_3 - K_3 \tag{4}$$

If the values of n^- and [L] were known, plotting of $(n^- -1)/(2-n^-)[L]$ v/s $(3-n^-)[L]/(2-n^-)$, give straight line equation with y-intercept=K_3 and slope = K_2 K_3.

The other form of equation (4) can be obtaining on division by K_2 K_3 and this give nearly the same values x-intercept $=1/K_2$ and slope $1/K_2K_3$ which useful check on the consistency of the data.

$$\frac{(\bar{n}-1)}{(2-\bar{n})[L]} \times \frac{1}{K_2K_3} + \frac{1}{K_2} = \frac{(3-\bar{n})[L]}{(2-\bar{n})} \tag{5}$$

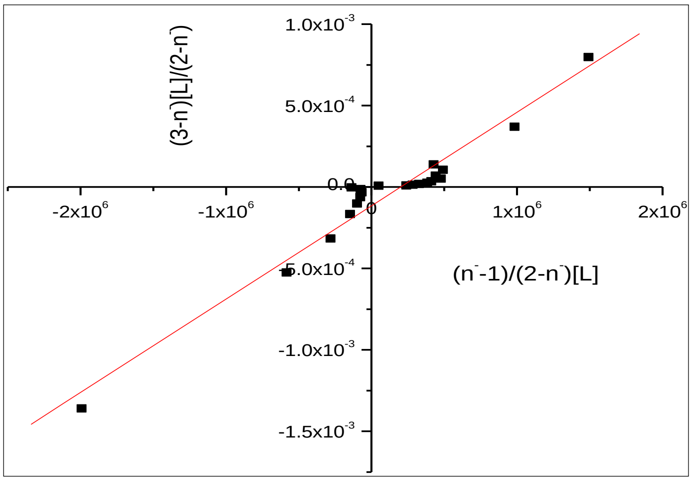

Fig. 12: Least Squares Method Logk$_2$=5.2368 & Logk$_3$=4.3010. (Titanium Acetate)

Linear Regression for: Y = A + B * X

Parameter	Value	Error	R^2
Intercept	-0.0001	0.00002	
Slope	5.7975E-10	2.80147E-11	0.97962

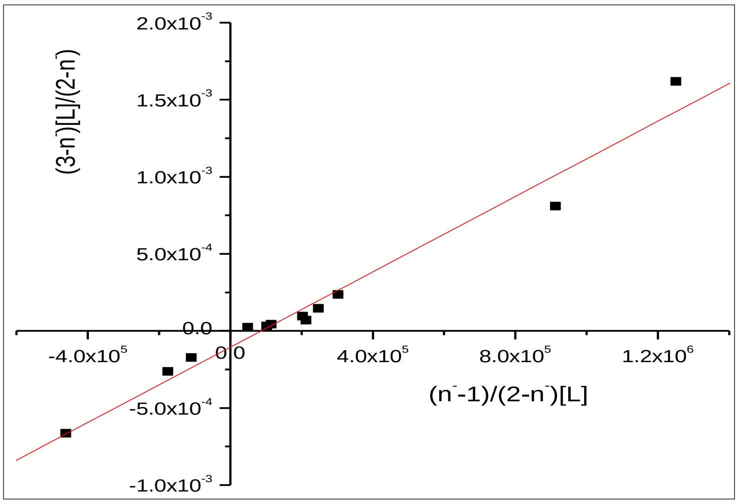

Fig. 13: Least Squares Method, Logk$_2$=4.913 & Logk$_3$ =4.3010. (Titanium Oxalate)

Linear Regression for: Y = A + B * X

Parameter	Value	Error	R^2
Intercept	-0.0001	0.00003	0.9854
Slope	1.22219E-9	6.67725E-11	

Any errors in the values of $\beta_1 \ldots \beta_{t-1}$will accumulate in the value of β_t. (Where t=N-1) [2].

3.2.5. Henderson's or hasselbalch's equation: (Ti-oxalacetate system)

This equation is used when only one complex or chelate is formed.

$$\log\left(\frac{\bar{n}}{(1-\bar{n})}\right)=\log\beta_1+\log[L]$$

The equation is familiar as Henderson's or Hasselbalch's equation, and has been widely used for determination of the dissociation constants of monobasic acids. It is also useful for determining constants from n$^-$ and [L] data over a very limited range e.g. if very strong or very weak complexes are formed, or if precipitation occurs at low value of n$^-$ which is the case in this investigation. [3]

Table 11: Logk$_2$ by Henderson's or Hasselbalch's Equation. Average Logk$_2$= 8.6384 (Titanium Oxalacetate)

n^-	[L]	$\log\left(\frac{(n^{-}-1)}{(2-n_{A})}\right)$	Log([L])	logK$_2$	n^-	[L]	$\log\left(\frac{(n^{-}-1)}{(2-n_{A})}\right)$	Log([L])	logK$_2$
1.2653	6.92E-12	-0.4423	-11.1601	10.7178	1.6439	4.36E-09	0.2573	-8.3602	8.6175
1.2712	9.92E-12	-0.4293	-11.0035	10.5741	1.6558	5.45E-09	0.2800	-8.2636	8.5436
1.3132	1.38E-11	-0.3409	-10.8617	10.5207	1.6616	6.84E-09	0.2912	-8.1651	8.4563
1.3412	1.90E-11	-0.2858	-10.7222	10.4364	1.6670	8.58E-09	0.3017	-8.0666	8.3682
1.3438	2.62E-11	-0.2807	-10.5817	10.3010	1.6733	1.08E-08	0.3140	-7.9684	8.2824
1.3754	3.51E-11	-0.2211	-10.4543	10.2332	1.6789	1.35E-08	0.3251	-7.8701	8.1952
1.3937	4.69E-11	-0.1875	-10.3286	10.1411	1.6850	1.69E-08	0.3374	-7.7720	8.1094
1.4275	6.14E-11	-0.1268	-10.2119	10.0851	1.6907	2.12E-08	0.3489	-7.6738	8.0227
1.4057	8.24E-11	-0.1655	-10.0841	9.9186	1.6964	2.66E-08	0.3605	-7.5756	7.9361
1.4214	1.07E-10	-0.1377	-9.9702	9.8325	1.7026	3.33E-08	0.3734	-7.4776	7.8510
1.4418	1.38E-10	-0.1016	-9.8608	9.7593	1.7083	4.17E-08	0.3854	-7.3795	7.7649
1.4934	1.73E-10	-0.0115	-9.7632	9.7517	1.7142	5.23E-08	0.3977	-7.2815	7.6791
1.5409	2.15E-10	0.0713	-9.6671	9.7384	1.7204	6.55E-08	0.4111	-7.1835	7.5946
1.5459	2.75E-10	0.0799	-9.5605	9.6404	1.7265	8.21E-08	0.4242	-7.0856	7.5099
1.5503	3.51E-10	0.0877	-9.4552	9.5429	1.7327	1.03E-07	0.4378	-6.9877	7.4256
1.5554	4.45E-10	0.0966	-9.3515	9.4481	1.7408	1.29E-07	0.4561	-6.8905	7.3467
1.5600	5.64E-10	0.1046	-9.2486	9.3533	1.7481	1.61E-07	0.4728	-6.7931	7.2659
1.5654	7.13E-10	0.1143	-9.1469	9.2612	1.7559	2.01E-07	0.4910	-6.6958	7.1868
1.5701	9.00E-10	0.1226	-9.0456	9.1682	1.7664	2.51E-07	0.5161	-6.5996	7.1156
1.5754	1.13E-09	0.1319	-8.9450	9.0769	1.7767	3.14E-07	0.5413	-6.5032	7.0446
1.5805	1.43E-09	0.1410	-8.8449	8.9859	1.7857	3.92E-07	0.5641	-6.4065	6.9706
1.5862	1.80E-09	0.1513	-8.7453	8.8966	1.7889	4.92E-07	0.5725	-6.3077	6.8803
1.6010	2.25E-09	0.1778	-8.6487	8.8265	1.7926	6.18E-07	0.5823	-6.2092	6.7914
1.6149	2.80E-09	0.2032	-8.5522	8.7553	1.7954	7.76E-07	0.5897	-6.1103	6.7000
1.6297	3.50E-09	0.2306	-8.4562	8.68687	1.7987	9.74E-07	0.5984	-6.0116	6.6100

The higher the values of stability constants showed that the ligands under investigation are strong chelating agents [15].

4. Conclusion

The four graphical methods give nearly the same values for each titanium caboxylate system. The values of stability constants estimated by point-wise method, half integral method and linear plot method were in a good agreement specially half integral and linear plot method, but the results obtained by least squares method were slightly different specially in K_{n-1}, where the error accumulated, this method has many restriction which can be found in literature. Reader no doubt by now may ask the question "what method can I use, and which should give me the most accurate value". Each of four methods employed above seen satisfactorily to give the answer, with difference ≤ 0.2. For a system where $N \leq 3$, half integral method and linear plot one, give nearly unique answer for K_n values, whereas common fault is that, as n^- increase, K_n becomes more prone to error. Differences in magnitude between K_n values are due solely to errors inherent in the experimental data or non-rigorous data treatment, that is, least squares fit to curves with correlated errors.

In least squares method the slope and intercept obtained by adding trend line and display equation on chart is less accurate than that obtained by LINEST in excel program, or that obtain from origin program (view- result log or fit linear). In each case if the intercept and slope were divided by 2 as this found by extremely trail, the K_n value agreed with other values obtained by different methods and this minimize the error accumulated in K_{n-1}, this which has been done throughout this investigation. In Henderson's equation the stability constant should be taken as an average for values of e.g logK$_2$ in the range 1.2-1.8, in this way the value of stability constant meet values obtained by other methods. For all results $K_2>K_3$ this order implies no specific electronic or steric phenomenon.

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