



Stability constants and stoichiometries of chromium and zirconium carboxylates complexes calculated by four comparative methods

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Abstract

Four comparative methods for determination of stoichiometries and stability constants of chromium and zirconium complexes with citric and propanoic acids were studied, in purpose to select the most accurate and sensitive method, and to compare the formation of complexes of these two transition metals. (Cr 1st transition series group 6B, Zr 2nd transition series group 4B) Metal-ligand stability constants and stoichiometries of the above systems were determined by Calvin & Bjerrum pH-metric titration technique as adopted by Irving & Rossotti.

Four methods employed were point-wise calculation method, half integral method, linear plot method and least squares method. The result seems in a good agreement with each other and any method can represent the other.

Keywords: Half integral method; Henderson equation; Stability constants; Excel program; activity.

1. Introduction

Complexation studies are very important from the point of view of analytical and biochemical researchers, the extent to which the ligand binds to a metal ion is expressed in terms of stability constants (Sanjay et al, 2002). Dissociation of organic acid and their interactions with metal ions (complex formation) may be extremely sensitive to ionic strength of the medium (Santosh et al, 2011). Studies in metal-ligand complexes in a solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would interestingly throw a light on the mode of storage and transport of metal ions in biological kingdom (Summer et al, 2011). If the stability constant of a reaction between metal and ligand has found greater than zero, is perhaps one of the most convincing evidence for the existence of the complex species (Abdulbaset et al. 2012).

The equilibrium constants that refer to the interaction of metal cations and ligands are widely referred to as stability constants. In practice there are two types of stability, mainly thermodynamic and kinetic (Hartley et al. 1980). The main transition metal groups or d-block includes these elements that have partially filled d-shells, thus chromium is half-filled 3d-shells (Cr: [Ar] 4s13d5) and zirconium is partially filled 4d-shells, (Zr: [Kr] 5s2 4d2) (Cotton et al 1972, Boner et al 1996).

Citric acid is weak organic acid with formula C₆H₈O₇ a white crystalline powder with molar mass 192.124. It consists of three carboxylic groups. (http://en.wikipedia.org/wiki/Citric_acid, 2014) Propanoic acid also known as propionic acid from Greek words protos meaning first and pion meaning fat. It is a naturally occurring carboxylic acid with chemical formula CH₃CH₂COOH. It is a clear liquid with pungent odor, molecular formula 74.08, with one carboxylic group. The physical properties is intermediate

those smaller carboxylic acids and the largest fatty acids. (http://en.wikipedia.org/wiki/Propanoic_acid, 2014)

The factors that determine which ligand will coordinate best with a given metal ion are numerous, complicated and not completely understood. (Dodge et al. 1995) The bond between the metal ion and a ligand shows high dependency on the properties of the metal atom. The most important of these properties are the size of metal atom, its ionic charge, atomic number, electronic configuration, electronegativity and ionization potential (William et al. 1985).

Volumetric titrations are usually most conveniently performed with visual indicators. In cases where an indicator is unavailable, potentiometric detection of end point can often be used. Potentiometric titrations are among the most accurate known, because the potential follows actual change in activity and therefore the end point coincides with the equivalent point (Cary D Christian. 1980). Activity means the effective concentration of an ion in the presence of an electrolyte, and it can be used to describe quantitatively the effects of salt on equilibrium constants, and it is also important in potentiometric measurements (Louis Meites. 1981).

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±10°C, the sensitivity of the pH-meter is 0.01 unit, 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 sets of solution total volume of each (V_0) 200cm³ 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) (Gurdeep Raj 1986, p.67)

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 200cm³, after adding 1cm³ of potassium nitrate solution to maintain ionic strength constant, the titrations were carried out in 250cm³ beaker with magnet bar inside for stirring the solution.

On plotting the observed pH against the volume of alkali added, different trends were shown, 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 has been created for plotting the graph for volumes of alkali solution versus pH of each three sets of solution (acid, acid+ligand and acid+ligand+metal ion) and secondly to find the volume of alkali required for bringing each one of three sets 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 (Minaxi et al. 2011).

$$n_A = y - \frac{(V_1 - V_2)(N^0 + E^0)}{(V^0 + V_1)T_{CL}^0} \quad (1)$$

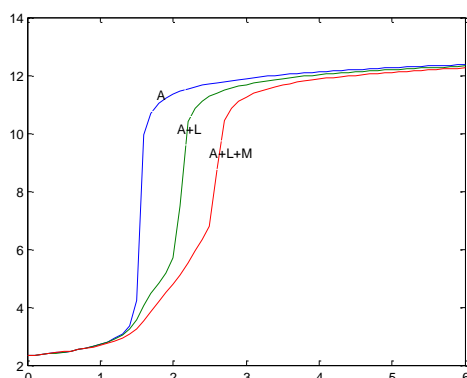


Fig. 1: Titration Curves of Three Sets of Solution. A-Free Acid (HNO₃), L-Ligand (Propanoic Acid) and M-Metal Ion (Zr)

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_{CL}^0 is the total ligand concentration, V_0 is the total volume of titration solution, V_1 and V_2 the volume of alkali added to acid, and acid +ligand respectively to bring each one to the 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:

$$n = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)n_A T_{cm}^0} \quad (2)$$

Where V_2 and V_3 are the volumes of alkali required to mixture of (acid + ligand) and (acid+ligand +metal) to bring them to the 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) (Ashwini et al. 2007)

$$pL = \log_{10} \left\{ \frac{1 + \beta_n^H}{[\text{anti log pH}]^n} \times \frac{(V^0 + V_3)}{V^0} \right\} - \frac{T_{CL}^0 - nT_{cm}^0}{T_{CL}^0 - nT_{cm}^0} \quad (3)$$

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. Point-wise calculation method

The calculation of free ligand exponent function (pL) of metal complexes requires a prior knowledge of the proton-ligand stability constant (Avinash et al. 2013) (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 propanoic acid and citric acid the ligand titration curve is well separated from the free acid titration curve at pH 2.5, indicating the dissociation of the ligand in the titration medium.

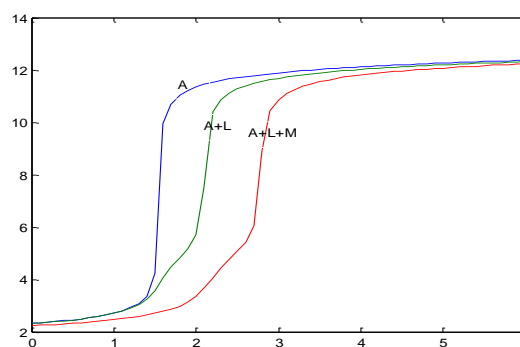


Fig. 2: Titration Curves Of Three Sest Of Solution. A-Free Acid (HNO₃), L-Ligand (Propanoic Acid) And M-Metal Ion (Cr)

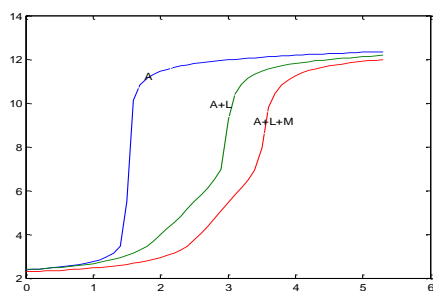


Fig. 3: Titration Curves of Three Sets of Solution. A-Free Acid (HNO₃), L-Ligand (Citric Acid) and M-Metal Ion (Zr).

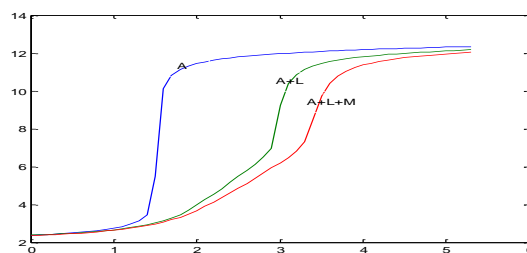


Fig. 4: Titration Curves of Three Sets of Solution. A-Free Acid (HNO₃), L-Ligand (Citric Acid) and M-Metal Ion (Cr)

According to point-wise calculation method the dissociation constants were calculated on tables below. Values of pKa₁, pKa₂ and pKa₃ were taken as an average on range of 0.2 to 0.8, 1.2 to 1.8 and 2.2 to 2.8 on n_A scale respectively (Sayyed et al. 2011).

Table 1: Proton-Ligand Stability Constant of Propionic Acid. Average pka₁ =4.8259

pH(B)	V1	V2	.n _A	$\log\left(\frac{n_A}{1-n_A}\right)$	pKa ₁
2.9	1.1833	1.2000	0.9708	1.5223	4.4223
3.0	1.2500	1.2714	0.9626	1.4111	4.4111
3.1	1.3074	1.3300	0.9606	1.3866	4.4866
3.2	1.3444	1.3800	0.9379	1.1789	4.3789
3.3	1.3815	1.4188	0.9349	1.1574	4.4574
3.4	1.4056	1.4500	0.9225	1.0760	4.4760
3.5	1.4169	1.4813	0.8877	0.8977	4.3977
3.6	1.4281	1.5078	0.8610	0.7919	4.3919
3.7	1.4393	1.5275	0.8462	0.7404	4.4404
3.8	1.4506	1.5471	0.8317	0.6939	4.4939
3.9	1.4618	1.5567	0.8345	0.7026	4.6026
4.0	1.4730	1.5863	0.8024	0.6087	4.6087
4.1	1.4843	1.6071	0.7859	0.5647	4.6647
4.2	1.4955	1.6310	0.7637	0.5096	4.7096
4.3	1.5011	1.6548	0.7320	0.4364	4.7364
4.4	1.5028	1.6786	0.6935	0.3546	4.7546
4.5	1.5046	1.7029	0.6543	0.2770	4.7770
4.6	1.5063	1.7314	0.6075	0.1898	4.7898
4.7	1.5081	1.7600	0.5608	0.1062	4.8062
4.8	1.5098	1.7886	0.5139	0.0242	4.8242
4.9	1.5116	1.8172	0.4672	-0.0571	4.8429
5.0	1.5134	1.8457	0.4206	-0.1390	4.8610
5.1	1.5151	1.8743	0.3737	-0.2242	4.8758
5.2	1.5169	1.9019	0.3288	-0.3100	4.8900
5.4	1.5204	1.9404	0.2678	-0.4369	4.9631
5.5	1.5221	1.9596	0.2373	-0.5071	4.9929

Table 2: First Dissociation Constant of Citric Acid. Average pka₁=3.1459

pH	.n _A	$\log\left(\frac{n_A - 2}{3 - n_A}\right)$	pKa ₁	pH	.n _A	$\log\left(\frac{n_A - 2}{3 - n_A}\right)$	pKa ₁
2.5	2.8833	0.8789	3.3789	3.1	2.5201	0.0349	3.1349
2.6	2.8426	0.7287	3.3287	3.2	2.4525	-0.0828	3.1172
2.7	2.7587	0.4975	3.1975	3.3	2.3850	-0.2034	3.0966
2.8	2.6978	0.3635	3.1635	3.4	2.3429	-0.2825	3.1175
2.9	2.6370	0.2443	3.1443	3.5	2.2838	-0.4021	3.0979
3.0	2.5772	0.1353	3.1353	3.6	2.2164	-0.5587	3.0413

Table 3: Second Dissociation Constant of Citric Acid. Average pka₂=4.8270

pH	.n _A	$\log\left(\frac{n_A - 1}{2 - n_A}\right)$	pKa ₂	pH	.n _A	$\log\left(\frac{n_A - 1}{2 - n_A}\right)$	pKa ₂
4.3	1.8275	0.5389	4.8389	5.1	1.4364	-0.1865	4.9135
4.4	1.7757	0.4191	4.8191	5.2	1.3943	-0.2722	4.9278
4.5	1.7241	0.3105	4.8105	5.3	1.3483	-0.3633	4.9367
4.6	1.6715	0.2086	4.8086	5.4	1.3023	-0.4624	4.9376
4.7	1.6178	0.1120	4.8120	5.5	1.2564	-0.5867	4.9133
4.8	1.5641	0.0330	4.8330	5.6	1.2057	-0.7365	4.8635
4.9	1.5190	-0.0388	4.8612	5.7	1.1550	-0.9340	4.7660
5.0	1.4777	-0.1111	4.8889	5.8	1.1043	-1.2472	4.5528

Table 4: Third Dissociation Constant of Citric Acid. Average pKa3=8.3813

pH	nA	$\log \frac{nA}{(1-nA)}$	pKa3	pH	nA	$\log \frac{nA}{(1-nA)}$	pKa3
6.4	0.8159	0.6465	7.0465	8.3	0.5630	0.1101	8.4101
6.5	0.7714	0.5279	7.0279	8.4	0.5592	0.1034	8.5034
6.6	0.7362	0.4458	7.0458	8.5	0.5556	0.0970	8.5970
6.7	0.7012	0.3705	7.0705	8.6	0.5518	0.0903	8.6903
6.8	0.6662	0.3001	7.1001	8.7	0.5480	0.0836	8.7836
6.9	0.6314	0.2337	7.1337	8.8	0.5442	0.0769	8.8769
7.0	0.6119	0.1977	7.1977	8.9	0.5405	0.0706	8.9706
7.1	0.6082	0.1910	7.2910	9.0	0.5367	0.0639	9.0639
7.2	0.6044	0.1841	7.3841	9.1	0.5329	0.0573	9.1573
7.3	0.6006	0.1772	7.4772	9.2	0.5291	0.0506	9.2506
7.4	0.5968	0.1703	7.5703	9.3	0.5223	0.0388	9.3388
7.5	0.5932	0.1638	7.6638	9.4	0.5107	0.0186	9.4186
7.6	0.5895	0.1572	7.7572	9.5	0.4990	-0.0017	9.4983
7.7	0.5855	0.1501	7.8501	9.6	0.4874	-0.0219	9.5781
7.8	0.5819	0.1436	7.9436	9.7	0.4757	-0.0422	9.6578
7.9	0.5781	0.1368	8.0368	9.8	0.4641	-0.0625	9.7375
8.0	0.5743	0.1300	8.1300	9.9	0.4524	-0.0829	9.8171
8.1	0.5705	0.1233	8.2233	10.0	0.4408	-0.1033	9.8967
8.2	0.5669	0.1168	8.3168	10.1	0.4292	-0.1237	9.9763

3.2. Metal-ligand stability constant

3.2.1. Point-wise calculation method

Metal titration curve showed a displacement with respect to the ligand titration curve along the volume axis indicating the affinity of ligand with metal ions which release protons and produced the volume difference (V3-V2) (Mane et al. 2011). This is utilized to calculate the values n- and pL and further to evaluate the metal-ligand stability constants. Chromium complexes:

For propanoic acid the variation of n- is from 0.0260 to 1.9031, since the ligand is monoprotic, this indicates the formation of two complex species ML1 and ML2. For tribasic ligand citric acid, the values of n- extend between 0.0633 and 2.9925, indicate formation of ML chelate.

Zirconium complexes

For propanoic acid n- extends in the range 2.4881 to 2.9968 this indicates the formation of 1:3 complex only. For citric acid The n-'s values extend between 1.0892 to 2.8752, indicating formation of 1:1 chelate only because the ligand is tribasic.

Table 5: Point-Wise Calculation Method Cr-Propanoate LogK1 (Average Value = 4.5499)

V2	V3	pL	.n-	$\log \left(\frac{n^-}{(1-n^-)} \right)$	logK1
0.8200	0.8500	5.0772	0.1539	-0.7403	4.3369
0.9827	1.0250	4.9885	0.2207	-0.5480	4.4406
1.1000	1.1500	4.8962	0.2621	-0.4496	4.4465
1.2000	1.2600	4.8074	0.3238	-0.3199	4.4875
1.2714	1.3462	4.7226	0.4069	-0.1636	4.5589
1.3300	1.4167	4.6355	0.4725	-0.0478	4.5877
1.3800	1.4722	4.5450	0.5145	0.0252	4.5702
1.4188	1.5185	4.4553	0.5580	0.1013	4.5566
1.4500	1.5556	4.3660	0.5989	0.1741	4.5401
1.4813	1.5926	4.2805	0.6559	0.2802	4.5607
1.5078	1.6250	4.1962	0.7120	0.3931	4.5892
1.5275	1.6563	4.1188	0.7961	0.5915	4.7103
1.5471	1.6875	4.0440	0.8828	0.8769	4.9210

Table 6: Point-Wise Calculation Method Cr-Propionate LogK2 (Average Value =3.6038)

V2	V3	pL	n	$\log \left(\frac{(n^- - 1)}{(2-n^-)} \right)$	logK2
1.6310	1.8030	3.7624	1.1772	-0.6667	3.0957
1.6548	1.8333	3.7073	1.2745	-0.4220	3.2853
1.6786	1.8636	3.6637	1.3942	-0.1867	3.4770
1.7029	1.8939	3.6304	1.5255	0.04436	3.6748
1.7314	1.9286	3.6185	1.6959	0.35958	3.9780

Table 7: Point-Wise Calculation Method Cr-Citrate LogK1 (Average Value= 6.1327)

V2	V3	n-	pL	$\log \frac{n^-}{(1-n^-)}$	logK1
1.7611	1.8438	0.1844	8.7155	-0.6457	8.0697
1.8130	1.9053	0.2111	8.4197	-0.5726	7.8471
1.8565	1.9579	0.2389	8.1242	-0.5033	7.6209
1.9000	2.0091	0.2650	7.8284	-0.4430	7.3854
1.9370	2.0546	0.2932	7.5330	-0.3820	7.1510
1.9741	2.1000	0.3225	7.2379	-0.3223	6.9156
2.0104	2.1455	0.3556	6.9434	-0.2581	6.6853
2.0448	2.1909	0.3948	6.6500	-0.1856	6.4644
2.0793	2.2333	0.4275	6.3557	-0.1269	6.2288
2.1138	2.2750	0.4600	6.0615	-0.0696	5.9918
2.1483	2.3167	0.4945	5.7678	-0.0096	5.7582
2.1828	2.3583	0.5306	5.4748	0.0533	5.5282
2.2179	2.4000	0.5678	5.1828	0.1186	5.3013
2.2536	2.4400	0.6004	4.8911	0.1769	5.0680
2.2893	2.4800	0.6353	4.6023	0.2410	4.8433
2.3200	2.5192	0.6832	4.3206	0.3337	4.6543
2.3486	2.5577	0.7371	4.0487	0.4477	4.4964
2.3772	2.5962	0.7940	3.7934	0.5861	4.3795

Table 8: Point-Wise Calculation Method Zr-Propanoate LogK3 (Average Value 11.5165)

V2	V3	.n-	.pL	$\log \frac{(n^- - 2)}{(3-n^-)}$	logK3
0.3333	0.8000	2.4881	11.4807	-0.0207	11.4661
0.6200	1.1000	2.4974	11.3885	-0.0045	11.3883
0.820	1.3167	2.5456	11.3325	0.0795	11.4156
0.9827	1.4833	2.6101	11.2990	0.1944	11.4962
1.1000	1.6222	2.7356	11.3686	0.4443	11.8160

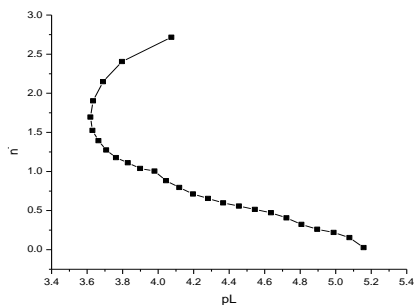
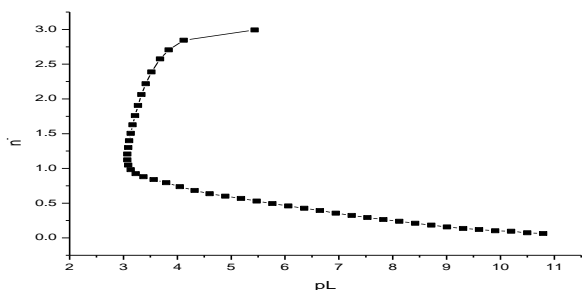
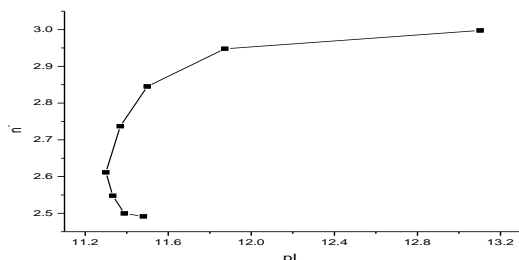
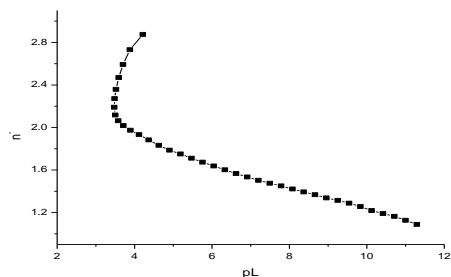
3.2.2. Half integral method

If a graph is plotted between n- and pL, then the corresponding values of pL at n- equal to 0.5 and 1.5 gives logK1 and logK2 respectively (Gurdeep Raj 1986, p.67).

Generally for log Kn the value of pL at which n-= n-0.5 corresponds to logKn. Other expression for this

Table 9: Point-Wise Calculation Method Zr-Citrate LogK1 (Average Value 7.5967)

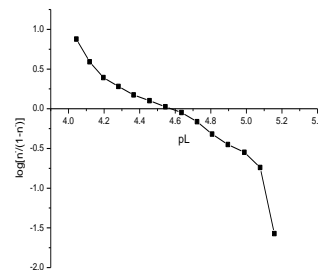
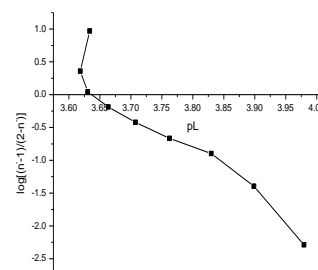
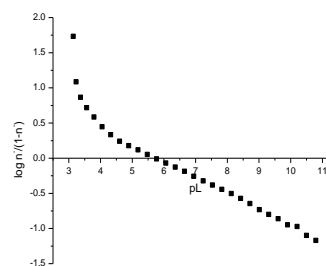
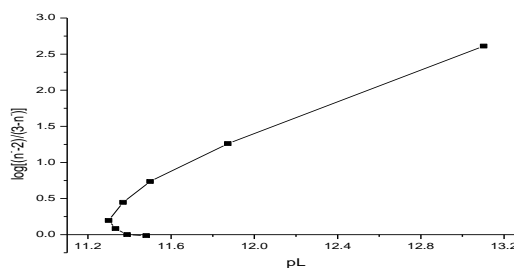
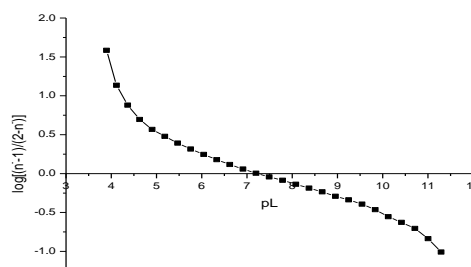
V2	V3	n-	.pL	$\log \frac{(n^- - 1)}{(2 - n^-)}$	logK2
1.4700	2.0700	1.2179	10.1245	-0.5549	9.5696
1.5583	2.1636	1.2560	9.8341	-0.4633	9.3708
1.6357	2.2400	1.2880	9.5423	-0.3930	9.1492
1.7056	2.3056	1.3146	9.2492	-0.3383	8.9109
1.7611	2.3611	1.3378	8.9554	-0.2922	8.6631
1.8130	2.4111	1.3678	8.6634	-0.2353	8.4281
1.8565	2.4482	1.3939	8.3705	-0.1871	8.1834
1.9000	2.4852	1.4215	8.0781	-0.1375	7.9406
1.9370	2.5188	1.4508	7.7863	-0.0858	7.7005
1.9741	2.5500	1.4754	7.4933	-0.0429	7.4505
2.0104	2.5813	1.5028	7.2013	0.0049	7.2062
2.0448	2.6125	1.5339	6.9105	0.0590	6.9695
2.0793	2.6438	1.5669	6.6205	0.1169	6.7375
2.1138	2.6750	1.6014	6.3314	0.1787	6.5101
2.1483	2.7061	1.6379	6.0432	0.2459	6.2891
2.1828	2.7364	1.6739	5.7555	0.3152	6.0708
2.2179	2.7667	1.7113	5.4692	0.3917	5.8609
2.2536	2.7970	1.7504	5.1850	0.4781	5.6631
2.2893	2.8257	1.7868	4.9026	0.5672	5.4698

**Fig. 5:** Chromium Propanoate LogK1=4.54 and LogK2=3.632 (Half Integral Method)**Fig. 6:** Chromium Citrate LogK1=5.72 (Half Integral Method)**Fig. 7:** Zirconium Propanoate LogK3=11.382**Fig. 8:** Zirconium Citrate LogK1=7.2

$$K_n = \left(\frac{1}{[L]} \right)_{\text{at } n^- = n - 0.5}$$

3.2.3. Linear plot method:

Plotting $\log(n/n-1)$ and $\log(n-1)/(2-n)$ versus corresponding pL gives logK1 and logK2 respectively (Anjani et al. 2011).

**Fig. 9:** Chromium Propanoate LogK1=4.626 (Linear Plot Method)**Fig. 10:** Chromium Propanoate LogK2=3.63 (Linear Plot Method)**Fig. 11:** Chromium Citrate LogK1=5.72 (Linear Plot Method)**Fig. 12:** Zirconium Propanoate LogK3=11.382 (Linear Plot Method)**Fig. 13:** Zirconium Citrate LogK1=7.41 (Linear Plot Method)**3.2.4. Least squares method**

For estimation of K2 and K3 for chromium propanoate and chromium citrate by this method, linear equation of Rossotti and Rossotti as expressed below has been employed:

$$n^- = (1-n^-)[L]K_1 + (2-n^-)[L]K_1K_2$$

This on division by $(1-n^-)[L]K_1$ and further rearranging becomes:

$$\frac{n^-}{(1-n^-)[L]} = \frac{(2-n^-)[L]}{(1-n^-)} \times K_1K_2 + K_1$$

If the values of n^- and $[L]$ were known, plotting of $(2-n^-)[L]/(1-n^-)$ V/s $n^-/(1-n^-)[L]$, give straight line equation with y-intercept= K_1 and slope = K_1K_2 (Gurdeep Raj 1986, p.67).

Table 10: Determination of Chromium Propanoate Stability Constants by Least Squares Method (Averg. Value Logk1=4.2198 and Logk2 (Average Value = 3.7344)

pL	n	[L]	$\frac{(2-n^-)[L]}{(1-n^-)}$	$\frac{n^-}{(1-n^-)[L]^2}$
5.1571	0.0260	6.9647E-06	1.4116E-05	3838.8930
5.0772	0.1539	8.3716E-06	1.8266E-05	21723.1864
4.9885	0.2207	1.0267E-05	2.3442E-05	27579.1226
4.8962	0.2621	1.2701E-05	2.9912E-05	27960.5246
4.8074	0.3238	1.5583E-05	3.8626E-05	30723.2399
4.7226	0.4069	1.8943E-05	5.0881E-05	36218.9184
4.6355	0.4725	2.3148E-05	6.7031E-05	38701.2932
4.5450	0.5145	2.8513E-05	8.7244E-05	37171.0648
4.4553	0.5580	3.5049E-05	0.00014351	36023.8284
4.3660	0.5989	4.3056E-05	0.0002	34678.2783
4.2805	0.6559	5.2416E-05	0.0002	36368.7292
4.1962	0.7120	6.3656E-05	0.0003	38837.3431
4.1188	0.7961	7.6076E-05	0.0004	51320.6695
4.0440	0.8828	9.0363E-05	0.0009	83359.2057
3.9795	1.0051	0.0001	-0.0203	-1870517.592
3.8987	1.0386	0.0001	-0.0031	-212882.0742
3.8297	1.1123	0.0001	-0.0012	-66924.1810
3.7624	1.1772	0.0002	-0.0008	-38434.2168
3.7073	1.2745	0.0002	-0.0005	-23662.7599
3.6637	1.3942	0.0002	-0.0003	-16303.5508
3.6304	1.5255	0.0002	-0.0002	-12394.8823
3.6185	1.6959	0.0002	-0.0001	-10122.9771
3.6337	1.9031	0.0002	-2.4942E-05	-9066.0208
3.6895	2.1486	0.0002	2.6452E-05	-9150.3771

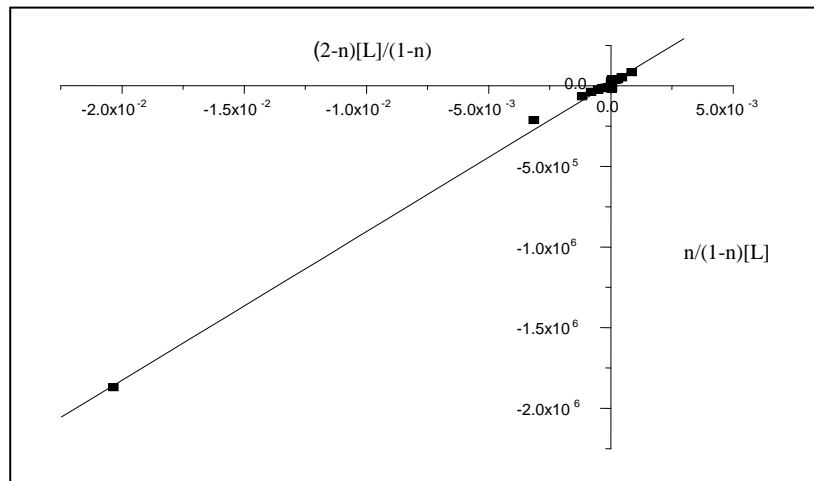


Fig. 14: Least Squares Method (Chromium Propanoate Logk1=4.2198 and Logk2=3.7447)

Linear Regression for Data1_B:

$$Y = A + B * X$$

Parameters	Value	Error	R2
Intercept	16590.2608	4192.90636	0.99849
Slope	9.2152E7	1.03405E6	

R2 is coefficient of determination. This is the famous number people quote to prove how good the fit is. It is quite useless for evaluating a working curve unless you count the "number of nines" you get. (0.978 is a pretty bad working curve. 0.999 is probably a good one.) For estimation of chromium citrate stability constant by this method, and because only one complex is formed, equation familiar as Henderson or Hasselbalch's equation was employed as follows: (Rossotti et al. 1955).

$$\frac{n^-}{(1-n^-)} = \beta_1[L] \quad \log \frac{n^-}{(1-n^-)} = \log \beta_1 + \log[L]$$

Table 11: Determination of Chromium Citrate Stability Constant by Hasselbach's Equation. Logk1 (Average. Value =6.0509)

pL	n	log[L]	$\log \frac{n^-}{(1-n^-)}$	$\log \frac{n^-}{(1-n^-)} - \log[L]$	pL	n	Log[L]	$\log \frac{n^-}{(1-n^-)}$	$\log \frac{n^-}{(1-n^-)} - \log[L]$
11.7244	0.2634	-11.7244	0.2796	12.0040	5.4748	-5.4748	-5.4748	0.2517	5.7265
11.4032	0.1214	-11.4032	0.2918	11.6950	5.1828	-5.1828	-5.1828	0.2471	5.4299
11.0994	0.0923	-11.0994	0.2941	11.3935	4.8911	-4.8911	-4.8911	0.2430	5.1341
10.7956	0.0633	-10.7956	0.2963	11.0919	4.6023	-4.6023	-4.6023	0.2384	4.8407
10.4975	0.0740	-10.4975	0.2955	10.7930	4.3206	-4.3206	-4.3206	0.2318	4.5523
10.2012	0.0965	-10.2012	0.2938	10.4949	4.0487	-4.0487	-4.0487	0.2238	4.2726
9.9022	0.1015	-9.9022	0.2934	10.1955	3.7934	-3.7934	-3.7934	0.2149	4.0083
9.6053	0.1212	-9.6053	0.2918	9.8971	3.5624	-3.5624	-3.5624	0.2073	3.7697
9.3079	0.1371	-9.3079	0.2905	9.5984	3.3701	-3.3701	-3.3701	0.1999	3.5701
9.0111	0.1562	-9.0111	0.2889	9.2999	3.2277	-3.2277	-3.2277	0.1917	3.4193
8.7155	0.1844	-8.7155	0.2866	9.0020	3.1378	-3.1378	-3.1378	0.1800	3.3178
8.4197	0.2111	-8.4197	0.2843	8.7040	3.0903	-3.0903	-3.0903	0.1653	3.2556
8.1242	0.2389	-8.1242	0.2818	8.4060	3.0723	-3.0723	-3.0723	0.1469	3.2192
7.8284	0.2650	-7.8284	0.2795	8.1079	3.0738	-3.0738	-3.0738	0.1228	3.1966
7.5330	0.2932	-7.5330	0.2768	7.8099	3.0875	-3.0875	-3.0875	0.0914	3.1789
7.2379	0.3225	-7.2379	0.2741	7.5119	3.1082	-3.1082	-3.1082	0.0520	3.1602
6.9434	0.3556	-6.9434	0.2708	7.2142	3.1356	-3.1356	-3.1356	-0.0027	3.1328
6.6500	0.3948	-6.6500	0.2668	6.9168	3.1715	-3.1715	-3.1715	-0.0892	3.0823
6.3557	0.4275	-6.3557	0.2634	6.6190	3.2149	-3.2149	-3.2149	-0.2356	2.9793
6.0615	0.4600	-6.0615	0.2598	6.3213	3.2692	-3.2692	-3.2692	-0.5897	2.6795
5.7678	0.4945	-5.7678	0.2559	6.0237	-	-	-	-	-

Since only one complex zirconium propanoate is formed Henderson's equation is employed.

Table 12: Determination of Zirconium Propanoate Stability Constant by Hasselbach's Equation Logk3 (Average Value =11.5124)

pL	n	log[L]	$\log \frac{n^-}{(1-n^-)}$	$\log \frac{(n^- - 2)}{(3-n^-)} - \log[L]$	pL	n	log[L]	$\log \frac{(n^- - 2)}{(3-n^-)}$	$\log \frac{(n^- - 2)}{(3-n^-)} - \log[L]$
11.4817	2.4881	-11.4807	-0.0207	11.4600	11.3686	2.7356	-11.3686	0.44434	11.8129
11.3885	2.4974	-11.3885	-0.0045	11.3840	11.4992	2.8442	-11.4992	0.73401	12.2332
11.3325	2.5456	-11.3325	0.07949	11.4120	11.8720	2.9470	-11.8720	1.25219	13.1242
11.2990	2.6101	-11.2990	0.19436	11.4934	13.1023	2.9968	-13.1023	2.49601	15.5984

Table 13: Determination of Zirconium Citrate Stability Constant, by Hasselbach's Equation Logk1 (Average Value =7.5152)

pL	n	log[L]	$\log \frac{n^-}{(1-n^-)}$	$\log \frac{n^-}{(1-n^-)} - \log[L]$	pL	n	log[L]	$\log \frac{n^-}{(1-n^-)}$	$\log \frac{n^-}{(1-n^-)} - \log[L]$
11.2928	1.0892	-11.2928	1.0868	12.3797	6.04322	1.6379	-6.0432	0.4095	6.4528
11.0021	1.1274	-11.0021	0.9469	11.9490	5.75553	1.6739	-5.7555	0.3951	6.1507
10.7112	1.1649	-10.7112	0.8491	11.5603	5.46924	1.7113	-5.4692	0.3813	5.8505
10.4177	1.1910	-10.4177	0.7949	11.2127	5.18504	1.7504	-5.1850	0.3678	5.5529
10.1245	1.2179	-10.1245	0.7472	10.8718	4.90260	1.7868	-4.9026	0.3562	5.2588
9.83406	1.2560	-9.8341	0.6907	10.5248	4.62838	1.8324	-4.6284	0.3427	4.9711
9.54227	1.2880	-9.5423	0.6505	10.1928	4.36531	1.8834	-4.3653	0.3288	4.6941
9.24920	1.3146	-9.2492	0.6210	9.8703	4.11750	1.9318	-4.1175	0.3166	4.4341
8.95536	1.3378	-8.9554	0.5977	9.5531	3.89417	1.9746	-3.8942	0.3066	4.2008
8.66337	1.3678	-8.6634	0.5704	9.2338	3.71066	2.0177	-3.7107	0.2972	4.0079
8.37046	1.3939	-8.3705	0.5488	8.9193	3.57813	2.0635	-3.5781	0.2879	3.8660
8.07807	1.4215	-8.0781	0.5280	8.6060	3.50019	2.1173	-3.5002	0.2776	3.7778
7.78627	1.4508	-7.7863	0.5077	8.2939	3.47490	2.1909	-3.4749	0.2647	3.7396
7.49330	1.4754	-7.4933	0.4919	7.9852	3.48490	2.2715	-3.4849	0.2520	3.7369
7.20129	1.5028	-7.2013	0.4755	7.6768	3.52143	2.3589	-3.5214	0.2395	3.7610
6.91052	1.5339	-6.9105	0.4583	7.3688	3.59307	2.4686	-3.5931	0.2255	3.8186
6.62055	1.5669	-6.6205	0.4415	7.0621	3.70390	2.5931	-3.7039	0.2116	3.9155
6.33138	1.6014	-6.3314	0.4253	6.7567	3.88073	2.7308	-3.8807	0.1980	4.0788

4. Conclusion

The three graphical method half integral method, linear plot method and least squares method in addition to the two algebraic ones (point-wise and Henderson's equation) give nearly the same results, but in using least squares method for determination of chromium-propanoic acid which forms 1:1 and 1:2 complexes, the results obtained were slightly different specially in Kn-1, where the error accumulated, this method has many restriction which can be found in literature.

Citric acid forms only one chelate with chromium and zirconium (1:1). Propanoic acid forms 1:1 and 1:2 complexes with chromium and with zirconium forms a 1:3 complex only.

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 these methods employed above seen satisfactorily to give the an-

swer, with difference ≤ 0.3 , for a system where $N \leq 3$ (N is the possible coordination sites).

The most important thing in this work that matlab program is used for determination of the volume of alkali that required to bring the three sets of solution to the same pH, which is important for determination of formation functions nA , n^- and pL .

Interaction of metal ion with carboxylic acid shows high dependency on the salt that added to maintain the ionic strength of the medium, so potassium nitrate with nitric acid as free acid is adequate, for nitrate ion has very slight complexing tendency and the competition between nitrate ion and the ligands under study is of minor importance.

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