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Research Paper

Potentiometric studies on complexes of Cr (Ⅲ) and Zr (IV)with some carboxylic acids

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Abstract

The present work, deals with the study of proton-ligand (pK) and metal-ligand (logK) of acetic acid, oxalic acid, and oxalacetic acid with Cr (Ⅲ) and Zr (IV) by potentiometric titration technique. The stoichiometries and stability constants of these complexes were evaluated, usingCalvin-Bjerrum pH-titration technique as adopted by Irriving and Rossotti.
Graphic and algebraic methods have been employed, for determination of the stability constants, in purpose to select the most accurate and sensitive method. Furthermore, aiming to determine, the factor that effectingthe precision of those methods under investigation, and to compare the complexes of these ligands with first and second series transition elements of D-block Cr and Zr taken as an example. The obtained results were in a good agreement with each other.

Keywords:*Oxalacetic Acid; Point-Wise; Stability Constants; Least Squares Method.*

1. Introduction

Potentiometric titrations are among the most accurate known, because the potential followsactual change in activity and therefore the end point coincide with the equivalent point (Louis Meites. 1981) ; (Gurdeep, 1986)]. The study of metal-ligand complexes in a solution would be interesting which throw a light on the mode of storage and transport of metal ion in biological kingdom with a view to understand the bi-inorganic chemistry of the metal ions.(Maldhure et al., 2012); (Sumer et al., 2011)
All metal complexes or chelates may be considered as being formed by displacement of one or more usually weakly acidic protons of the complexing or chelating agent by a metal ion in a solution, which result in pH drop. (Cotton, 2006). The work of coordination chemistry was first begun in the twentieth century; it was mostly related to step-wise formation of complexes. (Praveen, et al., 2009). The fundamental assumption that the complex formation is step-wise process, if this is true then the ratios of various stability constants could in theory is predicted by statistical considerations. (Hartley &Alcock, 1980). The stability constant of the reaction between metal and ligand has been found to be greater than zero, is perhaps the most convincing evidence for the existence of the complex species. (Abdulbast, 2012).

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 experiment were prepared in doubly distilled water. The pH-meter is denver instrument ultra-basic pH/mVmeter with combine electrode, 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.

2.2. Procedure

All measurements were carried out at 29±10C. 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.
It was shown by Calvin and Wilson that pH measurement done during titration with alkali, solution of ligand in presence and absence of metal ion could be used to calculate the formation functions n-, nA and pL.(Gurdeep, 1986.). (Where nA average number of proton associated with ligand, n-the average number of ligand attached with metal ion and pL is the free ligand exponential function). (Ashwini, 2007); (Anjani, 2011).
Irving and Rossotti titrated the three sets of the following solutions against carbonate free standard alkali solution keeping the total volume constant. (Minaxi&Shah, 2011); (Avinash&Marutil, 2013).

i) Free acid.(A)
ii) Free acid +ligand. (A+L).
iii) Free acid +ligand +metal. (A+L+M).

Three sets of solutions were completed with double distilled water to 200cm3. The ionic strength was maintained constant, by addition 1cm3 of 1M KNO3. The three sets of solutions were titrated against free carbonate standard KOH. A matlab program was used for plotting a graph of the pH of three sets of solutions versus the volume of alkali added, and then to calculate required volume that bringing the three sets of solutions to same pH.

The proton-ligand stability constants calculated according to following relationships: for dibasic acid. (Abdulbast, 2012); (Gurdeep, 1986.).

$$pK_1 = pH + \log\frac{n_A - 1}{2 - n_A} \quad pK_2 = \mathrm{pH} + \log\frac{n_A}{1 - n_A}$$

For monobasic acids: $pK_1 = \mathrm{pH} + \log\frac{n_A}{1 - n_A}$

The formation functions were calculated by the following relations: (Anjani, et al., 2011); (Ashwini, Ashok & Malik, 2007); (Santosh, 2011)

$$\bar{n}_A = y - \frac{(V_1 - V_2)(N^0 + E^0)}{(V^0 + V_1)T_L^0} \quad \bar{n} = \frac{(V_3 - V_2)(E^0 + N^0)}{(V^0 + V_2)\bar{n}_A T_m^0}$$

$$PL = \log_{10}\{\frac{1 + \beta_n^H \frac{1}{[anti\ \log \mathrm{pH}]^n}}{T_L^0 - \bar{n}T_m^0} X \frac{(V^0 + V_3)}{V^0}\}$$

Where y= the number of dissociable protons, N0 is the concentration of the alkali, E0 is the concentration of the free acid, T_L^0 is the total ligand concentration, T_m^0 is the total metal ion concentration, V0 is the total volume of titration solution, V1, V2 and V3 the volumes of alkali added to acid, acid +ligand and acid + ligand + metal ion respectively bringing each of them to same pH value.

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 required a prior knowledge of the proton-ligand stability constant. Cr-titration curves, with the three ligands:

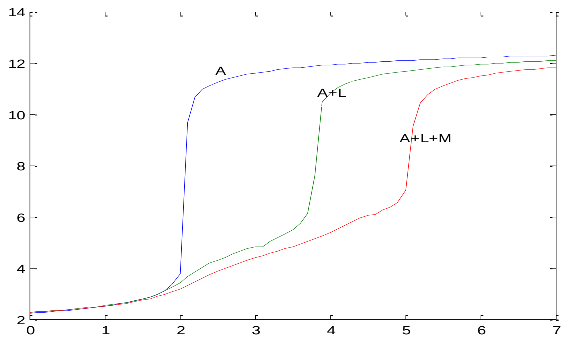

Fig. 1: Volume of Alkali Added Versus Three Sets of Solutions. A(HNO3), L (Acetic Acid) and M(Cr).

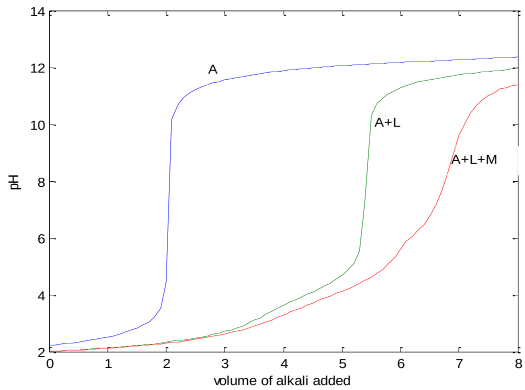

Fig. 2: Volume of Alkali Added Versus Three Sets of Solutions. A(HNO3), L (Oxalic Acid) and M(Cr)

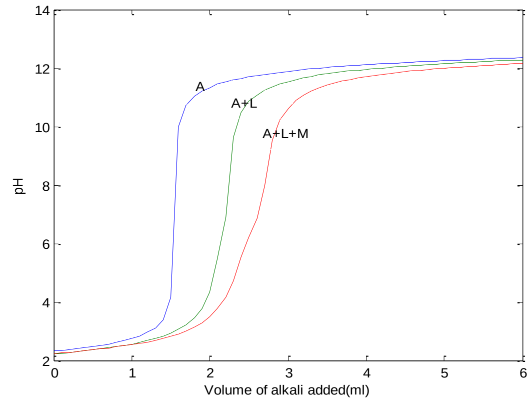

Fig. 3: Volume of Alkali Added Versus Three Sets of Solutions. A(HNO3), L (Oxalacetic Acid) and M(Cr)

Zr-titration curves with the three ligands

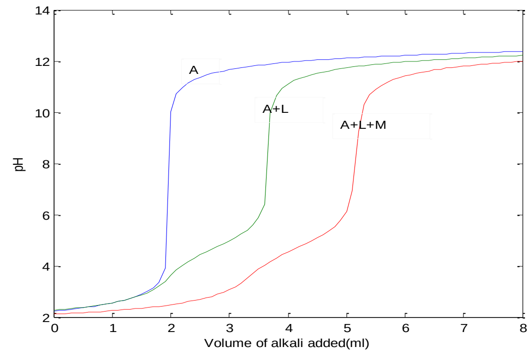

Fig. 4: Volume of Alkali Added Versus Three Sets of Solutions. A(HNO3), L (Acetic Acid) and M(Zr)

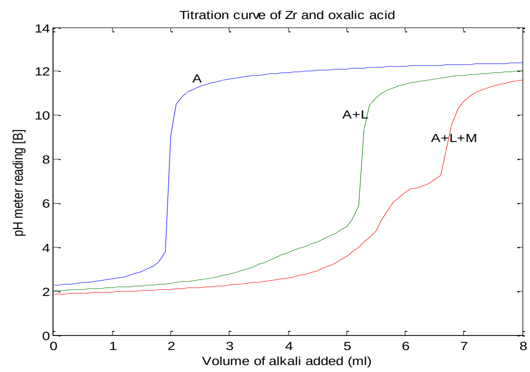

Fig. 5: Volume of Alkali Added Versus Three Sets of Solutions. A(HNO3), L (Oxalic Acid) and M(Zr)

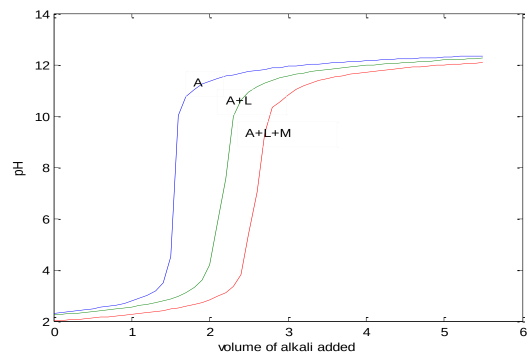

Fig. 6: Volume of Alkali Added Versus Three Sets of Solutions. A (HNO3), L (Oxalacetic Acid) and M (Zr)

Dissociation constants of the three ligands were calculated as follows:

Table 1: Pka of Acetic Acid (Average Value =4.8365)

pH	V1	V2	.nA	$\log\left(\frac{n_A}{(1-n_A)}\right)$	pKa
3.1	1.7157	1.8063	0.9523	1.3001	4.4001
3.2	1.8364	1.8688	0.9829	1.7607	4.9607
3.3	1.8818	1.9278	0.9758	1.6054	4.9054
3.4	1.9143	1.9833	0.9637	1.4240	4.8240
3.5	1.9381	2.0318	0.9507	1.2852	4.7852
3.6	1.9619	2.0773	0.9393	1.18962	4.7896
3.7	1.9857	2.1250	0.9267	1.1020	4.8020
3.8	2.0007	2.1750	0.9083	0.9960	4.7960
3.9	2.0024	2.2278	0.8815	0.8713	4.7713
4.0	2.0041	2.2833	0.8532	0.7642	4.7642
4.1	2.0058	2.3467	0.8207	0.6606	4.7606
4.2	2.0075	2.4154	0.7855	0.5637	4.7637
4.3	2.0092	2.4923	0.7459	0.4678	4.7678
4.4	2.0109	2.5818	0.6998	0.3675	4.7675
4.5	2.0126	2.6727	0.6529	0.2743	4.7743
4.6	2.0143	2.7636	0.6060	0.1869	4.7869
4.7	2.016	2.8600	0.5562	0.0980	4.7980
4.8	2.0177	2.9600	0.5045	0.0078	4.8078
4.9	2.0194	3.1286	0.4167	-0.1459	4.7540
5.0	2.0211	3.1762	0.3926	-0.1895	4.8104
5.1	2.0228	3.2385	0.3608	-0.2484	4.8515
5.2	2.0244	3.3143	0.3217	-0.3238	4.8761
5.3	2.0261	3.3857	0.2851	-0.3992	4.9007
5.4	2.0278	3.4440	0.2553	-0.4648	4.9351

Table 2: Pka1 of Oxalic Acid (Average Value=1.7799)

pH	V1	V2	.nA	$\log\left(\frac{(n_A-1)}{(2-n_A)}\right)$	pKa1
2.3	0.3500	1.8667	1.1958	-0.6143	1.6865
2.4	0.7000	2.2334	1.1884	-0.6343	1.7657
2.5	0.9751	2.5501	1.1675	-0.6964	1.8036
2.6	1.1801	2.7801	1.1552	-0.7360	1.8640
2.7	1.3429	2.9801	1.1362	-0.8022	1.8978
2.8	1.4751	3.1429	1.1206	-0.8627	1.9373
2.9	1.5801	3.2858	1.1011	-0.9488	1.9516
3.0	1.6667	3.4001	1.0869	-1.0214	1.9786
3.1	1.7353	3.5101	1.0654	-1.1548	1.9452
3.2	1.7942	3.6092	1.0445	-1.3315	1.8685
3.3	1.8300	3.7001	1.0157	-1.7970	1.5030

Table 3: Pka2 of Oxalic Acid (Average Value 4.5708)

pH	V1	V2	.nA	$\log\left(\frac{n_A}{(1-n_A)}\right)$	pKa2
3.5	1.8967	3.8819	0.9555	1.3316	4.8316
3.6	1.9097	3.9801	0.91071	1.0086	4.6086
3.7	1.9204	4.0801	0.8638	0.8022	4.5022
3.8	1.9312	4.1802	0.8169	0.6494	4.4494
3.9	1.942	4.2891	0.7653	0.5134	4.4134
4.0	1.9527	4.3902	0.7178	0.4056	4.4056
4.1	1.9635	4.5102	0.6605	0.2890	4.3889
4.2	1.9742	4.6102	0.6136	0.2008	4.4008
4.3	1.985	4.7085	0.5676	0.1182	4.4182
4.4	1.9957	4.7918	0.5295	0.0514	4.4514
4.5	2.0011	4.8752	0.4886	-0.0199	4.4801
4.6	2.0028	4.9502	0.4500	-0.0871	4.5129
4.7	2.0045	5.0168	0.4159	-0.1475	4.5525
4.8	2.0063	5.0724	0.3876	-0.1986	4.6014
4.9	2.0082	5.1209	0.3631	-0.2440	4.6560
5.0	2.0098	5.1626	0.3421	-0.2841	4.7159
5.1	2.0115	5.2023	0.3221	-0.3232	4.7768
5.2	2.0133	5.2245	0.3114	-0.3447	4.8553
5.3	2.0150	5.2467	0.3006	-0.3667	4.9333

Table 4: Pka1 of Oxalacetic Acid (Average Value=2.9252)

B	V1	V2	nA	$\log\left(\frac{(n_A-1)}{(2-n_A)}\right)$	pK1
2.4	0.3000	0.6250	1.4267	-0.1283	2.2717
2.5	0.5750	0.8750	1.4715	-0.0495	2.4505
2.6	0.7667	1.0667	1.4720	-0.0487	2.5513
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	2.9505
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	-0.4461	3.1539
3.7	1.4403	1.8765	1.2349	-0.5129	3.1871
3.8	1.4532	1.9035	1.2102	-0.5749	3.2251
3.9	1.4662	1.9211	1.2022	-0.5961	3.3039

Table 5: Pk2 of Oxalacetic Acid Average Value 10.5172

B	V1	V2	nA	$\log\left(\frac{(n_A)}{(1-n_A)}\right)$	pK2
8.5	1.5743	2.2584	0.8009	0.6044	9.1044
8.7	1.5777	2.2657	0.7940	0.5861	9.2861
8.9	1.5812	2.2730	0.7874	0.5687	9.4687
9.1	1.5846	2.2803	0.7806	0.5512	9.6512
9.3	1.5880	2.2876	0.7738	0.5341	9.8341
9.5	1.5914	2.2949	0.7670	0.5173	10.0174
9.7	1.5946	2.3072	0.7510	0.4795	10.1795
9.9	1.5983	2.331	0.7158	0.4012	10.3012
10.1	1.6137	2.3548	0.7012	0.3705	10.4705
10.3	1.6411	2.3786	0.7077	0.3840	10.6840
10.5	1.6685	2.4054	0.7089	0.3866	10.8866
10.7	1.6959	2.4595	0.6623	0.2926	10.9926
10.9	1.7567	2.5218	0.6601	0.2882	11.1882
11.1	1.8389	2.6126	0.6456	0.2604	11.3604
11.3	1.9751	2.7501	0.6442	0.2579	11.5579
11.5	2.1859	2.9626	0.6427	0.2549	11.7549
11.7	2.5202	3.2802	0.6740	0.3155	12.0155

3.2. Metal-ligand stability constant

3.2.1. Point-wise calculation method

Determination of metal-ligand stability constants requires the accurate values of proton-ligand stability constants (Anil &Maroti, 2008). Metal titration curves crossed over ligand titration curve indicated the formation of complex upon proton release (Santosh, et al.,2011). If the values of n- are within range 0.2-0.8 and 1.2-18 this indicates the formation of 1:1 and 1:2 complexes (Sayyed&Mazahar, 2012).

In this investigation chromium acetate, n- ranges from 0.1044 to 2.1991indicating the formation of ML and ML2 complex species. The pH range of 2.5 to 5.2, showed that complexes are stable in acidic medium. For chromium oxalate, metal-ligand titration curve cross over the ligand titration curve at pH 2.3 indicating starting point of formation of the chelates. n- Extends between 0.1334 and 2.08indicating the formation of chelate species ML and ML2. For chromium oxalacetate, the values of n- extends from 0.0305 to 2.9997 indicate the formation of complex species ML and ML2 and ML3. For Zirconium acetate n- extends from 2.1992 to 3.9504, indicating the formation of complex species ML3 and ML4. Zirconium oxalate the n- found in range 2.336-3.9128 implies the formation of chelate 1:2 only. Zirconiumoxalacetate the value of n- in range 2.0206-2.9607 indicating the formation of only chelate 1:3.

In general K1>K2>K3 etc. any reversal of this order implies specific electronic or steric phenomenon (Vogel, 1978). As it has seen that there is no appreciable difference between logK1 and logK2 which indicates the complex species were formed simultaneously, except for chromium oxalacetate the difference between logK1and logK2 is > 1.8 which indicates that the complexes formed, in stepwise manner (Sayyed&Mazahar, 2011). The higher values of logK1 and logK2 showed that the ligand is strongest chelating agent (Anil &Maroti, 2008).

The average values were taken as correct value of logK1 and logK2.

Table 6: Point-Wise Method, Cr-Acetate Logk1 (AverageValue =3.6175)

V2	V3	n-	pL	$\log\left(\frac{n^-}{(1-n^-)}\right)$	Log K1
1.1750	1.225	0.1053	2.3146	-0.9291	3.6040
1.3667	1.4333	0.1405	4.5331	-0.7864	3.6517
1.5125	1.6000	0.1836	4.4382	-0.6481	3.6961
1.6300	1.7222	0.1946	4.3443	-0.6169	3.6299
1.7250	1.8300	0.2224	4.2469	-0.5436	3.6081
1.8063	1.9250	0.2625	4.1516	-0.4487	3.6094
1.8688	2.0077	0.2974	4.0582	-0.3733	3.5913
1.9278	2.0846	0.3381	3.9645	-0.2917	3.5805
1.9833	2.1571	0.3794	3.8722	-0.2137	3.5668
2.0318	2.2286	0.4354	3.7806	-0.1129	3.5787
2.0773	2.3000	0.4985	3.6916	-0.0025	3.6022
2.1250	2.3714	0.5589	3.6047	0.1029	3.6217
2.1750	2.4462	0.6275	3.5188	0.2265	3.6622
2.2278	2.5273	0.7139	3.4357	0.3972	3.7541
2.2833	2.6167	0.8209	3.3569	0.6611	3.9446

Table 7: Point-Wise Method, Cr-Acetate Logk2 (Average Value = 3.0439)

V2	V3	n-	pL	$\log\left(\frac{n^- -1}{(2-n^-)}\right)$	Log K2
2.4154	2.8000	1.0278	3.1456	1.6025	1.6025
2.4923	2.9000	1.1469	3.0850	2.3210	2.3210
2.5818	3.0100	1.2835	3.0320	2.6293	2.6293
2.6727	3.1111	1.4078	2.9827	2.8207	2.8207
2.7636	3.2250	1.5956	2.9509	3.1191	3.1191
2.8600	3.3444	1.8243	2.9351	3.6064	3.6064

Table 8: Point-Wise Method Cr-Oxalate Logk1 (Average Value =3.7762)

V2	V3	n-	pL	$\log\left(\frac{n^-}{(1-n^-)}\right)$	Log K1
1.8667	1.9667	2.3248	0.1334	-0.8128	3.9179
2.2334	2.3637	2.3319	0.1745	-0.6748	3.9423
2.5501	2.7001	2.3372	0.2042	-0.5908	3.9147
2.7801	2.9501	2.3422	0.2336	-0.5159	3.8809
2.9801	3.1601	2.3454	0.2512	-0.4742	3.8150
3.1429	3.3501	.35241	0.2930	-0.3826	3.8054
3.2858	3.5001	2.3551	0.3082	-0.3512	3.7335
3.4001	3.6501	.36446	0.3640	-0.2423	3.7476
3.5101	3.7751	2.3695	0.3934	-0.1880	3.7047
3.6092	3.9001	2.3776	0.4403	-0.1042	3.6959
3.7001	4.0223	2.3882	0.5013	0.0023	3.7141
3.791	4.1376	2.3979	0.5555	0.0968	3.7211
3.8819	4.2557	409173	0.6177	0.2084	3.7487
3.9801	4.3668	2.4189	0.6700	0.3077	3.7646
4.0801	4.4877	2.4331	0.7443	0.4640	3.8440

Table 9: Point-Wise Method Cr-Oxalate Logk2 (Average Value =2.9479)

V2	V3	pL	n-	$\log\left(\frac{(n^- -1)}{(2-n^-)}\right)$	pKa2
4.5102	4.9752	3.1224	1.1082	-0.9162	2.2063
4.6102	5.0891	3.0769	1.2280	-0.5299	2.5470
4.7085	5.2002	3.0418	1.3621	-0.2458	2.7960
4.7918	5.3093	3.0262	1.5362	0.0629	3.0891
4.8752	5.4002	3.0150	1.6884	0.3443	3.3593
4.9502	5.4911	3.0326	1.8878	0.8985	3.9312

Table 10: Point-Wise Method Cr-Oxalacetate Logk1 Average Value = 10.2385

V2	V3	pL	n-	$\log\left(\frac{n^-}{(1-n^-)}\right)$	Log K1
1.0667	1.1400	11.1082	0.2605	-0.4531	10.6551
1.2167	1.3167	10.9230	0.3501	-0.2687	10.6544
1.3556	1.4714	10.7334	0.4107	-0.1567	10.5767
1.4600	1.5889	10.5424	0.4624	-0.0655	10.4769
1.5500	1.6900	10.3509	0.5100	0.0174	10.3683
1.6267	1.7750	10.1575	0.5467	0.0813	10.2388
1.6933	1.8438	9.96256	0.5742	0.1299	10.0924
1.7391	1.9050	9.77481	0.6409	0.2516	10.0264
1.7826	1.9550	9.58116	0.6746	0.3167	9.89785
1.8177	2.0035	9.39529	0.7485	0.4737	9.86902
1.8471	2.0379	9.20263	0.7859	0.5647	9.76732

Table 11: Point-Wise Method Cr-Oxalacetate Logk2 Average Value = 6.0183

V2	V3	pL	n-	$\log\left(\frac{(n^{-}-1)}{(2-n^{-})}\right)$	Log K2
2.0225	2.2786	7.2961	1.2124	-0.5692	6.7269
2.0315	2.2964	7.1100	1.2686	-0.4350	6.6750
2.0405	2.3099	6.9193	1.3051	-0.3574	6.5619
2.0496	2.3222	6.7275	1.3366	-0.2947	6.4329
2.0586	2.3346	6.5363	1.3696	-0.2319	6.3044
2.0676	2.3469	6.3454	1.4029	-0.1709	6.1745
2.0766	2.3593	6.1551	1.4375	-0.1092	6.0459
2.0856	2.3716	5.9652	1.4725	-0.0479	5.9173
2.0946	2.384	5.7760	1.5088	0.0153	5.7914
2.1028	2.3963	5.5881	1.5477	0.0831	5.6712
2.1097	2.4105	5.4051	1.6005	0.1770	5.5821
2.1167	2.4254	5.2249	1.6581	0.2843	5.5092
2.1236	2.4403	5.0467	1.7170	0.4037	5.4504
2.1306	2.4552	4.8710	1.7768	0.5417	5.4127

Table 12: Point-Wise Method, Zr-Acetate Logk3 Average Value =5.1050

V3	V2	n-	pL	$\log\frac{(n^{-}-2)}{(3-n^{-})}$	Log K3
1.2500	0.1500	2.1992	5.2285	-0.6043	4.6242
1.7000	0.5500	2.3336	5.1635	-0.3004	4.8631
2.0500	0.8500	2.4991	5.1100	-0.0016	5.1084
2.3000	1.0800	2.5511	5.0264	0.0891	5.1155
2.5200	1.2833	2.6338	4.9530	0.2382	5.1912
2.7000	1.4286	2.7070	4.8780	0.3826	5.2606
2.8250	1.5556	2.7299	4.7870	0.4319	5.2188
2.9400	1.6500	2.7818	4.7065	0.5541	5.2606
3.0308	1.7267	2.8265	4.6244	0.6778	5.3022
3.1071	1.7933	2.8661	4.5413	0.8107	5.3521
3.1786	1.8474	2.9171	4.4638	1.0438	5.5076
3.2389	1.9000	2.9624	4.3853	1.4081	5.7934

Table 13: Point-Wise Method Zr-Acetate Logk4 Average Value =4.1095

V3	V2	n-	pL	$\log\frac{(n^{-}-3)}{(4-n^{-})}$	Log K4
3.3474	1.9909	3.0934	4.2523	-0.9870	3.2653
3.400	2.0381	3.1572	4.1897	-0.7293	3.4605
3.4556	2.0857	3.2301	4.1361	-0.5246	3.6114
3.5143	2.1389	3.3105	4.0927	-0.3465	3.7462
3.5857	2.1944	3.4565	4.1068	-0.0757	4.0311
3.6533	2.2563	3.6048	4.1583	0.18485	4.3432
3.7214	2.3214	3.7657	4.3013	0.51425	4.8155

Table 14: Point-Wise Method Zr-Oxalate Logk2 Average Value=3.4985

V2	V3	pL	n-	$\log\frac{(n^{-}-2)}{(4-n^{-})}$	Log K3
3.1875	4.4667	4.6005	2.3884	-0.6179	3.9826
3.3000	4.5700	4.4984	2.3962	-0.6073	3.8911
3.4091	4.6700	4.4039	2.4261	-0.5675	3.8364
3.5000	4.7538	4.3101	2.4532	-0.5332	3.7769
3.5909	4.8267	4.2147	2.4691	-0.5137	3.7010
3.6750	4.8933	4.1232	2.4939	-0.4842	3.6390
3.7636	4.9529	4.0331	2.5181	-0.4564	3.5767
3.8545	5.0100	3.9430	2.5370	-0.4353	3.5077
3.9500	5.0600	3.8491	2.5372	-0.4351	3.4140
4.0500	5.1087	3.7571	2.5370	-0.4353	3.3219
4.1500	5.1522	3.6719	2.5520	-0.4188	3.2530
4.2500	5.1957	3.5900	2.5691	-0.4004	3.1896
4.3556	5.2409	3.5118	2.5884	-0.3801	3.1317
4.4545	5.2864	3.4408	2.6189	-0.3486	3.0922
4.5500	5.3304	3.3752	2.6536	-0.3139	3.0613
4.6417	5.3739	3.3174	2.6971	-0.2716	3.0458
4.7231	5.4160	3.2702	2.7557	-0.2166	3.0536
4.8000	5.4560	3.2318	2.8212	-0.1570	3.0748
4.8667	5.4960	3.2100	2.9111	-0.0774	3.1326
4.9263	5.5184	3.1699	2.9370	-0.0548	3.1150
4.9789	5.5388	3.1369	2.9657	-0.0298	3.1071
5.0200	5.5592	3.1185	3.0142	0.0123	3.1308
5.0533	5.5796	3.1140	3.0786	0.0684	3.1824
5.0867	5.6000	3.1200	3.1498	0.1311	3.2511
5.1095	5.6217	3.1491	3.2483	0.2203	3.3693
5.1254	5.6435	3.1992	3.3611	0.3284	3.5277
5.1413	5.6652	3.2705	3.4785	0.4525	3.7231
5.1571	5.6870	3.3743	3.6023	0.6052	3.9795
5.1730	5.7105	3.5542	3.7440	0.8333	4.3875

Table 15:Point-Wise Method Zr-Oxalacetate Logk3 Average Value =4.4584

V2	V3	pL	n-	$\log\frac{(n^{-}-2)}{(3-n^{-})}$	logK3
2.0639	2.4879	6.4090	2.1287	-0.8308	5.5782
2.0703	2.4943	6.2175	2.1451	-0.7702	5.4474
2.0766	2.5006	6.0263	2.1615	-0.7154	5.3109
2.0829	2.5067	5.8351	2.1771	-0.6672	5.1679
2.0892	2.5127	5.6441	2.1924	-0.6230	5.0211
2.0956	2.5188	5.4542	2.2083	-0.5798	4.8744
2.1017	2.5249	5.2655	2.2245	-0.5382	4.7272
2.1073	2.5309	5.0787	2.2415	-0.4970	4.5818
2.1129	2.5370	4.8947	2.2593	-0.4559	4.4388
2.1184	2.5430	4.7139	2.2769	-0.4170	4.2969
2.1240	2.5491	4.5385	2.2951	-0.3782	4.1603
2.1296	2.5552	4.3707	2.3136	-0.3403	4.0304
2.1352	2.5612	4.2132	2.3318	-0.3041	3.9091
2.1408	2.5673	4.0705	2.3508	-0.2674	3.8031
2.1464	2.5733	3.9458	2.3695	-0.2321	3.7137
2.1520	2.5794	3.8430	2.3885	-0.1969	3.6461
2.1575	2.5855	3.7640	2.4085	-0.1608	3.6032
2.1631	2.5915	3.7073	2.4280	-0.1260	3.5813
2.1687	2.5976	3.6712	2.4484	-0.0900	3.5811
2.1743	2.6026	3.6464	2.4627	-0.0649	3.5815
2.1799	2.6070	3.6309	2.4738	-0.0456	3.5853
2.1855	2.6114	3.6241	2.4850	-0.0260	3.5981
2.1911	2.6157	3.6228	2.4958	-0.0072	3.6155
2.1967	2.6201	3.6261	2.5074	0.0129	3.6390
2.2016	2.6245	3.6324	2.5193	0.0336	3.6660
2.2058	2.6288	3.6412	2.5320	0.0556	3.6968
2.2099	2.6332	3.6521	2.5454	0.0791	3.7311
2.2140	2.6376	3.6641	2.5589	0.1029	3.7670
2.2181	2.6419	3.6765	2.5720	0.1260	3.8025
2.2222	2.6463	3.6903	2.5858	0.1507	3.8409
2.2263	2.6507	3.7050	2.5998	0.1757	3.8806
2.2305	2.6550	3.7195	2.6131	0.2000	3.9195
2.2346	2.6594	3.7350	2.6268	0.2252	3.9602
2.2387	2.6638	3.7520	2.6411	0.2520	4.0040
2.2428	2.6681	3.7690	2.6550	0.2784	4.0474
2.2469	2.6725	3.7878	2.6696	0.3067	4.0945
2.2510	2.6769	3.8076	2.6843	0.3360	4.1436
2.2551	2.6812	3.8277	2.6986	0.3650	4.1927
2.2593	2.6856	3.8498	2.7135	0.3964	4.2461
2.2634	2.6900	3.8734	2.7287	0.4292	4.3026
2.2675	2.6943	3.8976	2.7434	0.4620	4.3596
2.2716	2.6987	3.9236	2.7583	0.4965	4.4201
2.2757	2.7071	4.0056	2.7999	0.6017	4.6073
2.2798	2.7172	4.1395	2.8530	0.7635	4.9030

3.2.2. Half integral method

In half integral method, if a graph is plottedn- versus pL, (formation curve), then the corresponding values of pL at n- equal to 0.5 and 1.5, gives logK1and logK2 respectively (Hartley, Burgess, & Alcock.1980). It follows that:

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

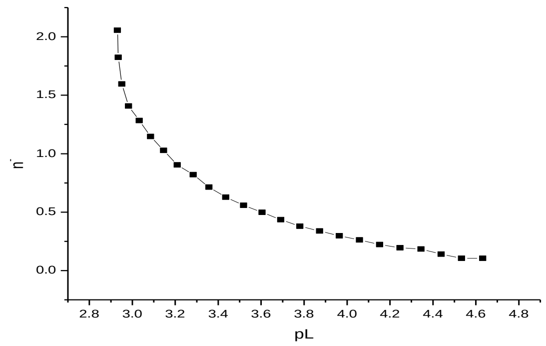

Fig. 7: Cr-Acetate Formation Curve Logk$_1$=3.6 &Logk$_2$=2.958

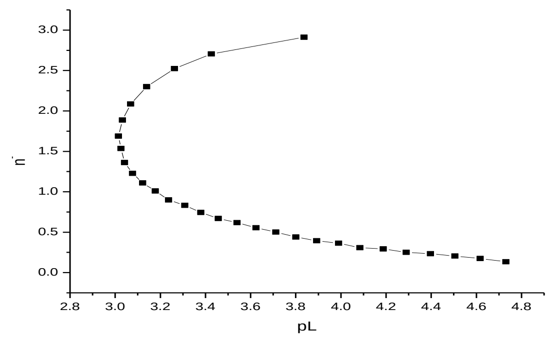

Fig. 8: Cr-Oxalate FormatiomCurve Logk$_1$= 3.71& Logk$_2$=3.04.

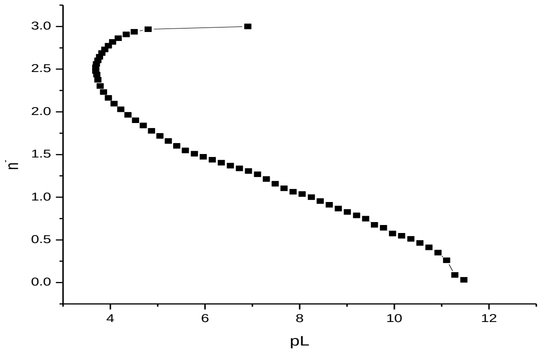

Fig. 9: Cr-Oxalacetate Formation Curve $Logk_1$=10.4 & $Logk_2$=5.76.

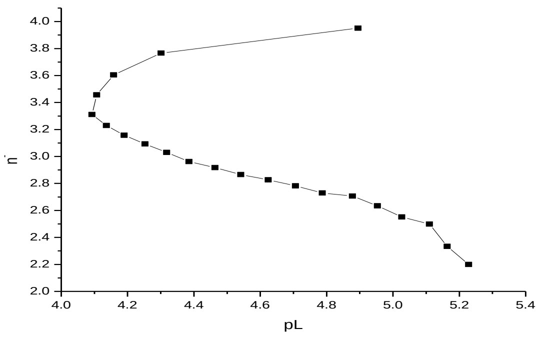

Fig. 10: Zr-Acetate Formation Curve Logk3= 5.11& Logk4=4.113

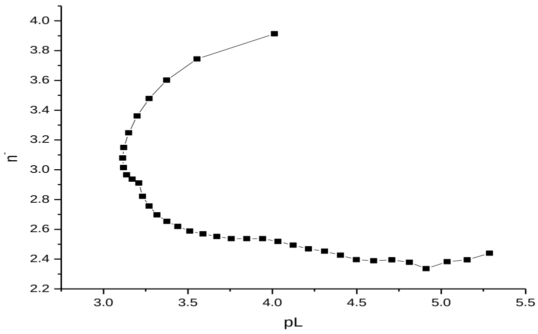

Fig. 11: Zr-Oxalate Formation Curve Logk2=3.3

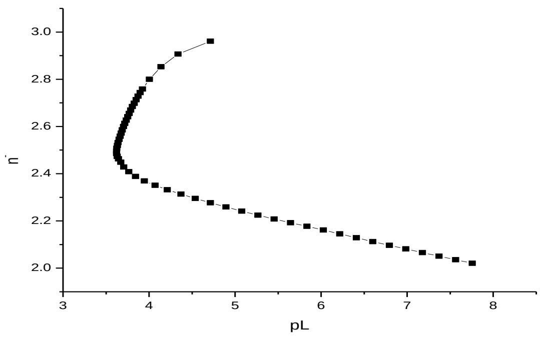

Fig. 12: Zr-Oxalacetate Formation Curve Log K3=3.616

3.2.3. Linear plot method

To estimate the stability constants of chromium acetate by this method log n- /(1-n-) and log(n- -1)/(2-n-) were plotted against corresponding pL for determination of logK1, and logK2 respectively (Anjani et al., 2011).

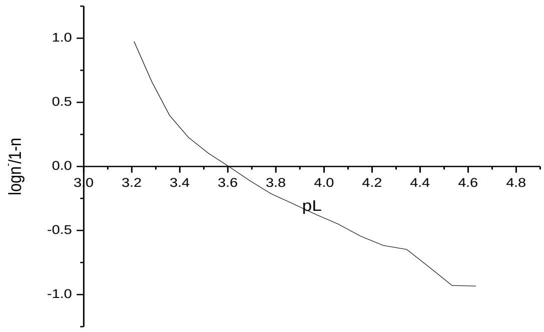

Fig. 13: Linear Plot Method, Cr-Acetate Logk1= 3.6

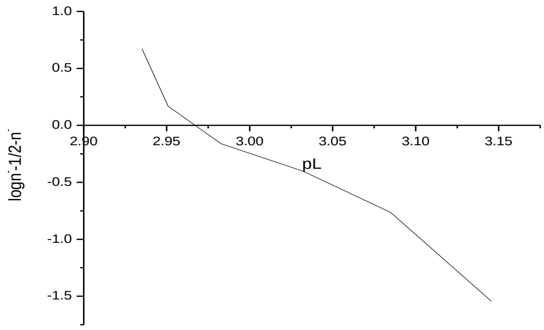

Fig. 14: Linear Plot Method Cr-Acetate Logk2= 2.96

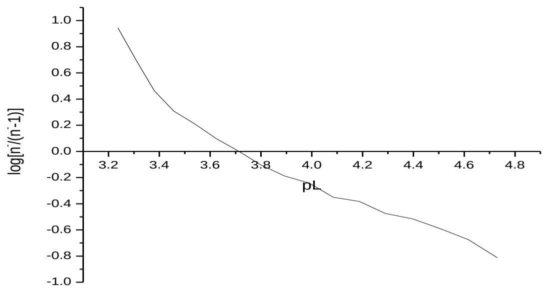

Fig. 15: Linear Plot Method Cr-Oxalate Logk1=3.71

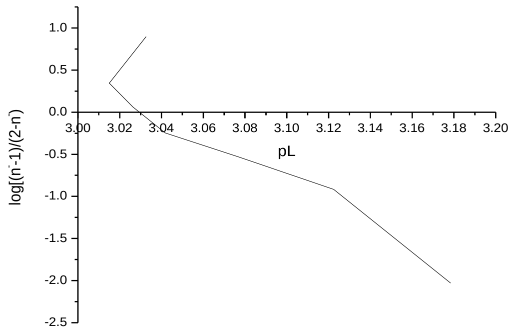

Fig.16: Linear Plot Method Cr-Oxalate Logk2 =3.03

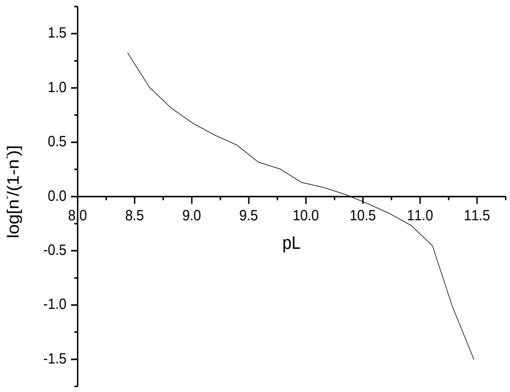

Fig. 17: Linear Plot Method Cr-Oxalacetate Logk1= 10.2

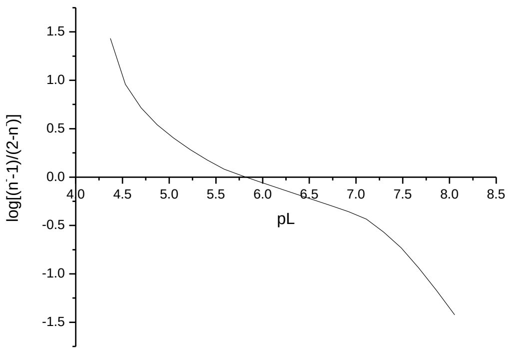

Fig. 18: Linear Plot Method Cr-Oxalacetic Logk2 =5.76

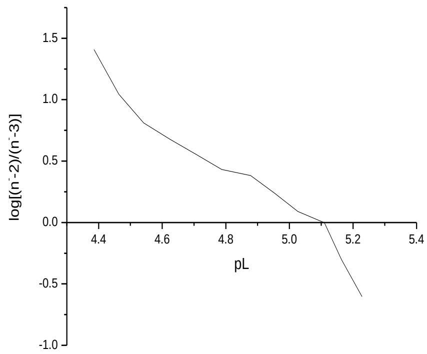

Fig. 19: Linear Plot Method Zr-Acetate Logk3=5.11

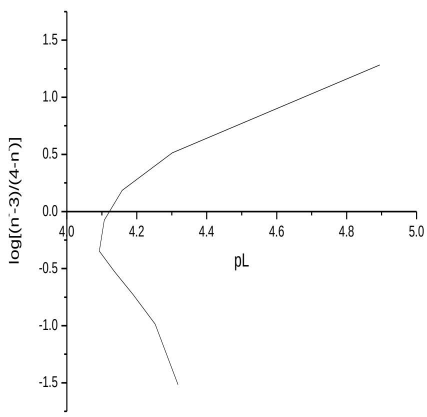

Fig. 20: Linear Plot Method Zr-Acetate Logk4=4.125

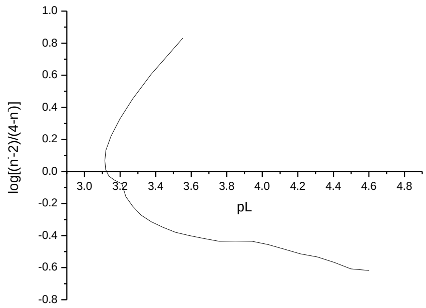

Fig. 21: Linear Plot Method Zr-Oxalate Logk2 = 3.126

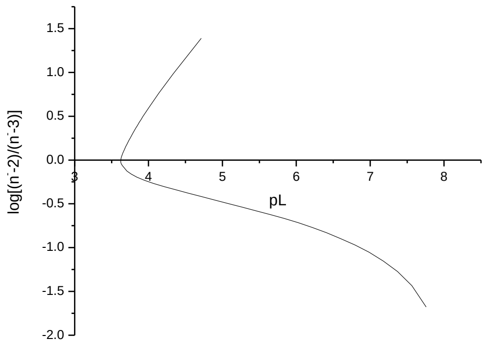

Fig. 22: Linear Plot Method, Zr-Oxalacetic Logk3 =3.64

3.2.4. Least squares method

For N=2 (N is all possible coordination sites), (Hartley, Burgess, & Alcock.1980).

$$\bar{n} = (1-\bar{n})[L]K_1 + (2-\bar{\bar{n}})[L]^2 K_1 K_2.$$

This is equation can be rearrange to give

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \left(\frac{(2-\bar{n})[L]}{(1-\bar{n})}\right) K_1 K_2 + K_1$$

Or

$$\frac{\bar{n}}{(1-\bar{n})[L]} \times \frac{1}{K_1 K_2} - \frac{1}{K_2} = \left(\frac{(2-\bar{n})[L]}{(1-\bar{n})}\right)$$

If only one complex is formed, Hendeson’s or Hasselbalch’s equation can be used (Rossotti & Rossotti, 1955)

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

R2 on caption above is an excel label, names as coefficient of determination, it is a 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).

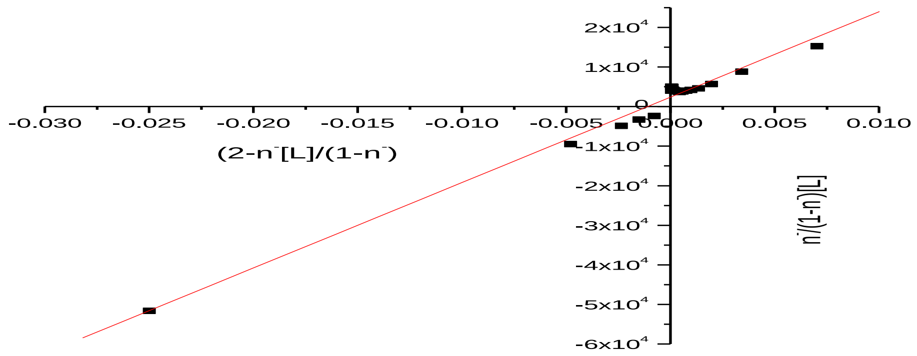

Fig. 23: Least Squared Method Cr-Acetate Logk1=3.3768 & Logk2=2.9242 Linear Regression for Y= Mx + C

Parameter	Value	Error	R^2
Intercep	2381.38229	360.54328	0.99163
Slope	2.15881E6	62833.38787	

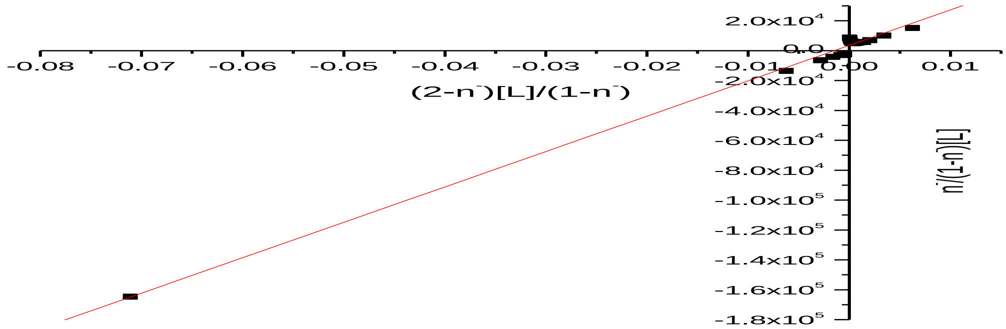

Fig. 24: Least Squares Method Cr-Oxalate Logk1=3.5525&Logk2=2.8221 Linear Regression

Parameter	Value	Error	R2
Intercept	3569.26285	647.38547	0.99652
Slope	2.36902E6	43212.15133	

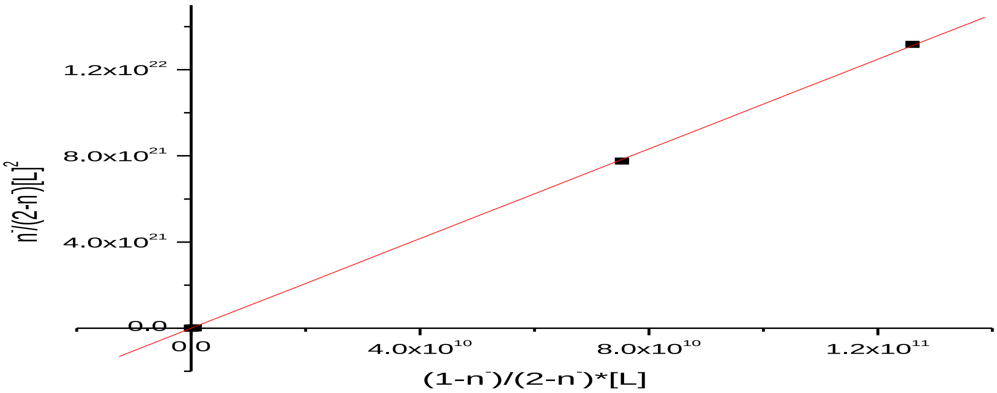

Fig. 25: Least Squares Method Cr-Oxalacetate Logk$_1$= 11.0174 & K$_2$= 7.4604 Linear Regression

Parameter	Value	Error	R2
Intercept	2.91168E7	2.39491E7	0.99997
Slope	9.60579E-12	1.10809E-14	

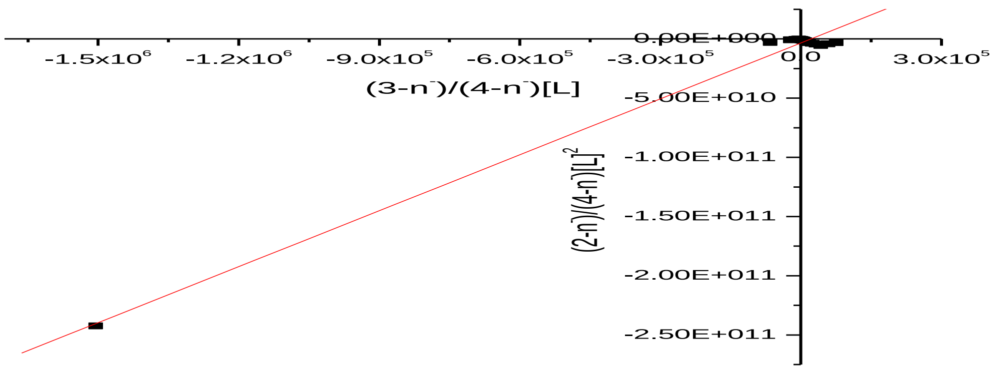

Fig. 26: Least Squares Method Zr-Acetate $Logk_3$=5.1974 & $Logk_4$=4.3259 Linear Regression

Parameter	Value	Error	R2
Intercept	-3.33637E9	1.28213E9	0.9943
Slope	157541.99547	3888.59382	

Table 16: Henderson's Equation Zr-Oxalate, Logk2 Average Value =3.4768

n-	pL	Log[L]	$\log\frac{(n^{-}-2)}{(4-n^{-})}$	Log K2
2.4396	5.2858	-4.4984	-0.6073	3.8911
2.3952	5.1546	-4.4039	-0.5675	3.8364
2.3831	5.0357	-4.3101	-0.5332	3.7769
2.3360	4.9105	-4.2147	-0.5137	3.7010
2.3788	4.8117	-4.1232	-0.4842	3.6390
2.3950	4.7082	-4.0331	-0.4562	3.5767
2.3884	4.6005	-3.9430	-0.4353	3.5077
2.3962	4.4984	-3.8491	-0.4351	3.4140
2.4261	4.4039	-3.7571	-0.4352	3.3219
2.4532	4.3101	-3.6719	-0.4188	3.2530
2.4691	4.2147	-3.5900	-0.4004	3.1896
2.4939	4.1232	-3.5118	-0.3801	3.1317
2.5181	4.0331	-3.4408	-0.3486	3.0922
2.5370	3.9430	-3.3752	-0.3139	3.0613
2.5372	3.8491	-3.3174	-0.2716	3.0458
2.5370	3.7571	-3.2702	-0.2166	3.0536
2.5520	3.6719	-3.2318	-0.1570	3.0748
2.5691	3.5900	-3.2100	-0.0774	3.1326
2.5884	3.5118	-3.1699	-0.0548	3.1150
2.6189	3.4408	-3.1369	-0.0298	3.1071
2.6536	3.3752	-3.1185	0.0123	3.1308
2.6971	3.3174	-3.1140	0.0684	3.1824
2.7557	3.2702	-3.1200	0.1311	3.2511
2.8212	3.2318	-3.1491	0.2203	3.3693
2.9111	3.2100	-3.1992	0.3284	3.5277
2.9370	3.1699	-3.2705	0.4525	3.7231
2.9657	3.1369	-3.3743	0.6052	3.9795
3.0142	3.1185	-3.5542	0.8333	4.3875
3.0786	3.1140	-4.0130	1.3414	5.3544
3.1498	3.1200	-4.4984	-0.6079	3.8911
3.2483	3.1491	-4.4039	-0.5675	3.8364
3.3611	3.1992	-4.3101	-0.5332	3.7769
3.4785	3.2705	-4.2147	-0.5137	3.7010
3.6023	3.3743	-4.1232	-0.4842	3.6390
3.7440	3.5542	-4.0331	-0.4564	3.5767

Table 17: Henderson's Equation, Zr-Oxalacetate Logk3 Average Value =4.4584

pL	n-	log[L]	$\log\left(\frac{(n^{-}-2)}{(3-n^{-})[L]}\right)$	logK3
7.7578	2.0206	-7.7578	-1.6775	6.0802
7.5644	2.0354	-7.5644	-1.4351	6.1294
7.3713	2.0506	-7.3713	-1.2729	6.0984
7.1783	2.0656	-7.1783	-1.1537	6.0246
6.9857	2.0813	-6.9857	-1.0534	5.9323
6.7931	2.0967	-6.7931	-0.9706	5.8224
6.6008	2.1123	-6.6008	-0.8980	5.7028
6.4090	2.1287	-6.4090	-0.8308	5.5782
6.2175	2.1451	-6.2175	-0.7702	5.4474
6.0263	2.1615	-6.0263	-0.7154	5.3109
5.8351	2.1771	-5.8351	-0.6672	5.1679
5.6441	2.1924	-5.6441	-0.6230	5.0211
5.4542	2.2083	-5.4542	-0.5798	4.8744

5.2655	2.2245	-5.2655	-0.5383	4.7272
5.0787	2.2415	-5.0787	-0.4970	4.5818
4.8947	2.2593	-4.8947	-0.4559	4.4388
4.7139	2.2769	-4.7139	-0.4170	4.2969
4.5385	2.2951	-4.5385	-0.3782	4.1603
4.3707	2.3136	-4.3707	-0.3403	4.0304
4.2132	2.3318	-4.2132	-0.3041	3.9091
4.0705	2.3508	-4.0705	-0.2674	3.8031
3.9458	2.3695	-3.9458	-0.2321	3.7137
3.8430	2.3885	-3.8430	-0.1969	3.6461
3.7640	2.4085	-3.7640	-0.1608	3.6032
3.7073	2.4280	-3.7073	-0.1260	3.5813
3.6712	2.4484	-3.6712	-0.0900	3.5811
3.6464	2.4627	-3.6464	-0.0649	3.5815
3.6309	2.4738	-3.6309	-0.0456	3.5853
3.6241	2.4850	-3.6241	-0.0260	3.5981
3.6228	2.4958	-3.6228	-0.0072	3.6155
3.6261	2.5074	-3.6261	0.0129	3.6390
3.6324	2.5193	-3.6324	0.0336	3.6660
3.6412	2.5320	-3.6412	0.0556	3.6968
3.6521	2.5454	-3.6521	0.0791	3.7311
3.6641	2.5589	-3.6641	0.1029	3.7670
3.6765	2.5720	-3.6765	0.1260	3.8025
3.6903	2.5858	-3.6903	0.1506	3.8409
3.7049	2.5998	-3.7049	0.1757	3.8806
3.7195	2.6131	-3.7195	0.2000	3.9195
3.7350	2.6268	-3.7350	0.2252	3.9602
3.7520	2.6411	-3.7520	0.2520	4.0040
3.7690	2.6550	-3.7690	0.2784	4.0474
3.7878	2.6696	-3.7878	0.3067	4.0945
3.8076	2.6843	-3.8076	0.3360	4.1436
3.8277	2.6986	-3.8277	0.3650	4.1927
3.8498	2.7135	-3.8498	0.3964	4.2461
3.8734	2.7287	-3.8734	0.4292	4.3026
3.8976	2.7434	-3.8976	0.4620	4.3596
3.9236	2.7583	-3.9236	0.4965	4.4201
4.0056	2.7999	-4.0056	0.6017	4.6073
4.1395	2.8530	-4.1395	0.7635	4.9030
4.3364	2.9066	-4.3364	0.9869	5.3234

4. Conclusion

The results obtained were nearly the same for all methods, except for least squares method the value of stability constant is lesser than the values obtained by other methods (≤ 0.3). Even in this method we used all data gained from experiment, whereas the data compensate in a linear equation, and the values determined form the intercept and slope, these steps may propagate the error, and the error accumulate on Kn-1. For chromium oxalacetate n- (the average number of ligand attached to metal ion) extends from 0.0305 to 2.9997 which indicates the complexing of 1:3, (and complexes 1:1 and 1:2), that revealsoxalacetic acid binds to chromium as monodentate ligand, even though oxalacetic acid is strongest complexing agent (logK1 >10). Oxalic acid and acetic acid form two complexes with chromium ion 1:1 and 1:2. The difference between the two stability constants for chromium acetate is 0.57 and chromium oxalate 0.8283, this reveals, that the complexes form simultaneously and not in step-wise manner, also the 1:2 may be in trans structure with water.

Zirconium with the monodentate ligand (acetic acid) n- range from 2.1992-3.9504 implies the formation of complexes 1:3 and 1:4 with a difference in stability constants greater than unity, with the bidentate ligand (oxalic acid) n- extends between 2.336 and 3.9128 this reveals the formation of chelate 1:2, that elucidate the four primary valence of zirconium ion, the possible sites for coordination. Zirconium oxalacetate n- lies between 2.0206 and 2.9607, that is complex 1:3, this indicates the themonodendate interaction of the bidentate ligand as same as with chromium, this may be due to the long carbon chain (C4H4O5) in respect to size of metal ions.

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