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

Abdalazeem A. Omar *, Elmugdad A. Ali

Department of chemistry, faculty of science, Sudan University of Science and Technology, Sudan
*Corresponding author E-mail: abdeenomar78@hotmail.com

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 represents 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 bind 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 Creek 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. (Dodle 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 coincide 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±10C, 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 (V0) 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 nA, nL, nT (where nA average number of proton associated with ligand, nL average number of ligand attached to metal ion and nT 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) 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 nA, nL and nT.

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)

\[ n_A = \frac{y}{(V_1 - V_2)(N_0 + E_0)} \]

\[ n_L = \frac{y}{(V_0 + V_1)n_{CL}} \]

\[ n_T = \frac{y}{(V_0 + V_1)n_{CL} + V_2} \]

Where y= the number of dissociable protons, N0 is the concentration of the alkali, E0 is the concentration of the free acid, \( T_{CL} \) is the total ligand concentration, V0 is the total volume of titration solution, V1 and V2 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:

\[ \frac{V_3 - V_2}{V_0} \frac{(E + N)}{(V_0 + V_2)} \]

\[ n = \frac{0}{V_0} - \frac{0}{V_0} \]

Where V2 and V3 are the volumes of alkali required to mixture of (acid + ligand) and (acid+ligand +metal) to bring them to the same pH value, Tcm 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)

\[ PL = \log_{10}[1 + \rho_H \frac{1}{[\text{anti log pH}]^N + V_0 \frac{V_0 + V_3}{V_0}}] \]

Where V3 = 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 nA 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.

\[ y = \frac{y}{(V_1 - V_2)(N_0 + E_0)} \]

Where y= the number of dissociable protons, N0 is the concentration of the alkali, E0 is the concentration of the free acid, \( T_{CL} \) is the total ligand concentration, V0 is the total volume of titration solution, V1 and V2 the volume of alkali added to acid, and acid +ligand respectively to bring each one to the same pH value.

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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 nA scale respectively (Sayyed et al. 2011).

**Table 1: Proton-Ligand Stability Constant of Propionic Acid. Average pKα1=4.8259**

| pH(B) | V1       | V2       | nA       | log \( \frac{n_A}{(1-n_A)} \) | pKα1 |
|-------|----------|----------|----------|--------------------------------|------|
| 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                          | 4.4066 |
| 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                          | 4.4400 |
| 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 |
| 5.3   | 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 pKα1=3.1459**

| pH    | nA       | log \( \frac{(n_A-2)}{(3-n_A)} \) | pKα1 | pH    | nA       | log \( \frac{(n_A-2)}{(3-n_A)} \) | pKα1 |
|-------|----------|---------------------------------|------|-------|----------|---------------------------------|------|
| 2.5   | 2.8833   | 0.8789                          | 3.3789 | 3.1   | 2.5201 | 0.0349                          | 3.3149 |
| 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 pKα2=4.8270**

| pH    | nA       | log \( \frac{(n_A-1)}{(2-n_A)} \) | pKα2 | pH    | nA       | log \( \frac{(n_A-1)}{(2-n_A)} \) | pKα2 |
|-------|----------|---------------------------------|------|-------|----------|---------------------------------|------|
| 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 |
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 ligand titration curve along the volume axis. This is utilized to calculate the values of 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 monoprotonic, 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, indicating 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 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)

| 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 | 0.5297 | 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 |

3.2.2. 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 logKn the value of pL at which n = 0.5 and 1.5 gives logK1 and logK2 respectively. For propanoic acid, third dissociation constant of citric acid.

Table 6: Third Dissociation Constant of Citric Acid. Average pKa=3.8313

Table 7: Point-Wise Calculation Method Cr-Citrate Logk1 (Average Value = 6.1327)

Table 8: Point-Wise Calculation Method Zr-Propanoate Logk3 (Average Value = 11.5165)
Table 9: Point-Wise Calculation Method Zr-Citrate Logk1 (Average Value 7.5967)

| V2  | V3  | n- | \( \text{pL} \) | \( \log \left( \frac{n-1}{2-n} \right) \) | \( \log K2 \) |
|-----|-----|----|-------|----------------|----------|
| 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 | 1.3880 | 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 | 6.6107 | 0.1169  | 6.7375 |
| 2.1138 | 2.6750 | 1.6014 | 6.3148 | 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 |

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

3.2.3. Linear plot method:

Plotting \( \text{pL} (n/n-1) \) and \( \log (n-1)/(2-n) \) versus corresponding \( \text{pL} \) gives \( \log K1 \) and \( \log K2 \) respectively (Anjani et al. 2011).

3.2.4. Least squares method

For estimation of \( K2 \) and \( K3 \) for chromium propanoiate and chromium citrate by this method, linear equation of Rossoiti and Rossotti as expressed below has been employed:
\[ n^- = (1-n^-) [L] K_1 + (2-n^-) [L] K_2 K_1 K_2 \]

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

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

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   | \(n\) | \([L]\) | \((2-n^-)[L]/(1-n^-)\) | \(n^-\) \((1-n^-)[L]\) |
|------|-------|--------|------------------------|------------------------|
| 5.1571| 0.0260| 6.9647E-06| 1.4116E-05             | 3838.3930              |
| 5.0772| 0.1539| 8.3716E-06| 1.8266E-05             | 21723.1864             |
| 4.9885| 0.2207| 1.0267E-05| 2.3442E-05             | 27759.1226             |
| 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             | 36023.8284             |
| 4.4553| 0.5580| 3.5049E-05| 1.0051E-05             | 37171.0648             |
| 4.3660| 0.5989| 4.3056E-05| 0.00014351             | 36478.2783             |
| 4.2805| 0.6359| 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| 1.0000    | -0.0203                | -187051.7592           |
| 3.8987| 1.0386| 0.0001    | -0.0301                | -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    | -2.4942-05             | -9066.0208             |
| 3.6895| 2.1468| 0.0002    | 2.6452E-05             | -9180.3771             |

**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).

\[
\frac{n^-}{(1-n^-)} = \beta_1 [L] \quad \log \frac{n^-}{(1-n^-)} = \log \beta_1 + \log [L]
\]
Since only one complex zirconium propionate is formed, Henderson’s equation is employed.

### Table 12: Determination of Zirconium Propionate Stability Constant by Hasselbach’s Equation Log3 (Average Value = 7.5152)

| n  | log[L] | log \( n^- \) | log \( \frac{n^-}{1 - n^-} \) | log \( \frac{n^- - \log L}{1 - n^-} \) | n  | log[L] | log \( n^- \) | log \( \frac{n^-}{1 - n^-} \) | log \( \frac{n^- - \log L}{1 - n^-} \) |
|----|--------|--------------|-----------------|-----------------|----|--------|--------------|-----------------|-----------------|
| 11.1024 | 0.2107 | 0.2918 | 11.6970 | 5.1828 | 11.1024 | 0.2107 | 0.2918 | 11.6970 | 5.1828 |
| 11.1434 | 0.2207 | 0.2918 | 11.6970 | 5.1828 | 11.1434 | 0.2207 | 0.2918 | 11.6970 | 5.1828 |
| 11.1844 | 0.2307 | 0.2918 | 11.6970 | 5.1828 | 11.1844 | 0.2307 | 0.2918 | 11.6970 | 5.1828 |
| 11.2254 | 0.2407 | 0.2918 | 11.6970 | 5.1828 | 11.2254 | 0.2407 | 0.2918 | 11.6970 | 5.1828 |
| 11.2664 | 0.2507 | 0.2918 | 11.6970 | 5.1828 | 11.2664 | 0.2507 | 0.2918 | 11.6970 | 5.1828 |

### Table 13: Determination of Zirconium Citrate Stability Constant, by Hasselbach’s Equation Log1 (Average Value = 7.5152)

| n  | log[L] | log \( n^- \) | log \( \frac{n^-}{1 - n^-} \) | log \( \frac{n^- - \log L}{1 - n^-} \) | n  | log[L] | log \( n^- \) | log \( \frac{n^-}{1 - n^-} \) | log \( \frac{n^- - \log L}{1 - n^-} \) |
|----|--------|--------------|-----------------|-----------------|----|--------|--------------|-----------------|-----------------|
| 11.2928 | 0.1092 | 0.1129 | 12.3797 | 6.04322 | 11.2928 | 0.1092 | 0.1129 | 12.3797 | 6.04322 |
| 11.0021 | 0.1174 | 0.1102 | 9.4699 | 5.75553 | 11.0021 | 0.1174 | 0.1102 | 9.4699 | 5.75553 |
| 10.7112 | 0.1266 | 0.1077 | 8.8491 | 5.46924 | 10.7112 | 0.1266 | 0.1077 | 8.8491 | 5.46924 |
| 10.4177 | 0.1191 | 0.1047 | 8.4799 | 4.97007 | 10.4177 | 0.1191 | 0.1047 | 8.4799 | 4.97007 |
| 10.1245 | 0.1276 | 0.1024 | 8.1079 | 5.06250 | 10.1245 | 0.1276 | 0.1024 | 8.1079 | 5.06250 |
| 9.83406 | 0.1560 | 0.0934 | 7.6907 | 4.62838 | 9.83406 | 0.1560 | 0.0934 | 7.6907 | 4.62838 |
| 9.54227 | 0.1280 | 0.0943 | 7.5050 | 4.3653 | 9.54227 | 0.1280 | 0.0943 | 7.5050 | 4.3653 |
| 9.24902 | 0.1346 | 0.0924 | 7.0030 | 4.11750 | 9.24902 | 0.1346 | 0.0924 | 7.0030 | 4.11750 |
| 8.95536 | 0.1378 | 0.0855 | 6.5797 | 3.89417 | 8.95536 | 0.1378 | 0.0855 | 6.5797 | 3.89417 |
| 8.66337 | 0.1378 | 0.0764 | 6.0693 | 3.57106 | 8.66337 | 0.1378 | 0.0764 | 6.0693 | 3.57106 |
| 8.37046 | 0.1339 | 0.0705 | 5.5488 | 3.57813 | 8.37046 | 0.1339 | 0.0705 | 5.5488 | 3.57813 |
| 8.07807 | 0.1421 | 0.0807 | 5.0280 | 3.50019 | 8.07807 | 0.1421 | 0.0807 | 5.0280 | 3.50019 |
| 7.78627 | 0.1458 | 0.0783 | 4.5077 | 3.47490 | 7.78627 | 0.1458 | 0.0783 | 4.5077 | 3.47490 |
| 7.49330 | 0.1475 | 0.0743 | 4.9191 | 3.48490 | 7.49330 | 0.1475 | 0.0743 | 4.9191 | 3.48490 |
| 7.20129 | 0.1502 | 0.0721 | 4.7578 | 3.52143 | 7.20129 | 0.1502 | 0.0721 | 4.7578 | 3.52143 |
| 6.91052 | 0.1539 | 0.0695 | 4.5838 | 3.59307 | 6.91052 | 0.1539 | 0.0695 | 4.5838 | 3.59307 |
| 6.62055 | 0.1569 | 0.0625 | 4.4145 | 3.52000 | 6.62055 | 0.1569 | 0.0625 | 4.4145 | 3.52000 |
| 6.33138 | 0.1604 | 0.0534 | 4.2535 | 3.56756 | 6.33138 | 0.1604 | 0.0534 | 4.2535 | 3.56756 |

### 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 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 answer, with difference ≤ 0.3, for a system where N≥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 \( \alpha_n \), n- and \( \alpha \).

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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