Gran Plot

Ion selective electrodes respond to the activity of ions and not to the concentration, in it's strictest definition. pH electrode is a H-ion sensitive electrode.

Thus pH electrodes respond to the activity of hydrogen ions, a_{H+}, by way of pH = -log a_{H+} where $a_{H+} = \gamma_{H+}\, c_{H+}$.

When acid -base titrations are monitored following the pH as a function of the volume of the titrant added, an expression for the pH at the the point a certain volume of the titrant added can be derive as follows (before the end point).

Assume V_a ml of an acid HA, here KHP, of concentration C_{HA} was titrated with the strong base of concentration C_b ; the **volume of NaOH added at a point be V_b.** Let the volume of NaOH reqired to reach the **equivalence point be V_e.**

By Definition: $K_a = \dfrac{a_H \cdot a_A}{a_{HA}}$ charges on H, HA and A the ions not shown

$$K_a = \frac{\gamma_H \cdot C_H \cdot \gamma_A \cdot C_A}{\gamma_{HA} \cdot C_{HA}}$$

$$C_A = \frac{V_b \cdot C_b}{V_a + V_b}$$

because every OH- ion reacted produce A, and is distributed in the new volume.

$$C_{HA} = \frac{V_a \cdot C_a - V_b \cdot C_b}{V_a + V_b}$$

HA left in the new volume

Substituting for concentrations of A and HA in the K_a expresssion;

$$K_a = \frac{\gamma_H \cdot C_H \cdot \gamma_A \cdot C_A}{\gamma_{HA} \cdot C_{HA}}$$

$$K_a = \gamma_H \cdot C_H \cdot \gamma_A \cdot V_b \cdot \frac{C_b}{\left[\left(V_a + V_b\right) \cdot \left(\gamma_{HA} \cdot C_{HA}\right)\right]}$$

Substituting for C_A

$$K_a = \gamma_H \cdot C_H \cdot \gamma_A \cdot V_b \cdot \frac{C_b}{\left[\gamma_{HA} \cdot \left(V_a \cdot C_a - V_b \cdot C_b\right)\right]}$$

Substituting for C_{HA}

upon rearrangement; $$V_b \cdot C_H \cdot \gamma_H = \frac{\gamma_{HA}}{\gamma_A} \cdot K_a \cdot \frac{V_a \cdot C_a - V_b \cdot C_b}{C_b}$$

rewriting; $V_b \cdot 10^{-\,pH} = \frac{\gamma_{HA}}{\gamma_A} \cdot K_a \cdot \frac{V_a \cdot C_a - V_b \cdot C_b}{C_b}$

because by definition; $pH = -\log(a_H)$

further, the third term on the right hand side simplifies to, where V_e is the equivalence point. $\frac{V_a \cdot C_a}{C_b} - V_b = V_e - V_b$

because $C_a \cdot V_a = C_b \cdot V_e$

i.e. $V_b \cdot 10^{-\,pH} = \frac{\gamma_{HA}}{\gamma_A} \cdot K_a \cdot (V_e - V_b)$

Expanding the above expression and upon rearrangement:

$$\left(V_b \cdot 10^{-\,pH}\right) = -\left(\frac{\gamma_{HP}}{\gamma_P} \cdot K_a \cdot V_b\right) + \frac{\gamma_{HP}}{\gamma_P} \cdot K_a \cdot V_e$$

In the region very close to the end point the ratio of the *activity coefficient ratio is practically constant*. Thus a plot of $V_b \cdot 10^{-\,pH}$ vs V_b will yield a straight line of which the slope:

slope = $\frac{\gamma_{HA}}{\gamma_A} \cdot K_a$; if the activity ratio can be calculated we can estimate K_{aHA}.
and the intercept on x axis is the equivalence point !!!

The usefulness of the gran plot is that it allows determination of the end point with data, obtained before the end point. This is closer to the equivalence point than those determined with indicators (which are really end points; such points are often detected 'after the fact').

Submit the following calculations (well documented):

i. Determine the equivalence point from best fit line, compare with the theoretical value.

ii. Spreadsheet or mathcad work sheet to plot $V_b \cdot 10^{-\,pH}$ vs V_b.
ii. Calculation of the activity coefficient ratio at ~95% to the end point.
iv. Second dissociation constant of Phthalic acid, $K_{a,HA} = K_{2aH2A}$ (literature value, find out from the appropriate places)

An example data set worksheet in **Mathcad** is shown below. You may follow the logic of it not necessarily the Mathcad syntax.

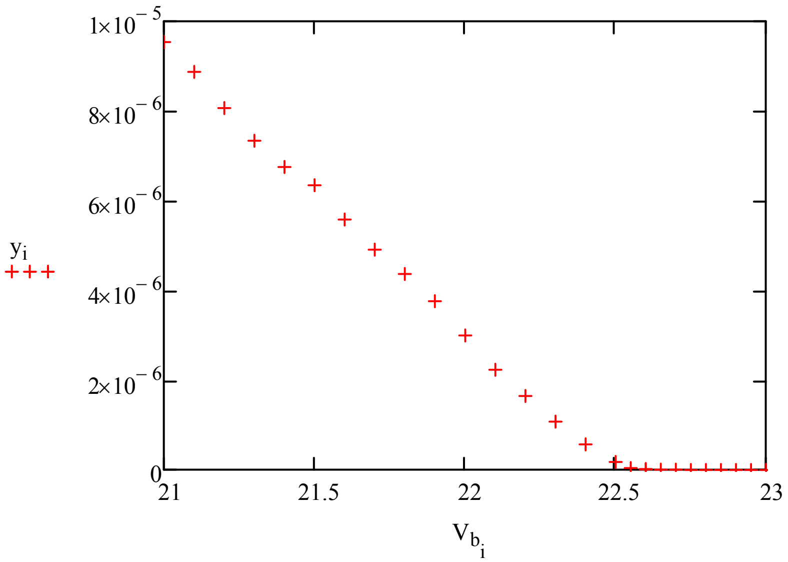
Data from the titration Volume of base added and the pH of the solution after addition of the base :

$$V_b := \begin{pmatrix} 21.000 \\ 21.100 \\ 21.200 \\ 21.300 \\ 21.400 \\ 21.500 \\ 21.600 \\ 21.700 \\ 21.800 \\ 21.900 \\ 22.000 \\ 22.100 \\ 22.200 \\ 22.300 \\ 22.400 \\ 22.500 \\ 22.550 \\ 22.600 \\ 22.600 \\ 22.650 \\ 22.700 \\ 22.750 \\ 22.800 \\ 22.850 \\ 22.900 \\ 22.950 \\ 23.000 \end{pmatrix} \qquad pH := \begin{pmatrix} 6.3424 \\ 6.3760 \\ 6.4192 \\ 6.4624 \\ 6.5008 \\ 6.5296 \\ 6.5872 \\ 6.6448 \\ 6.6976 \\ 6.7648 \\ 6.8656 \\ 6.9952 \\ 7.1296 \\ 7.3168 \\ 7.5952 \\ 8.1088 \\ 8.6944 \\ 9.0736 \\ 9.2992 \\ 9.5536 \\ 9.7024 \\ 9.8416 \\ 9.9472 \\ 10.053 \\ 10.130 \\ 10.211 \\ 10.269 \end{pmatrix}$$

Gran Plot: As Derived before the relationship for Gran plot is:

Set y as; $i := 0..26$ $y_i := V_{b_i} \cdot 10^{-pH_i}$

Plot y vs V_b;



To plot the line; selection of points upto 22.40 mL, before end point from the data above.

$$\text{Vbs} := \begin{pmatrix} 21.000 \\ 21.100 \\ 21.200 \\ 21.300 \\ 21.400 \\ 21.500 \\ 21.600 \\ 21.700 \\ 21.800 \\ 21.900 \\ 22.000 \\ 22.100 \\ 22.200 \\ 22.300 \\ 22.400 \end{pmatrix} \qquad \text{pHs} := \begin{pmatrix} 6.3424 \\ 6.3760 \\ 6.4192 \\ 6.4624 \\ 6.5008 \\ 6.5296 \\ 6.5872 \\ 6.6448 \\ 6.6976 \\ 6.7648 \\ 6.8656 \\ 6.9952 \\ 7.1296 \\ 7.3168 \\ 7.5952 \end{pmatrix}$$

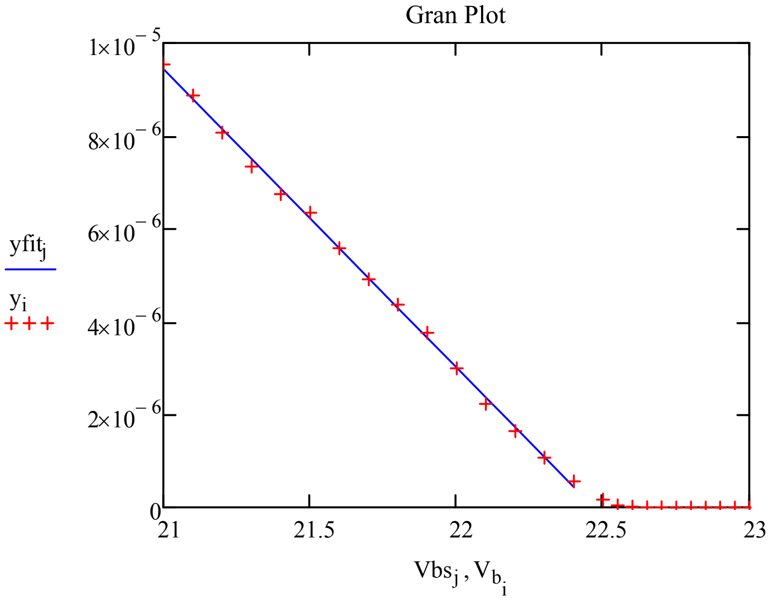
V_bs is the Gran Plot x axis
15 points use here.

Gran Plot y axis $j := 0 .. 14$ $yaxis_j := Vbs_j \cdot 10^{-pHs_j}$

Plot Parameters of the Gran plot best fit line:

$slope(Vbs, yaxis) = -6.42464 \times 10^{-6}$ $intercept(Vbs, yaxis) = 1.44356 \times 10^{-4}$

Best fit line equation: $yfit_j := slope(Vbs, yaxis) \cdot Vbs_j + intercept(Vbs, yaxis)$



Activity Coefficeints for Gran Plot.

The activity coefficients for HA^{-1} and A^{-2} (HP^{-1} and P^{-2}, here) are required to calculate K_a from the Gran plot output. The activity coefficients at about $0.95V_e$ (V_e = equivalence point) will be used here (assuming they do not vary significantly in that region). To calculate activity coefficients, among other factors, μ, is needed. This is how you may calculate μ: assuming the variation of μ near the end point to be minimal.

Find your $0.95V_e$ value first (for the titration involving 50.00mL of KHP). At that point H^+ and OH^- ion concentrations are negligible (so disregard the ionic contribution from them) compared to K^+, Na^+, HP^- and P^{-2} concentrations and the *concentrations* of which are (symbolized as K, Na etc):

$V_e := 22.46 \qquad C_{OH} := 0.100$

Concentrations
assumed for this example

$$C_{KHP} := \frac{C_{OH} \cdot V_e}{50.00}$$

$$K := \frac{50}{0.95 \cdot V_e + 50} \cdot C_{KHP}$$

$$Na := \frac{0.95 \cdot V_e}{0.95 \cdot V_e + 50} \cdot C_{OH}$$

$$HP := 0.050 \cdot \left(\frac{50}{0.95 \cdot V_e + 50} \cdot C_{KHP} \right)$$

$$P := 0.95 \cdot \left(\frac{50}{0.95 \cdot V_e + 50} \cdot C_{KHP} \right)$$

$$\mu := \frac{1}{2} \cdot \left[K \cdot 1^2 + Na \cdot 1^2 + HP \cdot (-1)^2 + P \cdot (-2)^2 \right] \qquad \mu = 0.091$$

Use DHE to estimate γ_P andγ_{HP} for the above μ: assume both pthalate ions have same α.

From the tables:

$$\alpha_P := 600 \qquad \alpha_{HP} := \alpha_P \qquad z_P := -2 \qquad z_{HP} := -1$$

DHE

$$\log(\gamma_P) = \frac{-0.51 \cdot (z_P)^2 \cdot \sqrt{\mu}}{1 + \frac{\alpha_P \cdot \sqrt{\mu}}{305}} \qquad \log(\gamma_{HP}) = \frac{-0.51 \cdot (z_{HP})^2 \cdot \sqrt{\mu}}{1 + \frac{\alpha_{HP} \cdot \sqrt{\mu}}{305}}$$

$\gamma_{HP} := 0.800 \qquad \gamma_P := 0.411$

Calculation of K_a:

Equating the slope to the derived expression for the slope, and solving for K_a;

$$-\left(\frac{\gamma_{HP}}{\gamma_P} \cdot K_a \right) = -6.42464 \times 10^{-6}$$

$$K_a := \frac{6.42464 \times 10^{-6} \cdot \gamma_P}{\gamma_{HP}}$$

$K_a = 3.301 \times 10^{-6}$ at room temperature.