Scholars Academic Journal of Pharmacy
Abbreviated Key Title: Sch Acad J Pharm
ISSN 2347-9531 (Print) | ISSN 2320-4206 (Online)
Journal homepage: http://saspublishers.com

OPEN ACCESS

Pharmacy

Finding Singular Points of the Titration Curve by Solving the Equation of State of the Electrolyte Solution

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DOI: 10.36347/sajp.2023.v12i03.004 | **Received:** 08.02.2023 | **Accepted:** 25.03.2023 | **Published:** 28.03.2023

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Abstract

Original Research Article

Electrolyte solutions consisting of acids, bases, and their salts have one or more singular points. These special points include the equivalence points of the titration curves and the coordinates (composition) of the maximum buffer capacity of the buffer solution. Knowledge of these points is necessary for solving problems of analytical and preparative chemistry. This paper describes a method for finding singular points of an electrolyte solution by solving the general equation of state derived in our previous work.

Keywords: Acid-base titration curve, equivalence point, buffer capacity, electrolyte, general equation of state.

INTRODUCTION

Having a general equation for a titration curve has been a dream of chemists for a long time. The first scientist known to us to advance in this direction was Charlote G, he derived the Charlote equation relating the concentration of hydrogen ions, the dissociation constant of a weak acid, the initial concentrations of an acid and a strong base, and the Delta - the value equal to the difference in the concentrations of hydrogen ions and hydroxide ions in a solution (Charlot G 1947). The Charlote equation can be converted to a polynomial of the third degree (Charlotte Equation 2023), the resolution of which with respect to hydrogen ion concentrations leads to a theoretical curve for the titration of a weak monobasic acid with a strong base. De Levie derived equations for acid-base titration for various acids and their mixtures, the variables in his equations are the volumes of analyte and titrant and the variable Delta introduced by Charlotte (De Levie R 1995). Our task was: 1) To derive a general equation of state for an electrolyte solution using natural variables and parameters. 2) The solution of this equation with respect to the concentration of hydrogen ions and, hence, the derivation of the equation of the titration curve. 3) Use of the general equation of state to find singular points of state of the solution, namely, equivalence points and points of maximum buffer capacity of the solution. In our previous work (Yefimov S 2023), we described the derivation of the general equation of state for an electrolyte solution at the constant unit volume, and the solution of this equation with respect to the concentration of hydrogen ions. We showed good agreement between the theoretical model and experimental data, which allowed us to verify the correctness of the theory. In this paper, we show how, by solving the general equation of state, to find singular points, namely, equivalence points and points of maximum buffer capacity of the solution. Theoretical calculations are compared with the previously accumulated experimental data.

MATERIALS AND METHODS

Microsoft EXCEL spreadsheet was used for calculations and the creation of graphs. The experiment was performed on HI2221 Calibration check pH/ORP Meter “HANNA instrument” with glass electrode HI1131. The instrument was calibrated using 3 standard solutions: pHRed-4, pHYellow-7, and pHBlue-10 “Inorganic Ventures”. Reagents: Hydrochloric acid 1.0M standard solution “Lab Chem”; Acetic acid glacial “Sigma-Aldrich”; Phosphoric acid for HPLC 85% Sigma-Aldrich”; Sodium hydroxide solid “Sigma-Aldrich”; Water for HPLC “TEDIA”. A secondary standard solution of NaOH 0.9–1.1 M was prepared by dissolving 40 g of solid NaOH in water, followed by titration with a standard HCl solution to check the concentration. Solutions of acids with a concentration of about 0.001 M were prepared by dissolving aliquots of acids in 1L of water, followed by titration with standard NaOH solution to control the concentration. Experimental titration curves were obtained by titrating

Citation: Stanislav V. Yefimov. Finding Singular Points of the Titration Curve by Solving the Equation of State of the Electrolyte Solution. Sch Acad J Pharm, 2023 Mar 12(3): 74-78.

10^{-3} mol of acids diluted in 1 L of water with a 1.0 M standard NaOH titrant. Such an analyte/titrant concentration ratio makes it possible to consider the volume constant since its change during the titration process is negligibly small. The basis of the method of finding the singular points is as follows: The singular points of the electrolyte solution are visible on the curve of acid-base titration; these are the points of the inflection of the curve. At the inflection points, the second derivative of the function vanishes. Knowing the function, we can find the coordinates of singular points, that is, the composition of the solution. The function whose graph is the titration curve is known to us (Yefimov S 2023); this is the transformed general equation of state. Thus, the determination of equivalence points and points of maximum buffer capacity of the solution is reduced to the mathematical problem of determining the coordinates of the inflection points of the curve (BYU’S Inflection point 2023).

RESULTS AND DISCUSSION

The general equations of state for electrolyte solutions, which we use here to find singular points, are presented in Table 1. The derivation of these equations is given in (Yefimov S 2023).

Table 1: Polynomial coefficients of the general equation of state of an electrolyte solution at a constant unit volume, consisting of a weak or strong acid and a strong base

Max. degree.	triprotic acid. (AH_3) $h^5 + a*h^4 + b*h^3 + c*h^2 + d*h + e = 0$	diprotic acid. (AH_2) $h^4 + a*h^3 + b*h^2 + c*h + d = 0$	monoprotic acid. (AH) $h^3 + a*h^2 + b*h + c = 0$	Strong acid. $h^2 + a*h + b = 0$
h^5	1	0	0	0
h^4	B + K1+K2+K3	1	0	0
h^3	K1*K2 + K1*K3 + K2*K3 + B*(K1 + K2 + K3) – W – A*K1	B + K1 + K2	1	0
h^2	K1*K2*K3 + B*(K1*K2 + K1*K3 + K2*K3) – W*(K1 + K2 + K3) – A*(2*K1*K2 + K1*K3)	B*(K1 + K2) + K1*K2 - W – A*K1	B + K1	1
h	B*K1*K2*K3 – W*(K1*K2 + K1*K3 + K2*K3) – 3*A*K1*K2*K3	B*K1*K2 – W*(K1 + K2) -2*A*K1*K2	B*K1 – W – A*K1	B - A
h^0 (const.)	-W*K1*K2*K3	-W*K1*K2	-W*K1	-W

***Note 1**: The equation of state for an aqueous solution of a weak base and a strong acid is symmetrical to those in the table. The acid dissociation constants are replaced by the base dissociation constants, A is replaced by B, B is replaced by A, and h is the number of moles of hydroxide ions in the solution.*

Determination of Equivalence Points by Double Differentiation of the Equation of State

The equivalence point corresponds to the inflection of the titration curve (B=B(ph)). To find this point, we need to calculate the second derivative (B") with respect to ph of the equation of state B=B(h), equate it to zero, and find the roots of the resulting equation (BYU’S Inflection point 2023). Finding the roots of equation B”=0 is somewhat easier than finding the roots of the Equation of State (Yefimov S 2023) since we only need the numerical values of the singular points, that is, we can use any numerical method, for example, Newton’s *root-finding algorithm*. Here we will apply an illustrative method of finding the roots, the Zooming Method. We will not calculate anything, but we will scale the plot of B" =B"(ph) and find the coordinate of the point of intersection of the curve with the O-ph axis.

To find out the first and second derivative of B, let's make a change of variables: $h=10^{-y}$, where y=ph.

The derivative of h with respect to y is equal to $-10^{-y}*\ln(10)$, i.e. h'= -h*&, where &=ln(10).

The procedure for finding derivatives consists of 5 consecutive operations:

1) From the equation of state in normal form ($P=0=h^5 + a*h^4 + b*h^3 + c*h^2 + d*h + e$) extract B=B(h).
2) Find the first derivative of P' with respect to ph, given that h'= -h*&.
3) Extract B'=B'(h).
4) Find the second derivative of P" with respect to ph, given that h'= -h*&
5) Extract the desired second derivative: B"=B"(h)

Strong Acid and Strong Base

$h^2 + (B - A)*h - W = P = 0$

$B = (W + h*A - h^2)/h = W/h + A – h$

$P'_{(y)} = -2*h^2*\& - h*B_{(y)}*\& + B'_{(y)}*h + h*A*\& \to$

$B'_{(y)}/\& = 2*h + B_{(y)} – A$ (first derivative)

$P''_{(y)} = 4*h*\&^2 + h*B_{(y)}*\&^2 – 2*h*(B'_{(y)}/\&)*\&^2 + h*B''_{(y)}*\&^2 – h*A*\&^2 \to$

$B''_{(y)}/\&^2 = A - B_{(y)} + 2*(B'_{(y)}/\&) – 4*h$ (second derivative)

$B''_{(y)}/\&^2 = W/h – h$

One singular point is the point of equivalence. $B''(y)/\&^2 = 0 = W/h - h$, $h= \pm sqrt(W)$, We choose positive root; $h = sqrt(10^{-14}) = 10^{-7}$, or ph= 7. The Zooming Method (Figure 1 c) gives us the same result pH=7.

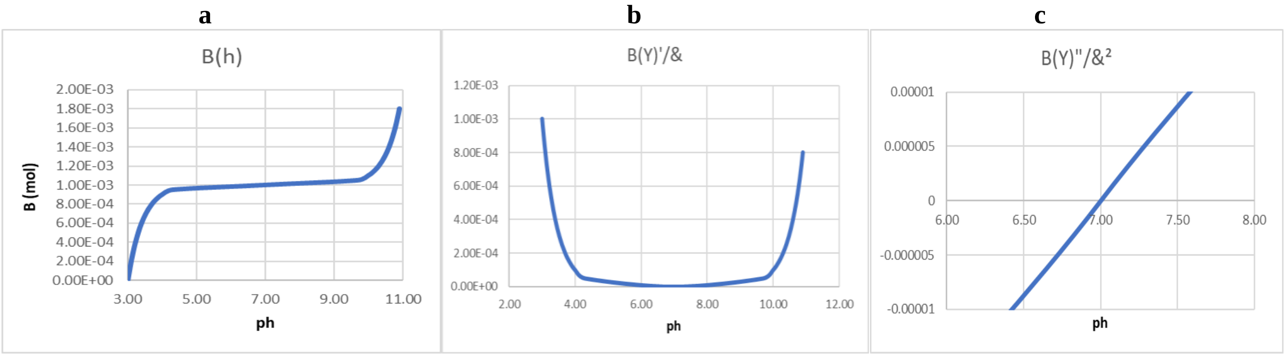

Figure 1 (a, b, c): Hydrochloric acid 10^{-3} mol in 1L, a- theoretical titration curve B=B(ph), b – first derivative, and c – second derivative

Week Monoprotic Acid

The equation of state, its first and second derivatives look like this:

$P=h^3+h^2*(B+K)+h*(B*K-W-A*K)-W*K=0$, extract B:

$B = (W*K + h*(W + A*K) - h^2*K - h^3)/(h^2 + K*h)$

$P'= -3*h^3*\&-2*h^2*(B+K)*\&+h^2*B'-h*(B*K-W-A*K)*\&+h*B'*K=0$, extract B':

$B'/\&= (B * (2h^2 + K*h) + 3h^3 + 2h^2*K - h*(W+A*K))/(h^2 + K*h)$

$P''=9*h^3*\&^2+4*h^2*(B+K)*\&^2-4*h^2*B'*\&+B''*h^2+h*(B*K-W-A*K)*\&^2-2*h*B'*\&+B''*h*K=0$, extract B'':

$B''/\&^2= (B'/\& *(4*h^2 + 2*h*K) - B*(4*h^2 + h*K) - 4*K*h^2 - 9*h^3 + h*(W + A*K))/(h^2 + h*K)$

The estimated pH in the equivalence point by Zooming Method is 7.88 (Figure 2 c).

Calculation by the formula [$$]: ph=7 + (pK-pB)/2 (Yefimov S 2023) gives us the same result: 7+(pK-pB)/2=7+(4.759-3)/2=7.88

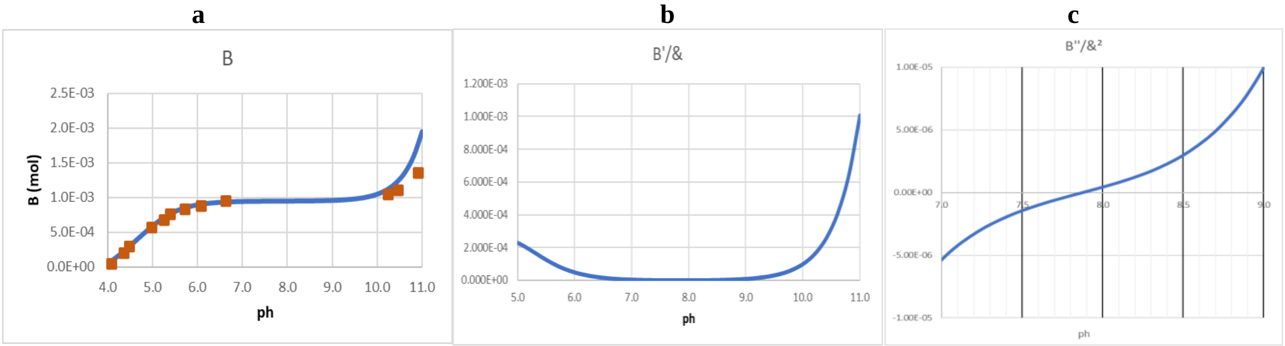

Figure 2 (a, b, c): Acetic acid $0.95*10^{-3}$ mol in 1L, $K= 1.75*10^{-5}$. a- theoretical titration curve B=B(ph) and experimental points (symbols)**, b – first derivative, and c – second derivative**

Week diprotic acid (AH2), $h^4 + a*h^3 + b*h^2 +c* h + d = P=0$.

$P= h^4+ B*h^3+h^3*(k1+k2) + B*h^2*(k1+k2) +h^2*(k1*k2 - W - A*k1) + B*h*k1*k2 - h*((k1+k2)*W+ 2*A*k1*k2) - W*k1*k2 = 0$, extract B:

$B=(-h^4-h^3*K1-h^3*K2- h^2*(K1*K2-W-K1*A)+h*((K1+K2)*W+2*A*K1*K2)+W*K1*K2)/(h^3+ h^2*(K1+K2)+h*K1*K2)$

$P'= -4*h^4*\& - 3*B*h^3*\&+ B'*h^3 - 3*h^3*(k1+k2)*\& - 2*B*h^2*(k1+k2)*\& + B'*h^2*(k1+k2) - 2*h^2*(k1*k2 - W - A*k1)*\& - B*h*k1*k2*\&+ B'*h*k1*k2 + h*((k1+k2)*W+ 2*A*k1*k2)*\& = 0$ extract B':

$B'=(4*h^4+3*h^3*(K1+K2)+2*h^2*(K1*K2-W-A*K1)-h*(W*(K1+K2)+2*A*K1*K2)+B*(3*h^3+2* h^2*(K1+K2)+h*K1*K2))/(h^3+ h^2*(K1+K2)+h*K1*K2)$

$P''= 16*h^4*\&^2 + 9*h^3*B*\&^2-6*B'/\&*h^3*\&^2 + B''*h^3 + 9*h^3*(k1+K2) *\&^2 + 4*h^2*B*(k1+k2) *\&^2 - 4*B'/\&*h^2*(k1+k2) *\&^2 + B''*h^2*(k1+k2) + 4*h^2*(k1*K2-W-AK1) *\&^2 + h*B*k1*k2*\&^2 - 2*B'/\&*h*k1*k2*\&^2 + B''*h*k1*k2 - h*(W*(k1+k2)+2*A*k1*k2) *\&^2= 0$, extract B'':

$B''/\&^2=(-16*h^4-9*h^3*(K1+K2)-4*h^2*(K1+K2-W-A*K1)+h*(W*K1*K2+2*A*K1*K2)+B'/\&*(6*h^3+4* h^2*(K1+K2)+2*h*K1*K2)-B*(9*h^3+4* h^2*(k1+K2)+h*K1*K2))/(h^3+ h^2*(K1+K2)+h*K1*K2)$

The roots of the B''/&2=0 equation are found by the Zooming Method (Figure 3 c). We have three roots that correspond to two points of equivalence and one point of maximum buffer capacity between them. The points of equivalence are 5.1 pH (AH2 +BOH = AHB + HOH) and 9.1 pH (AHB +BOH = AB2 + HOH). The point of maximum buffer capacity is pH=7.19.

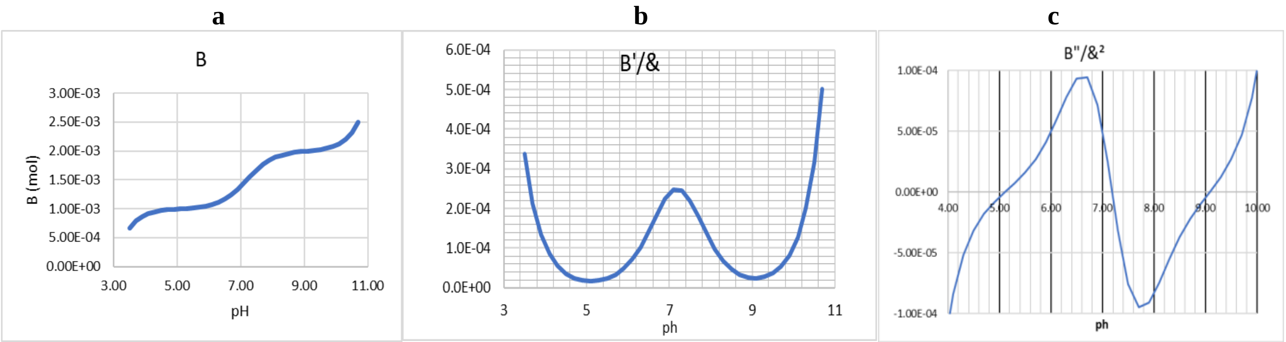

Figure 3 (a, b, c): Sulfurous acid, 0.001 mol in 1L, K1= 1.4*10^{-2}, K2= 6.5*10^{-8}. a- theoretical titration curve B=B(ph), b – first derivative, and c – second derivative

Week triprotic acid (AH3).

To reduce the length of formulas, we introduce the following notation:

a=K1+K2+K3

b=K1*K2+K1*K3+K2+K3

c=K1*K2*K3

d=b-W-A*K1

e=c-W*a-A*(2*K1*K2+K1*K3)

f=W*b+3*A*c

g=W*c

Equation of state:

P=h5+h4*(B+a)+h3*(B*a+d)+h2*(B*b+e)+h*(B*c-f)-g=0. extract B:

B= (-h5-h4*a-h3*d-h2*e+h*f+g) / (h4+h3*a+h2*b+h*c)

Remember: h’=-h*&

P’= -5*h5*&-4*h4*(B+a)*&+h4*B’-3*h3*(B*a+d)*&+h3*B’*a-2*h2*(B*b+e)*&+h2*B’*b- h*(B*c -f)*&+ h*B’c= 0. extract B’:

B’/&= [B*(4*h4+3*h3*a+2*h2*b+h*c) +5*h5+4*h4*a+3*h3*d+2*h2*e-h*f)] / (h4+h3*a+h2*b+h*c)

P”=25*h5*&2+16*h4*(B+a)*&2-8*h4*B’*&+h4*B”+9*h3*(B*a+d)*&2-6*h2*B’*a*&+h3*B”*a+ 4*h2*(B*b+e)*&2-4*h2*B’*b*&+h2*B”*b+h*(B*c-f)*&2-2*h*B’*c*&+h*B”*c=0. extract B”:

B”/&2= [2*B’/&*(4*h4+3*h3*a+2*h2*b+h*c)-B*(16*h4+9*h3*a+4*h2*b+h*c) -25*h5-16*h4*a-9*h3*d-4*h2*e+h*f)] / (h4+h3*a+h2*b+h*c)

The roots of the B”/&2=0 equation are found by the Zooming Method (Figure 4 c). We have three roots that correspond to two points of equivalence and one point of maximum buffer capacity between them. The points of equivalence are 5.2 pH (AH3 +BOH = AH2B + HOH) and 9.0 pH (AH2B +BOH = AHB2 + HOH). The point of maximum buffer capacity is pH=7.2.

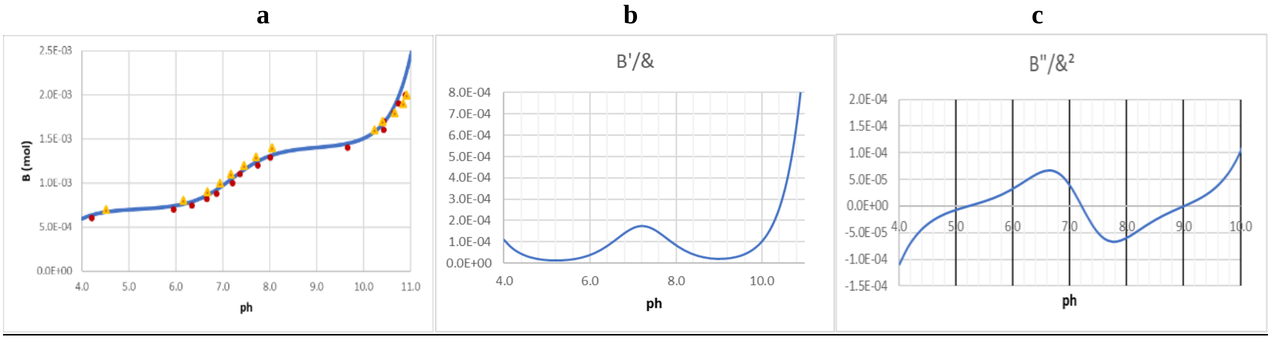

Figure 4 (a, b, c): Phosphoric acid 7*10-4 mol in 1L, K1= 6.9*10-3, K2=6.2*10-8; K3=4.8*10-13 ,. a- theoretical titration curve B=B(ph) and experimental points (symbols), b – first derivative, and c – second derivative

CONCLUSION

This work completes a series of two papers devoted to the derivation of the General Equation of State of an electrolyte solution and its application for analytical purposes. The general equation of state is used to find the function of the acid-base titration curve and to determine the singular points, namely the equivalence points and points of maximum buffer capacity of the solution. The theory agrees well with experiments and with calculations made by other, independent methods. The derived equations will help to create and analyze solutions with a given acidity and buffer capacity. In the future, it is planned to extend the theory to more concentrated solutions, and here one cannot do without the use of activity coefficients.

Abbreviations:

K1, K2, and K3 - dissociation constants of the first, second, and third stages, respectively.

A – a number of moles of acid added to the solution.

B – a number of moles of base added to the solution.

h – a number of moles of hydrogen ions (H^+) in solution

W – the Water Ionization Constant (Kw)

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