

## CHAPTER. I



### INTRODUCTION

Potentiometric Titration (Christian, 1986) is the method, which involves measuring the potential of a suitable indicator electrode or pH as a function of titrant volume. This method is widely applicable and provides inherently more accurate data than the corresponding method that makes use of indicators. It is particularly useful for titration of colored or turbid solutions and for detecting the presence of unsuspected species in a solution. It is readily applied with automatic titration devices.

There are many methods for the determination of equivalent volume in potentiometric titration. Titration curve method can determine the equivalent volume by plotting the curve between potential or pH as a function of volume of titrant. The equivalent point will be located on the steeply rising portion of the curve. The procedure for determination of equivalent volume in this method are Tubb's or circle fitting procedure (Tubb, 1954), the Kohn-Zitko procedure (Anfalt and Jagner, 1971), the bisection procedure (Jeffery et al. 1978) and the parallel tangent

procedure (Jeffery et al.). Differential method (Skoog, West and Holler, 1990) can be used to determine the equivalent volume by plotting the difference in potential or pH between each of the addition of titrant as the function of average volume. This method involves the procedure of first derivative, second derivative, Cohen (Cohen, 1966) and Liteanu-cormos (Liteanu and Cormos, 1960).

Moreover, the Gran's method is used for determination of the equivalent volume. This method was studied by many scientists, such as; Gran(1952), Rossotti (1956), Ingman and Still(1966), Seksiri(1986) and Juthamas (1988). It is based on mass balance, charge balance and equilibrium equation. This method can be used to determine the equivalent volume of weak acid solution by extrapolation of the straight lines before equivalent point called G plot and after equivalent point called V plot. This method has several advantages when compared to potentiometric titration curves and differential plots. The graphical analysis is a straight line rather than a curve, so fewer points are needed to define it; and the points can be taken at regular intervals instead of being bunched in a narrow region around the equivalent point. The portions of the curve, which are used in this technique, are before the equivalent point or after the

equivalent point. Also, the linear extrapolation used in this method can provide more precise results than those obtained by the differential method, especially for asymmetrical titration curves. The results of these study suggested that Gran's method would yield the equivalent volume which were statistical indifference from the official method in USP XX.

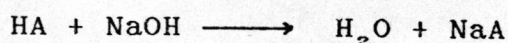
The derivation of Gran's equation could be described, as followed.

Derivation of Gran Equation for Titration Data Prior to Equivalent Point

The weak acidic compound could be classified into neutral and ionized weak acid.

1. Neutral Weak Acid

When a weak acid, HA, was titrated with a strong base (sodium hydroxide)



Dissociation reaction of weak acid



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$
 Eq. 1

which  $K_a$  = The dissociation constant of weak acid.

The solution must be electrically neutral, meaning that

$$[\text{A}^-] + [\text{OH}^-] = [\text{Na}^+] + [\text{H}^+]$$
 Eq. 2

and at the equivalent point

$$V_E N = (V_o + V) C_{HA}$$
 Eq. 3

which  $V_E$  = Volume of base equivalent to weak acid,  
called equivalent volume

$N$  = Normality of titrant

$V_o$  = Initial volume of solution

$V$  = Volume of titrant

$C_{HA}$  = The concentration of weak acid

The concentration of sodium ion at any volumes of titrant was

$$[\text{Na}^+] = \frac{VN}{(V_o + V)}$$
 Eq. 4



and the fact that

$$C_{HA} = [HA] + [A^-] \quad \text{Eq. 5}$$

When combined Equation 2 and 4 , gave

$$[A^-] = VN / (V_o + V) + [H^+] - [OH^-] \quad \text{Eq. 6}$$

substitution of Equation 6 into Equation 5 and combining it with Equation 3

$$V_E N / (V_o + V) = [HA] + VN / (V_o + V) + [H^+] - [OH^-]$$

Which might be rearranged to ,

$$[HA] = V_E N / (V_o + V) - \{ VN / (V_o + V) + [H^+] - [OH^-] \} \quad \text{Eq. 7}$$

Substitution of Equation 6 and Equation 7 into Equation 1

$$K_a = \frac{[H^+] \{ VN / (V_o + V) + [H^+] - [OH^-] \}}{V_E N / (V_o + V) - \{ VN / (V_o + V) + [H^+] - [OH^-] \}} \quad \text{Eq. 8}$$

and rearrangement gave

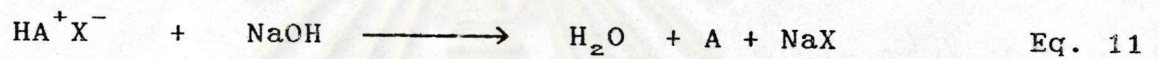
$$G [H^+] = K_a V_E N - K_a G \quad \text{Eq. 9}$$

where

$$G = VN + (V_0 + V) ([H^+] - [OH^-]) \quad \text{Eq. 10}$$

## 2. Ionized Weak Acid

When ionized weak acid, such as  $HA^+X^-$  was titrated, the reaction was



and dissociation reaction of weak acid was



$$K_a = [H^+] [A] / [HA^+] \quad \text{Eq. 13}$$

charge balance of this titration solution was

$$[H^+] + [Na^+] + [HA^+] = [OH^-] + [X^-] \quad \text{Eq. 14}$$

At the equivalent point

$$C_{HA^+} = [X^-] = V_E N / (V_0 + V) \quad \text{Eq. 15}$$

which  $C_{HA^+}$  = The concentration of ionized weak acid

and

$$C_{HA^+} = \frac{V_E N}{(V_o + V)} = [HA^+] + [A] \quad \text{Eq. 16}$$

Substitution Equation 4 in Equation 14

$$[HA^+] + [H^+] + \frac{VN}{(V_o + V)} = [OH^-] + [X^-] \quad \text{Eq. 17}$$

Substitution Equation 15 into Equation 17

$$[HA^+] = \frac{V_E N}{(V_o + V)} - \frac{VN}{(V_o + V)} - [H^+] + [OH^-] \quad \text{Eq. 18}$$

Equation 16 was subtracted by Equation 18, yielded

$$[A] = \frac{VN + [H^+] - [OH^-]}{(V_o + V)} \quad \text{Eq. 19}$$

Substitution Equation 18 and 19 in Equation 13, gave

$$K_a = \frac{[H^+] \{ VN / (V_o + V) + [H^+] - [OH^-] \}}{V_E N / (V_o + V) - \{ VN / (V_o + V) + [H^+] - [OH^-] \}} \quad \text{Eq. 20}$$

and rearrangement gave

$$G [H^+] = K_a V_E N - K_a G \quad \text{Eq. 21}$$

Eventhough the ionized weak acid was in the form of  $K^+HA^-$ , the Gran equation could obtain in the same manner as Equation 21, which the ionized weak acid was in the form of  $HA^+X^-$ .

It was found that Equation 9 and 21 were identical. The slope of these linear equation was the dissociation constant ( $K_a$ ) and the term of  $K_a V_E N$  was the intercept of these equations. So, the equivalent volume of weak acidic compound could be obtained from the intercept of the equation.

#### Derivation for Titration Data after Equivalent Point

The weak acidic compound could be classified into neutral and ionized weak acid.

##### 1. Neutral Weak Acid

After equivalent point, the concentration of HA was negligible. The charge balance of the solution was



$$[A^-] + [OH^-] = [Na^+] + [H^+] \quad \text{Eq. 22}$$

Where  $[A^-]$  was the concentration of conjugate base of a weak acid, HA.

The mass balance of weak acid was

$$[A^-] = C_{HA} = V_E N / (V_o + V) \quad \text{Eq. 23}$$

Equation 23 was substituted in Equation 22, and rearrangement gave

$$[OH^-] - [H^+] = [Na^+] - V_E N / (V_o + V) \quad \text{Eq. 24}$$

In the alkaline region, generally  $[OH^-] \gg [H^+]$ , Equation 24 could be reduced to

$$[OH^-] = [Na^+] - V_E N / (V_o + V) \quad \text{Eq. 25}$$

Equation 4 was substituted in Equation 25 and  $K_w = [H^+][OH^-]$  gave,

$$K_w / [H^+] = V_N / (V_o + V) - V_E N / (V_o + V) \quad \text{Eq. 26}$$

which  $K_w =$  The ionization constant of water

Which could be rearranged to

$$KwV_T / [H^+] = (V - V_E) N \quad \text{Eq. 27}$$

Where  $V_T = V_o + V$

In this case, the plot of  $KwV_T$  vs  $V$  would give a linear relationship of which  $N$  was slope and from intercept,  $V_E$  could be obtained.

## 2. Ionized Weak Acid

If an ionized weak acid, such as  $HA^+X^-$ , was titrated, charge balance of the solution after equivalent point was

$$[X^-] + [OH^-] = [Na^+] + [H^+] \quad \text{Eq. 28}$$

and the mass balance of the weak acid was

$$[X^-] = C_{HA^+} = V_E N / (V_o + V) \quad \text{Eq. 29}$$

which  $C_{HA^+}$  = The concentration of ionized weak acid

In the similar way as derived early, Equation 28 and 29 would give

$$K_w V_T / [H^+] = (V - V_E)N \quad \text{Eq. 30}$$

Eventhough the ionized weak acid was in the form of  $K^+HA^-$ , the derivation of Gran equation for titration data after equivalent point could be made in the same manner as for  $HA^+K^-$ . So the equation was identical to equation 30.

Equation 27 and 30 were identical equations which were employed in equivalent volumes determination of weak acids for titration data after equivalent point.

Various methods for the determination of equivalent volumes in potentiometric titration, as described above, were the method for evaluation only the equivalent volume of the single weak acid solution, not mixture of acidic compounds. When there were the mixture of two acidic compounds in the solution, it could find both the equivalent volumes of the acidic compounds by these methods (Titration curve, Differential method, Gran's method, etc), if there was an appreciable difference in their strengths. There must generally be a difference in pKa values at least 4 (Skoog, West and Holler, 1992).

Moreover, there were many methods for the equivalent volumes determination of weak acid mixtures and could be

described, as followed.

The Titration of Mixed Acidic Compound in Nonaqueous.

In this method, there were some extra precautions to be considered, such as; moisture and temperature. Moisture was generally to be avoided in using non-aqueous procedures, because water, being a weak acid, would compete with the weak acid for the basic titrant. Experimentally (Jenkins, 1977), it had been found that the moisture content in non-aqueous titrimetry should be held to less than 0.05 % so as not to have any appreciable effect on equivalent determination. Temperature (Skoog and West, 1992) must be strictly constant throughout the titration because of the high coefficient of expansion of organic solvent. So it could be seen that the determination in nonaqueous solvent was not appropriate and could give the uncorrect results. For example (Huber, 1967), the potentiometric Titration in nonaqueous solvent was the stepwise titration of mandelic acid and 2-aceto-1-naphthol in acetonitrile with 0.1 N potassium methoxide as titrant.

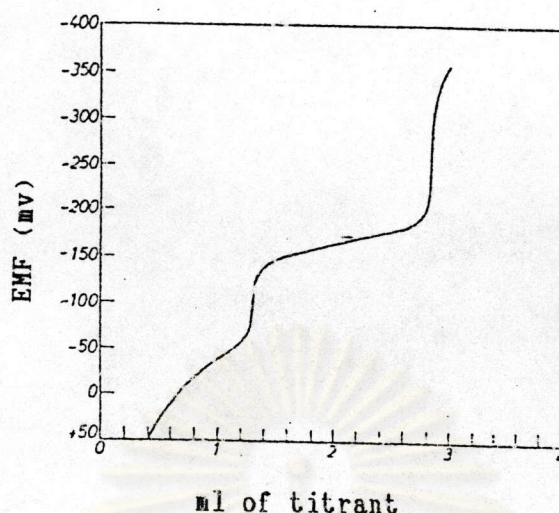


FIGURE 1 : Stepwise titration of mandelic acid + 2-aceto-1-naphthol in acetonitrile with 0.1 N potassium methoxide.

Linear Titration Plot for The Potentiometric Determination of Mixtures of Strong and Weak Acid.

1. The Method Applied from the Gran's Plot.

Boiani (1986) applied this method from the Gran's plot. The basic premise of a Gran's plot was a linear relationship, which could be found between the analyte concentration during titration and the volume of titrant added,  $V$ , such that a plot of this relationship versus  $V$  would yield a straight line that intercepted the  $V$  axis at the equivalent volume for the analyte,  $V_E$ . For a complete dissociated strong acid sample of concentration  $C_s$  and volume  $V_s$ , being titrated with a base titrant of concentration,  $N$ , the

hydrogen ion concentration during the titration up to the equivalent point could be expressed as

$$[\text{H}^+] = (C_s V_s - NV) / (V_s + V) \quad \text{Eq. 31}$$

The substitution of  $N V_E$  for  $C_s V_s$  could be made for  $V_E$ , the equivalent volume, and rearrangement of equation 31 yielded

$$(V_s + V) [\text{H}^+] = N(V_E - V) \quad \text{Eq. 32}$$

Substitution of  $10^{-\text{pH}} = a_{\text{H}^+} = \gamma_{\text{H}^+} [\text{H}^+]$  into Equation 32 and rearrangement gave

$$(V_s + V) 10^{-\text{pH}} = N \gamma_{\text{H}^+} (V_E - V) \quad \text{Eq. 33}$$

It could be seen that a plot of  $(V_s + V) 10^{-\text{pH}}$  versus  $V$  should be a straight line intercepting the  $V$  axis at  $V_E$ , see in Figure 2, provided that the activity coefficient,  $\gamma_{\text{H}^+}$ , and the junction potentials remained constant during the titration.

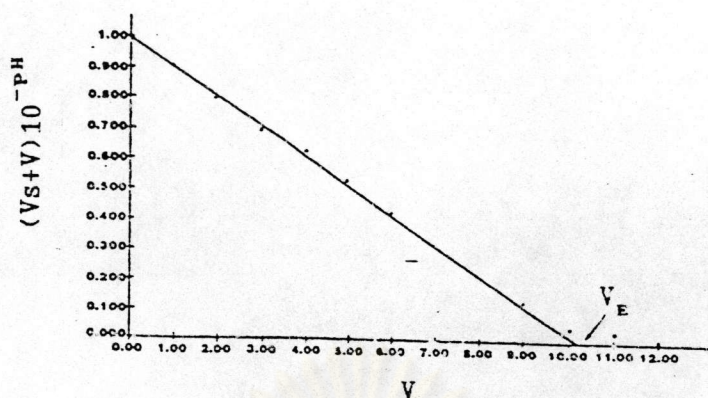


FIGURE 2 : Typical Gran plot for the determination of the equivalent volume of the strong acid component of an unknown mixture.

The relationship used for a weak acid, HA, differed from Equation 33 because of the equilibrium existing between HA,  $H^+$  and  $A^-$ , which could be summarized by the acid dissociation constant expression,

$$K_a = \gamma_{H^+} [H^+] \gamma_{A^-} [A^-] / (\gamma_{HA} [HA]) \quad \text{Eq. 34}$$

For a sample of HA with initial concentration,  $C_s$ , volume,  $V_s$  and volume of titrant,  $V$ , of concentration,  $N$ .

$$[HA] = C_s V_s - NV / (V_s + V) = N (V_E - V) / (V_s + V) \quad \text{Eq. 35}$$

and  $[A^-] = NV / (V_s + V) \quad \text{Eq. 36}$

Substitution of Equation 35 and 36 into Equation 34 and rearrangement gave

$$V \gamma_{H^+} [H^+] = V 10^{-pH} = K_a \gamma_{HA} (V_E - V) / \gamma_{A^-} \quad \text{Eq. 37}$$

A plot of  $V 10^{-pH}$  versus  $V$  (Figure 3) yielded a linear region, which could be extrapolated to intercept the  $V$  axis at  $V_E$ . It was also possible to obtain the value of  $K_a$  from the slope of the line.

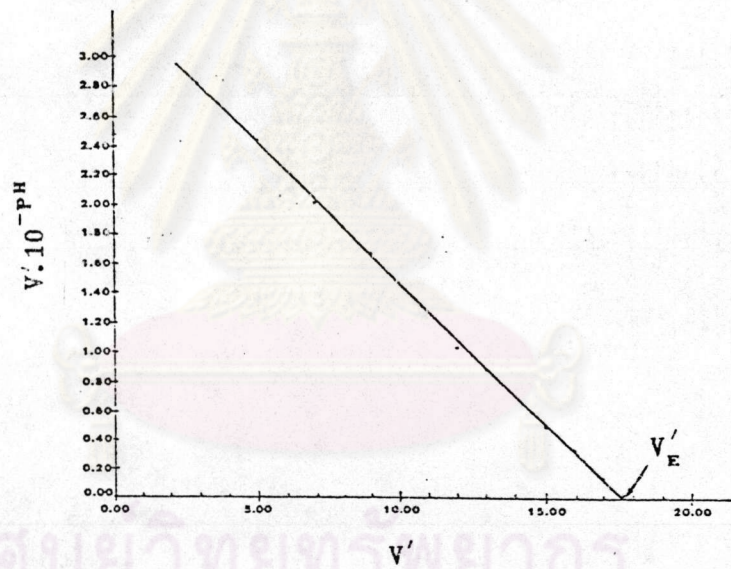


FIGURE 3 : Gran plot for the determination of the equivalent volume of the weak acid component in the same mixture as Figure 2.

It should be realized that the strong acid would be titrated first so that Equation 33 would be used



for the first graph. Also the titrant volume used to find the weak acid equilibrium point must be corrected for the volume needed to titrate the strong acid. This meant Equation 36 was substituted the term  $V'$  for  $V$  where  $V' = V - V_E$  (strong acid)

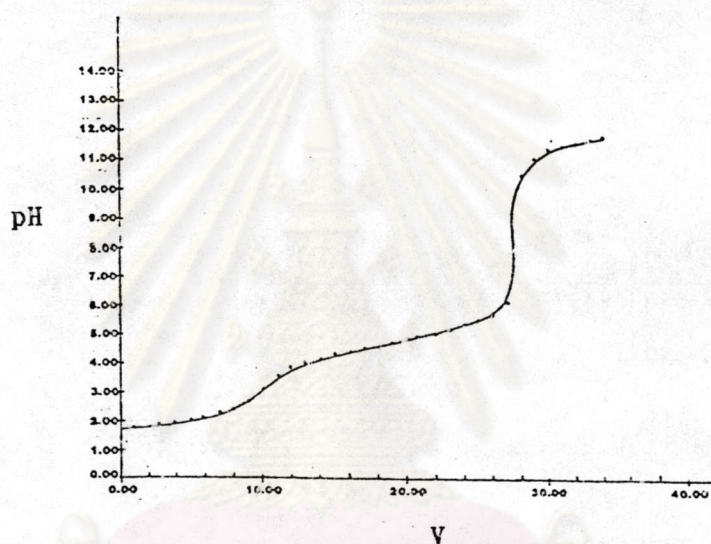


FIGURE 4 : The pH titration curve of the same acid mixture as in Figures 2 and 3.

## 2. The Mathematical and Graphical Procedure in Determination of A Mixture of Two Acids.

From the study of Boiani, the data obtained in a potentiometric titration of a mixture of acetic acid and hydrochloric acid with standard sodium hydroxide could be used to access the concentration of each acid by a linear treatment of the Gran plots that best fit the pertinent equations. For the determination of the equivalent volumes,

two different relationships and two plots were needed. Carios, Castillo and Alonso (1989) proposed the mathematical and graphical procedure in determination of a mixture of two acids in difference strength, example for hydrochloric acid and acetic acid. In this method, an alternative procedure was presented that allowed us to get the same kind of information using a single equation (Equation 38) plus a graph (Figure 5), which was better than the method of Boiani.

The equation could be derived and showed the relationship between many parameters, as followed

$$V = V_E + KaV_E' / ([H^+] + Ka) - (V_o + V) d/B \quad \text{Eq. 38}$$

where  $A_1$  = Molar concentration of hydrochloric acid

$A_2$  = Molar concentration of acetic acid

$B$  = Molar concentration of sodium hydroxide

$$V_E = A_1 V_o / B$$

$$V_E' = A_2 V_o / B$$

$$\text{and } d = [H^+] - Kw / [H^+] \quad \text{Eq. 29}$$

A plot of  $V$  versus  $(V_o + V) d$  was then constructed. Figure 5 showed two breaks of the graph. The first corresponds to  $V_E$ , the equivalent volume of the strong acid component in the mixture, and

the difference between the two breaks is  $V_E'$ , the equivalent volume of the weak acid component of the mixture.

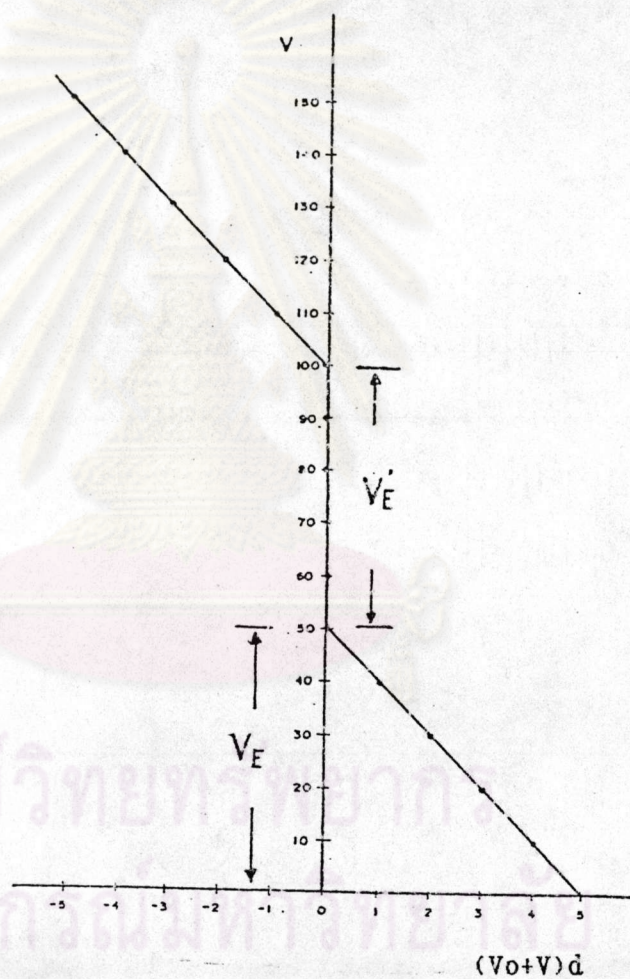


FIGURE 5 : The plot of  $V$  vs  $(V_0 + V)d$  for the determination of the equivalent volumes of an acid mixture.

### 3. The Use of Linear Plot as The Function of $F_{mix}$ and Gran's Plot.

McCallum and Midgley (1975) described that in this method, the linear titration plots for potentiometric titration were applied to a mixture of a strong acid and a weak acid, which might have any number of dissociation steps of any strength. The resultant linear titration plot was used to determine the strong acid, together with a Gran's plot to determine the total acid concentrations of the mixture. In order to resolve the mixture into its components by this method, it was necessary to know the total acidity of the solution. This value might be obtained in a separate experiment, by any suitable method, or by continuing the titration into the basic region and using either the S-shaped titration curve or the appropriate Gran function.

By the application of the charge- and mass-balance equations, together with the equilibrium constants of the system, linear titration plots had been obtained in the function of  $r'_{mix}$ .

$$F_{mix} = N (V_s - V) / h$$

Eq. 40



A function  $F_{mix}$  could be calculated from the equilibrium constants  $K_w$ ,  $K_i$  and the experimental data  $V_o$ ,  $V$ ,  $N$ ,  $V_E$  and  $[H]$ , as followed

$$F_{mix} = \frac{\{(V_o + V) \frac{[H^+]}{f_1} - \frac{K_w}{[H^+] f_1} (1 + \beta) + N(V - V_E) (1 + \beta - \alpha)\}}{h}$$

which

$$f_{H^+} = f_{OH^-} = f_1$$

$f_1$  = The activity coefficients of the i-th protonated form of weak acid

$f_a$  = The activity coefficient of the unionized weak acid

$V_s$  = Volume of base equivalent to the strong acid

$[H^+]$  = The experimentally observed hydrogen ion activity

$h$  = The number of protons removable by titration

$K_i$  = The ith association constant of weak acid

$$\beta = \frac{\sum K_i [H]^i f_a}{f_1}$$

$$\alpha = \frac{\sum i K_i [H]^i f_a}{f_1}$$

From Equation 40, the function was linear when plotted against  $V$ , intercepting the  $V$ -axis at  $V = V_s$ . Thus, once the total acidity was known, the concentration of the strong acid could be calculated and hence the

concentration of the weak acid found by different. The Figure 6 showed the  $F_{mix}$  and Gran plot for a typical titration and for comparison the pH vs  $V$  curve (Figure 7).

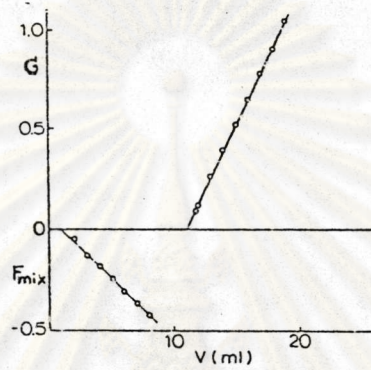


FIGURE 6 : Gran plot and  $F_{mix}$  curves for the titration of oxalic acid-nitric acid mixture.

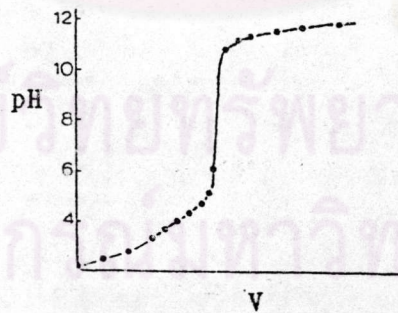


FIGURE 7 : Titration curve of oxalic acid-nitric acid mixture.

Determination of The Mixtures of Two Weak Acids by Potentiometric Titration and Non-Linear Regression.

This method was the study of Betti, Papoff and Meites (1986). It dealt with potentiometric titrations in which mixtures of two monobasic weak acids were titrated with a strong base, and in which weighted non-linear regression analysis was used to find the concentrations for both acids. The precisions of the resulting values of the concentrations depend on the difference between the values of pKa, on the ratio of the initial concentrations, and on the standard error of measurement of both the pH and the volume of base.

The fundamental equation for the titration of such a mixture might be written in the form

$$[\text{H}^+] - [\text{OH}^-] = \left\{ \frac{\text{Ka}_A}{(\text{Ka}_A + [\text{H}^+])} + x \frac{\text{Ka}_B}{(\text{Ka}_B + [\text{H}^+])} - f \right\} C_A / (1 + rf) \quad \text{Eq. 41}$$

where  $\text{Ka}_A$ ,  $\text{Ka}_B$  = The dissociation constant of the two acid

$x$  = The ratio of concentration ( $x = C_B / C_A$ )

$C_A$  = The analytical concentration of the stronger acid

- $C_B$  = The analytical concentration of the weaker acid
- $r$  = dilution parameter
- $f$  = titration parameter

This method was based on synthesizing the pair data of  $f$  and  $[H^+]$ , at each point, which the value of  $[H^+]$  was obtained by solving Equation 41, using a Newton-Raphson procedure, and was then converted into a value of the pH and the value of  $f$  at each subsequent point was obtained by adding an increment  $\Delta f$  to the last preceding value, which the first point always corresponded to  $f = 0$  (the start of the titration). The algorithm employed to generate the values of  $\Delta f$  was

1. if  $2 < N < 5$ ,  $\Delta f = 0.02$
2. if  $N > 5$ ,  $\Delta f = 1-f / 2$
3. if  $f > 1.05$ ,  $\Delta f = (1+x)-f / 2$

where  $N$  is the ordinal number of the point being generated and  $f$  denotes the value at the  $(N-1)$ th point.

The resulting data pair were combined with a general program (VARPWR) for estimating the variances of the parameters in weighted non-linear regression analysis. For any given values of the ratio of concentrations and the standard errors of measurement, the precision with which



the concentration of the stronger acid can be evaluated is, in general, poorest when the difference between the pKa values ( $\Delta$ ) is approximately 1.5, and improves if  $\Delta$  is either larger or smaller than that value.

These methods (the titration in nonaqueous solvent and the linear titration plot for the potentiometric titration), as described above, were used to find the equivalent volume of the mixture of acidic compound only the mixture of strong acid and weak acid or the two acids which had the difference in  $-\log$  (dissociation constant) more than 4. The last method (Betti, Papoff and Meites) was studied about the determination of the mixtures of two weak acids. Moreover, it was not suitable in determination, when the difference of pKa value between two weak acids was about 1.5.

The third method (Betti, Papoff and Meites) was only theoretical research. There was no support by the actual experimentation. Eventhough it was the method in theoretical, there was the error in determination, when the difference of pKa between two acids was about 1.5. It might be described that the fitting of equation's model from the derivation was uncorrect. Thus, the propose of the new method was occured. The previous study was the modification and development of equation from the former methods in order to

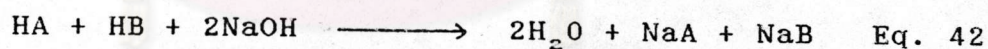
determine the equivalent volume of weak acid mixtures. This method was studied both in theoretical and experimental.

The modified equation, which based on the basic principles of mass balance, charge balance and equilibrium equation, could be derived, as followed.

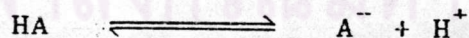
### Titration of Weak Acidic Mixtures

#### Derivation of Equation for Titration The Mixture of Two Neutral Weak Acids.

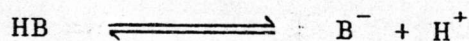
When 2 neutral weak acids, HA and HB, were titrated with a strong base



The dissociation reaction of two weak acids were



$$K_{a_A} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{Eq. 43}$$



$$K_{a_B} = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} \quad \text{Eq. 44}$$

The mass balance of two weak acids gave

$$C_A V_o / (V_o + V) = [\text{HA}] + [\text{A}^-] \quad \text{Eq. 45}$$

$$C_B V_o / (V_o + V) = [\text{HB}] + [\text{B}^-] \quad \text{Eq. 46}$$

charge balance of this titration solution was

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{A}^-] + [\text{B}^-] \quad \text{Eq. 47}$$

The concentration of sodium ion at any volumes of titrant was

$$[\text{Na}^+] = NV / (V_o + V) \quad \text{Eq. 48}$$

Substitution Equation 48 in Equation 47 gave

$$[\text{H}^+] + NV / (V_o + V) = [\text{OH}^-] + [\text{A}^-] + [\text{B}^-] \quad \text{Eq. 49}$$

Substitution Equation 45 in Equation 43 and Equation 46 in Equation 44

$$K_{a_A} = \frac{[\text{H}^+] [\text{A}^-]}{\{ C_A V_o / (V_o + V) - [\text{A}^-] \}}$$

which  $C_A V_o = V_{EA} N$

$$C_B V_o = V_{EB} N$$

$$V_{EA} = \text{Equivalent volume of weak acid A}$$

$$V_{EB} = \text{Equivalent volume of weak acid B}$$

$$[A^-] = \frac{K_{aA} V_{EA} N}{(V_o + V) (K_{aA} + [H^+])} \quad \text{Eq. 50}$$

$$[B^-] = \frac{K_{aB} V_{EB} N}{(V_o + V) (K_{aB} + [H^+])} \quad \text{Eq. 51}$$

Substitution Equation 50 and 51 in Equation 49 gave

$$[H^+] + \frac{NV}{V_o + V} = [OH^-] + \frac{K_{sA} V_{EA} N}{(V_o + V) (1/(K_{aA} + [H^+]))} + \frac{K_{aB} V_{EB} N}{(V_o + V) (K_{aB} + [H^+])} \quad \text{Eq. 52}$$

Equation 52 could be rearranged to

$$[H^+] + \frac{NV}{V_o + V} - [OH^-] = \frac{K_{aA} V_{EA} N}{(V_o + V) (K_{aA} + [H^+])} + \frac{K_{aB} V_{EB} N}{(V_o + V) (K_{aB} + [H^+])}$$

Eq. 53

Equation 53 can be written in term of variable Y, X<sub>1</sub> and X<sub>2</sub>

$$Y = a_1 X_1 + a_2 X_2 \quad \text{Eq. 54}$$

$$\text{which } Y = \frac{[H^+] + NV - [OH^-]}{(V_o + V)} \quad \text{Eq. 55}$$

$$X_1 = \frac{1}{(V_o + V)(K_{a_A} + [H^+])} \quad \text{Eq. 56}$$

$$X_2 = \frac{1}{(V_o + V)(K_{a_E} + [F^+])} \quad \text{Eq. 57}$$

$$a_1 = K_{a_A} V_{EA} N \quad \text{Eq. 58}$$

$$a_2 = K_{a_B} V_{EB} N \quad \text{Eq. 59}$$

From the partially regression coefficient, a<sub>1</sub> and a<sub>2</sub>, which obtained from solving the equation (Eq. 53) by the multiple regression analysis and computer program, SPSS / PC<sup>+</sup>, we could find the equivalent volume of 2 weak acids, V<sub>EA</sub> and V<sub>EB</sub>. The dissociation constant of each weak acid could be obtained from G plot (as shown in equation 9 and 21, the slope of these equation was the

dissociation constant) from the titration of the single weak acidic solution. The normality of titrant could be obtained from the standardization of titrant solution with the standard acid solution.

For the derivation of equation for titration the mixture of neutral and ionized weak acids, such as; HA and  $K^+HA^-$  or the mixture of two ionized weak acids, such as;  $K^+HA^-$  and  $HB^+X^-$ , it could be derived in the same manner as for the equation of two neutral weak acids. Thus, the equations were the same character as Equation 53 and the volumes of titrant, which equivalent to the two weak acids, were obtained from the value of partially regression coefficient, as shown in Equation 58 and 59.

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