

CHAPTER IV



RESULT AND DISCUSSION

The computer curve fitting program, SPSS/PC⁺, is important for the interpretation of data in this method. To test the possibility of using, the data was simulated in theoretical. Before the analysis of experimental data, we must first prove theoretically that this program can be used to solve the modified equation (Eq. 53) for determination of weak acidic mixture.

Testing The Applicability of SPSS/PC⁺ Program

The sets of data were synthesized by solving the polynomial equation. The set of data was the concentration of hydronium ion as the function of the volume of titrants. The principle of polynomial equation was based on mass balance, charge balance and equilibrium equation. The polynomial equation could be derived, as followed.

The initial steps of derivation were in the same pattern as for the derivation of Equation 53.

$$[\text{H}^+] + \frac{NV}{V_0+V} - [\text{OH}^-] = \frac{K_{a_A} V_{EA} N}{(V_0+V)(K_{a_A} + [\text{H}^+])} + \frac{K_{a_B} V_{EB} N}{(V_0+V)(K_{a_B} + [\text{H}^+])}$$

refer to Eq. 53

Multiplying Equation 53 with $[\text{H}^+]$ gave

$$[\text{H}^+]^2 + VN[\text{H}^+] - K_w = \frac{K_{a_A} V_{EA} N [\text{H}^+] (K_{a_A} + [\text{H}^+])}{(V_0+V)(K_{a_A} + [\text{H}^+])} + \frac{K_{a_B} V_{EB} N [\text{H}^+] (K_{a_B} + [\text{H}^+])}{(V_0+V)(K_{a_B} + [\text{H}^+])}$$

Eq. 60

Multiplying Equation 60 with $(K_{a_A} + [\text{H}^+]) (K_{a_B} + [\text{H}^+])$ could give

$$\begin{aligned} & \{K_{a_A} K_{a_B} + (K_{a_A} + K_{a_B})[\text{H}^+] + [\text{H}^+]^2\} \left\{ [\text{H}^+] + \frac{VN[\text{H}^+] - K_w}{V+V_0} \right\} \\ & = \frac{\{K_{a_A} V_{EA} N [\text{H}^+] (K_{a_B} + [\text{H}^+])\}}{(V+V_0)} + \frac{\{K_{a_B} V_{EB} N [\text{H}^+] (K_{a_A} + [\text{H}^+])\}}{(V+V_0)} \end{aligned}$$

Eq. 61

Equation 61 could be rearranged to

$$[H^+]^4 + (K_{a_A} + K_{a_B} + \frac{VN}{V+V_0}) [H^+]^3 +$$

$$\left\{ \frac{K_{a_A} K_{a_B}}{V+V_0} + \frac{(K_{a_A} + K_{a_B})VN}{V+V_0} - \frac{K_w}{V+V_0} - \frac{K_{a_A} V_{EA} N}{V+V_0} - \frac{K_{a_B} V_{EB} N}{V+V_0} \right\} [H^+]^2 +$$

$$\left\{ \frac{K_{a_A} K_{a_B} VN}{V+V_0} - K_w (K_{a_A} + K_{a_B}) - \frac{K_{a_A} K_{a_B} V_{EA} N}{V+V_0} - \frac{K_{a_A} K_{a_B} V_{EB} N}{V+V_0} \right\} [H^+]$$

$$- K_{a_A} K_{a_B} K_w = 0$$

Eq. 62

Equation 62 could be written in polynomial form

$$a_4 [H^+]^4 + a_3 [H^+]^3 + a_2 [H^+]^2 + a_1 [H^+] + a_0 = 0$$

where

$$a_4 = 1$$

$$a_3 = K_{a_A} + K_{a_B} + \frac{VN}{V_0+V}$$

$$a_2 = K_{a_A} + K_{a_B} + \frac{(K_{a_A} + K_{a_B})VN}{V_0+V} - \frac{K_w}{V_0+V} - \frac{K_{a_A} V_{EA} N}{V_0+V}$$

$$- \frac{K_{a_B} V_{EB} N}{V_0+V}$$

$$a_1 = \frac{K_{a_A} K_{a_B} V N}{V_0 + V} - K_w (K_{a_A} + K_{a_B}) - \frac{K_{a_A} K_{a_B} V_{E_A} N}{V_0 + V} - \frac{K_{a_A} K_{a_B} V_{E_B} N}{V_0 + V}$$

$$a_0 = K_{a_A} K_{a_B} K_w$$

When each of weak acid or both of weak acids were in the ionized form, the polynomial equation can be derived in the same manner as both of weak acids were in the neutral form and the polynomial equation was identical to Equation 62.

The variable in polynomial equation (Eq. 62) was hydronium ion concentration. The parameters in the coefficient ($a_0 - a_4$) of polynomial equation (K_{a_A} , K_{a_B} , V_{E_A} , V_{E_B} , N , V_0 and K_w) were fixed except the volume of titrants. Thus, solving the polynomial equation could give the set of data, which was the hydronium ion concentration as a function of the volume of titrant. Newton's approximation method (Butler, 1964 and Geenspan, 1988) and computer program, Macro Lotus were used in order to solve this polynomial equation. This newton's approximation method was included in the textbooks of Maron (1987); Maron and Lopez (1991); Mendenhall, Scheaffer and Wackerly (1981) and Pizer (1983). Each set of data, hydronium ion concentration as a function of the volume of

titrant, was obtained from changing the pKa of each weak acid in the polynomial equation, which could give the difference of ΔpK_a , as shown in Table 3. The sets of data (hydronium ion concentration as a function of the volume of titrant, obtained from simulation) were the same character as obtained from the titration in the real experiment. The set of data, obtained from simulation, was applied to the modified equation (Eq. 53) for calculation of V_{EA} and V_{EB} values with the aid of SPSS/PC⁺ program.

Table 3 summarized the comparison between the theoretical V_{EA} and V_{EB} values with the calculated values of V_{EA} and V_{EB} obtained from multiple linear regression analysis (Draper and Smith, 1966; Johnson and Bhattacharyya, 1987; Byrkit, 1987 and Dunteman, 1984) of SPSS/PC⁺ program. The results as summarized in Table 3 suggested that this program, SPSS/PC⁺, was suitable for solving the modified equation (Eq. 53) in equivalent points determination of two weak acids.

Figure 8 - 43 showed the three-dimensional plot between the variables of the modified equation, Y, X1 and X2, in theoretical. For this case of two independent variables, X1 and X2, the equation for the value of Y

described a plane in the three-dimensional space with X1, X2 and Y as the coordinate axis .

$$\text{where } Y = [\text{H}^+] + (\text{VN}/(\text{V}_0 + \text{V})) - [\text{OH}^-]$$

$$X1 = 1/((\text{V}_0 + \text{V})(\text{Ka1} + [\text{H}^+]))$$

$$X2 = 1/((\text{V}_0 + \text{V})(\text{Ka2} + [\text{H}^+]))$$

The Titration of Mixed Weak Acids with Strong Base

The weak acids chosen in this study were benzoic acid, potassium biphthalate, p-nitrophenol, pralidoxime chloride, boric acid and ephedrine hydrochloride. Their pKa was shown in Table 1. In these experiments, the pairs of weak acid were arranged in random form in order to reduce the bias, which might occur in matching the pairs of weak acids. The differences in ΔpKa of weak acid mixtures obtained from this matching were shown in Table 2.

The results of the titration were compared with the reference method, G plot, by the statistical procedure, student t-test, at 95% confidence interval (Devore, 1990). Gran's plot (G plot) could be used as the reference method, since it had been shown that in the former study there was no statistical difference between the result from G plot and the official method in USP XX.

The discussion of the two equivalent points determination for the weak acid mixtures could be divided into 3 categories, as followed: two neutral weak acid mixtures, neutral weak acid mixed with ionized weak acid and two ionized weak acid mixtures.

1. The Titration of The Neutral Weak Acidic Mixtures

The weak acidic mixtures in this group were

1.1 Benzoic acid and boric acid

The dissociation constant of these compounds as determine by G plot (Equation 9) were 7.871×10^{-5} ($pK_a = 4.104$, benzoic acid) and 8.017×10^{-10} ($pK_a = 9.096$, boric acid). The difference of pK_a between these weak acids was 4.992. From the titration each of weak acidic solution, the equivalent volume (see Table 4 and 5) could be determined from the titration curve, Gran's plot and the modified equation (Equation 53 with only one variable in the equation). The titration curves and Gran's plots were shown in Figure 44, 48, 50, 51, 58 and 59. For boric acid, the equivalent volume could not be determined from the titration curve, because the curve had poorly defined equivalent region, as shown in Figure 48.

The titration curve of weak acidic mixture and the three-dimensional plot of three variables in the modified equation (Y, X1 and X2) were shown in Figure 62 and 63. The equivalent volume of these weak acids (see Table 4 and 5) were found by solving the modified equation (Eq. 53).

The equivalent volumes for each weak acid obtained by solving the modified equation (Eq. 53) from the titration of weak acid mixture were statistical indifference from the equivalent volumes of the respective weak acid obtained by G plot (Equation 9) from the titration each of weak acid solution.

1.2 Benzoic acid and p-nitrophenol

The dissociation constant of these compounds as determine by G plot (Eq. 9) were 7.871×10^{-5} ($pK_a = 4.104$, benzoic acid) and 1.004×10^{-7} ($pK_a = 6.998$, p-nitrophenol). The difference of pK_a between these weak acids was 2.894. From the titration each of weak acidic solution, the equivalent volume (see Table 6 and 7) could be determined from the titration curve, Gran's plots and the modified equation (Eq. 53 with only one variable in the equation). The titration curves and Gran's plots were shown in Figure 44, 46, 50, 51, 54 and 55.

The titration curve of weak acidic mixture and the three-dimensional plot of three variables in the modified equation (Y, X1 and X2) were shown in Figure 64 and 65. The results of these titration followed in the same pattern as for the titration of the mixture of benzoic acid and boric acid.

1.3 p-Nitrophenol and boric acid

The dissociation constant of these compounds as determined by G plot (Eq. 9) were 1.004×10^{-7} (pKa = 6.998, p-nitrophenol) and 8.017×10^{-10} (pKa = 9.096, boric acid). The difference of pKa between these weak acids was 2.098. From the titration each of weak acidic solution, the equivalent volume (see Table 8 and 9) could be determined by the titration curve, Gran's plots and the modified equation (Eq. 53 with only one variable in the equation). The titration curves and Gran's plots were shown in Figure 46, 48, 54, 55, 58 and 59. For boric acid, the equivalent volume could not be determined from the titration curve, because the curve had poorly defined equivalent region, as shown in Figure 48.

The titration curve of weak acidic mixture and the three-dimensional plot of three variables in the modified equation (Equation 53) were shown in Figure 66

and 67. The results of these titrations followed in the same pattern as for the titration of the mixture of benzoic acid and boric acid.

From the results of this group (benzoic acid-boric acid mixture, benzoic acid- p-nitrophenol mixture and p-nitrophenol -boric acid mixture), it was concluded that the equivalent volumes of two neutral weak acids could be determined by the modified equation (Eq. 53).

2. The Titration of The Neutral Weak Acid Mixed with Ionized Weak Acid

The weak acidic mixtures in this group were

2.1 Benzoic acid and ephedrine hydrochloride

The dissociation constant of these compounds as determined by G plot (Equation 9 and 21) were 7.871×10^{-5} for benzoic acid ($pK_a = 4.104$) and 2.153×10^{-10} for ephedrine hydrochloride ($pK_a = 9.667$). The difference of pK_a between these weak acids was 5.563. The equivalent volume for each weak acid (see Table 11 and 12) could be determined from the titration curves, Gran's plots and the modified equation (with only one variable in the equation). The titration curves and Gran's plots were

shown in Figure 44, 49, 50, 51, 60 and 61. For ephedrine hydrochloride, the equivalent point could not be determined from the titration curve, because it had poorly defined equivalent region.

The titration curve of the weak acidic mixture and the three-dimensional plot of the variables in the modified equation (Eq. 53) were shown in Figure 68 and 69. The results of these titrations were summarized in Table 11 and 12.

The equivalent volumes obtained by solving the modified equation (Eq. 53) for the titration of weak acid mixture were statistical difference from the equivalent volume of each weak acid obtained by G plot (Eq. 9 and 21) from the titration each of weak acid solution. This was likely due to alkaline error as much of the data were in the range of high pH value. The error was due to the capability of the membrane for responding to other cation besides the hydrogen ion. As the hydrogen ion activity became very small, the Na^+ ions could compete successfully in the potential determining mechanism.

2.2 p-Nitrophenol and ephedrine hydrochloride

The dissociation constant of these compounds as determined by \bar{G} plot (Eq. 9 and 21) were 1.004×10^{-7} ($pK_a=6.998$, p-nitrophenol) and 2.153×10^{-10} ($pK_a =9.667$, ephedrine hydrochloride). The difference of pK_a between these weak acids was 2.669. The equivalent volume for each weak acid (see Table 13 and 14) could be determined from the titration curve. Gran's plots and the modified equation (Eq. 53 with only one variable in the equation). The titration curves and Gran's plots were shown in Figure 46, 49, 54, 55, 60 and 61. For ephedrine hydrochloride, the equivalent point could not be determined from the titration curve because the curve had poorly defined equivalent region, as shown in Figure 49.

The titration curve of the weak acidic mixture and the three-dimensional plot of three variables in the modified equation (Eq. 53) were shown in Figure 70 and 71. The results of these titrations were summarized in Table 13 and 14 and followed in the same pattern as for the titration of benzoic acid - ephedrine hydrochloride mixture.

2.3 Boric acid and ephedrine hydrochloride

The dissociation constant of these compounds as determined by \bar{G} plot (Eq. 9 and 21) were 8.017×10^{-10} ($pK_a = 9.096$, boric acid) and 2.153×10^{-10} ($pK_a = 9.667$, ephedrine hydrochloride). The difference of pK_a between these weak acids was 0.571. The equivalent volume for each weak acid (see Table 15 and 16) could be determined from Gran's plots and the modified equation (Eq. 53 with only one variable in the equation). The titration curves and Gran's plots were shown in Figure 48, 49, 58-61. The equivalent volumes of these weak acids could not be determined from the titration curves because the curves had poorly defined equivalent region, as shown in Figure 48 and 49.

The titration curve of the weak acidic mixture and the three-dimensional plot of three variables in the modified equation (Eq. 53) were shown in Figure 72 and 73. The results of these titrations were summarized in Table 15 and 16 and followed in the same pattern as for the titration of benzoic acid - ephedrine hydrochloride mixture.

2.4 Potassium biphthalate and boric acid

The dissociation constant of these compounds as determined by G plot (Equation 9 and 21) were 9.156×10^{-6} ($pK_a = 5.038$, potassium biphthalate) and 8.017×10^{-10} ($pK_a = 9.096$, boric acid). The difference of pK_a between these weak acids was 4.058. The equivalent volume for each weak acid could be determined from titration curves (Figure 45 and 48), Gran's plots (Figure 52, 53, 53 and 59) and the modified equation (with only one variable in the equation). For boric acid, the equivalent point could not be determined from the titration curve, because the curve had poorly defined equivalent region.

The titration curve of the weak acidic mixture and the three-dimensional plot of variables in the modified equation (Eq. 53) were shown in Figure 74 and 75. The results of these titrations were summarized in Table 17 and 18. The equivalent volumes for each weak acid obtained from solving the modified equation (Equation 53) in the titration of weak acid mixture were statistically indistinguishable from the equivalent volumes of the corresponding compound as obtained from G plot (Equation 9 and 21) for the titration of each weak acid solution.

2.5 Benzoic acid and pralidoxime chloride

The dissociation constant of these compounds as determined by G plot (Equation 9 and 21) were 7.871×10^{-5} ($pK_a = 4.104$, benzoic acid) and 1.240×10^{-8} ($pK_a = 7.907$, pralidoxime chloride). The difference of pK_a between these weak acids was 3.803. The equivalent volume for each weak acid could be determined from titration curves (Figure 44 and 47), Gran's plots (Figure 50, 51, 56 and 57) and the modified equation (with only one variable in the equation).

The titration curve of the weak acidic mixture and the three-dimensional plot of variables in the modified equation (Eq. 53) were shown in Figure 76 and 77. The results of these titrations (Table 19 and 20) followed in the same pattern as for the titration of potassium biphthalate-boric acid mixture.

2.6 Potassium biphthalate and p-nitrophenol

The dissociation constant of these compounds as determined by G plot (Equation 9 and 21) were 9.156×10^{-6} ($pK_a = 5.038$, potassium biphthalate) and 1.004×10^{-7} ($pK_a = 6.998$, p-nitrophenol). The difference of pK_a between these weak acids was 1.960. The

equivalent volume for each weak acid could be determined from the titration curves (Figure 45 and 46), Gran's plots (Figure 52-55) and the modified equation (with only one variable in the equation).

The titration curve of the weak acidic mixture and the three-dimensional plot of variables in the modified equation (Eq. 53) were shown in Figure 78 and 79. The results of these titrations (Table 19 and 20) followed in the same pattern as for the titration of potassium biphthalate-boric acid mixture.

2.7 p-Nitrophenol and pralidoxime chloride

The dissociation constant of these compounds as determined by G plot (Equation 9 and 21) were 1.004×10^{-7} ($pK_a = 6.998$) for p-nitrophenol and 1.240×10^{-8} ($pK_a = 7.907$) for pralidoxime chloride. The difference of pK_a between these weak acids was 0.909. The equivalent volume for each weak acid could be determined from the titration curves, Gran's plots and the modified equation (with only one variable in the equation). The titration curves and Gran's plots were shown in Figure 46, 47, 54 - 57.

The titration curve of the weak acidic mixture and the three-dimensional plot of variables in the modified equation (Eq. 53) were shown in Figure 80 and 81. The results of these titrations were summarized in Table 23 and 24. It could be seen that there were statistical difference between equivalent volume for each weak acid, obtained by solving the modified equation (Equation 53) from the titration of two-weak acidic solution and the equivalent volume of the corresponding compound as obtained from G plot (Equation 9 and 21), which the data obtained from titration each of the single weak acidic solution.

In this mixture, we could not determined the equivalent volumes of two weak acid mixtures by the modified equation (Equation 53). When the dissociation constant of two weak acid were quite close, the range of data applied into the modified equation reflected high buffer capacity. The measurement of pH values in this region was not sensitive enough to change in volume of titrant. Thus, the modified equation (Equation 53) could not be used to accurately separate the effect of each weak acid on the pH of solution.

2.8 Pralidoxime chloride and boric acid

The dissociation constant of these compounds as determined by G plot (Eq. 9 and 21) were 1.240×10^{-8} ($pK_a = 7.907$, pralidoxime chloride) and 8.017×10^{-10} ($pK_a = 9.096$, boric acid). The difference of pK_a between these weak acids was 1.189. The equivalent volume for each weak acid could be determined from the titration curves (Figure 47 and 48), Gran's plots (Figure 56-59) and the modified equation (with only one variable in the equation). For boric acid, the equivalent point could not be determined from the titration curve because it had poorly defined equivalent region.

The titration curve of the weak acidic mixture and the three-dimensional plot of variables in the modified equation (Eq. 53) were shown in Figure 80 and 81. The results of these titrations were summarized in Table 25 and 26 and followed the same pattern as the titration of p-nitrophenol and pralidoxime chloride.

2.9 Benzoic acid and potassium biphthalate

The dissociation constant of these compounds as determined by G plot (Eq. 9 and 21) were 7.871×10^{-5} ($pK_a = 4.104$, benzoic acid) and 9.156×10^{-6}

($pK_a = 5.038$, potassium biphthalate). The difference of pK_a between these weak acids was 0.334. The equivalent volume for each weak acid could be determined from the titration curve (Figure 44 and 45), Gran's plots (Figure 50-53) and the modified equation (with only one variable in the equation).

The titration curve of the weak acidic mixture and the three-dimensional plot of variables in the modified equation (Eq. 53) were shown in Figure 82 and 83. The results of these titrations (Table 27 and 28) followed the same pattern as the titration of p-nitrophenol and pralidoxime chloride.

3. The Titration of The Ionized Weak Acidic Mixtures

The weak acidic mixtures in this group were

3.1 Potassium biphthalate and ephedrine hydrochloride

The dissociation constant of these compounds as determined by G plot (Equation 21) were 9.156×10^{-5} ($pK_a = 5.038$, potassium biphthalate) and 2.153×10^{-10} ($pK_a = 9.667$, ephedrine hydrochloride).



The difference of pK_a between these weak acids was 4.629. The equivalent volume for each weak acid could be determined from the titration curves, Gran's plots and the modified equation (with only one variable in the equation). The titration curves and Gran's plot were shown in Figure 45, 49, 52, 53, 60 and 61. For ephedrine hydrochloride, the equivalent volume could not be determined by the titration curve, because it had poorly defined equivalent region.

The titration curve of the weak acidic mixture and the three-dimensional plot of variables in the modified equation (Eq. 53) were shown in Figure 86 and 87. The results of these titrations were summarized in Table 29 and 30.

The equivalent volumes for each weak acid, obtained by solving the modified equation (Eq. 53) from the titration of weak acid mixture, were statistical difference from the equivalent volumes of the corresponding compound as obtained by G plot (Eq. 9, 21) from the titration each of weak acid solution. This was likely due to alkaline error as much of the data were in the range of high pH value. The error was due to the capability of the membrane for responding to other cation besides the hydrogen ion. As the hydrogen ion activity became very small, the Na^+

ions could compete successfully in the potential determining mechanism.

3.2 Pralidoxime chloride and ephedrine hydrochloride

The dissociation constant of these compounds as determined by G plot (Eq. 21) were 1.240×10^{-8} ($pK_a=7.907$, pralidoxime chloride) and 2.153×10^{-10} ($pK_a = 9.667$, ephedrine hydrochloride). The difference of pK_a between these weak acids was 1.760. The equivalent volume for each weak acid (see Table 31 and 32) could be determined by the titration curves, Gran's plots and the modified equation (with only one variable in the equation). The titration curves and Gran's plots were shown in Figure 47, 49, 56, 57, 60 and 61. For ephedrine hydrochloride, the equivalent volume could not be determined from the titration curve because the curve had poorly defined equivalent region, as shown in Figure 49.

The titration curve of the weak acidic mixture and the three-dimensional plot of three variables in the modified equation (Eq. 53) were shown in Figure 88 and 89. The results of these titrations were summarized in Table 31 and 32 and followed the same pattern as the

titration of potassium biphthalate-ephedrine hydrochloride mixture.

3.3 Potassium biphthalate and pralidoxime chloride

The dissociation constant of these compounds as determined by G plot were 9.156×10^{-5} ($pK_a = 5.038$) for potassium biphthalate and 1.240×10^{-8} ($pK_a = 7.907$) for pralidoxime chloride. The difference of pK_a between these weak acids was 2.869. The equivalent volume for each weak acid could be determined from the titration curves (Figure 45, 47), Gran's plots (Figure 52, 53, 56 and 57) and the modified equation (with only one variable in the equation).

The titration curve of the weak acidic mixture and the three-dimensional plot of variables in the modified equation (Eq. 53) were shown in Figure 90 and 91. The results of these titrations were summarized in Table 33 and 34. The equivalent volumes of two-weak acids, which obtained from solving the modified equation (Equation 53) in the titration of weak acid solution, were statistically indistinguishable from the equivalent volumes, which obtained from G plot (titration each of weak acidic solution).

From the results of the experiments (Table 4), it was anticipated that there were many factors which concern on these results, such as; alkaline error and the difference of pKa between two weak acids. The experimental results were differed from the theoretical results because of these factors.

Alkaline Error Effect

The titration results of the following weak acid mixtures;

- benzoic acid and ephedrine hydrochloride
- potassium biphthalate and ephedrine hydrochloride
- p-nitrophenol and ephedrine hydrochloride
- pralidoxime chloride and ephedrine hydrochloride
- boric acid and ephedrine hydrochloride

showed that, there were statistical difference between the equivalent volumes, obtained from solving the modified equation and the equivalent volume of the corresponding compound as obtained from G plot. It was due to the alkaline error as much of the data were in the range of high pH value. The pH measurement of glass electrode in the range of high pH value (pH value was more than about 9) did not reflect the true concentration of hydronium ions. The H^+ concentration was very small, when it was compared with the other ions such as Na^+ , K^+ and other

cations. This alkaline error was due to the capability of the membrane for responding to other cation (Na^+) besides the hydrogen ion. As the hydrogen ion activity became very small, these other ions could compete successfully in the potential-determining mechanism.

The Effect of ΔpK_a

As we already pointed out that the titration of the following weak acidic mixtures;

- benzoic acid and potassium biphthalate
- p-nitrophenol and pralidoxime chloride
- pralidoxime chloride and boric acid

were statistical difference between the equivalent volume, obtained from solving the modified equation (Eq. 53) and the equivalent volume, obtained from the reference method, G plot (Eq. 9 and 21). It could be seen that this method had the error in determination, when the dissociation constant of two weak acids in the mixtures were quite close.

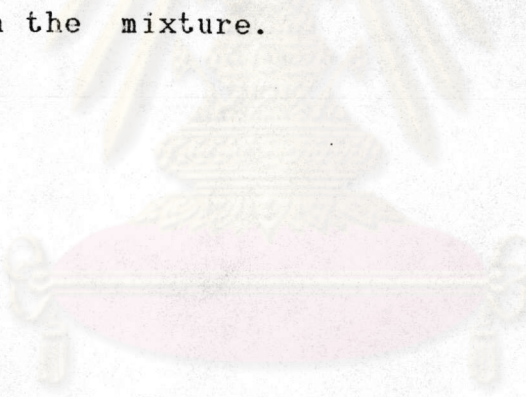
The reason was that the range of data which were used in the calculation of the modified equation (Eq. 53) was in the range of high buffer capacity, as shown in Figure 80, 82 and 84. These figures showed the titration

curves of these weak acid mixtures, which the slope of their buffer regions were less than the titration curve of other weak acid mixtures, which their ΔpK_a were more than about 2. In this region, the measurement of pH values was not sensitive enough to the change of titrant volume. Thus, the modified equation (Eq. 53) could not be used to accurately separate the effect of each weak acid on the pH of solution.

The factor which would affect the numerical value of slope of the buffer region include concentration of each weak acid and the ΔpK_a . The values of slopes for mixed weak acids as shown in Table 35 reflects the "apparent minimum slope value". To clarify this, let us look at mixture of potassium biphthalate-boric acid and the mixture of potassium biphthalate-p-nitrophenol. The slope value for potassium biphthalate-boric acid ($\Delta pK_a = 4.058$) is 0.685 and the slope for potassium biphthalate-p-nitrophenol ($\Delta pK_a = 1.960$) is 0.725. The reason for potassium biphthalate-p-nitrophenol has higher apparent slope than potassium biphthalate-boric acid mixture is because the buffer region of potassium biphthalate and p-nitrophenol significantly overlapped with each other and calculation of the apparent slope include both the buffer region of potassium biphthalate and p-nitrophenol. Where as in the case of potassium biphthalate-boric acid, there is no overlapping of the buffer regions and hence the apparent slope of this

mixture is actually the slope of potassium biphthalate only.

Moreover, there was a small uncertainty in the pH measurement. Normally, this does not lead to error in determination of equivalent volumes of each weak acid in the mixture. Error would arise only when the change in pH of solution was small when compared to change in volume of titrant (see Table 35) and for the weak acidic mixtures, this would occur when ΔpK_a was less than 2. This would lead to error in determination of equivalent point for each weak acid in the mixture.



ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย