

Investigación

Potentiometric Analysis of a Reaction System of Organic Acids

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Abstract. A new potentiometric titration method for the quantitative analysis of a reaction system of diprotic organic acids is presented. The method uses the individual potentiometric titration data for calculating the dissociation constants. With this information a set of " $n - 1$ " linear equations and " $n - 1$ " unknowns is solved; " n " is the number of organic acids present in the reaction mixture. This method was applied to tartaric acid process production from maleic acid. In this process two successive reactions take place: firstly the maleic acid epoxidizes to epoxysuccinic acid and secondly the epoxysuccinic acid hydrolyzes to tartaric acid, leaving three organic acids present in the reaction system. It is necessary to quantify the concentration of all three acids in order to determine the progress of the reaction. This paper describes a fast, economical and easy to carry out analytical method for determining the concentration of all three acids simultaneously by potentiometric titration.

Keywords: Acid-Base Chemistry, Quantitative Analysis, Potentiometric Titration.

Resumen. Se presenta un nuevo método de titulación potenciométrica para el análisis cuantitativo de un sistema de reacción de ácidos orgánicos diprotónicos. El método parte de los datos de la titulación potenciométrica para cada uno de los ácidos de manera individual para determinar sus respectivas constantes de disociación. Se plantea un sistema de " n " ecuaciones lineales con " n " incógnitas, donde " n " es el número de ácidos presentes en el sistema de reacción. Este método fue aplicado en el proceso de producción de ácido tartárico a partir del ácido maleico. En este proceso suceden dos reacciones sucesivas: el ácido maleico se convierte en ácido epoxisuccínico para posteriormente este último hidrolizarse a ácido tartárico, por lo que se forma una mezcla en la que están presentes los tres ácidos. Para determinar el grado de avance de la reacción se requiere cuantificar la concentración de los tres ácidos. El artículo describe un método analítico rápido, económico y fácil de implementar para determinar simultáneamente la concentración de los tres ácidos por titulación potenciométrica.

Palabras clave: Titulación potenciométrica, análisis cuantitativo, química ácido-base.

Introduction

Acid-base potentiometric titration is the most common analytical technique for determining the concentration of one acid in solution. Dashek and Micales [1] presented a summary of procedures employed for the detection and quantification of organic acids. They reported ten methods (Capillary electrophoresis, colorimetry, conductimetric titration, differential pulse polarography, enzymatic method, gas chromatography, high-pressure liquid chromatography, ion exchange chromatography, photometric determination and silica gel chromatography with gradient elution), but did not consider a potentiometric titration. A generalization of this technique for a mixture of acids is very important. Kankare [2] proposed a simple linear relationship between the deprotonation degree of the mixture and the mole fraction of the acids. He concluded that it is possible to determine by a potentiometric titration the concentration of weak acids in a mixture. Betti *et al.* [3] carried out a potentiometric titration of mixtures of two weak monoprotic acids. They found that the method precision was a function of the dissociation constants and the ratio of the acid concentrations. Gordus [4] carried out similar experiments but using polyprotic acids. He concluded that it is impossible to determine, by a potentiometric titration, the concentration of

the individual acids in a mixture. Papanastasiou *y col.* [5] presented an iterative method for a potentiometric titration of a mixture of monoprotic weak acids and found that it is possible to obtain accurate results even for acids with similar dissociation constants. De Levie [6] developed a single equation describing the entire progress of the titration, but did not calculate the concentration of acids in the mixture. This work describes the potentiometric method developed by Castro [7] for calculating the concentration of three organic acids present in the catalytic peroxidation of maleic acid. This method can be extended to systems without reaction.

Fundamentals

When the maleic acid reacts, it produces epoxysuccinic acid and tartaric acid. The concentration of hydrogen ions present in the reaction system changes due to the different ionization constants of the three organic acids. Fig. 1 shows the titration curves for the three 0.1 N organic acids when titrated with 0.1 N sodium hydroxide. Potentiometric titrations are easy, fast and reliable techniques when the added volume and pH can be measured with high precision and the system is well stirred. The dissociation expressions for the reaction system are:

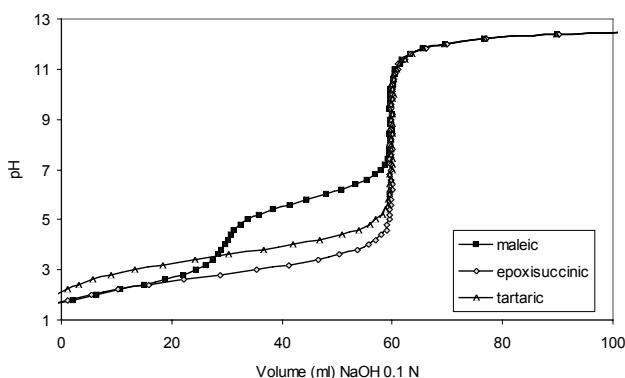
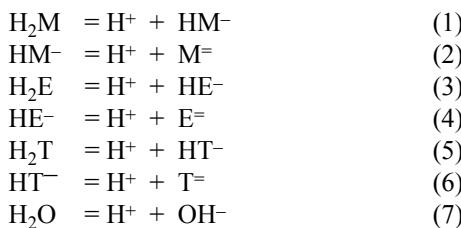


Fig. 1. Titration curves for three diprotic acids.



Where:

H_2M , HM^- , $\text{M}^=$ = Maleic acid species: no, partially and complete dissociated respectively
 H_2E , HE^- , $\text{E}^=$ = Epoxysuccinic acid species: no, partially and complete dissociated respectively
 H_2T , HT^- , $\text{T}^=$ = Tartaric acid species: no, partially and complete dissociated respectively
 H_2O = Water
 H^+ = Hydrogen ion
 OH^- = Hydroxide ion

Applying the electroneutrality principle to equations 1-7 gives:

$$[\text{H}^+] + [\text{Na}^+] = [\text{HM}^-] + 2[\text{M}^=] + [\text{HE}^-] + 2[\text{E}^=] + [\text{HT}^-] + 2[\text{T}^=] + [\text{OH}^-] \quad (8)$$

Formulating the mass balance relations that include the dilution of the sample as result of the addition of titrant and the degree of advance of two successive reactions, we get:

$$[\text{H}_2\text{M}] + [\text{HM}^-] + [\text{M}^=] = \frac{C_{mi} V_a}{V_a + V_b} (1 - X) \quad (9)$$

$$[\text{H}_2\text{E}] + [\text{HE}^-] + [\text{E}^=] = C_{ei} + \frac{C_{mi} V_a}{V_a + V_b} X (1 - Y) \quad (10)$$

$$[\text{H}_2\text{T}] + [\text{HT}^-] + [\text{T}^=] = C_{ti} + \frac{C_{mi} V_a}{V_a + V_b} X Y \quad (11)$$

$$[\text{Na}^+] = \frac{C_b V_b}{V_a + V_b} \quad (12)$$

where:

C_{mi} , C_{ei} , C_{ti} = Initial concentration of maleic, epoxysuccinic and tartaric acid respectively

V_a = Initial volume of acid (sample)

V_b = Add volume of NaOH during the titration

The species acid fractions (α_{HiA}) and K_i values are identical to De Levi [6] expressions:

$$\alpha_{HiA} = \frac{[H^+] K_1 K_2 \dots K_{n-i}}{[H^+] + [H^+]^{-1} K_1 + [H^+]^{-2} K_1 K_2 + \dots + K_1 K_2 \dots K_n} \quad (13)$$

with $i = 1, 2, \dots, n$, and

$$K_i = \frac{[H^+] [H_{n-i} A]}{[H_{n-i+1} A]} \quad (14)$$

Combining the charge balance relation (Eq. 8), with the species acid fractions (Eq. 13) and mass balance relations (Eqs. 9-12), and considering that initially epoxysuccinic acid and tartaric acid are zero, we obtain:

$$\frac{V_b}{V_a} = \frac{C_{mi} (1 - X) (\alpha_{HM}^- + 2\alpha_M^=) + C_{mi} X (1 - Y) (\alpha_{HE}^- + 2\alpha_E^=) + C_{mi} X Y (\alpha_{HT}^- + 2\alpha_T^=) - [H^+] + [OH^-]}{C_b + [H^+] - [OH^-]} + \frac{C_{mi} X Y (\alpha_{HT}^- + 2\alpha_T^=) - [H^+] + [OH^-]}{C_b + [H^+] - [OH^-]} \quad (15)$$

where: X and Y are the conversion of maleic acid to epoxysuccinic acid and the conversion of epoxysuccinic acid to tartaric acid respectively. By definition X and Y are:

$$X = \frac{C_{mi} - C_m}{C_{mi}} \quad (16)$$

$$Y = \frac{C_T}{C_{mi} - C_m} \quad (17)$$

Combining the conversion definitions (Eqs. 16-17) with Eq. 15, we obtain:

$$\frac{V_b}{V_a} = \frac{C_M (F_{am} - F_{ac}) + C_T (F_{at} - F_{ac}) + C_{mi} F_{ac} - [H^+] + [OH^-]}{C_b + [H^+] - [OH^-]} \quad (18)$$

where:

F_{ai} = $\alpha_{Hi}^- + 2\alpha_i$

C_m , C_T = Maleic and tartaric acid concentration at any time

Experimental

All measurements were done with a MSE Spectro-Plus, model 41113-2244 with multiple options. The temperature was controlled by a Cole-Parmer High-Performance Utility Baths and was maintained at 25 ± 0.15 °C. The reagents used were ana-

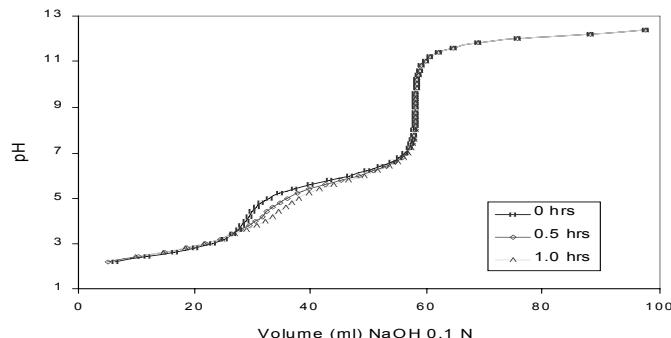


Fig. 2. Titration curves for the reaction system samples at different times

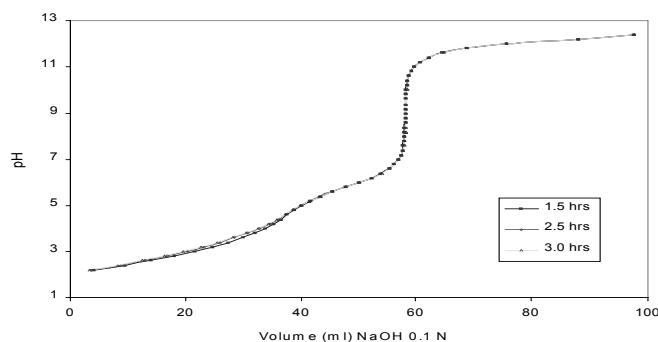


Fig. 3. Titration curves for the reaction system samples at different times

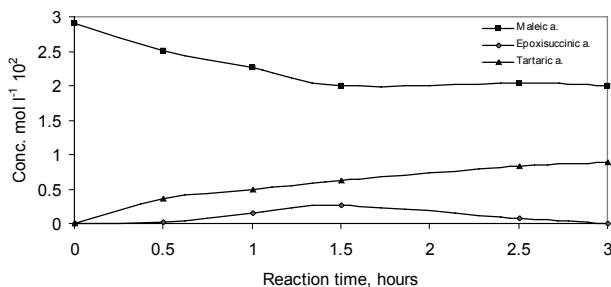


Fig. 4. Concentration profiles for the reaction system.

lytical grade (Aldrich, 99 %). The procedure included titrations of each pure acid (for the dissociation constants determination) and titrations of the mixture of all three acids. An aliquot of the sample, V_m , was taken from the reactor at different times (from $t = 0$ until the reaction system became stabilized), diluted to 100 mL with distilled water, and titrated with a 0.1 N sodium hydroxide solution. Figs. 2 and 3 show the titration curves for the reaction system samples at different times. Fifty values of volume of NaOH added and pH were registered. Titrations of the samples were done twice.

Calculations

The dissociation constants (K_i) of pure acid were determined by non linear multiple regression from the titration data at 25

Table 1. Dissociation constants at 25 °C.

Acid	K_1	K_2
Maleic	5.0370E-3	1.5365E-6
Epoxysuccinic	3.6520E-3	6.6872E-4
Tartaric	6.4120E-4	1.0618E-4

Table 2. Known and calculated concentration of Maleic acid.

Known concentration mol L⁻¹	Calculated Concentration mol L⁻¹	Relative error %
0.0263	0.0262	0.3802
0.0443	0.0442	0.2257
0.0491	0.0502	2.2403
0.0505	0.0504	0.1980

Table 3. Known and calculated concentration of Epoxysuccinic acid.

Known concentration mol L⁻¹	Calculated Concentration mol L⁻¹	Relative error %
0.0284	0.0280	3.4483
0.0471	0.0450	4.4586
0.0518	0.0510	1.5444
0.0605	0.0609	0.6612

Table 4. Known and calculated concentration of Tartaric acid.

Known concentration mol L⁻¹	Calculated Concentration	Relative error % mol L⁻¹
0.0279	0.0284	1.7921
0.0453	0.0455	0.4415
0.0507	0.0510	0.5917
0.0509	0.0512	0.5894

°C of the pure acids (Fig. 1). Table 1 shows the dissociation constants for all three acids in the reaction system found by a non linear regression algorithm.

Calculating F_{ai} (Eq. 19) for two pH levels in the titration curves of the mixture of acids and substituting the others variables (V_b , V_a , C_{mi} [H₊], C_b) with $[\text{OH}^-] = 1\text{e-}14 / [\text{H}^+]$ in eq. 18, we generated a set of two linear equations and two unknowns (C_M and C_T). We can use any pair of pH values, but it is recommended to select them in a range where the slope of the titration curve is small. For example for reaction time of 1.0 hour and pH values of 3.6 and 4.2 the equations are:

$$0.736538 C_M + 0.678041 C_T = 0.020017 \quad (20)$$

$$0.899531 C_M + 0.341249 C_T = 0.022036 \quad (21)$$

The concentration for the epoxysuccinic acid (C_E) is found by subtraction using equation (22).

Table 5. Known and calculated concentration of different mixtures of acids.

Known concentration mol L ⁻¹			Calculated Concentration mol L ⁻¹			Relative error %		
AM	AE	AT	AM	AE	AT	AM	AE	AT
0.0280	0.0120	0.0000	0.0282	0.0121	0.0000	0.7143	0.8333	0.0000
0.0240	0.0080	0.0080	0.0240	0.0079	0.0081	0.0000	1.2500	1.2500
0.0160	0.0120	0.0120	0.0161	0.0119	0.0120	0.6250	0.8333	0.0000
0.0000	0.0080	0.0320	0.0000	0.0079	0.0320	0.0000	1.2500	0.0000

Table 6. Test of hypothesis.

Acid	Mean	Standard deviation	Lower limit	Upper limit
Maleic known	0.0426	0.0112	0.0248	0.0603
Maleic calculated	0.0428	0.0114	0.0246	0.0689
Epoxysuccinic known	0.0470	0.0136	0.0254	0.0685
Epoxysuccinic calculated	0.0462	0.0138	0.0243	0.0682
Tartaric known	0.0437	0.0108	0.0264	0.0610
Tartaric calculated	0.0440	0.0108	0.0269	0.0611

$$C_E = C_{mi} - C_M - C_T \quad (22)$$

Results

We validated the developed method by analysis of the pure acids as well as the by mixture of all of them. Tables 2, 3 and 4 show the known and calculated concentrations (Eq. 18) for each acid when they were titrated separately. Table 5 shows the known and calculated concentration for different mixtures of the three acids.

In the example, solving the set of two linear equations and two unknowns (eqs. 20-21) and applying eq. 22, we obtain: $C_M = 2.2619 \times 10^{-2}$ mol L⁻¹, $C_T = 0.4951 \times 10^{-2}$ mol L⁻¹ and $C_E = 0.1480 \times 10^{-2}$ mol L⁻¹. The Fig. 4 shows the concentration profiles for the reaction system, calculated by this method.

Discussion

Test of hypotheses on the equality of the calculated and known concentration for each pure acid means were done. It was assumed that both variables were normally distributed with variances unknown. The process for the statistical analysis is described by Montgomery [8]. The null hypothesis was: "there is no statistical difference between the theoretical and experimental mean values".

$$H_0: m_1 = m_2 \quad (23)$$

$$H_1: m \neq m_2 \quad (24)$$

The test is based on the t-test:

$$t_o = \frac{\bar{X}_1 - \bar{X}_2}{S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \quad (25)$$

Where S_p is a single estimate of the common variance, \bar{X}_1 and \bar{X}_2 are the means of calculated and known concentration, n_1 and n_2 are the samples sizes. The null hypothesis is accepted if: $|t_o| > t_{\alpha/2, n_1+n_2-2}$, where $t_{\alpha/2, n_1+n_2-2}$ is the t-student distribution at the a significant level and $n_1 + n_2 - 2$ degrees of freedom. Table 6 shows the results when Montgomery's method was applied.

For $\alpha = 0.05$ and $n_1 = n_2 = 4$ the t-value is equal to 2.447. For all cases the null hypothesis was accepted. There is no difference between the calculated and the known means. Therefore, the method proposed in this work is suitable to be used successfully. Of course, the ionic strength affect the dissociation constants determination, but when the sample concentration is too small, the activity coefficient are almost unity, so the measured (or apparent) dissociation constants are very close to obtained to zero ionic strength [9]. Additionally, Albert and Serjeant [10] recommended that the ionic strength corrections be applied when an instrument calibrated in 0.005 pH units or less has been used.

Conclusions

This work presents a fast, economical and easy to carry out potentiometric method for the quantitative analysis of a mixture of organic acids. The results indicate that it can be used in chemical or physical systems for simultaneous determination of the concentrations of all acids present in a ternary mixture and can compete with others methods as gas chromatography.

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