The Gran Plot Analysis of an Acid Mixture

An Undergraduate Experiment to Highlight This Alternate Method

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The use of a Gran plot (1) for finding the equivalence point of a potentiometric titration has several advantages over the more commonly used procedure of inflection point determination of a sigmoidal logarithmic plot such as a pH titration curve. The advantages were pointed out by Rossotti and Rossotti (2), and many well-known analytical chemistry textbooks have by now included a discussion of this alternate method (3–7). However, only one of the textbooks surveyed (3) contains the description of an experiment utilizing a Gran plot and it does not demonstrate the usefulness of the procedure for the quantitative analysis of an unknown. Several applications of the Gran plot have appeared in the literature recently. It has been incorporated into an experiment for the determination of fluoride concentration by use of a specific ion electrode (8) and one for acid rain analysis (9). And the Gran plot has been applied to the measurement of percent strong acid found in atmospheric aerosols over the Northeastern United States (10).

The experiment presented here is an adaptation of this last application. It is a straightforward one, designed to introduce students to the method by applying it to a system where it can be easier to use and more precise than a titration curve, namely, the determination of strong and weak acid concentrations in an unknown. It is designed to show students the procedure for analyzing free ions as well as those involved in an equilibrium. The experiment can be used to acquaint students with the concept of activities and with the application of the method of least squares for data analysis. It involves a system where accurate unknowns can be made easily. And it shows that Gran plots are as useful for the study of acids as they are for other analytes in solution.

Background

The Gran plot technique has several advantages when compared to potentiometric titration curves and differential plots of them. The graphical analysis is of 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 equivalence point. There is no need to anticipate the approach of the equivalence point in order to slow down the addition of titrant, and, concurrently, there is no need to redo a titration if it is overshot. It can be used when only a portion of the titration curve is accessible to measurement such as in the analysis of a strong acid in the presence of hydrolyzable metal ions or weak acid molecules. Also, the linear extrapolation used in the method can provide more precise results than those obtained by the differential method, especially for nonsymmetric titration curves. Finally, students now have access to hand-held calculators or computers with linear regression programs to make the unbiased determination of intercepts easier. Gran plots do require a certain amount of repetitive calculations; but these are no more time-consuming than those needed for differential plots and are simple enough to do between the collection of data points, with the use of calculators. Such calculations can even be eliminated in most cases if one chooses to use the specially prepared skewed semi-antilog paper available for this type of titration (Orion Research Incorporated, Cambridge, MA).

Theory

The basic premise of a Gran plot is that a linear relationship can be found between the analyte concentration during titration and the volume of titrant added, V_T, such that a plot of this relationship versus V_T will yield a straight line that intercepts the V_T axis at the equivalence volume for the analyte, V_E. Specific ion electrodes (the pH electrode in this case) are used to monitor the analyte concentration. The form of the relationship depends on whether or not the analyte is involved in an equilibrium.

For the case of a completely dissociated strong acid sample of concentration C_S and volume V_S, being titrated with a base titrant of concentration C_T, the hydrogen ion concentration during the titration up to the equivalence point can be expressed as

$$[H^+] = \frac{C_S V_S - C_T V_T}{V_S + V_T} \tag{1}$$

Recalling that V_E is the equivalence volume, the substitution of $C_T V_E$ for $C_S V_S$ can be made and rearrangement of eq 1 yields

$$(V_S + V_T)[H^+] = C_T(V_E - V_T) \tag{2}$$

Because pH electrodes, like other specific ion electrodes, respond to activities rather than concentrations, the expression $10^{-pH} = a_{H^+} = \gamma_{H^+}[H^+]$ must be used to relate the measured quantity to the desired one. Substitution and rearrangement gives

$$(V_S + V_T)10^{-pH} = C_T \gamma_{H^+}(V_E - V_T) \tag{3}$$

It can be seen that a plot of $(V_S + V_T)10^{-pH}$ versus V_T should be a straight line intercepting the V_T axis at V_E, provided that the activity coefficient, γ_{H^+} and the junction potentials remain constant during the titration. The latter assumption is generally acceptable as long as the electrodes stay in the same solution and, for dilute solutions, the assumption of nonvarying activity coefficients is reasonable. Naturally, $(V_S + V_T)10^{-pH}$ never really goes to zero because 10^{-pH} is never zero due to other sources of hydrogen ion in solution; however, there will be a linear region of the plot that can be extrapolated to the V_T axis to obtain V_E.

The relationship used for a weak acid, HA, differs from eq 3 because of the equilibrium existing between HA, H^+, and A^-, which can be summarized by the acid dissociation constant expression,

$$K_a = \frac{\gamma_{H^+}[H^+]\gamma_{A^-}[A^-]}{\gamma_{HA}[HA]} \tag{4}$$

For a sample of HA with initial concentration, C_S, and volume, V_S, it is a good approximation to say that after the addition of V_T of titrant of concentration C_T,

$$[HA] = \frac{C_S V_S - C_T V_T}{V_S + V_T} = \frac{C_T(V_E - V_T)}{V_S + V_T} \tag{5}$$

and

$$[A^-] = \frac{C_T V_T}{V_S + V_T} \tag{6}$$

Substitution of eqs 5 and 6 into eq 4, followed by cancellation of $C_T(V_S + V_T)$ and rearrangement, gives

$$V_T \gamma_{H^+}(H^+) = V_T 10^{-pH} = K_a \frac{\gamma_{HA}}{\gamma_{A^-}}(V_E - V_T) \qquad (7)$$

If the assumptions mentioned above hold, a plot of $V_T 10^{-pH}$ versus V_T yields a linear region that can be extrapolated to intercept the V_T axis at V_E. It is also possible to obtain the value of K_a from the slope of the line and calculated values of γ_{HA} and γ_{A^-}. This was not done in the experiment described here but the procedure to do so is detailed in reference 3, page 622.

In order to apply the Gran plot method to a mixture of strong and weak acids, it should be realized that the strong acid will titrate first so that eq 3 will 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 would mean substituting into eq 6 the term V'_T for V_T where $V'_T = V_T - V_E$ (strong acid). Therefore the equivalence volume of the strong acid must be determined before the second Gran plot can be made.

Experimental

This experiment was incorporated into a new lecture/laboratory course in analytical chemistry designed for sophmore chemistry and junior biochemistry majors. Students were given a reading assignment on Gran plots and activities from the lecture text (3) and a handout elaborating on the method and its background. During the prelaboratory lecture mention was made of the concept of activities but a more detailed discussion was deferred to the lecture and a later experiment involving a fluoride ion-selective electrode. During the previous week the students had done a potentiometric titration curve of an unknown chloride/bromide mixture and so were familiar with this method for comparison.

Students were given unknown mixtures containing hydrochloric acid in the concentration range 0.040 M to 0.060 M and acetic acid in the range 0.080 M to 0.11 M. These mixtures allow for the complete titration of a 25.0-mL aliquot by less than 50 mL of 0.1000 N sodium hydroxide solution. The students were required to prepare and standardize their own sodium hydroxide solutions. The operation of the pH meter was reviewed and the electrodes were standardized against a pH 7 buffer.

The students were instructed to pipet 25.0 mL of their unknown and 25.0 mL of distilled water into a dry 150-mL beaker. The beaker was placed on a magnetic stirrer and the electrodes and a stirbar were inserted. The stirrer was turned on and an initial reading was taken. Then the sodium hydroxide was added in 1.00 mL aliquots from a buret and after a 30- to 60-second wait to allow the reading to stabilize the pH was recorded. Students were cautioned not to rinse the sides of the beaker or the buret tip with distilled water because of the importance of knowing the exact solution volume at all times.

An efficient method for performing the measurements is to have the students spend the time between additions of titrant calculating the values needed for doing the first Gran plot. The aliquots of sodium hydroxide are added until the rapid rise in pH due to the onset of the second equivalence point is encountered. The first equivalence point is not easily seen and so only one sharp rise occurs.

The Gran plot for the hydrochloric acid was obtained first and its equivalence volume was used to calculate V'_T for the acetic acid plot. The students were given the option of determining the best straight lines graphically "by eye" or mathematically by using a least-squares-fit program. In the latter case the plots still need to be done in order to select the range of points which best represent a straight line. For the strong acid plot, an ordinate range of an order of magnitude is sufficient to define the line. The weak acid plot should be
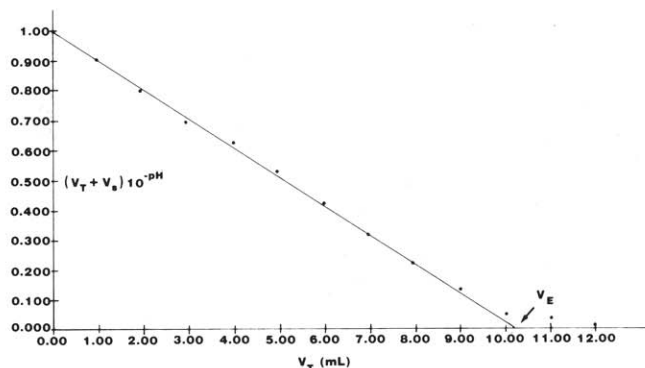

Figure 1. Typical Gran plot for the determination of the equivalence volume of the strong acid component (hydrochloric) of an unknown mixture.
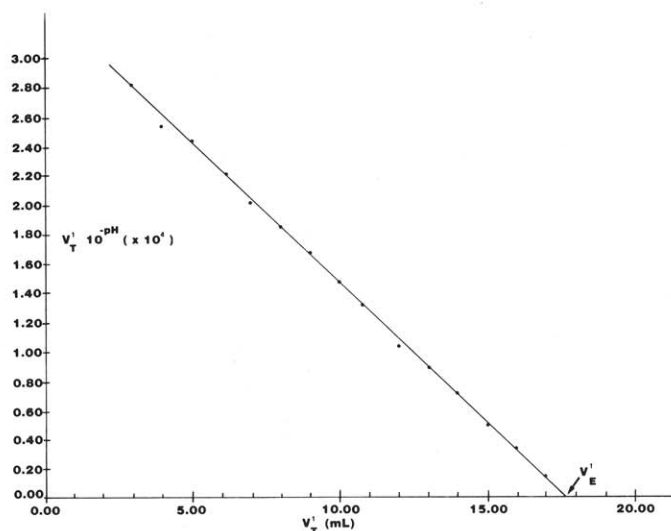

Figure 2. Gran plot for the determination of the equivalence volume of the weak acid component (acetic) in the same mixture as Figure 1.

between the first equivalence point and the observable sharp rise in pH. The students were also asked to prepare a pH titration curve plot from their data so that they could compare the ease of recognizing the equivalence points by the two methods.

It should be noted that normal least-squares-fit programs determine the y intercept whereas students will need the x intercept of the Gran plot. This can be obtained from the slope, m, and the y intercept, b, gotten from the program, by recognizing that setting $y = 0$ in the equation for a straight line will give the x intercept value as $-b/m$.

Results

Typical Gran plots for the hydrochloric and acetic acids are shown in Figures 1 and 2. For comparison, Figure 3 is a plot of the pH titration curve obtained for the same sample mixture. Note that whereas the weak acid equivalence point can be distinguished equally well from both types of plots, the strong acid equivalence point is ill defined in the pH titration curve but easily found by the Gran plot. Also note the obvious nonlinear region in Figure 1 near the equivalence point.

This experiment has been used for two years in the course. During the most recent year two-thirds of the students reported results for the hydrochloric acid concentration that were within 3% of the correct value and acetic acid concentrations that were within 4%. The higher uncertainty in acetic acid results is to be expected because the value ob-
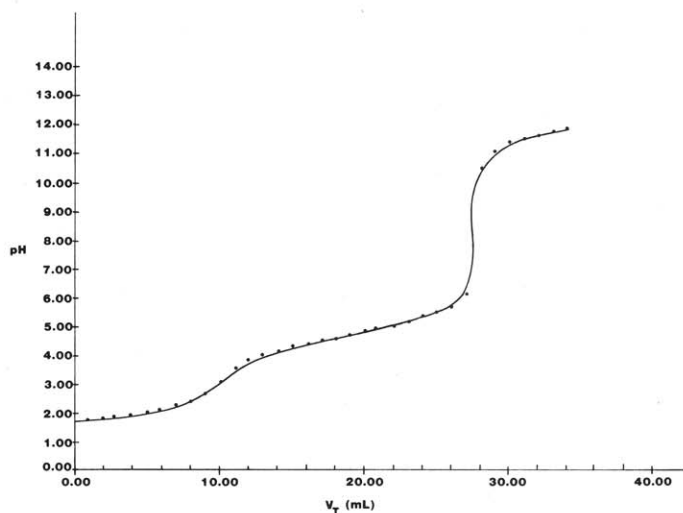
Figure 3. The pH titration curve of the same acid mixture as in Figures 1 and 2.

tained for its equivalence volume depends on the value obtained for hydrochloric acid.

Conclusion

The Gran plot method for finding equivalence points is a convenient and often more efficient procedure than those more commonly used. The experiment described here has proven successful in introducing it to students who will be using such procedures in their future careers. Further modifications of the method can include replacing the burette with a constant volume pipetter and computerizing the titrant addition and data analysis. The author is currently studying both areas.

Acknowledgment

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