Linear Graphs for Understanding Acid–Base Titrations

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Abstract: The dependence of the various concentrations on the progress of an acid–base titration can be visualized in the form of linear graphs.

1. Introduction

In evaluations of the effectiveness of teaching chemistry, equilibria and titrations are often mentioned as among the most difficult topics. This has several possible reasons, such as (1) the nontransparency of the traditional, piecemeal theory, and (2) the nonlinear shape of the titration curve. The issue may be further complicated by (3) considering activity effects at an early stage, an eminently avoidable [1, 2] but often self-inflicted problem. The first two of these are inherent in any titration, and must therefore be dealt with. In the preceding communication [3] we have tried to simplify the *theory* as much as possible. In the present note we will consider some *graphical aids* that may help us understand what titrations are all about, and, specifically, where their peculiar shape comes from. In the discussion we will comment on the third-mentioned difficulty.

The best-known example of using linear graphs to represent titrations are the Gran plots [4], in which appropriate functions of $[H^+]$ or $[OH^-]$ are plotted versus the titrant volume V_t. Actually, Gran plots are always nonlinear, but they often exhibit near-linear sections that can be extrapolated to their intersection in order to obtain the equivalence volume V_{eq}. For polyprotic acids and bases, as well as for mixtures, Gran plots are often too curved to be useful. An elegant, truly linear plot for the titration of a single monoprotic acid or base was more recently described by Schwartz [5]. Unfortunately, neither Gran nor Schwartz plots are extendable to polyprotic acids and bases, where the number of parameters is too large to make such a linearization possible.

Below we will describe another class of graphs, which are linear over the entire progress of the titration, even for polyprotic systems and mixtures. Such graphs can be very useful in visualizing what titrations are all about. On the other hand, they are of no help in locating the equivalence volume V_{eq}. Fortunately, that requirement is no longer so pressing, now that we can fit the progress of the entire titration directly to a single, closed-form algebraic expression in order to find the unknown total analytical concentrations C and/or the relevant equilibrium constants K_a [1, 2, 6]. In fact, such a fit completely obviates the need for an intermediary calculational parameter such as the equivalence volume V_{eq}, and the associated, nontrivial analysis of propagated uncertainty.

2. A Simple Model

We will first give an outline of our approach, valid when we have available a titrant delivery system that can accurately deliver known, small volumes of a concentrated titrant, such as a precision displacement buret. We will assume, as is customary in such a case, that the titrant concentration is much higher than that of the sample, so that mutual dilution effects can be neglected. In section 3 we will see how to modify our results when dilution must be taken into account.

Apart from this just-mentioned but soon to be lifted constraint, the theory on which we will base our graphs will be exact, and will treat the entire titration curve as a whole. The traditional theory is usually both approximate and piecemeal. Approximations can serve very useful functions in science, but should only be used when needed.

We will restrict our discussion to the titration of acidic samples (acids, acid salts, or mixtures thereof) with a single, strong, monoprotic base. Since we are free to choose the titrant, and a strong base is optimal for the titration of acids, this should not be a problem. As our main parameter we will use the proton excess $\Delta = [H^+] - [OH^-]$.

2a. Titrating a Strong Monoprotic Acid

We examine the titration of an aqueous sample of HCl, of concentration C_a and sample volume V_a, with a variable volume V_b of aqueous NaOH, of concentration C_b. Both HCl and NaOH will be considered to be fully ionized, so that the solution will only contain water molecules plus the ions H^+, Cl^-, Na^+, and OH^- (or, if one prefers such notation, their hydrated forms, such as H_3O^+ for H^+).

The reaction of HCl with NaOH involves the reaction $H^+ + OH^- \rightarrow H_2O$, i.e., adding a solution of NaOH to a sample of HCl causes the added OH^- to react with the H^+ ions in the sample, but does not affect the ions Cl^- and Na^+ in any chemical sense. In this titration, Cl^- and Na^+ can therefore be considered to be mere *spectator* ions. Therefore, when the titrant is sufficiently concentrated, so that $V_b \ll V_a$ over the entire course of the titration, and hence the resulting sample dilution can be neglected, we have

$$[Cl^-] = C_a V_a/(V_a + V_b) \approx C_a \qquad (1)$$

and

$$[Na^+] = C_b V_b/(V_a + V_b) \approx C_b V_b/V_a \qquad (2)$$

where the term V_b/V_a accounts for the unavoidable dilution of the sodium ions by the much larger volume V_a of the acid sample already in the titration vessel.

Since there are only four different kinds of ions present, the relevant electroneutrality condition is

$$[H^+] + [Na^+] = [Cl^-] + [OH^-] \quad (3)$$

for the mixture of sample plus titrant, *at any point during the titration*. Upon substitution of eqs (1) and (2) into eq (3) we obtain

$$[H^+] + C_b V_b / V_a = C_a + [OH^-] \quad (4)$$

which, after some algebraic manipulation, yields

$$\Delta = [H^+] - [OH^-] = C_a - C_b V_b / V_a \quad (5)$$

From eq (5) we conclude that the proton excess Δ will be a linear function of the volume V_b of titrant added to the sample. Specifically, a plot of Δ versus V_b should start (at the beginning of the titration, where $V_b = 0$) at $\Delta = C_a$, and cross the horizontal axis at the equivalence volume, i.e., at $V_b = V_{eq} = C_a V_a / C_b$, see eq (2).

Why this special role for the proton *excess* Δ rather than for the proton *concentration* $[H^+]$? Because the autoprotolysis of water generates both H^+ and OH^-, and the titration only deals with the *excess* of protons H^+ over hydroxide ions OH^-, i.e., with $\Delta = [H^+] - [OH^-]$.

2b. The Shape of the Titration Curve

We now consider the peculiar shape of the titration curve. This curve, i.e., the plot of pH vs. V_b, is S-shaped. Why is this so?

We have seen in the previous section that Δ is a linear function of V_b. Here we will illustrate that the shape of the titration curve results from the dependence of pH on Δ. In Figure 1a we plot pH = – log $[H^+]$ as a function of $[H^+]$. It is a curve all right, but it doesn't look like a complete titration curve. Figure 1b shows the pH as a function of $[OH^-]$. Again, no luck. But when we plot pH as a function of Δ, as in Figure 1c, we obtain a curve that indeed has the shape of a titration curve. And, in retrospect, it will be clear that the curve of pH vs. Δ should indeed have that shape, because we just demonstrated, in eq (5), that Δ is a linear function of V_b.

This short detour again illustrates the central role of the proton *excess* in acid–base titrations. In Figure 1c we have plotted pH vs. *minus* Δ in view of the minus sign of the V_b-term in eq (5).

3. The Complete Theory

When titrations are performed manually, with simple volumetric glassware, the concentration C_a of an acid sample is usually of the same order of magnitude as the concentration C_b of the base used as its titrant, in order to minimize the effects of volumetric reading errors. Dilution effects must then be considered for precise quantitative results, and we will do so now.

3a. Titrating a Strong Monoprotic Acid

We reconsider the concentrations of these spectator ions. When a significant volume of titrant is added to the sample, the concentrations of the components in the original sample are also diluted. In our example of the titration of HCl with NaOH, this applies to the chloride anions. Conservation of mass then requires that

$$[Cl^-] = C_a V_a/(V_a + V_b) \quad (1')$$

where the term $V_a/(V_a + V_b)$ describes the dilution of chloride ions by the addition of NaOH. Likewise, the sodium concentration will be given by

$$[Na^+] = C_b V_b/(V_a + V_b) \quad (2')$$

where the term $V_b/(V_a + V_b)$ accounts for the dilution of sodium ions by the volume of HCl already present in the titration vessel. Equations (1') and (2') revert to eqs (1) and (2) respectively for $V_b \ll V_a$.

Substituting eqs (1') and (2') into eq (3) yields

$$[H^+] + \frac{C_b V_b}{V_a + V_b} = \frac{C_a V_a}{V_a + V_b} + [OH^-] \quad (4')$$

or, after some algebraic manipulation,

$$\frac{V_b}{V_a} = \frac{C_a - [H^+] + [OH^-]}{C_b + [H^+] - [OH^-]} = \frac{C_a - \Delta}{C_b + \Delta} \quad (6)$$

This equation for the titration of a single, strong, monoprotic acid with a single, strong, monoprotic base has the form of the *general* result for *any* acid–base titration [1, 2, 6].

In Figure 2a we display the various concentrations of the four ions involved, H^+, Cl^-, Na^+, and OH^-, for the titration of 25 mL of 0.08 M HCl with 0.10 M NaOH, and in Figure 2b the corresponding proton excess Δ.

All concentrations in Figure 2 are now represented by *curves*. This is not surprising, because all concentrations, including those of the spectator ions, are subject to dilution.

In order to compensate for this dilution effect, we multiply the concentration terms $[H^+]$, $[OH^-]$, $[Cl^-]$ and Δ by the factor $(V_a + V_b)/V_a$, and $[Na^+]$ by the factor $(V_a + V_b)/V_b$. Figure 3a displays the resulting, dilution-corrected concentrations, identified as such by a prime mark ('): $[H^+]' = [H^+]\ (V_a + V_b)/V_a$, $[Na^+]' = [Na^+]\ (V_a + V_b)/V_b$, etc. As a result, the corrected concentrations $[Na^+]'$ and $[Cl^-]'$ of the spectator ions become constant (except for $[Na^+]'$ when $V_b = 0$), and the corrected concentrations $[H^+]'$ and $[OH^-]'$ exhibit approximately linear sections as a function of V_b before and beyond the equivalence point respectively. Moreover, the dilution-corrected proton excess $\Delta' = \Delta\ (V_a + V_b)/V_a = ([H^+] - [OH^-])\ (V_a + V_b)/V_a$ becomes a linear function of the volume V_b of titrant added throughout the *entire* range of the titration.

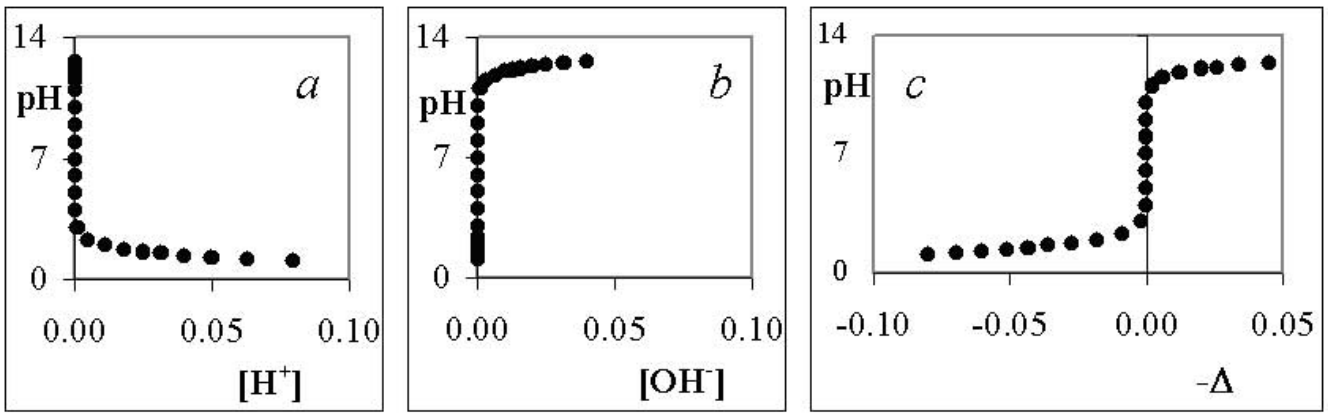

Figure 1. (a): The pH as a function of $[H^+]$. (b): The pH as a function of $[OH^-]$. (c): The pH as a function of $-\Delta = -([H^+] - [OH^-])$.

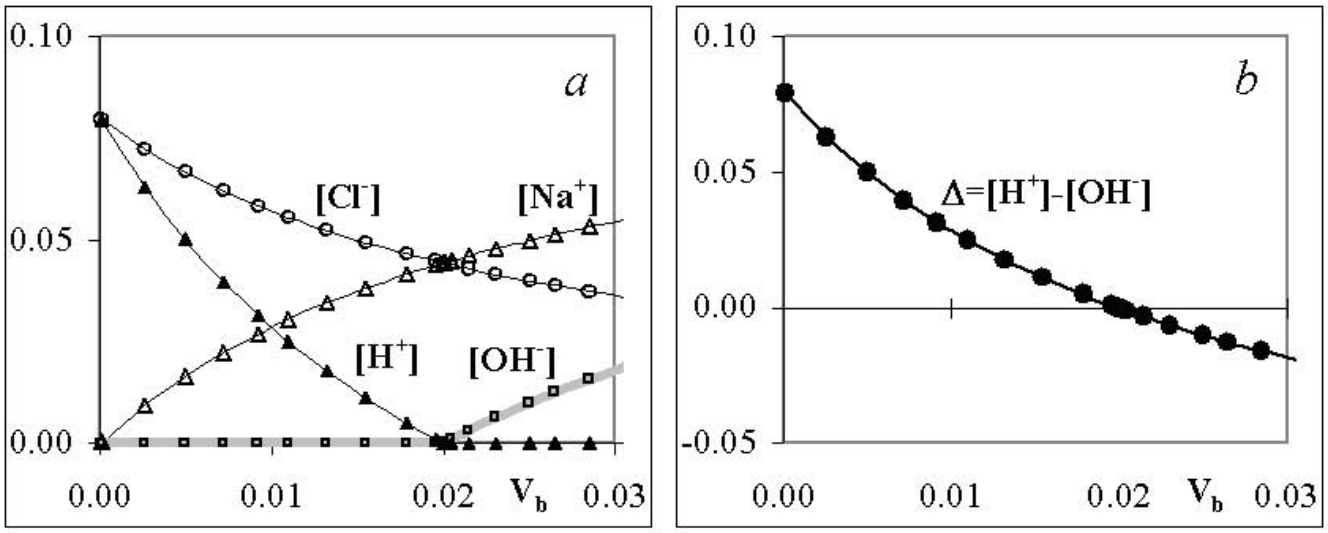

Figure 2. (a): The concentrations $[H^+]$, $[Na^+]$, $[Cl^-]$, and $[OH^-]$ as a function of titrant volume V_b for the titration of 25 mL of 0.08 M HCl with 0.10 M NaOH. (b): The corresponding proton excess, $\Delta = [H^+] - [OH^-]$ as a function of V_b.

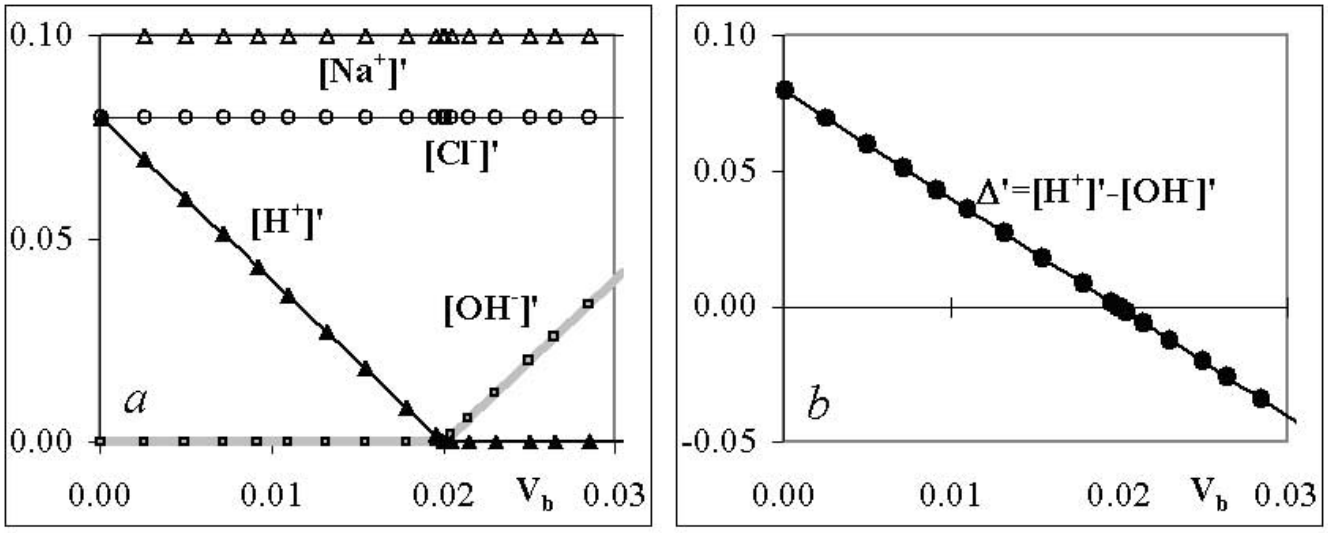

Figure 3. (a): The dilution-corrected concentrations $[Na^+]'$, $[Cl^-]'$, $[H^+]'$, and $[OH^-]'$ as a function of titrant volume V_b. (b): The dilution-corrected proton excess Δ' as a function of V_b.

In fact, the linear dependence of $\Delta' = \Delta\,(V_a + V_b)/V_a$ on V_b is *exact*, as follows by rewriting equation (5') as

$$\Delta = \frac{C_a V_a - C_b V_b}{V_a + V_b} = \left(C_a - \frac{C_b}{V_a} V_b\right)\left(\frac{V_a}{V_a + V_b}\right) \qquad (7)$$

so that the dilution-corrected proton excess is given by

$$\Delta' = \Delta\,\left(\frac{V_a + V_b}{V_a}\right) = C_a - \frac{C_b}{V_a} V_b \qquad (7')$$

which is indeed a linear function of the titration volume V_b, with the same slope and intercept as in eq (7).

The linear relation in Figure 3b is again definable by two readily computed points. At the beginning of the titration, where $V_b = 0$, the charge balance for HCl reads $[H^+] = [Cl^-] + [OH^-] = C_a + [OH^-]$ so that $\Delta = C_a$ as well as $\Delta' = C_a$, since $(V_a + V_b)/V_a = 1$ for $V_b = 0$. At the equivalence point, $V_b = V_{eq} = C_a V_a/C_b$, hence $\Delta = 0$ and $\Delta' = 0$. Thus, the line specified by eq (7') passes through the points $\Delta' = C_a$ for $V_b = 0$, and $\Delta' = 0$ for $V_b = V_{eq}$. Note that these are the same as for the line for Δ in the absence of dilution effects.

Consequently we now understand the titration of a strong acid with a strong base as the gradual reduction of the proton excess by the added base. *After correction for the effect of dilution, the proton excess decreases in a linear fashion with the amount of base added.*

Dilution can be taken into account in various ways: either as described above, or by plotting Δ versus $V_a\,V_b/(V_a + V_b)$. Here we have illustrated the former, since it leaves at least one axis of the usual titration curve unaffected.

3b. Titrating a Weak Monoprotic Acid

We now consider the titration of a weak monoprotic acid HA with NaOH. This case is slightly more complicated, because a (sufficiently) weak acid is mostly present in its protonated form, HA, with relatively few free anions (A^-).

The mathematical analysis is analogous to that of section 2, except that the acid anion is no longer a spectator ion, so that equation (1') must now be replaced by the mass balance

$$[HA] + [A^-] = C_a V_a/(V_a + V_b) \qquad (8)$$

and equation (3) by the charge balance

$$[H^+] + [Na^+] = [A^-] + [OH^-] \qquad (9)$$

The relation between $[HA] + [A^-]$ in eq (10) and $[A^-]$ in eq (11) follows from the acid dissociation constant $K_a = [H^+]\,[A^-]/[HA]$ as

$$\frac{[A^-]}{[HA] + [A^-]} = \frac{K_a}{[H^+] + K_a} = \alpha_0 \qquad (10)$$

where the index on α denotes the number of exchangeable protons on the species. Consequently, $[A^-] = \alpha_0\,\{[HA] + [A^-]\} = \alpha_0 C_a V_a/(V_a + V_b)$, so that we must replace eq (4') by

$$[H^+] + \frac{C_b V_b}{V_a + V_b} = \frac{\alpha_0 C_a V_a}{V_a + V_b} + [OH^-] \qquad (11)$$

from which we immediately obtain the solution

$$\frac{V_b}{V_a} = \frac{\alpha_0 C_a - \Delta}{C_b + \Delta} \qquad (12)$$

because equations (4') and (11) differ only in the substitution of $\alpha_0 C_a$ for C_a. Equation (12) can be written more explicitly in terms of $[H^+]$ as

$$\frac{V_b}{V_a} = \frac{\dfrac{K_a}{[H^+] + K_a} C_a - [H^+] + \dfrac{K_w}{[H^+]}}{C_b + [H^+] - \dfrac{K_w}{[H^+]}} \qquad (13)$$

A plot of the various concentrations, corrected for their dilution, is shown in Figure 4a. In this case a strictly linear dependence on V_b, throughout the entire titration, is found for the quantity $\Delta' + [HA]' = ([H^+] - [OH^-] + [HA])\,(V_a + V_b)/V_a$, see Figure 4b. And, again, the intersections of this line with the axes are simple: $\Delta' + [HA]' = C_a$ at $V_b = 0$, and $\Delta' + [HA]' = 0$ at the equivalence point.

This result can be understood as follows. The titratable protons are now of two kinds: the excess of free H^+ ions over OH^- ions, and the dissociable protons locked up in HA. Consequently, the titration of a weak monoprotic acid with strong base involves two chemical reactions, $H^+ + OH^- \rightarrow H_2O$ as well as $HA + OH^- \rightarrow A^- + H_2O$. Clearly, the reactions of *both* are reflected in the linear dependence of $[H^+]' - [OH^-]' + [HA]'$ with the amount of base added.

3c. Titrating a Polyprotic Acid with a Strong Monoprotic Base

The above approach can be carried further. For instance, an analysis starting from the exact result for the progress of the titration of a diprotic acid with a single, strong monoprotic base yields a linear relation of $L_2' = \Delta' + 2[H_2A]' + [HA^-]' = (\Delta + 2[H_2A] + [HA^-])\,(V_a + V_b)/V_a$ with the volume or amount of base added, reflecting the fact that titratable protons are now available from three sources: the excess protons in $\Delta = [H^+] - [OH^-]$, as well as H_2A (which can contribute two of them), and HA^- (for a one-proton contribution). Likewise, in the titration of a triprotic acid with NaOH, a corresponding linear function is given by $L_3' = \Delta' + 3[H_3A]' + 2\,[H_2A^-]' + [HA^{2-}]' = (\Delta + 3[H_3A] + 2\,[H_2A^-] + [HA^{2-}]) \times (V_a + V_b)/V_a$, as illustrated in Figure 5 for citric acid (where the pK_as lie closely together), and in Figure 6 for phosphoric acid (with widely spaced pK_as). For citric acid, using the third equivalence point would be the logical value to use, but for H_3PO_4 one might prefer the first or second equivalence point, since the third equivalence point has little analytical usefulness. Fortunately we can also use linear plots based on the first or second equivalence points. Throughout the titration, $[H_3A]' + [H_2A^-]' + [HA^{2-}]' + [A^{3-}]' = C_a$, so that we can generate a linear plot for $L_2' = \Delta' + 2[H_3A]' + [H_2A^-]' - [A^{3-}]'$ versus V_b, which passes through the points

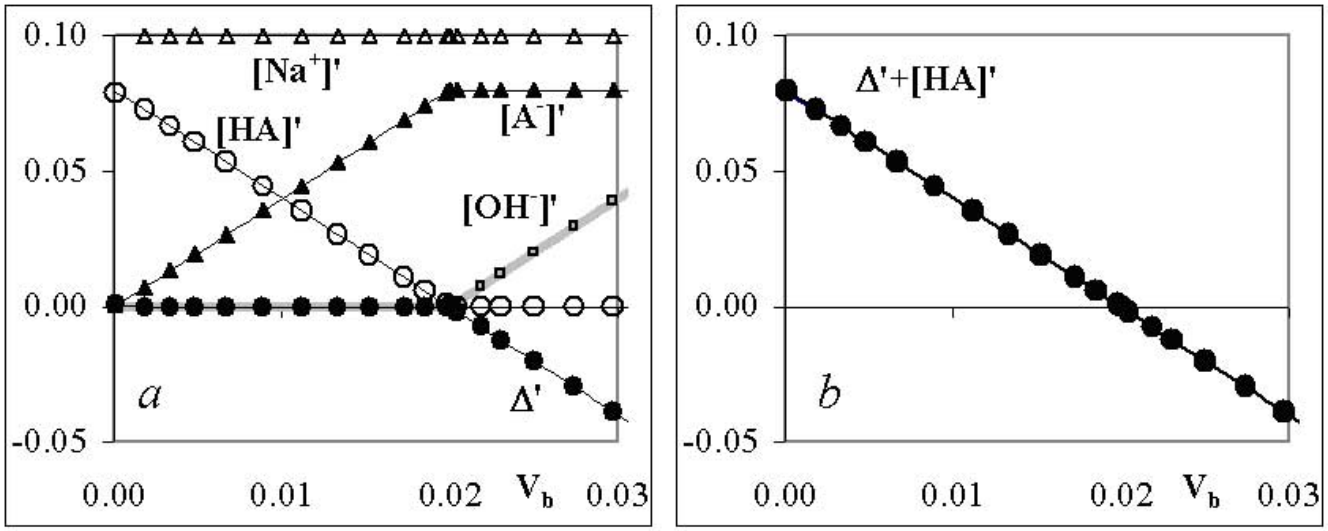

Figure 4. (a): The dilution-corrected concentrations $[Na^+]'$, [HA]', $[A^-]'$, and $[OH^-]'$ as a function of V_b during the titration of 25 mL of a 0.08 M solution of a weak monoprotic acid ($pK_a = 5$) with a 0.10 M solution of a strong monoprotic base. Note that the curves for [HA]' and Δ' visually (though not quite mathematically) overlap before the equivalence point while, on this scale, $[H^+]'$ would be visually indistinguishable from 0 over the entire range of V_b values. (b): The dilution-corrected quantity Δ' + [HA]' = ($[H^+] - [OH^-] + [HA]$) $(V_a + V_b)/V_a$ as a function of V_b during this titration.

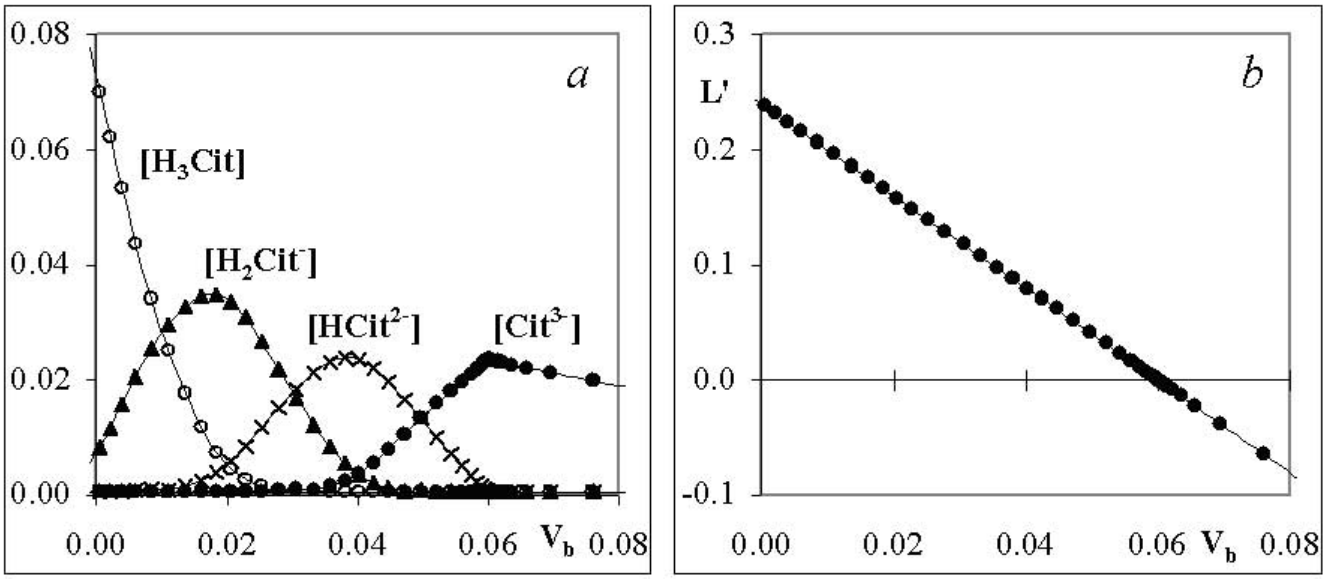

Figure 5. (a): The concentrations of the various citrate species during the titration of 25 mL of 0.08 M citric acid with 0.1 M NaOH, as a function of the titrant volume V_b in mL. (b): The parameter $L_3' = \Delta' + 3[H_3Cit]' + 2[H_2Cit^-]' + [HCit^{2-}]'$ as a function of V_b. Equilibrium constants used: $pK_{a1} = 3.13$, $pK_{a2} = 4.76$, $pK_{a3} = 6.40$. Note the absence of sharp knees in the curves for $[H_2Cit^-]$ and $[HCit^{2-}]$ at the equivalence points at $V_b = 20$ and 40 mL respectively, caused by the presence of significant concentrations of other citrate species at those points.

$L_2' = 2C_a$ at $V_b = 0$, and $L_2' = 0$ at the second equivalence point, or $L_1' = \Delta' - [H_2A^-]' - 2[HA^{2-}]' - 3[A^{3-}]'$ which goes through $L_1' = C_a$ at $V_b = 0$, and $L_2' = 0$ at the first equivalence point. These linear plots are illustrated in Figure 6b.

Again, instead of correcting the linear function L_i by multiplying each of its concentration terms by $(V_a + V_b)/V_a$ we can correct V_b through multiplication by $V_a/(V_a + V_b)$, as illustrated in Figure 7 for the titration of H_3PO_4 with NaOH. As before, this results in a somewhat simpler computation, but the direct correspondence with the experimental volume scale V_b is lost.

4. Discussion

The traditional approach to titration curves computes two (or more) special points, at the beginning of the titration, and at its equivalence point(s), and between them uses approximate curve segments that connect with neither of those points but that, instead, go to –∞ or +∞ at those points. The plots discussed in the present communication use the very same special points, but connect them by straight lines that are exact.

At the beginning of the titration of a strong monoprotic acid such as HCl we have the electroneutrality condition $[H^+] = [Cl^-] + [OH^-] = C_a + [OH^-]$ or $\Delta = C_a$, where C_a is the

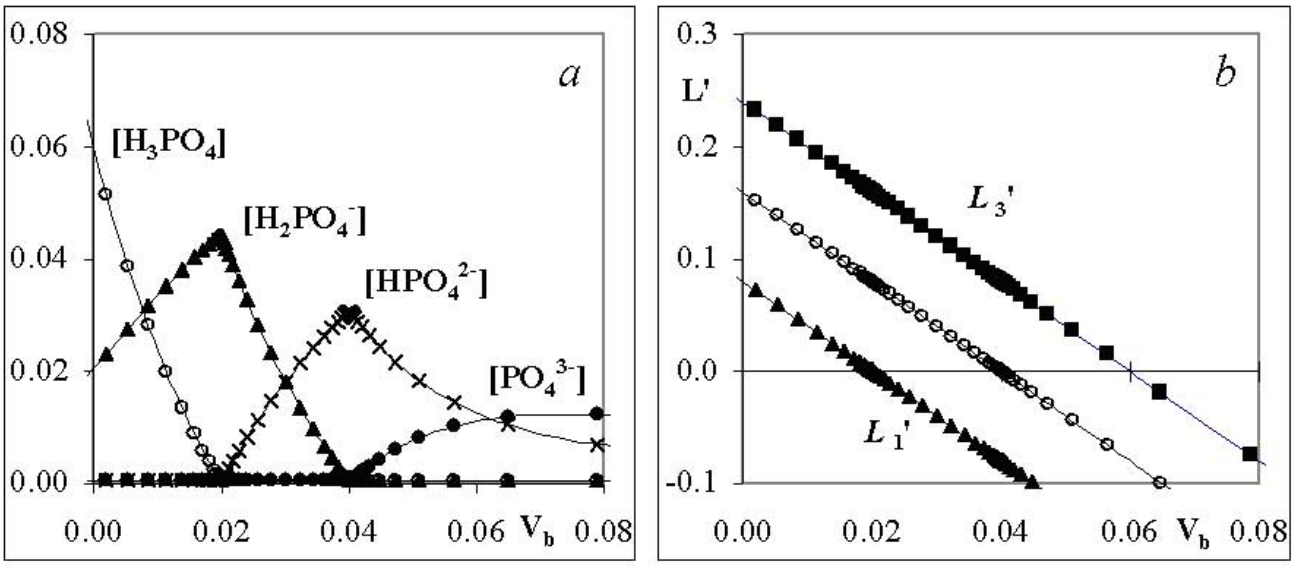

Figure 6. (a): The concentrations of the various phosphate species during the titration of 25 mL of 0.08 M H_3PO_4 with 0.1 M NaOH, as a function of the titrant volume V_b in mL. In this case the three equivalence volumes are V_{eq1} = 20 mL, V_{eq2} = 40 mL, and V_{eq3} = 60 mL. Equilibrium constants used: pK_{a1} = 2.15, pK_{a2} = 7.20, pK_{a3} = 12.15. Note the absence of a knee in the curves for $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ in Fig. 6a at the third equivalence point, at $V_b = V_{eq3}$ = 60 mL, because of the leveling effect of water. (b): The linear functions $L_3' = \Delta' + 3[H_3PO_4]' + 2[H_2PO_4^-]' + [HPO_4^{2-}]'$, $L_2' = \Delta' + 2[H_3PO_4]' + [H_2PO_4^-]' - [PO_4^{3-}]'$, and $L_1' = \Delta' + [H_3PO_4]' - [HPO_4^{2-}]' - 2[PO_4^{3-}]'$, each plotted as a function of V_b. (The subscript 1 to 3 defines the equivalence point used as internal reference, i.e., the equivalence point at which the curve crosses the horizontal axis.) Because the data were generated at constant pH intervals, they appear to cluster around the first and second equivalence point, as they do also in Figs. 2b through 5b, as well as in Figure 7.

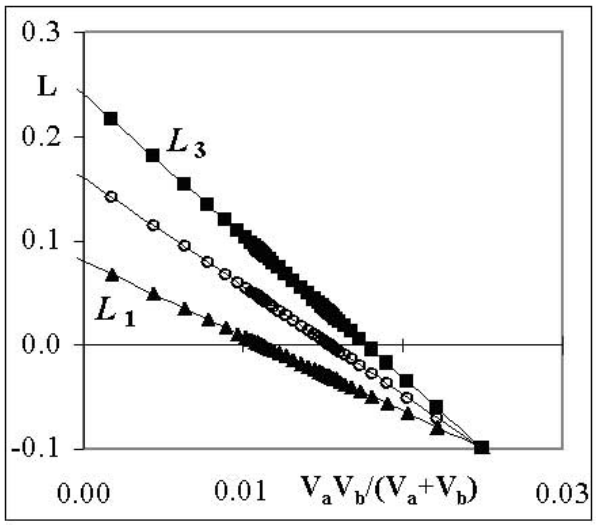

Figure 7. The linear concentration combinations $L_3 = \Delta + 3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^{2-}]$ (filled squares), $L_2 = \Delta + 2[H_3PO_4] + [H_2PO_4^-] - [PO_4^{3-}]$ (open circles), and $L_1 = \Delta + [H_3PO_4] - [HPO_4^{2-}] + 2[PO_4^{3-}]$ (filled triangles), all as a function of $V_a V_b/(V_a + V_b)$, during the titration of 25 mL of 0.08 M H_3PO_4 with 0.1 M NaOH. Equilibrium constants used: pK_{a1} = 2.15, pK_{a2} = 7.20, pK_{a3} = 12.15. Note that the lines start at $L_i = iC_a$ for $V_b = 0$, and all tend to converge at $L = -C_b$ when $V_b \gg V_a$ so that $V_a V_b/(V_a + V_b) \rightarrow V_a$. In practice, that point of convergence is seldom approached since it requires a large excess of titrant past the last equivalence point.

concentration of the acid in the sample. Since no titrant has yet been added (i.e., $V_b = 0$), dilution effects are zero at this point, so that we can also write this as $\Delta' = C_a$. For the onset of the titration of the weak monoprotic acid HA of concentration C_a we have, likewise, $\Delta + [HA] = C_a$ and $\Delta' + [HA]' = C_a$. At the start of the titration of a diprotic acid we have $L_2 = \Delta + 2[H_2A] + [HA^-] = L_2' = \Delta' + 2[H_2A]' + [HA^-]' = 2C_a$ or $L_1 = \Delta + [H_2A] - [A^{2-}] = L_1' = \Delta' + [H_2A]' - [A^{2-}]' = C_a$. For a triprotic acid we likewise have $L_3' = \Delta + 3[H_3A] + 2[H_2A^-] + [HA^{2-}] = L_3' = \Delta' + 3[H_3A]' + 2[H_2A^-]' + [HA^{2-}]' = 3C_a$, $L_2' = \Delta + 2[H_3A] + [H_2A^-] - [A^{3-}] = L_2' = \Delta' + 2[H_3A]' + [H_2A^-]' - [A^{3-}]' = 2C_a$, etc. These are the starting points of our linear graphs in Figures 2b, 3b, 4b, 5b, 6b, and 7.

The second "anchoring" point is that at the equivalence point. For the equivalence point of the titration of HCl with NaOH we have $\Delta = 0$, while for that of the titration of HA with have $\Delta' + [HA]' = 0$. Similarly, in the titration of C_a M H_2A we have $L_2' = 0$ for the second equivalence point, and $L_1' = 0$ for the first equivalence point, for a triprotic acid $L_i' = 0$ at the ith equivalence point, etc.

Thus, we have taken the exact, fixed points of the traditional computation of the titration curve, and shown how to connect them by a straight line in an exact fit, instead of by approximate curve segments that never actually go through those points.

The relations shown here can readily be extended to titrations of mixtures with a single strong monoprotic base, or to the titration of bases and mixtures of bases with a single strong monoprotic acid. The limitations of the above approach can be appreciated by going back to the general expressions for the progress of acid–base titrations [1, 2, 6],

$$\frac{V_b}{V_a} = \frac{C_a F_a - \Delta}{C_b F_b + \Delta} \qquad (14)$$

so that

$$\frac{\Delta\ (V_a + V_b)}{V_a} = C_a F_a - \frac{C_b V_b F_b}{V_a} \qquad (15)$$

where the acid dissociation function F_a, the base dissociation function F_b, and the volume V_b of base added, all vary during the titration. When we use a single, strong monoprotic base as the titrant, F_b is equal to 1, and the right-most term in eq (15) is V_b times a constant. In that case we can rewrite eq (15) as

$$L' = \frac{\Delta\ (V_a + V_b)}{V_a} - C_a(F_a - 1) = C_a - \frac{C_b V_b}{V_a} \qquad (16)$$

which is what we have exploited here. It does show, though, that the linear relations illustrated in this communication are restricted to titrations with a *single*, *strong* titrant. This is not a serious limitation since, at the introductory level, one seldom if ever needs to discuss titrations where the titrant is a weak acid or base, or a mixture.

The linear relations derived so far illustrate the role of the proton excess. They can also be used to analyze experimental data, in which case Δ' and any applicable concentration terms [..]' must be expressed explicitly in terms of a single parameter, typically $[H^+]$, and the appropriate concentrations and equilibrium constants. At that point, the equation will become a nonlinear expression in $[H^+]$, which we can then fit with a *nonlinear* least-squares routine to the experimental data, and so determine $[H^+]$ and the various constants involved. This is equivalent to fitting V_b/V_a to the more general expressions, using $[H^+]$ as the adjustable parameter, an approach already advocated by Waser [7] more than thirty years ago, and detailed in section 4.6 of reference 6.

While the relations shown here yield linear plots for a large number of acid–base titrations, they are in general unsuited to *linear* least-squares fitting, because they contain $[H^+]$ as an implicit (rather than explicit) parameter. This cannot be helped, because in general we deal here with more than two adjustable parameters. For instance, in the titration of a triprotic acid, the adjustable parameters are C_a, K_{a1}, K_{a2}, K_{a3}, and K_w. The linear plot advocated by Schwartz [5] for the analysis of a single (strong or weak) monoprotic acid or base with a strong monoprotic titrant assumes K_w, and is then able to find C_a and K_a for a single, monoprotic weak acid. The Schwartz plot constitutes the obvious limit of the applicability of a linear least-squares fit to a straight-line representation of an acid–base titration. In principle, there appear to be no limits to what functions can be fitted with nonlinear least squares.

The quantities plotted versus the titrant volume V_b in Figures 2 through 6 of this communication are all linear functions of the concentrations of the participating species. Insofar as they are derived from pH measurements, they are encumbered with a fairly large relative uncertainty, the result of the conversion of a logarithmic quantity such as pH into a concentration. The present method shares this inherent weakness with, for example, Gran and Schwartz plots.

In the treatment of ionic equilibria, which typically includes the discussion of titrations, it is customary to introduce ionic activity, as distinct from ionic concentration, at this level. For the purposes of chemical *analysis*, where the primary goal is to derive the concentration(s) of the unknown(s), it is unnecessary to consider activity effects. One can usually fit the experimental data without considering activity effects, and while the resulting equilibrium constants may differ significantly from their thermodynamic counterparts, neither the equivalence volume(s) nor the concentration(s) of the unknown(s) will be measurably affected [8].

The activity coefficient is, of course, a rather subtle concept, which can easily confuse the students. And it would be outright misleading if the students were left with the incorrect impression that they should simply replace all concentrations by the corresponding activities. The derivations of sections 2a and 3a clearly illustrate this. Equations (1) through (6), or their dilution-corrected counterparts through eq (9), are correct as written in terms of concentrations, and would be *incorrect* in terms of activities, because we have merely used the mass and charge balance equations, which count numbers rather than energies. Activity effects come into play only when we deal with equilibrium constants such as K_a and K_w, and with electrometric (but not with spectrometric) pH measurements.

In teaching quantitative analysis, it may therefore be wiser to delay a discussion of activity effects until the students know to what purpose they perform the titration (to determine the concentration of an unknown sample, or to determine the equilibrium constants of a known compound), until they appreciate the difference between balance equations (which involve concentrations) and thermodynamic constants (which require activities), and until they have learned to distinguish between electrochemical measurements (which approximately yield ionic activities) and optical pH measurements (which, through Beer's law, yield concentrations instead). Ionic activity is a concept far too subtle to inflict on beginning students.

References and Notes

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