

A New Method for the Evaluation of Acid-Base Titration Curves and Buffer Capacity of Soils

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Introduction

Acid-base buffer efficiency of soils can most readily be characterized by potentiometric titration curves of the soil suspension. However, the results of such studies are significantly influenced by the following factors:

- the method of suspension preparation (solution/soil ratio; whether salt solution or pure water is used to make the suspension; whether the CO₂ has been removed or not, etc.);

- the way titration is carried out (number of measured points, time allowed for equilibration);

- the method of evaluation of the titration curves.

Thus, it seems particularly important to establish optimal experimental conditions, as well as to improve the methods of evaluation.

Buffer capacity is generally defined as the area between the titration curve of the soil suspension and that of the soil-free solution, or, alternatively, as the quantity of acid or base that causes the pH to change by unity. However, the susceptibility of soil to an acid or base (i. e. the curvature of the titration curve) may differ significantly in different pH regions, thus the buffer capacity also depends on the pH region considered. Therefore, in our opinion, the traditional methods of determining buffer capacity allow only a qualitative description of the buffering mechanism.

This communication presents principles and equations for evaluating the rate of pH change as well as for calculating the buffer capacity of the soil at any pH and for any amount of acid or base added.

Materials and Methods

The derivation of the presented mathematical relationships is based on titration curves taken from the literature and from our studies. Titration curves based on few (6-8) measured points usually can be approximated by some stan-

standard curves and thus are readily described (REMEZOV, 1957; VOZBUTSKAYA, 1964; ZUSEVICH, 1980; FEDERER & HORNBECK, 1985; HARTIKAINEN, 1986; MURÁNYI & RÉDLY, 1986; MOWBRAY & SCHLESINGER, 1988). As these curves express only the general features of the behaviour of the system, they will be referred to as „feature curves”. On the other hand, curves that contain more experimental data points (> 18) display a more complex shape and must be treated differently (FILEP & RÉDLY, 1988). These curves have more detailed features and also allow the study of partial processes.

Results and Discussion

Feature curves may be classified into four basic groups (Figure 1). Titration with a base can yield curves of either type A or B, while an acid titration curve will have a shape of either C or D. We propose the following equation to describe A and B types of titration curves:

$$pH_x = pH_0 + k(m_b)^p \quad (1)$$

where pH_x is the equilibrium pH of the soil suspension following the addition of base of amount m_b ; pH_0 is the initial pH of the suspension (starting point of the titration); k and p are parameters that depend on the soil. For curves of type A $p < 1$, for type B $p > 1$.

k and p can most easily be obtained from the linearized form of Eq. (1):

$$\log(pH_x - pH_0) = \log k + p \log(m_b) \quad (2)$$

Plotting $(pH_x - pH_0)$ as a function of m_b on a log-log paper will yield a straight line with an intercept k and slope p . If $m_b = 1$, then $\log(pH_x - pH_0) = \log k$. Thus, k equals the pH change occurring upon addition of unit mass of base, while p is a constant indicative of the rate of the pH change. The closer the value of p to unity, the lower the basic buffer intensity (efficiency) of the soil.

Feature curves of acidic titrations (types C and D) can be described by the following equations:

$$pH_x = pH_0 - k'(m_a)^q \quad (3)$$

or in linear form

$$\log(pH_0 - pH_x) = \log k' + q \log(m_a) \quad (4)$$

where m_a is the mass of acid added. The evaluation of these relations is the same as that of Eqs. (1) and (2), with constants k' and q having the same meaning as that of the corresponding constants (k , p).

Curves that level off at either high or low pH (which indicates an increased buffer capacity) are convenient to break down into two separate sections (I and II). Sometimes only the steep part (section I) is analyzed.

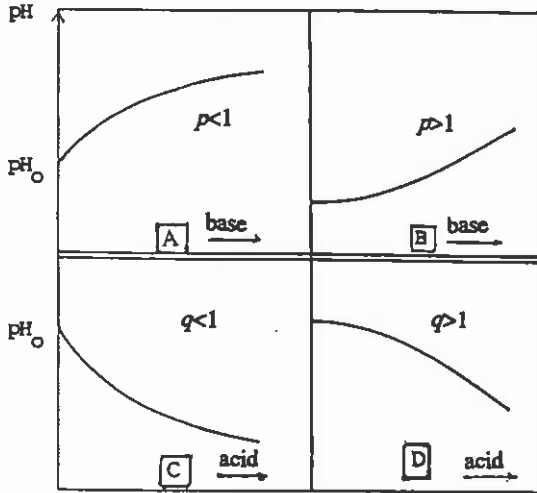


Figure 1
Basic type of „feature curves” of acid-base treatments

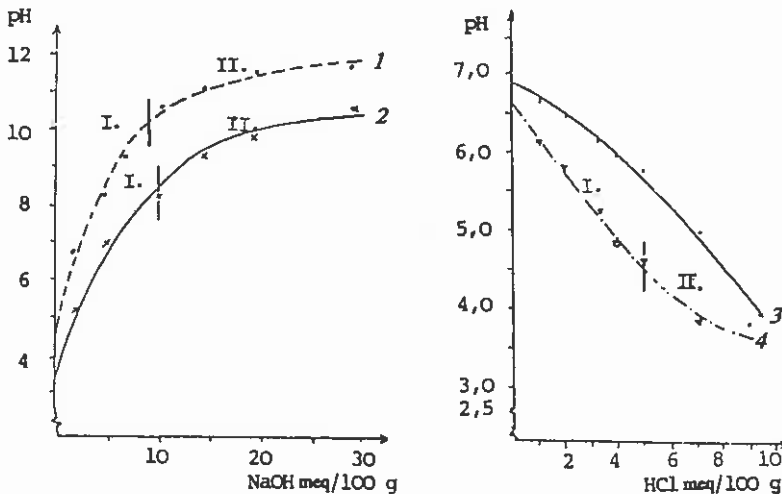


Figure 2
Alkaline (left) and acid (right) titration curves of soil samples 1-4,
with equations describing the pH change:

1. $pH = 4.6 + 1.04 (mb_1)^{0.86}$; $p_I = 0.86$; $p_{II} = 0.15$
2. $pH = 3.5 + 0.91 (mb_1)^{0.75}$; $p_I = 0.75$; $p_{II} = 0.21$
3. $pH = 6.9 - 0.14 (mb_1)^{1.33}$; $q = 1.33$
4. $pH = 6.65 - 0.46 (mb_1)^{0.91}$; $q_I = 0.91$; $q_{II} = 0.63$

Feature titration curves of some soil samples along with values of characteristic constants k , k' , p and q are illustrated in Figure 2. Curves 1 and 2 show the results of an alkaline titration of an acidic sand with low organic matter content from Nyírtelek and of an acidic loam from Kákkápolna, respectively. Curves 3 and 4 were obtained from acidic titrations of two different neutral loams (from Rábakecöl). It can be seen from this Figure that, as the pH of the system passes a certain value the buffer capacity of the soils increases markedly. This can also be inferred from parameters p and q calculated for sections I and II of the curves. This increase in the buffer capacity occurs at $\text{pH} > 10$ for soil 1, and at $\text{pH} \sim 8.3$ for soil 2. The buffer capacity of sample 4 becomes significantly greater at $\text{pH} < 4.5$. (The buffer capacity of soil 3 does not change much in the pH region studied).

Complex (detailed) titration curves can be partitioned into steep or flat portioned sections that can be approximated with curves of types A, B, C or D (Figure 3). Therefore, the evaluation of such curves can be carried out by the method described above, after division into adequate parts. As indicated by Figure 3, the end point of each section (i. e. the corresponding pH and m_b or m_s values) can be considered as the starting point of the next section, thus we have for an *alkaline titration*:

$$\text{pH}_{x_1}(\text{max}) = \text{pH}_{0_2}; \quad \text{pH}_{x_2}(\text{max}) = \text{pH}_{0_3}; \quad \text{pH}_{x(n-1)}(\text{max}) = \text{pH}_{0_n}$$

and for an *acidic titration*:

$$\text{pH}_{x_1}(\text{min}) = \text{pH}_{0_2}; \quad \text{pH}_{x_2}(\text{min}) = \text{pH}_{0_3}; \quad \text{pH}_{x(n-1)}(\text{min}) = \text{pH}_{0_n}$$

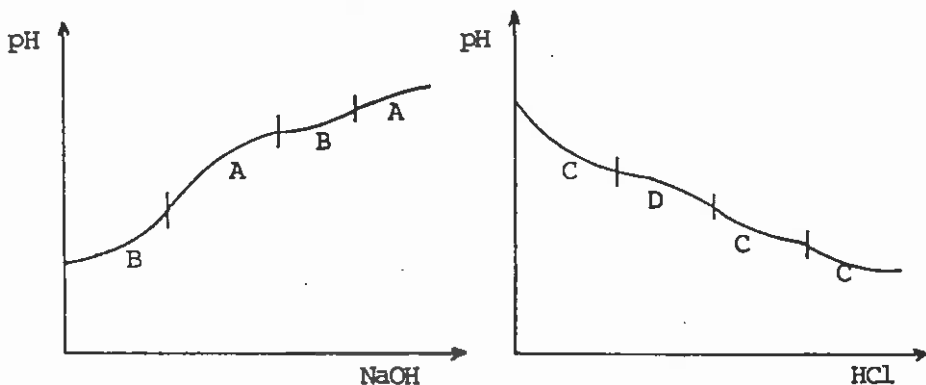


Figure 3

The principle of partitioning non-standard shaped titration curves

Equations that describe the separate sections can be cast in the following form:

$$pH_{x1} = pH_{01} \pm k_1 \cdot (m_1)^{p_1} \tag{5a}$$

$$pH_{x2} = pH_{02} \pm k_2 \cdot (m_2)^{p_2} \tag{5b}$$

$$pH_{xn} = pH_{0n} \pm k_n \cdot (m_n)^{p_n} \tag{5c}$$

$p_1, p_2, p_n, q_1, q_2, q_n$ are parameters that characterize the buffering efficiency of the soil in the various sections (pH regions) of the titration curve.

From the fundamental relationships (Eqs. (1) and (3)) one can express the buffer capacity of the system (β). The buffer capacity is defined by VAN SLYKE (1922) as

$$\beta = \frac{dm_b}{dpH} = - \frac{dm_s}{dpH} \tag{6}$$

The differentiation of Equations (1) and (3) readily leads us to the definition of $1/\beta$. It then follows that

$$\frac{dpH}{dm_b} = \frac{1}{\beta} = k \cdot p \cdot (m_b)^{p-1} \tag{7}$$

and

$$\frac{dpH}{dm_s} = \frac{1}{\beta} = k' \cdot q \cdot (m_s)^{q-1} \tag{8}$$

The buffer capacity can be readily calculated by these equations (knowing k, p or k' and q values for the different sections). In the case of soils, buffer capacity shows more than one maximum. A more elaborate characterization of the buffering by the soil can be done with the aid of the function $\beta = f(pH)$ (called buffer curve) (FILEP & RÉDLY, 1988). These buffer curves can be constructed from $\beta \cdot m_b$ or $\beta \cdot m_s$ values of the separate sections, calculated by Eqs. (7) and (8) (taking into account the corresponding pH-m values). The information content of the buffer curve depends strongly on the number of data points, on the error introduced by division into sections and on the number of data pairs β -m or pH-m used.

Figure 4 shows the detailed (comprising many data points) titration curves of samples 2 and 3 as well as the corresponding $\beta = f(pH)$ buffer curves. These plots indicate the strict correspondence between the titration and buffer curves as well as demonstrate the validity of our approach. The method of evaluation of such buffer curves was published earlier (FILEP & RÉDLY, 1988).

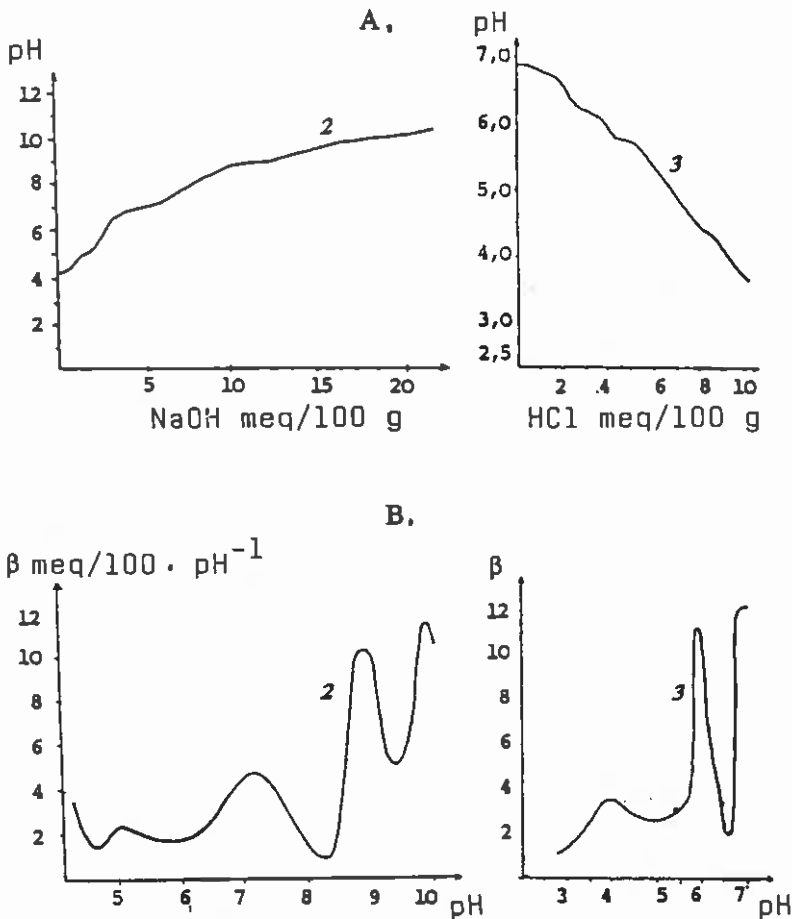


Figure 4

Detailed (several data points) titration curves of samples 2 and 3 (A) and the corresponding buffer curves (B), which indicate the changes in buffer capacity (β) as a function of time

As illustrated by the above results, parameters p and q of „feature curves” could find use in the following applications:

- when comparing the susceptibility of various soils to an acid or a base or quantitatively evaluating the change in pH upon lime application („lime dose curves”; FILEP & CSUBÁK, 1990);
- preparation of more precise maps on the susceptibility of soils to acidity;

– quantitative studies on relations between the characteristic soil parameters (clay content, types of clay minerals, organic matter content, CEC, etc.) and the observed buffering action.

Detailed titration curves, as well as the $\beta = f(pH)$ buffer curves are in turn useful when changes of buffer capacity as a function of pH are studied or when the role, range of activity and mechanism of major buffer systems are to be characterized.

Summary

New parameters are presented to describe the susceptibility of soils to the amount of acid or base added.

Titration curves based on a small number of data and assumed to have a standard shape (termed „feature curves“) have been described by Equations (1) and (3); parameters p and q characterize the rate of the pH change, while constant k indicates the initial pH change.

Complex (detailed) titration curves can be evaluated in a similar manner, after these curves are partitioned into adequate sections of standard shape. New expressions of buffer capacity (Equations (7) and (8)) have enabled us either to calculate the β values corresponding to various amounts of acid or base added or to construct the entire $\beta = f(pH)$ curve.

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