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The Conditions Needed for a Buffer to Set the pH in a System

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Abstract

It is a known fact that buffer systems are widely used in industry and diverse laboratories to maintain the pH of a system within desired limits, occasionally narrow. Hence, the aim of the present work is to study the *buffer capacity* and *buffer efficacy* in order to determine the useful conditions to impose the pH on a given system. This study is based on the electroneutrality and component balance equations for a mixture of protons polyreceptors. The added volume equations are established, V, for strong acids or bases, as well as the *buffer capacity* equations with dilution effect, β_{dil}, and the *buffer efficacy*, ε, considering that the analyte contains a mixture of the species of the same polyacid system or various polyacid systems. The ε index is introduced to define the performance of a buffer solution and find out for certain, whether the buffer is adequate to set the pH of a system, given the proper conditions and characteristics.

Keywords: buffer, buffer capacity, buffer efficacy, polyacid systems, electroneutrality equation.

1. Introduction

Currently, there are studies that examine the progress of an acid-base titration for one or various polydonor systems, extending sometimes this study to the theme of buffer capacity [1–16]. In the scientific literature, there are algorithms and simulators to construct acid-base titration curves, even considering a wide range of different mixtures of polydonor systems [17–20].

The buffer solutions have a certain buffering capacity that is used to maintain constant the pH of a system, having only a small uncertainty. The *buffer capacity*, β, has been defined as the quantity of strong acid or strong base (in the buffer solution) that gives rise to a change of one pH unit in 1 L of solution, as an intensive property of the system [15]. This involves using directly the concentration of either a strong base or an acid in the buffer solution, without considering the dilution effect, as King and Kester [2], Segurado [3], Urbansky and Schock [4], De Levie [8] did, among others. Urbansky and Schock also mentioned the use of concentration to simplify the maths. Nevertheless, the dilution effect on buffer capacity was first considered by Michałowski, as Asuero and Michałowski have established in a thorough and holistic review [6].

The buffer capacity considering the effect of dilution, β_{dil}, is defined as the added amount of strong base or strong acid required to change in one unit the pH of an initial V_o volume of the buffer solution formed by species of only one polydonor system [7]. By their definition, β is an intensive property by considering the concentration, while β_{dil} is an extensive property to include the amount of substance.

A buffer solution is used to impose the pH in a given system; generally speaking, the buffer is added to a working system selected to impose a given pH, thus giving rise to a mixture between both systems. It would be convenient to know the minimum concentration of the buffer components in the mixture as well as the minimum volume that must be added in order for it to fulfill its function. From the existing works in the literature, an evaluation of the buffer performance was attempted, in general a β was provided, although up to now this problem has not been dealt with quantitatively.

Figure 1 shows the scheme, in which a buffer solution is used to buffer the pH of a given system. It is observed that a mixture of both systems exists: the buffer system (BS) and the original system (OS). In general, it is necessary to define which would be the BS and the study system.
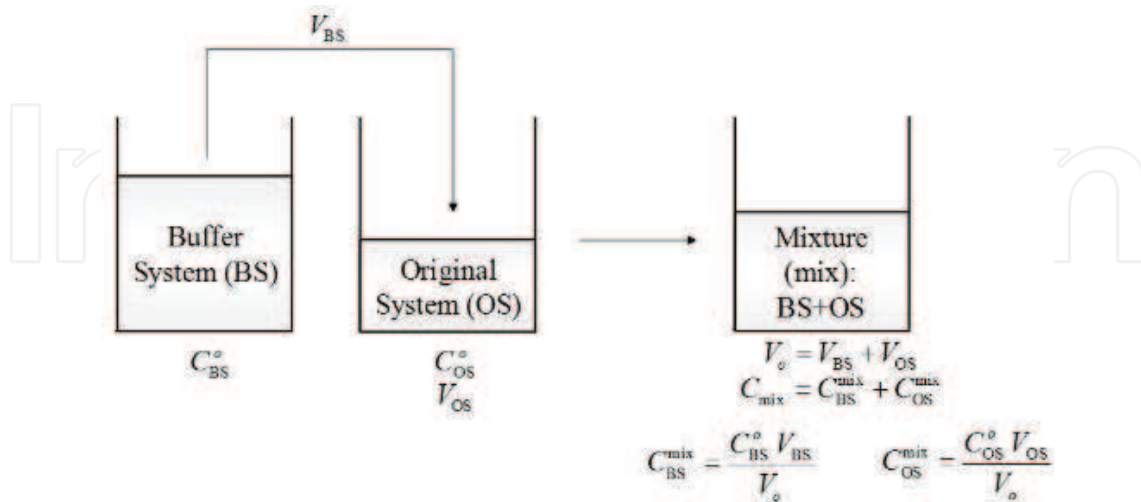
Figure 1. Schematization of the manner, in which the pH is generally set in an original system (OS) with a buffer system (BS). C_{BS}^o is the initial concentration of the buffer system before mixing, V_{BS} is the volume of BS added to OS, C_{OS}^o and V_{OS} are the initial concentration and initial volume of the original system before mixing, respectively; V_o is the mixture volume formed by the solutions with volumes V_{BS} and V_{OS}, C_{mix} is the overall concentration of the mixture, C_{BS}^{mix} is the buffer components' concentration in the mixture; and C_{OS}^{mix} is the original system's solute concentration in the mixture.

In many applications, it is convenient that the volume of the buffer solution that is added to the system of interest be $V_{BS} < V_{OS}$, in order not to alter much the composition of the study system.

The present work extends the study of β_{dil} that is contained in a mixture of polydonor systems. Moreover, a new concept is introduced, *buffer efficacy* (ε), as an index to estimate the performance of a buffer. Finally, it is shown how these indexes allow the determination of the useful conditions (minimum concentration and volume), for a buffer to enable imposing the pH in a system of interest.

2. Theoretical background

2.1. Description of the components, species, equilibria, and fractions in a mixture of polydonor systems

In order to evaluate the useful performance of a buffer to impose the pH in a given system, it is necessary to establish the expressions of β or of β_{dil} that consider mixtures of various polydonor systems.

Although Ref. [8] presented equations that describe the behavior of β for polydonor systems, the nomenclature, which has shown in Ref. [7] to study β_{dil}, is considered here to generalize its equations for the case of buffer solutions of mixtures of different polydonor systems.
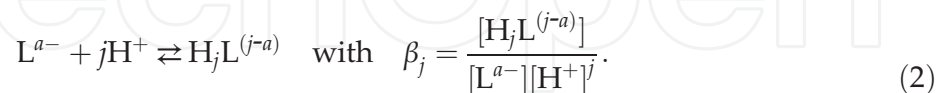
A polyprotic system [6, 7] can be represented as follows:

$$H_n L^{(n-a)}/\ldots/H_j L^{(j-a)}/\ldots L^{a-}/H^+, \quad \text{where } j \in \{0, 1, \ldots, a, \ldots, n\} \tag{1}$$

$H_n L^{(n-a)}$ is the polyprotic acid (weak acid in general), L^{a-} is the base of the system, and the neutral species is $H_a L$; H^+ is the exchanged particle in the reaction, n is the number of protons of the polyprotic acid, $a-$ is the charge of the base (expressed in elementary charge units).

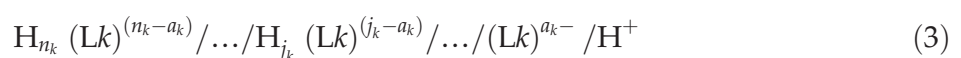The species that go from $H_{(n-1)} L^{(n-a)}$ up to $HL^{(a-1)}$ are the system's formal ampholytes.

The global formation equilibria of the species of a polydonor system are represented according to Eq. (2).

$$L^{a-} + jH^+ \rightleftarrows H_j L^{(j-a)} \quad \text{with} \quad \beta_j = \frac{[H_j L^{(j-a)}]}{[L^{a-}][H^+]^j}.$$
$$\text{where } j \in \{0, 1, \ldots, a, \ldots, n\} \tag{2}$$
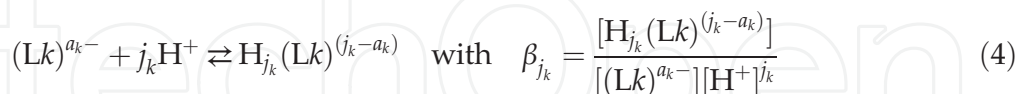
By definition $\beta_o = 1$.

When there is a mixture of c polydonor systems in aqueous solution with $(c + 1)$ components, a general representation of the set of polyprotic systems is given as:

$$H_{n_k} (Lk)^{(n_k - a_k)}/\ldots/H_{j_k} (Lk)^{(j_k - a_k)}/\ldots/(Lk)^{a_k-}/H^+ \tag{3}$$

where $k \in \{1, 2, \ldots, c\}$, $j_k \in \{0, 1, \ldots, a_k, \ldots, n_k\}$.

$H_{n_k}(Lk)^{(n_k-a_k)}$ is the polyprotic acid of the kth polydonor system, $(Lk)^{a_k-}$ is its polybase, n_k is the number of protons of the kth polyprotic acid, and a_k is the charge of the kth polybase. The species that go from $H_{(n_k-1)}(Lk)^{(n_k-a_k-1)}$ up to $H(Lk)^{(1-a_k)}$ are the system's ampholytes.

A representation of the kth polydonor system's global formation equilibria in a mixture is given as:

$$(Lk)^{a_k-} + j_k H^+ \rightleftarrows H_{j_k}(Lk)^{(j_k-a_k)} \quad \text{with} \quad \beta_{j_k} = \frac{[H_{j_k}(Lk)^{(j_k-a_k)}]}{[(Lk)^{a_k-}][H^+]^{j_k}} \tag{4}$$

where $k \in \{1, 2,\ldots, c\}$, $j_k \in \{0, 1,.., a_k,\ldots, n_k\}$.

Also, in this case $\beta_{0_k} \equiv 1$ needs to be considered.

It can be demonstrated that the molar fraction to describe each of the c distributions of the species of each of the polydonor systems in the mixture with respect to H^+ is given by Eq. (5):

$$f_{j_k} = \frac{[H_{j_k}(Lk)^{(j_k-a_k)}]}{[Lk]_T} = \frac{\beta_{j_k}[H^+]^{j_k}}{\sum\limits_{j_k=0}^{n_k} \beta_{j_k}[H^+]^{j_k}} \tag{5}$$

where $k \in \{1, 2,\ldots, c\}$, $j_k \in \{0, 1,.., a_k,\ldots, n_k\}$.

where $[Lk]_T$ is the total concentration of the kth component in the mixture. As can be observed, the molar fractions only depend on pH and on the equilibrium constants β_{j_k}.

2.2. Description of the mixture to be titrated

There are N solutions, each containing one $H_{j_k}(Lk)^{(j_k-a_k)}$ species in a C_{oj_k} molar concentration, assuming a volume V_{oj_k} is taken from each solution to form only one mixture with an overall volume V_o, then: $N = \sum_{k=1}^{c}\left\{\sum_{j_k=0}^{n_k}(1)\right\} = \sum_{k=1}^{c}\{n_k+1\}$ and $V_o = \sum_{k=1}^{c}\left\{\sum_{j_k=0}^{n_k} V_{oj_k}\right\}$. This mixture is titrated with a strong MOH base at C_b concentration or with a strong MX acid at C_a concentration, measuring the pH.

Each species has associated countercations or counteranions ($M^{z_{j_k}+}$ or $Z^{z_{j_k}-}$) depending on whether (j_k-a_k) they are negative or positive, which lack the acid-base properties.

2.3. Expressions for the titration plots of polydonor systems mixtures

Although Asuero and Michałowski [6] and De Levie [9] have presented some mathematical representations of added volume as a function of pH for these systems, we have preferred to follow the same procedure and notation used to deduce the added volume equations, proposed by Rojas-Hernández et al. [7]. Then, for the case of the mixtures of species of various polydonor systems, the following expressions can be deduced:

The added volume expression for a strong base, V_b, is

$$V_b = \frac{\sum_{k=1}^{c}\left\{\sum_{j_k=0}^{n_k}\{(j_k - a_k)(V_{oj_k}C_{oj_k})\} - \left[\sum_{j_k=0}^{n_k}(V_{oj_k}C_{oj_k})\right]\left[\sum_{j_k=0}^{n_k}\{(j_k - a_k)f_{j_k}\}\right]\right\} - V_o([H^+] - [OH^-])}{C_b + [H^+] - [OH^-]}$$

(6)

If one considers now that a strong acid is added to the mixture, then the V_a expression becomes:

$$V_a = \frac{-\sum_{k=1}^{c}\left\{\sum_{j_k=0}^{n_k}\{(j_k - a_k)(V_{oj_k}C_{oj_k})\} + \left[\sum_{j_k=0}^{n_k}(V_{oj_k}C_{oj_k})\right]\left[\sum_{j_k=0}^{n_k}\{(j_k - a_k)f_{j_k}\}\right]\right\} + V_o([H^+] - [OH^-])}{C_a - [H^+] + [OH^-]}$$

(7)

Eqs. (6) and (7), $[OH^-] = \frac{K_w}{[H^+]}$ agree with the water self-protolysis equilibrium.

As can be observed, the added volume equations obtained for a strong base or a strong acid bear the same mathematical form. It is relevant to note which comes from the component's balance of each polyprotic system must be independently added, thus giving rise to the double summations appearing in Eqs. (6) and (7).

When $c = 1$ hence giving $k = 1$, the equations are the same as those shown in reference [7], to determine the volume that is added to a strong base and a strong acid (V_b and V_a, respectively) in a system formed by species of the same polydonor system.

Eqs. (6) and (7) are exact analytic solutions to obtain titration plots $pH = f(V)$ (estimating the volume from the pH values). These equations also allow obtaining exact equations of dpH/dV, hence the expressions for β_{dil} will be shown in the next section. β_{dil} is the first index used to explore quantitatively the application conditions for a buffer.

2.4. General expressions of dpH/dV_b and $-dpH/dV_a$

Eqs. (6) and (7) are functions of the pH, thus it becomes possible to obtain analytic expressions for their first derivatives (dV/dpH). With the reciprocals of the first derivatives, exact algebraic expressions of the first derivative of the titration plot are obtained. This is to say dpH/dV_b and $-dpH/dV_a$, which are used to detect the volumes at the titration points when the reactions are quantitative.

Extending the expressions for dpH/dV_b and $-dpH/dV_a$ considering a mixture of the species of various polydonor systems, the expressions obtained are as follows:

$$\frac{dpH}{dV_b} = \frac{C_b + 10^{-pH} - 10^{pH-pK_w}}{-2.303\sum_{k=1}^{c}\left(\left[\sum_{j_k=0}^{n_k}(V_{oj_k}C_{oj_k})\right]\left[\sum_{j_k=0}^{n_k}\left\{j_k f_{j_k}\sum_{i_k=0}^{n_k}\left[(i_k - j_k)f_{i_k}\right]\right\}\right]\right) + 2.303(V_o + V_b)[10^{-pH} + 10^{pH-pK_w}]}$$

(8)

$$-\frac{d\text{pH}}{dV_a} = \frac{C_a - 10^{-\text{pH}} + 10^{\text{pH}-pK_w}}{-2.303\sum_{k=1}^{c}\left(\left[\sum_{j_k=0}^{n_k}(V_{oj_k}C_{oj_k})\right]\left[\sum_{j_k=0}^{n_k}\left\{j_kf_{j_k}\sum_{i_k=0}^{n_k}\left[(i_k-j_k)f_{i_k}\right]\right\}\right]\right) \\ +2.303(V_o+V_b)[10^{-\text{pH}}+10^{\text{pH}-pK_w}]} \tag{9}$$

where $k \in \{1, 2, …, c\}$, $i_k \in \{0, 1, …, n_k\}$ and $j_k \in \{0, 1, …, a_k, …, n_k\}$.

Equally, if $c = 1$ and $k = 1$, Eqs. (8) and (9) are the same as those shown in Ref. [7] to determine $d\text{pH}/dV_b$ and $-d\text{pH}/dV_a$ for a mixture of the species of only one polydonor system.

2.5. General expressions of β_{dil}

In order to determine the buffer capacity considering the dilution, β_{dil}, the derivative is applied to the quantity of strong base or strong acid added as follows:

$$\beta_{\text{dil}_b} = \frac{dV_bC_b}{d\text{pH}} = C_b\frac{dV_b}{d\text{pH}} \quad \text{or} \quad \beta_{\text{dil}_a} = -\frac{dV_aC_a}{d\text{pH}} = -C_a\frac{dV_a}{d\text{pH}} \tag{10}$$

where β_{dil_b} and β_{dil_a} are units of quantity of substance. The analytic mathematical expressions are shown in Eqs. (11) and (12).

$$\beta_{\text{dil}_b} = \frac{dV_bC_b}{d\text{pH}} = \frac{2.303C_b\left\{-\sum_{k=1}^{c}\left(\left[\sum_{j_k=0}^{n_k}(V_{oj_k}C_{oj_k})\right]\left[\sum_{j_k=0}^{n_k}\left\{j_kf_{j_k}\sum_{i_k=0}^{n_k}[(i_k-j_k)f_{i_k}]\right\}\right]\right)\\ +(V_o+V_b)[10^{-\text{pH}}+10^{\text{pH}-pK_w}]\right\}}{C_b+10^{-\text{pH}}-10^{\text{pH}-pK_w}} \tag{11}$$

$$\beta_{\text{dil}_a} = -\frac{dV_aC_a}{d\text{pH}} = \frac{2.303C_a\left\{-\sum_{k=1}^{c}\left(\left[\sum_{j_k=0}^{n_k}(V_{oj_k}C_{oj_k})\right]\left[\sum_{j_k=0}^{n_k}\left\{j_kf_{j_k}\sum_{i_k=0}^{n_k}[(i_k-j_k)f_{i_k}]\right\}\right]\right)\\ +(V_o+V_b)[10^{-\text{pH}}+10^{\text{pH}-pK_w}]\right\}}{C_a-10^{-\text{pH}}+10^{\text{pH}-pK_w}} \tag{12}$$

Furthermore, it is worth noting that the different plots presented along this work were constructed from spreadsheets done through Excel 2007 in Microsoft Office using the equations heretofore presented.

3. Some case studies

3.1. Application of expressions for the titration curves fitting experimental data of the Britton-Robinson buffer

Figure 2 shows the pH $= f(V_b)$ and curve of $d\text{pH}/dV_b = f(\text{pH})$ retaking experimental data from *Lange's Handbook of Chemistry* [21] (markers • and ▲, respectively). The experimental curve
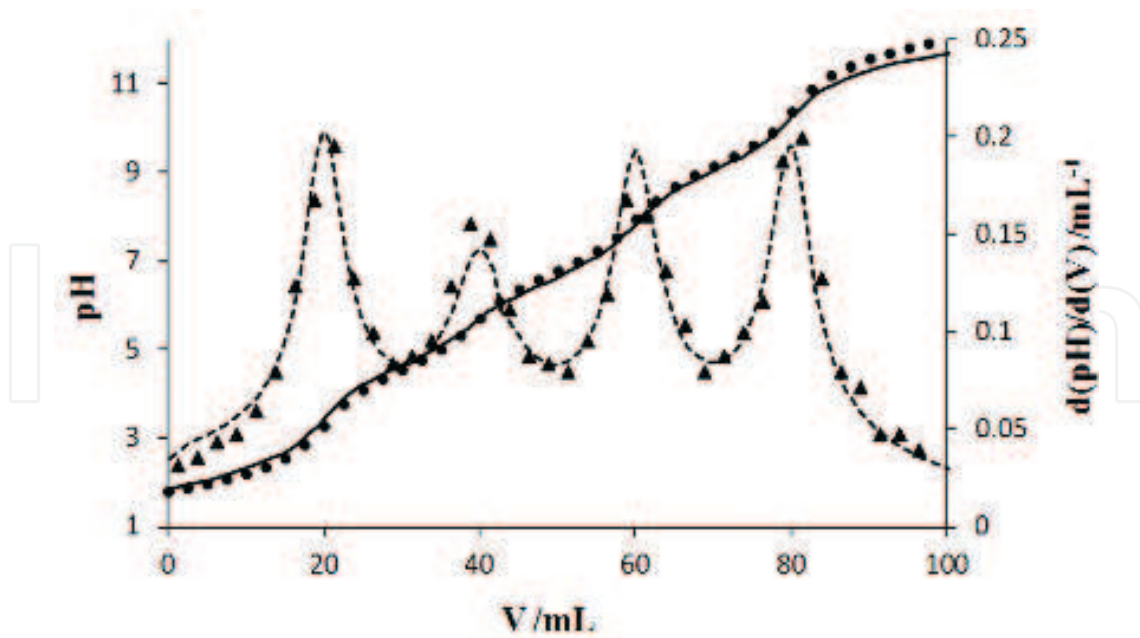
Figure 2. Titration of 100 mL of equimolar solution of Britton-Robinson 0.04 M ([AcO'] = [PO$_4$'] = [BO$_3$'] = C$_{SB}$ = 0.04 M) with NaOH 0.2M.—represents the calculated curve of pH = f(V_b), • denotes the experimental curve of pH = f(V_b), ----- denotes the calculated curve of dpH/dV_b = f(V_b), and ▲ denotes the experimental curve of ΔpH/ΔVb. The pK$_a$ values are as follows: pK$_a$ = 4.66 for acetic acid [23]; pK$_{a1}$ = 2.1 [24], pK$_{a2}$ = 6.75 [25], and pK$_{a3}$ = 11.71 [26] for phosphoric acid; and pK$_a$ = 9.15 for boric acid [27]. pK$_w$ = 13.73 [28, 29].

dpH/dV_b was calculated as the finite differences quotient of the pH values and the volumes measured during the titration (ΔpH/ΔV_b) using the average volumes for each interval. Also shown are the pH = f(V_b) and dpH/dV_b = f(pH) curves obtained using Eqs. (6) and (7) (solid and segmented lines, respectively) [22].

3.2. Effect of the quantity of a buffer solution on β_{dil}

Intuitively, it is known that the performance of a buffer solution is better whenever a larger volume is taken to set the pH. The β shown in the scientific literature [1–14, 20] does not consider this feature, for which it is necessary to have an index that evaluates the effect of the size of the buffer solution to impose the pH. For that purpose, the definition of β_{dil} is used to include in its mathematic expression, the term V_o, as observed in Eqs. (11) and (12). Subsequently, it is shown how β_{dil} takes this effect into account.

Figure 3 shows a series of β_{dil} = f(pH) plots for a 1000 and 10 mL buffer solutions containing the species H$_3$PO$_4$ and H$_2$PO$_4$$^-$ at different concentrations of the PO$_4$' (PO$_4$' = H$_3$PO$_4$/H$_2$PO$_4$$^-$/HPO$_4$$^{2-}$/PO$_4$$^{3-}$/H$^+$) system. In this case, these concentrations can be represented as C_{BS}^o = C_{mix} = C_{BS}^{mix} because the buffer system is a mixture, in agreement with **Figure 1**. It is necessary to underline that the axis β_{dil} is log, just as Urbansky and Schok [4] do, in order to compare β_{dil} within an ample PO$_4$' concentration range.

Figure 3a represents a larger buffer system than that represented in **Figure 3b**, because the initial volumes were 1000 and 10 mL, respectively. As can be observed in **Figure 3**, β_{dil} increases with
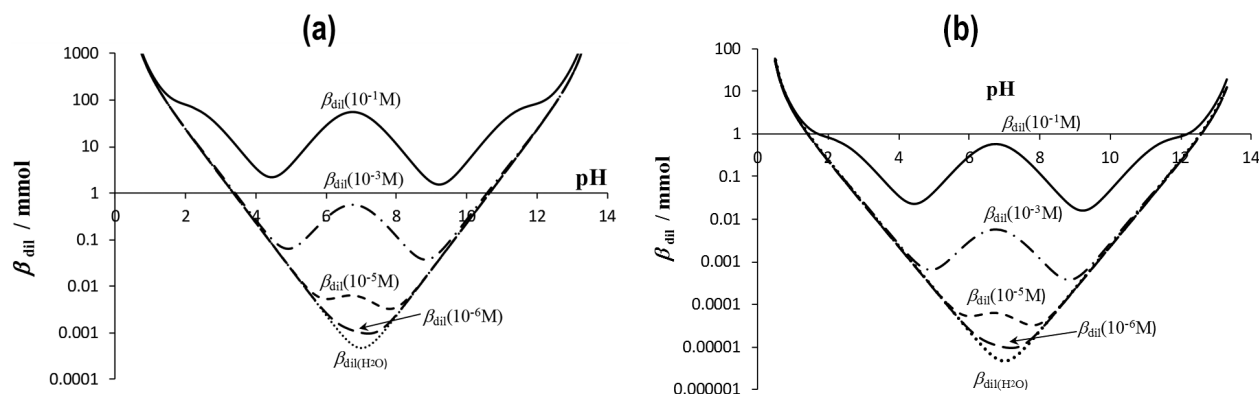
Figure 3. Calculated plots of $\beta_{dil} = f(\text{pH})$ of systems initially containing the H_3PO_4 and $H_2PO_4^-$ at PO_4' species at overall concentrations of 10^{-1}, 10^{-3}, 10^{-5} and 10^{-6} M. The broken line represents the plot of $\beta_{dil(H2O)} = f(\text{pH})$ for water and its basic and acid particles. $C_b = C_a = 0.5$ M. $pK_{a1} = 2.1$ [24], $pK_{a2} = 6.75$ [25], and $pK_{a3} = 11.71$ [26]. (a) $V_o = 1000$ mL. (b) $V_o = 10$ mL.

increasing quantity of the system (V_o). Hence, β_{dil} indicates well the expected behavior for a buffer system: the pH in a system is better imposed when the buffer amount is larger.

Figure 3 also shows the plot for water, $\beta_{dil(H2O)} = f(\text{pH})$, titrated with strong base and strong acid. It sets the lower limit given by this solvent and its acid and basic particles (broken line), with respect to all aqueous solutions. Therefore, it is established that any solution, including that of the same solvent, has certain β_{dil}. It can be observed that the concentration diminution of the PO_4' system provokes that β_{dil} diminishes and the width of the pH interval also decreases where the PO_4' system contributes more to β_{dil} than the solvent.

There is one *minimum concentration of the buffer system* (C_{BSmin}), small enough, where the PO_4' system almost does not contribute to β_{dil} ($C_{BSmin} \approx 10^{-6}$ M), so that the plot of β_{dil} of the PO_4' system can be discerned from the plot of $\beta_{dil(H2O)}$. Just as a minimum concentration is shown for the PO_4' system; whenever there is an acid-base pair (HL/L) with $pK_a \approx 7.0$, the C_{BSmin} will be the same (10^{-6} M). Although in other cases, when $pK_a < 7.0$ or $pK_a > 7.0$, it must be expected that the C_{BSmin} be larger; this is to say, for $pK_a = 5$ or $pK_a = 9$, the $C_{BSmin} \approx 10^{-5}$ M and for $pK_a = 3$ or $pK_a = 11$, the $C_{BSmin} \approx 10^{-3}$ M.

3.3. Buffer efficacy (ε) of a buffer system

The previous section showed that the β_{dil} has advantages over β in order to evaluate the buffer performance. However, the shortcomings of this situation refer to β_{dil}, which by definition is the quantity of strong base or strong acid added to change by one unit the system's pH, which is a fairly large change. Therefore, it is necessary to define a new index having a smaller change than β_{dil}.

Following the idea proposed by Christian in his textbook [30], it is possible to approximate the derivative by means of a finite difference quotient. Even when the pH change is acceptable for a buffer system, it depends on the application or on the system to be considered, a $\Delta pH \leq 0.1$ is sufficiently small to comply with the approximation established through Eq. (13).

$$\beta_{dil} = \frac{d(VC)}{dpH} \approx \frac{\Delta(VC)}{\Delta pH} \tag{13}$$

Then

$$\Delta(VC) \approx \beta_{dil} \Delta pH \tag{14}$$

In this work, the buffer performance will be assessed considering a $\Delta pH = 0.1$ [30]. The *buffer efficacy, ε,* is defined as the quantity of strong base or strong acid that provokes a pH change of only one-tenth in a system. The expression of ε is as follows:

$$\varepsilon \equiv \Delta(VC) \approx \beta_{dil} \Delta pH = 0.1 \beta_{dil} \tag{15}$$

3.4. Application of ε: buffer system's concentration threshold

A buffer system is used to set the pH, therefore, it is necessary to know its useful conditions to fulfill its function. Then, for the sake of a deeper understanding it is relevant to establish first a limit to determine the moment in which the buffer system's concentration sets pH conditions over those of the water and of its acid and basic particles, just as those of the system of interest.

3.4.1. Imposing the pH of the buffer system over the water and its acid and basic particles

Because the system's pH needs to be imposed, the efficacy of the system's buffer, the buffer (ε_{BS}) should be larger or at least equal to the *efficacy of the buffer amplified ten times that of the water, $\varepsilon_{10(H_2O)} = 10\varepsilon_{(H_2O)}$,* not just the *buffer efficacy of the water, $\varepsilon_{(H_2O)}$s.* In the present work, a factor of 10 is considered sufficiently large to assess a buffer's performance.

Figures 4a and **b** show the curves of $\varepsilon_{(H_2O)}$ for $V_o = 1000$ mL and $V_o = 10$ mL of water, respectively, titrated with a strong acid and a strong base at 1 M concentration (marker…). Also, it is shown the plot of $\varepsilon_{10(H_2O)}$ (marker…), which will be considered as the limit where the buffer concentration is useful to set the pH. It is also observed in **Figures 4a** and **b** that both $\varepsilon_{(H_2O)}$ and $\varepsilon_{10(H_2O)}$ depend, as expected, on the quantity of the system.

Figure 4c and **d** shows, apart from the $\varepsilon_{(H_2O)}$ and $\varepsilon_{10(H_2O)}$ plots, those of ε_{BS} of the NH_4^+/NH_3 buffer solutions at different concentrations for systems with $V_{BS} = V_o = 1000$ mL and $V_{BS} = V_o = 10$ mL, respectively, as those shown in **Figure 1**. In order to establish the limit in which a buffer works to set the pH, it is necessary to compare the ε_{BS} curve with that of the $\varepsilon_{10(H_2O)}$, so that compliance with $\varepsilon_{BS} \geq \varepsilon_{10(H_2O)}$ can be verified.

In this case, the lowest NH_4^+/NH_3 buffer concentration falls to a point that almost equals the $\varepsilon_{10(H_2O)}$ plot. Therefore, this concentration is termed as *threshold buffer concentration* (TC_{BS}) with a value of $TC_{BS} \approx 10^{-4}$ M. It can also be seen from **Figures 4c** and **d** that TC_{BS} does not depend on the size of the system (V_o).

Then, whenever there is a buffer formed by an acid-base pair HL/L with $pK_a \approx 7.0$ it must be expected a greater TC_{BS}, of approximately 10^{-5} M; when $pK_a = 5$ or $pK_a = 9$, the TC_{BS} will also be approximately 10^{-4} M; and for $pK_a = 3.0$ or $pK_a = 11.0$, the $TC_{BS} \approx 10^{-2}$ M.
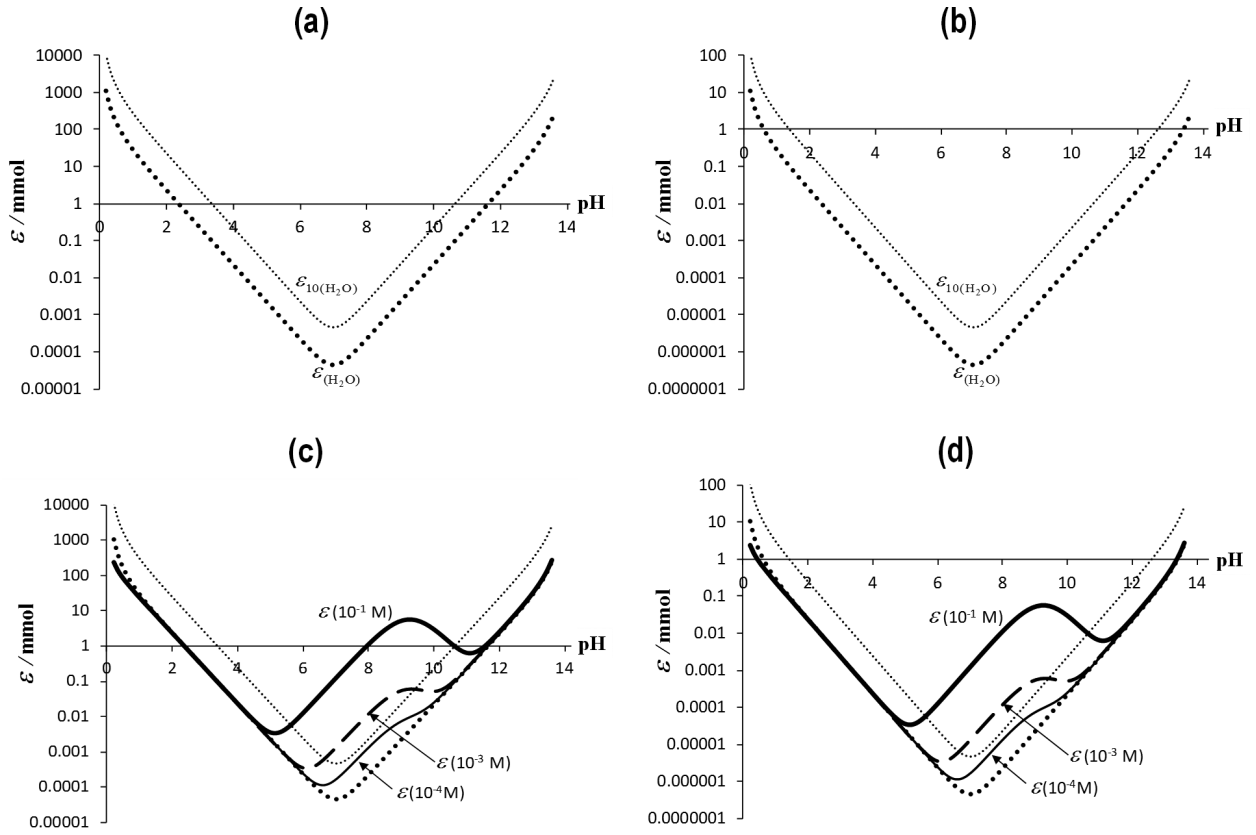
Figure 4. Calculated plots of $\varepsilon_{(H_2O)}$ and $\varepsilon_{10(H_2O)}$ for $V_o = 1000$ mL and $V_o = 10$ mL of water and its acid and basic particles (marker… and marker… , respectively). The ε_{BS} curves of NH_4^+/NH_3 buffer solutions at different concentrations, $[NH_3']_{Tot} = C_{BS}^o = C_{mix} = C_{BS}^{mix}$: -10^{-1} M, $---10^{-3}$ M, -10^{-5} M. $C_b = C_a = 1$ M. $pK_a = 9.25$ [31]. (a) and (c) 1000 mL. (b) and (d) 10 mL.

Furthermore, in **Figures 4c** and **d** it can also be noted that the useful interval for the BS to set the pH, when the $C_{BS}^o = C_{mix} = C_{BS}^{mix} = 10^{-1}$ M, is $pK_a - 1 < pH < pK_a + 1$ [32]. Whereas for $C_{BS}^o = C_{mix} = C_{BS}^{mix} = 10^{-3}$ M, the interval to set the pH is smaller because the ε_{BS} becomes closer to $\varepsilon_{10(H_2O)}$.

When the $\varepsilon_{BS} < \varepsilon_{10(H_2O)}$ strong acid or strong base must be used also at adequate concentration to set the pH. The strong base and strong acid in these extremes are used because the acid and basic particles of the solvent contribute more to ε than the buffer system components.

Finally, from the analysis of the plots in **Figure 4**, it can be determined that the pH limits of the buffer performance and the buffer system threshold concentration do not depend on the system's size.

3.4.2. Setting the buffer's system pH over that of the original system

It is necessary to set new limits (of pH and buffer concentration) whenever there is a mixture of the system of interest and the buffer system, because it is not sufficient to consider only the water effect.

The pH of a given system (OS) is set upon adding a buffer system (BS), hence, the buffer component concentration in the mixture (C_{BS}^{mix}) must be greater than the concentration of the

solutes of the original system (C_{OS}^{mix}), because both systems have their own ε, though how large is it? (**Figure 1**).

An example of the use of ε, to evaluate setting the pH to a 9.0 value at 100 mL (V_{OS}) of an acetylacetone solution (acac') (OS), is given next, at 10^{-3} M concentration (C_{OS1}^{o}), at different NH_4^+/NH_3 buffer concentrations in the mixture (C_{BS}^{mix}).

Figure 5a shows the ε of the acetylacetone solution (OS), stated in the previous paragraph (ε_{OS}, marker $\times\times\times\times$), the *buffer efficacy amplified 10 times that of the original system* (ε_{10OS}, marker ----), also presenting the plot of $\varepsilon_{(H_2O)}$ (marker…).

Figure 5b shows, apart from the $\varepsilon_{(H_2O)}$ curve, those corresponding to ε_{BS} for 100 mL of the NH_4^+/NH_3 system solution at different concentrations. The ε_{BS} magnitude depends on buffer's concentration and decreases until it reaches a TC_{BS}, which is given when the ε_{BS} curve almost becomes equal to that of $\varepsilon_{10(H_2O)}$. In this case, $TC_{BS} \approx 10^{-4}$ M.
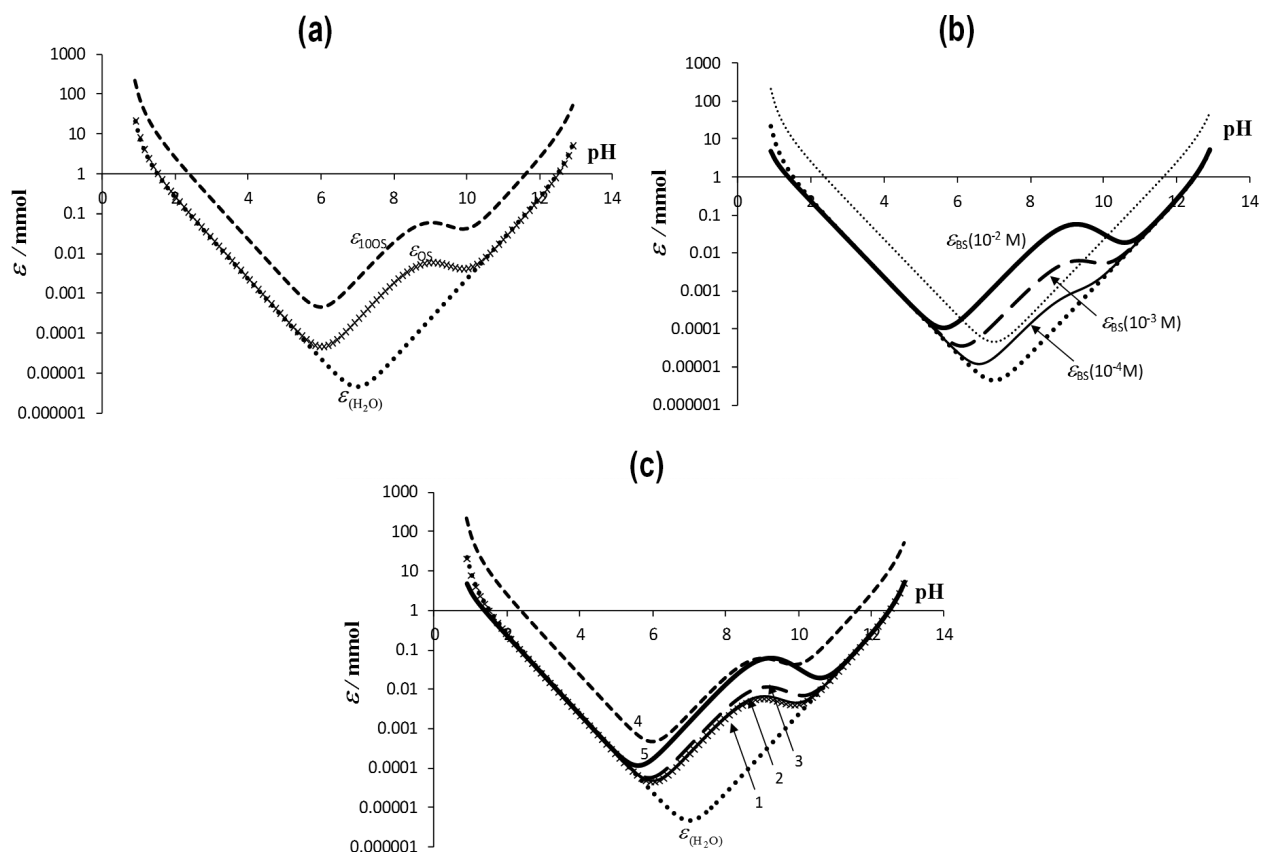
Figure 5. Curves of $\varepsilon = f(pH)$ for 100 mL solutions related to **Figure 1**. The line marked with ….in all cases represents the buffer efficacy of water, $\varepsilon_{(H_2O)}$, and its acid and basic particles. (a) Curves ε_{OS} and ε_{10OS} belong to an acac 10^{-3} M ([acac']$_{Tot} = C_{OS}^{o} = C_{mix} = C_{OS}^{mix}$) solution in the absence of the buffer system (markers $\times\times\times\times$ and ----, respectively). (b) Curves ε_{BS} belong to the NH_4^+/NH_3 buffer at different concentrations, $[NH_3']_{Tot} = C_{BS}^{o} = C_{mix} = C_{BS}^{mix}$: -10^{-2} M, $---10^{-3}$ M, -10^{-4} M. (c) Curves ε_{mix}, ε_{OS}, and ε_{10OS} belong to the solutions containing acac 10^{-3} M plus NH_4^+/NH_3 10^{-2} M buffer, 10^{-3} M, and 10^{-4} M in the mixture. 1: ε_{OS}, 2:$C_{OS}^{mix}=10^{-3}$ M $+C_{BS}^{mix} = 10^{-4}$ M, 3: $C_{OS}^{mix} = 10^{-3}$ M $+C_{BS}^{mix} = 10^{-3}$ M, 4:ε_{10OS}, and 5: $C_{OS}^{mix}=10^{-3}$ M $+ C_{BS}^{mix} = 10^{-2}$ M. $pK_a = 9.0$ for the system Hacac/acac$^-$ and $pK_a = 9.25$ for the NH_4^+/NH_3 system [31]. $C_b = C_a = 0.2$ M.

In order to impose the pH of the original system, the buffer efficacy of the mixture (ε_{mix}) should be greater or, at least equal to $\varepsilon_{10\text{OS}}$. Now, if the buffer is added to the original system to set the pH, the ε_{mix} has contributions of the original system and to the buffer system; thus, the buffer does not always set the pH in the system as shown in **Figure 5c**. The curve 1 that represents a ε_{OS} is practically identical to the curve 2 that corresponds to a mixture of the original system, with the buffer solution with concentration 10 times smaller than the solutes in the original system: in these cases, the pH of the system depends only on the original system, because $\varepsilon_{\text{mix}} \approx \varepsilon_{\text{OS}}$. The curve 3 shows that the buffer with 10^{-3} M concentration does already contribute to ε_{mix} apart from the original system, but has not set the pH yet because $\varepsilon_{\text{OS}} < \varepsilon_{\text{mix}} < \varepsilon_{10\text{OS}}$.

Finally, **Figure 5c** depicts the curve 4 as corresponding to $\varepsilon_{10\text{OS}}$, whereas the curve 5 represents a ε_{mix} corresponding to the *buffer threshold concentration for the buffer system component of the mixture*, $TC_{\text{BS}}^{\text{mix}}$ (whenever it is required to set the pH at a value of 9.0), for which $\varepsilon_{\text{mix}} \approx \varepsilon_{\text{BS}} = \varepsilon_{10\text{OS}}$, and therefore, there is an adequate buffer performance to set the pH of the system within the 8.25 < pH < 10.0 interval. It must be noted that if it is required to set pH > 10.0 values, a strong base must be used, apart from the buffer system. To the extent that $\varepsilon_{\text{mix}} \gg \varepsilon_{10\text{OS}}$ the buffer performance to set the system pH becomes better. Approximately $TC_{\text{BS}}^{\text{mix}}$ must be 10 times larger than $C_{\text{OS}}^{\text{mix}}$. Therefore, it is established that

$$C_{\text{BS}}^{\text{mix}} \geq TC_{\text{BS}}^{\text{mix}} \approx 10 C_{\text{OS}}^{\text{mix}} \tag{16}$$

Eq. (16) becomes specific whenever the original system is set to a pH = 9.0 when this system bears one acid-base pair with pK_a = 9.0 (Hacac/acac$^-$) [31]. This example is the most difficult case because this OS acid-base pair competes almost equally with the BS acid-base pair (NH$_4^+$/NH$_3$, pK_a = 9.25) to set the system's pH.

If the pK_a of some species in the original system moves away from the pH value that is desired to impose with the buffer system, the factor of 10 in Eq. (16) becomes smaller.

It must not be forgotten that the buffer system should have a conjugated acid-base pair with a pK_a value close to the pH that is desired to impose. As can be observed from **Figure 5c**, in this case it is difficult that the buffer system imposes the pH to a 9.0 value because both systems (BS and OS) have pK_a values similar to that pH value. It is worth clarifying that the NH$_4^+$/NH$_3$ buffer imposes more easily the pH to a 9.0 value to the extent that the pK_a of the acid-base pair original system drifts apart from pH = 9.0; of the $TC_{\text{BS}}^{\text{mix}}$ diminishes till it reaches a limit value given by $\varepsilon_{10(\text{H}_2\text{O})}$.

Consider now the case that a pH 9.0 shall be imposed to the 100 mL (V_{OS}) of the acetylacetone solution (acac') (OS), with a 10^{-3} M (C_{OS}^o) concentration, using now the Britton-Robinson [12, 21] buffer at different concentrations. For this example, the ε_{OS}, $\varepsilon_{10\text{OS}}$, and $\varepsilon_{(\text{H}_2\text{O})}$ are the same as those presented in **Figure 5a**.

Figure 6a shows, apart from the curve of $\varepsilon_{(\text{H}_2\text{O})}$, the curves of ε_{BS} for 100 mL solution of the Britton-Robinson buffer at different concentrations. In this case, the $C_{\text{BS}}^o = C_{\text{mix}} = C_{\text{BS}}^{\text{mix}}$ diminishes till reaching a TC_{BS}, having a value of $TC_{\text{BS}} \approx 10^{-5}$ M because at this point the ε_{BS} almost equals the $\varepsilon_{10(\text{H}_2\text{O})}$ curve.
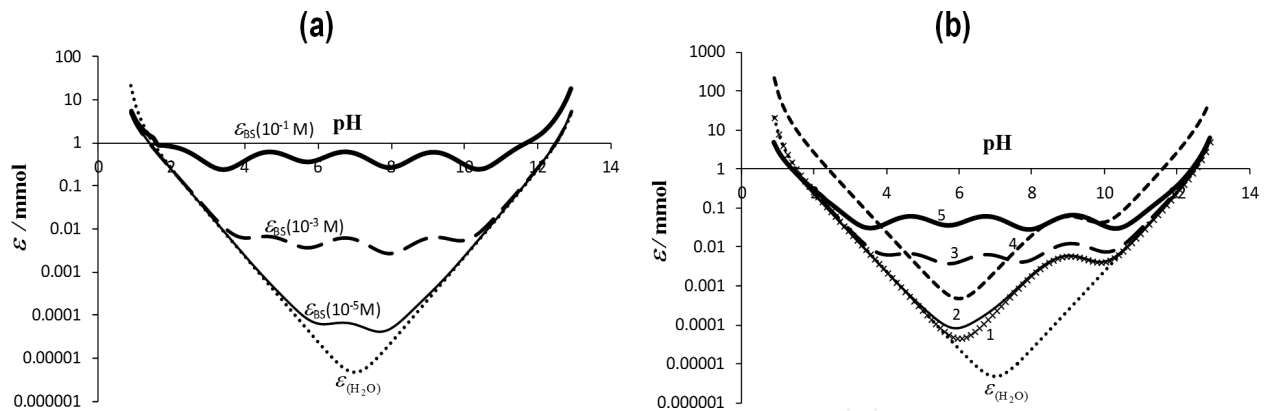
Figure 6. The curves $\varepsilon = f(pH)$ are for the 100 mL of the solutions related to **Figure 1**. The broken line in all cases represents the buffer efficacy of the water, $\varepsilon_{(H_2O)}$, and its acid and basic particles. (a) Curves ε_{BS} for equimolar Britton-Robinson buffer solutions at different concentrations, $[AcO']_{Tot} = [PO_4']_{Tot} = [BO_3']_{Tot} = C_{BS}^o = C_{BS}^{mix}$: $—10^{-1}$ M, $---$ 10^{-3} M, $—10^{-5}$ M. (b) Curves ε_{mix}, ε_{OS}, and ε_{10OS} of solutions that contain 10^{-3} M acac plus 10^{-2} M, 10^{-3} M, and 10^{-5} M Britton-Robinson's buffer in the mixture. 1: ε_{OS}, 2: $[acac'] = C_{OS}^{mix} = 10^{-3}$ M $+ C_{BS}^{mix} = 10^{-5}$ M, 3: $[acac'] = C_{OS}^{mix} = 10^{-3}$ M $+ C_{BS}^{mix} = 10^{-3}$ M, 4: ε_{10OS}, and 5: $[acac'] = C_{OS}^{mix} = 10^{-3}$ M $+ C_{BS}^{mix} = 10^{-2}$ M. The pK$_a$ values used in the model are as follows: pK$_a = 9.0$ for acac' [31]; pK$_a = 4.66$ for acetic acid [23]; pK$_{a1} = 2.1$ [24], pK$_{a2} = 6.75$ [25], and pK$_{a3} = 11.71$ [26] for phosphoric acid; and pK$_a = 9.15$ for boric acid [27]. pK$_w = 13.73$ [28, 29]. $C_b = C_a = 0.2$ M.

As stated, the ε_{mix} should be larger or at least equal to ε_{10OS}. Once again, the buffer efficacy of the mixture (ε_{mix}) is contributed from both the acac' system and the Britton-Robinson buffer; thus the buffer does not always set the pH in the system as shown in **Figure 6b**. Curve 1 represents the ε_{OS}, that is practically equal to curve 2 corresponding to a mixture of the original system with the buffer solution with a concentration 100 times smaller than the solutes in the original system: in these cases, the system's pH depends only on the original system, because $\varepsilon_{mix} \approx \varepsilon_{OS}$. Curve 3 shows that in the $4.5 < pH < 7.4$ interval, the buffer with 10^{-3} M concentration contributes more to the ε_{mix} than the original system, consequently, the buffer has the system's capacity to set the pH in this interval but not at pH = 9.0 as required in this example. Curve 3 also has another region where both systems contribute almost the same as ε_{mix} ($7.4 < pH < 10.7$) and because $\varepsilon_{mix} < \varepsilon_{10OS}$, the buffer is not capable of fulfilling its function in this interval.

Figure 6b also shows curve 4 that corresponds to ε_{10OS} and curve 5 that represents a ε_{mix} corresponding to a *threshold concentration for the buffer system's components in the mixture*, TC_{BS}^{mix} (when the pH to be imposed is 9.0), for which $\varepsilon_{mix} \approx \varepsilon_{BS} = \varepsilon_{10OS}$. At this same concentration, the buffer system's components show a good performance to impose the pH, not only at 9.0 but within the $3.8 < pH < 10.0$ interval; which is large because it corresponds to a wide spectrum buffer. Approximately TC_{BS}^{mix} must be 10 times larger than the C_{OS}^{mix} as established by Eq. (16), because the acid-base pair of the Britton-Robinson buffer is the $H_3BO_3/H_2BO_3^-$ with a pK$_a = 9.15$ value. It must be underlined that if it is intended to impose the pH to other value (pH < 8.1), the TC_{BS}^{mix} is smaller.

3.5. Application of ε: threshold volume of the buffer system

The concentration of the buffer components in the mixture (C_{BS}^{mix}) must be larger than the solute concentration in the system considered (C_{OS}^{mix}) to set the pH of the system. However, it is also

necessary to know the buffer minimum volume that must be added to the original system with the aim of fulfilling its function (**Figure 1**). Next, an example is given to determine this minimum volume on the acetylacetone case using Britton-Robinson buffer to impose pH 9.0 in the system.

If there are 100 mL of an acac (OS_1) solution at 10^{-3} M concentration (C_{OS1}^o), and two buffer (BS_1 y BS_2) solutions with components 10^{-1} M (C_{BS1}^o) and 1 M (C_{OS2}^o) concentration: which is the minimum volume that should be added to each buffer solution to set a pH = 9.0 in the system?

Figure 7a shows that the ε_{10OS} can be attained when 10 mL of the buffer solution with 10^{-1} M (SB_1) component concentration is added to the original system. Then, this minimum volume is the *threshold volume* (TV_{BS1}) for this specific buffer solution. If now, the buffer solution of 1 M (SB_2) component concentration is added to the system of interest, the threshold volume is different, as shown in **Figure 7b**, under these conditions the $TV_{BS2} = 1$ mL.

The TV_{BS} is related to TC_{BS}^{mix} in the mixtures, with total volumes of 110 mL for the first case and 101 mL for the second case, because in both cases TC_{BS}^{mix} are 10 times greater than the original system's solute concentrations in the mixture (C_{OS}^{mix}).

If now, a larger concentration of acac is used in the original system, for example 10^{-2} M (C_{OS2}^o), it is necessary to use the more concentrated buffer to impose the pH, for example SB_2, with 1 M (C_{BS2}^o) component concentration.

It is clear that if the original system solutes' concentrations in the mixture (C_{OS}^{mix}) grow, the TC_{BS}^{mix} also grows, consequently TV_{BS} does it too.

Observing the equations shown in **Figure 1**, it is possible to demonstrate that the threshold volume, TV_{BS}, can be determined from the initial working conditions using Eq. (15)

$$C_{BS}^{mix} \geq TC_{BS}^{mix} \approx 10 C_{OS}^{mix} \tag{19}$$

which can be rewritten as

$$\frac{C_{BS}^o \, V_{BS}}{V_o} \geq \frac{C_{BS}^o \, TV_{BS}}{V_o} = 10 \frac{C_{OS}^o \, V_{OS}}{V_o} \tag{17}$$

From Eq. (17), the following is obtained

$$V_{BS} \geq TV_{BS} = 10 \left(\frac{C_{OS}^o V_{OS}}{C_{BS}^o} \right) \tag{18}$$

Figure 7c shows that the TV_{BS} is equal to 10 mL, even if it is a volume added to the buffer solution with 1 M component concentration, because the original system is composed of 100 mL with 10^{-2} M solute concentration (C_{OS2}^o). It can be proved that the TC_{BS} fulfills the condition of being 10 times larger than the original system's solute concentration.
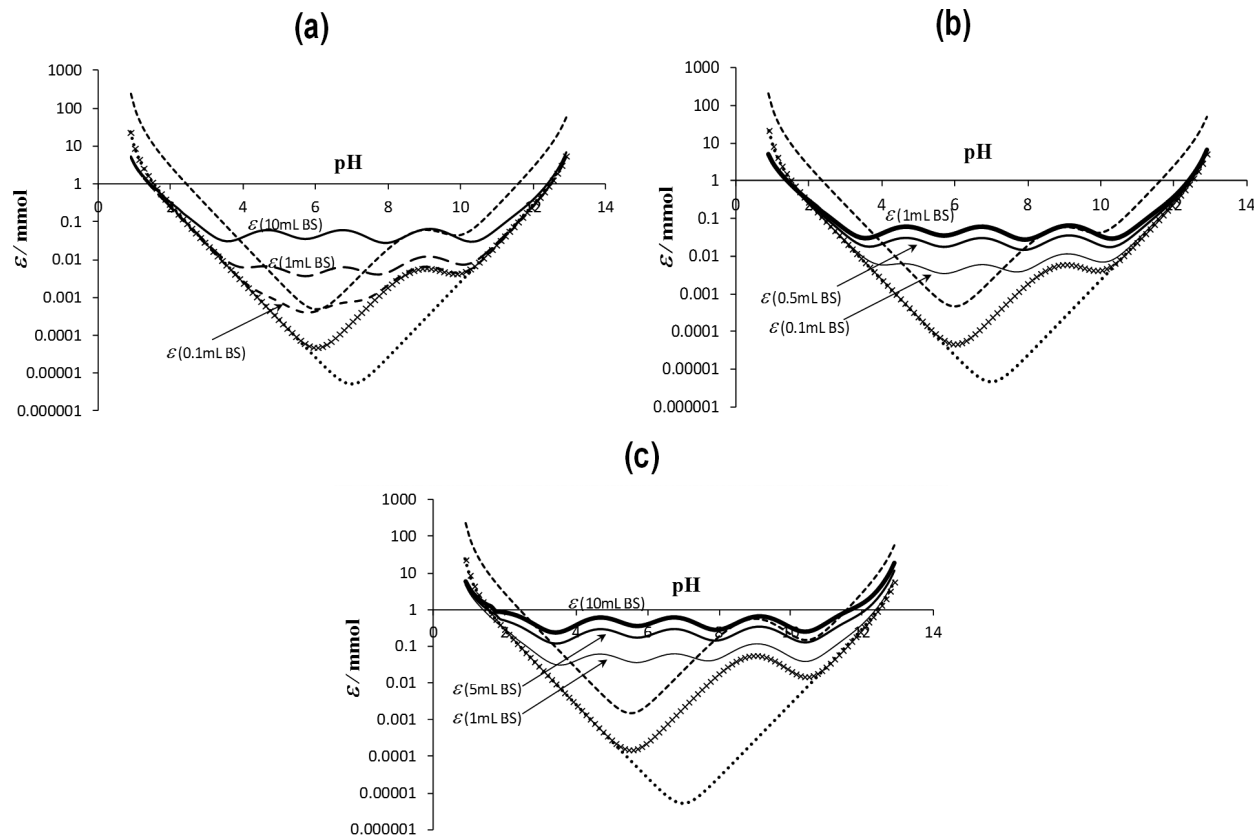
Figure 7. The curves for $\varepsilon = f(pH)$ for 100 mL of different solutions. The broken line in all cases represents the buffer efficacy of water, $\varepsilon_{(H_2O)}$, and its acid and basic particles. The curves of ε_{OS} and ε_{10OS} of acac solutions in the absence of the buffer system (markers $\times\times\times\times$ and ---, respectively). (a) Curves ε_{OS} and ε_{10OS} containing 100 mL of the acac solution with a 10^{-3} M solute concentration, curve ε_{mix} containing the same acac solution as ε_{OS} and different added volumes of the buffer solution with a concentration $C_{BS} = 0.1$ M. Volumes added: —10 mL, — — —1 mL and, 0.1 mL. (b) The curves ε_{OS} and ε_{10OS} are the same that in (a), curves ε_{mix} containing the same acac solution and different added volumes of the buffer solution with $C_{BS} = 1$ M. Added volumes: —1 mL, —0.5 mL and —0.1 mL. (c) Curves ε_{OS} and ε_{10OS} containing 100 mL of a acac solution with 10^{-2} M solute concentration, curves ε_{mix} containing 100 mL of the acac solution with a 10^{-2} M solute concentration and different volumes added to the buffer with $C_{BS} = 1$ M. Added volumes: —10 mL, —5 mL and, — 1 mL.

Just like in the case of the threshold concentration (TC_{BS}^{mix}) of Eq. (16), Eq. (18) also corresponds to the most difficult case. The factor of 10 can be smaller to the extent that the pK_a values of the original system move away from the pH that is to be set.

4. Conclusions

A model has been proposed to study the buffer capacity with dilution effect, β_{dil}, of mixtures of various polydonor systems in aqueous solutions. From the model, exact algebraic expressions were obtained that describe the buffer capacity with dilution.

Through the study of β_{dil} of solutions containing one or more polydonor systems with different conditions and characteristics, it is concluded that β_{dil} decreases when the total concentration of the polydonor systems (or mixtures of polydonor systems) decreases, and conversely.

When a polydonor system attains a very small concentration, this does not contributes practically to the buffer capacity, only the solvent's acid and basic particles determine this property. Then, it is stated that any solution, even the pure solvent, has a buffer capacity.

It is shown that the β_{dil} depends on the size of the system, which is information that is not considered in the β known and used in the common scientific literature.

A new index has been introduced, ε, to measure the buffer efficacy of a buffer solution such that the quantity added of strong base or strong acid causes a change of only one-tenth of a pH unit instead of one unit as β_{dil}.

From the construction of the different curves of $\varepsilon = f(pH)$, it is possible to identify a buffer threshold concentration in the mixture (TC_{BS}^{mix}), which allows knowing the minimum buffer concentration to set the desired pH of the system of interest. This concentration TC_{BS}^{mix} must be, at least 10 times greater than that of the original system's solutes in the mixture ($TC_{BS}^{mix} = C_{OS}^{mix}$) in the most difficult case.

Similarly, the different curves of $\varepsilon = f(pH)$ also allow determining the minimum volume (buffer threshold volume, TV_{BS}) that must be added to the system of interest to set its pH $\left(TV_{BS} = 10\left(\dfrac{C_{OS}^o V_{OS}}{C_{BS}^o}\right)\right)$ in the most difficult case.

Acknowledgements

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