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Dynamic Buffer Capacity in Acid–Base Systems

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Abstract   The generalized concept of 'dynamic' buffer capacity β_V is related to electrolytic systems of different complexity where acid–base equilibria are involved. The resulting formulas are presented in a uniform and consistent form. The detailed calculations are related to two Britton–Robinson buffers, taken as examples.

Keywords   Acid–base equilibria · Buffer capacity · Titration

1 Introduction

Buffer solutions are commonly applied in many branches of classical and instrumental analyses [1, 2], e.g. in capillary electrophoresis, CE [3–5], and polarography [6]. The effectiveness of a buffer at a given pH is governed mainly by its buffer capacity (β), defined primarily by Van Slyke [7]. The β-concept refers usually to electrolytic systems where only one proton/acceptor pair exists. A more general (and elegant) formula for β was provided by Hesse and Olin [8] for the system containing a n–protic weak acid H_nL together with strong acid, HB, and strong base, MOH; it was an extension of the β-concept from [9]. The formula for β found in the literature is usually referred to the 'static' case, based on an assumption that total concentration of the species forming a buffering system is unchanged. The dilution effects, resulting from addition of finite volume of an acid or base to such dynamic systems during titrations, was considered in the papers [2, 10], where finite changes (ΔpH) in pH, affected by addition of the strong acid or base, were closely related to the formulas for the acid–base titration curves. The ΔpH values, called

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'windows', were considered later [11] for a mixture of monoprotic acids titrated with MOH; the dynamic version of this concept was presented first in [10].

Buffering action is involved with mixing of two (usually aqueous) solutions. The mixing can be performed according to the titrimetric mode. In the present paper, the formula for dynamic buffer capacity, $\beta_V = \left| \frac{dc}{dpH} \right|$ related to the systems where V_0 mL of the solution being titrated (titrand, D) of different complexity, with concentrations [mol·L^{-1}] of component(s) denoted by C_0 or C_{0k}, is titrated with V mL of C mol·L^{-1} solution of: MOH (e.g. NaOH), HB (e.g. HCl), or a weak polyprotic acid H$_n$L or its salt of M$_m$H$_{n-m}$L ($m = 1,…,n$), or H$_{n+m}$LB$_m$ type as a reagent in titrant (T) are considered. This way, the D + T mixture of volume $V_0 + V$ mL, is obtained, if the assumption of additivity of the volumes is valid. It is assumed that, at any stage of the titration, D + T is a mono-phase system where only acid-base reactions occur. The formation function $\bar{n} = \bar{n}(pH)$ [12, 13] was incorporated, as a very useful concept, into formulas for acid-base titration curves, obtained on the basis of charge and concentration balances, referred to polyprotic acids.

2 Definition of Dynamic Buffer Capacity

In this work, the buffer capacity is defined as follows:

$$\beta_V = \left| \frac{dc}{dpH} \right| \tag{1}$$

where

$$c = C \cdot \frac{V}{V_0 + V} \equiv C - \frac{C \cdot V_0}{V_0 + V} \tag{2}$$

denotes the current concentration of a reagent R in a D + T mixture obtained after addition of V mL of C mol·L^{-1} solution of the reagent R (considered as titrant, T) into V_0 mL of a solution named as titrand (D). From Eqs. 1 and 2 we have:

$$\beta_V = \left| \frac{dc}{dV} \cdot \frac{dV}{dpH} \right| = \frac{C \cdot V_0}{(V_0 + V)^2} \cdot \left| \frac{dV}{dpH} \right| \tag{3}$$

The buffer capacity β_V is an intensive property, expressed in terms of molar concentrations, i.e., intensive variable. The expressions for $\frac{dV}{dpH}$ in Eq. 3 will be formulated below.

3 Formulation of Dynamic Buffer Capacity

Some particular systems can be distinguished. For the sake of simplicity in notation, the charges of particular species $X_i^{z_i}$ will can be omitted when put in square brackets, expressing molar concentration $[X_i]$.

System 1A: V mL of MOH (C, mol·L^{-1}) is added, as reagent R, into V_0 mL of K$_m$-H$_{n-m}$L (C_0, mol·L^{-1}). The concentration balances are as follows:

$$[\mathrm{M}] = CV/(V_0 + V); \ [\mathrm{K}] = m \cdot C_0 V_0/(V_0 + V); \ \sum_{i=0}^{q} [\mathrm{H}_i\mathrm{L}] = \frac{C_0 V_0}{V_0 + V} \tag{4}$$

Denoting:

$$[\mathrm{H}_i\mathrm{L}] = K_i^{\mathrm{H}} \cdot [\mathrm{H}]^i \cdot [\mathrm{L}]; \ b_i = K_i^{\mathrm{H}} \cdot [\mathrm{H}]^i; \ f_i = \frac{b_i}{\sum\limits_{j=0}^{q} b_j}$$

$$\alpha = [\mathrm{H}] - [\mathrm{OH}] = 10^{-\mathrm{pH}} - 10^{\mathrm{pH} - pK_{\mathrm{w}}} \tag{5}$$

and applying the formula for mean number of protons attached to L^{-n} [2]

$$\bar{n} = \frac{\sum\limits_{i=1}^{q} i \cdot [\mathrm{H}_i\mathrm{L}]}{\sum\limits_{i=0}^{q} [\mathrm{H}_i\mathrm{L}]} = \frac{\sum\limits_{i=0}^{q} i \cdot K_i^{\mathrm{H}} \cdot [\mathrm{H}]^i}{\sum\limits_{j=0}^{q} K_j^{\mathrm{H}} \cdot [\mathrm{H}]^j} = \frac{\sum\limits_{i=0}^{q} i \cdot b_i}{\sum\limits_{j=0}^{q} b_j} = \sum_{i=0}^{q} i \cdot f_i = \sum_{i=1}^{q} i \cdot f_i \tag{6}$$

in the charge balance equation

$$\alpha + [\mathrm{M}] + [\mathrm{K}] + \sum_{i=0}^{q} (i - n)[\mathrm{H}_i\mathrm{L}] = 0 \tag{7}$$

we get, by turns,

$$\alpha + \frac{C \cdot V}{V_0 + V} + m \cdot \frac{C_0 \cdot V_0}{V_0 + V} = (n - \bar{n}) \cdot \frac{C_0 \cdot V_0}{V_0 + V} \tag{8}$$

$$V = V_0 \cdot \frac{(n - m - \bar{n}) \cdot C_0 - \alpha}{C + \alpha} \tag{9}$$

$$\begin{aligned} V_0 + V &= V_0 \cdot \frac{(n - m - \bar{n}) \cdot C_0 + C}{C + \alpha} \\ &= ((n - m) \cdot C_0 + C) \cdot V_0 \cdot \frac{1}{C + \alpha} - C_0 \cdot V_0 \cdot \frac{\bar{n}}{C + \alpha} \end{aligned} \tag{10}$$

Differentiating Eq. 10 gives:

$$\begin{aligned} \frac{\mathrm{d}(V_0 + V)}{\mathrm{dpH}} &= \frac{\mathrm{d}V}{\mathrm{dpH}} \\ &= -((n - m)C_0 + C) \cdot V_0 \cdot \frac{1}{(C + \alpha)^2} \cdot \frac{\mathrm{d}\alpha}{\mathrm{dpH}} - C_0 \cdot V_0 \cdot \frac{\frac{\mathrm{d}\bar{n}}{\mathrm{dpH}} \cdot (C + \alpha) - \bar{n} \cdot \frac{\mathrm{d}\alpha}{\mathrm{dpH}}}{(C + \alpha)^2} \end{aligned} \tag{11}$$

Applying the relation:

$$\frac{\mathrm{d}z}{\mathrm{dpH}} = \frac{\mathrm{d}z}{\mathrm{d}[\mathrm{H}]} \cdot \frac{\mathrm{d}[\mathrm{H}]}{\mathrm{dpH}} = -\ln 10 \cdot [\mathrm{H}] \cdot \frac{\mathrm{d}z}{\mathrm{d}[\mathrm{H}]} \tag{12}$$

for $z = \alpha$ (Eq. 5) and $\bar{n}$ (Eq. 6), we get [2, 12]:

$$\frac{d\alpha}{dpH} = -\ln 10 \cdot ([H] + [OH]) \tag{13}$$

$$\frac{d\bar{n}}{dpH} = -\ln 10 \cdot \sum_{j>i=0}^{q} (j-i)^2 \cdot f_i f_j \tag{14}$$

and then from Eq. 11 we have:

$$\frac{dV}{dpH} = \frac{V_0 \cdot \ln 10}{(C+\alpha)^2} \cdot \left(\left((n-m) \cdot C_0 + C - C_0 \cdot \sum_{i=1}^{q} i \cdot f_i \right) \cdot ([H] + [OH]) \right.$$
$$\left. + C_0 \cdot (C+\alpha) \cdot \sum_{j>i=0}^{q} (j-i)^2 \cdot f_i f_j \right) \tag{15}$$

Note that $[H] + [OH] = (\alpha^2 + 4K_W)^{1/2}$ [12] (see Eq. 5), where $K_W = [H][OH]$.

System 1B: When V mL of HB (C, mol·L^{-1}) is added into V_0 mL of $K_m H_{n-m} L$ (C_0, mol·L^{-1}), we have $[B] = CV/(V_0+V)$. Then C is replaced by $-C$ in the related formulas, and we have:

$$V = V_0 \cdot \frac{(\bar{n}+m-n) \cdot C_0 + \alpha}{C - \alpha}$$
$$= V_0 \cdot \frac{-(\bar{n}+m-n) \cdot C_0 - \alpha}{-C + \alpha} = V_0 \cdot \frac{(n-m-\bar{n}) \cdot C_0 - \alpha}{-(C-\alpha)} \tag{16}$$

As we see, Eq. 16 can be obtained by setting $-C$ for C in the related formula. Applying it to Eq. 15, we get

$$\frac{dV}{dpH} = \frac{V_0 \cdot \ln 10}{(C-\alpha)^2} \cdot \left(\left((n-m) \cdot C_0 - C - C_0 \cdot \sum_{i=1}^{q} i \cdot f_i \right) \cdot ([H] + [OH]) \right.$$
$$\left. - C_0 \cdot (C-\alpha) \cdot \sum_{j>i=0}^{q} (j-i)^2 \cdot f_i f_j \right) \tag{17}$$

System 2A: V mL of C mol·L^{-1} MOH is added into V_0 mL of the mixture: $K_{m_k} H_{n_k-m_k} L_{(k)}(C_{0k}; \ m_k = 0,...,n_k; \ k = 1,...,P); \ H_{n_k+m_k} L_{(k)} B_{m_k}(C_{0k}; \ m_k = 0,...,q_k - n_k; \ k = P+1,...,Q),$ HB (C_{0a}) and MOH (C_{0b}). Denoting $-n_k$—charge of $L_{(k)}^{-n_k}$, we have the charge balance equation:

$$\alpha + [K] + [M] - [B] + \sum_{k=1}^{Q} \sum_{j=0}^{q_k} (j-n_k)[H_j L_k] = 0 \tag{18}$$

where:

$$\sum_{j=0}^{q_k} [H_j L_{(k)}] = \frac{C_{0k} V_0}{V_0 + V} \ (k = 1,..., \ P, \ P+1,...,Q); \ [K] = \frac{\sum_{k=1}^{P} m_k C_{0k} V_0}{V_0 + V} \tag{19}$$

$$[\mathrm{M}] = \frac{CV + C_{0b}V_0}{V_0 + V} \tag{20}$$

$$[\mathrm{B}] = \frac{\sum\limits_{k=P+1}^{Q} m_k C_{0k} V_0 + C_{0a} V_0}{V_0 + V} \tag{21}$$

The presence of strong acid HB (C_{0a}) and MOH (C_{0b}) in the titrand D can be perceived as a kind of pre-assumed/intentional "mess" done in stoichiometric composition of the salts. Denoting: $[\mathrm{H}_i\mathrm{L}_{(k)}] = K_{ki}^{\mathrm{H}} \cdot [\mathrm{H}]^i \cdot [\mathrm{L}_{(k)}]$; $b_{ki} = K_{ki}^{\mathrm{H}} \cdot [\mathrm{H}]^i$, and

$$f_{ki} = \frac{b_{ki}}{\sum\limits_{j=0}^{q_k} b_{kj}}; \quad \bar{n}_k = \frac{\sum\limits_{i=0}^{q_k} i \cdot [\mathrm{H}_i\mathrm{L}_{(k)}]}{\sum\limits_{j=0}^{q_k} [\mathrm{H}_j\mathrm{L}_{(k)}]} = \frac{\sum\limits_{i=0}^{q_k} iK_{ki}^{\mathrm{H}} \cdot [\mathrm{H}]^i}{\sum\limits_{j=0}^{q_k} K_{kj}^{\mathrm{H}} \cdot [\mathrm{H}]^j} = \frac{\sum\limits_{i=0}^{q_k} ib_{ki}}{\sum\limits_{j=0}^{q_k} b_{kj}} = \sum\limits_{i=1}^{q_k} i \cdot f_{ki} \tag{22}$$

we have:

$$\frac{\mathrm{d}\bar{n}_k}{\mathrm{dpH}} = -\ln 10 \cdot \sum\limits_{j>i=0}^{q_k} (j-i)^2 \cdot f_{ki} f_{kj} \tag{23}$$

Introducing Eqs. 19–23 into Eq. 18 we get, by turns:

$$\alpha + \frac{\sum\limits_{k=1}^{p} m_k C_{0k} V_0}{V_0 + V} + \frac{CV + C_{0b}V_0}{V_0 + V} - \frac{\sum\limits_{k=p+1}^{Q} m_k C_{0k} V_0 + C_{0a} V_0}{V_0 + V} + \sum\limits_{k=1}^{Q} \sum\limits_{i=0}^{q_k} (i - n_k)[\mathrm{H}_i\mathrm{L}_{(k)}] = 0$$

$$\alpha V_0 + \alpha V + \sum\limits_{k=1}^{p} m_k C_{0k} V_0 + CV + \Delta_0 V_0 - \sum\limits_{k=p+1}^{Q} m_k C_{0k} V_0 - \sum\limits_{k=1}^{Q} n_k \cdot C_{0k} V_0$$

$$+ \sum\limits_{k=1}^{Q} \bar{n}_k \cdot C_{0k} V_0 = 0$$

$$V_0 + V = V_0 \cdot \left(\sum\limits_{k=1}^{P} (n_k - m_k) \cdot C_{0k} + \sum\limits_{k=P+1}^{Q} (n_k + m_k) \cdot C_{0k} - \Delta_0 + C \right) \cdot \frac{1}{C + \alpha}$$

$$- V_0 \cdot \frac{\sum\limits_{k=1}^{Q} \bar{n}_k \cdot C_{0k}}{C + \alpha} \tag{24}$$

$$\frac{\mathrm{d}V}{\mathrm{dpH}} = \frac{V_0 \cdot \ln 10}{(C + \alpha)^2} \cdot \left(\sum\limits_{k=1}^{P} (n_k - m_k) \cdot C_{0k} + \sum\limits_{k=P+1}^{Q} (n_k + m_k) \cdot C_{0k} \right.$$

$$- \sum\limits_{k=1}^{Q} C_{0k} \cdot \sum\limits_{i=1}^{q_k} i \cdot f_{ki} - \Delta_0 + C \right) \cdot ([H] + [OH]) \tag{25}$$

$$+ (C + \alpha) \cdot \sum\limits_{k=1}^{Q} C_{0k} \cdot \sum\limits_{j>i=0}^{q_k} (j-i)^2 \cdot f_{ki} f_{kj} \Bigg).$$

where

$$\Delta_0 = C_{0b} - C_{0a} \tag{26}$$

System 2B: V mL of C mol·L^{-1} HB is added into V_0 mL of the mixture: $K_{m_k}H_{n_k-m_k}L_{(k)}$ (C_{0k}; $m_k = 0,...,n_k$; $k = 1,...,P$); $H_{n_k+m_k}L_{(k)}B_{m_k}(C_{0k}$; $m_k = 0,...,q_k - n_k$; $k = P+1,...,Q$), HB (C_{0a}) and MOH (C_{0b}). We have the balances Eqs. 18 and 19, and

$$[M] = \frac{C_{0b}V_0}{V_0 + V} \tag{27}$$

$$[B] = \frac{\sum\limits_{k=P+1}^{Q} m_k C_{0k} V_0 + C_{0a} V_0 + CV}{V_0 + V} \tag{28}$$

Introducing Eqs. 19, 27, 28 into Eq. 18 and applying Eqs. 13, 22, 23, 26 we obtain:

$$\frac{dV}{d\text{pH}} = \frac{V_0 \cdot \ln 10}{(C - \alpha)^2} \cdot \left(\left(\sum_{k=1}^{P} (n_k - m_k) \cdot C_{0k} + \sum_{k=P+1}^{Q} (n_k + m_k) \cdot C_{0k} \right. \right.$$
$$\left. - \Delta_0 - C - \sum_{k=1}^{Q} C_{0k} \cdot \sum_{i=1}^{q_k} i \cdot f_{ki} \right) \cdot ([H] + [OH])..$$
$$\left. -(C - \alpha) \cdot \sum_{k=1}^{Q} C_{0k} \cdot \sum_{j > i = 0}^{q_k} (j - i)^2 \cdot f_{ki} f_{kj} \right) \tag{29}$$

System 3A: V mL of C mol·L^{-1} $M_m H_{n-m}L$ is added into V_0 mL of the mixture: $K_{m_k}H_{n_k-m_k}L_{(k)}(C_{0k}$; $m_k = 0,...,n_k$; $k = 1,...,P$); $H_{n_k+m_k}L_{(k)}B_{m_k}(C_{0k}$; $m_k = 0,...,q_k - n_k$; $k = P+1,...,Q$), HB (C_{0a}) and MOH (C_{0b}). From charge

$$\alpha + [K] + [M] - [B] + \sum_{k=1}^{Q} \sum_{j=0}^{q_k} (j - n_k)[H_j L_{(k)}] + \sum_{j=0}^{q} (j - n)[H_j L] = 0 \tag{30}$$

and concentration balances, Eqs. 19 and 21 and

$$\sum_{j=0}^{q} [H_j L] = \frac{CV}{V_0 + V} \tag{31}$$

$$[M] = \frac{mCV + C_{0b}V_0}{V_0 + V} \tag{32}$$

after introducing Eqs. 19, 21, 31, 32 into Eq. 30 and applying Eqs. 6, 13, 14, 22, 23 and 26, we obtain:

$$V_0 + V = V_0 \cdot \left(-\sum_{k=1}^{P} (n_k - m_k)C_{0k} - \sum_{k=P+1}^{Q} (n_k + m_k)C_{0k} + (n - m) \cdot C + \Delta_0 \right) \cdot$$
$$\frac{1}{(n - m - \bar{n}) \cdot C - \alpha} + V_0 \cdot \frac{\sum\limits_{k=1}^{Q} \bar{n}_k \cdot C_{0k} - \bar{n} \cdot C}{(n - m - \bar{n}) \cdot C - \alpha} \tag{33}$$

and then

$$\frac{dV}{dpH} = \frac{V_0 \cdot \ln 10}{\left(\left(n - m - \sum\limits_{i=1}^{q} i \cdot f_i\right) \cdot C - \alpha\right)^2} \cdot \left(\left(\sum_{k=1}^{P}(n_k - m_k) \cdot C_{0k} + \sum_{k=P+1}^{Q}(n_k + m_k) \cdot C_{0k}\right.\right.$$
$$\left. - \sum_{k=1}^{Q} C_{0k} \cdot \sum_{i=1}^{q_k} i \cdot f_{ki} + \left(\sum_{i=1}^{q} i \cdot f_i - n + m\right) \cdot C - \Delta_0\right)$$
$$\cdot \left(C \cdot \sum_{j>i=0}^{q}(j-i)^2 \cdot f_i f_j + [H] + [OH]\right) - \left(\left(n - m - \sum_{i=1}^{q} i \cdot f_i\right) \cdot C - \alpha\right)$$
$$\left.\cdot \left(\sum_{k=1}^{Q} C_{0k} \cdot \sum_{j>i=0}^{q_k}(j-i)^2 \cdot f_{ki}f_{kj} - C \cdot \sum_{j>i=0}^{q}(j-i)^2 \cdot f_i f_j\right)\right)$$

$$(34)$$

System 3B: V mL of C mol·L^{-1} H$_{n+m}$LB$_m$ is added into V_0 mL of the mixture: K$_{m_k}$H$_{n_k-m_k}$L$_{(k)}$(C_{0k}; $m_k = 0,\ldots,n_k$; $k = 1,\ldots,$P); H$_{n_k+m_k}$L$_{(k)}$B$_{m_k}$(C_{0k}; $m_k = 0,\ldots,q_k - n_k$; $k = $P+1,$\ldots$,Q), HB ($C_{0a}$) and MOH ($C_{0b}$). Applying Eqs. 19, 27, 31 and

$$[B] = \frac{\sum\limits_{k=P+1}^{Q} m_k \cdot C_{0k}V_0 + C_{0a}V_0 + m \cdot CV}{V_0 + V} \qquad (35)$$

in Eq. 30, we obtain:

$$V_0 + V = V_0$$
$$\cdot \frac{-\sum\limits_{k=1}^{P}(n_k - m_k) \cdot C_{0k} - \sum\limits_{k=P+1}^{Q}(n_k + m_k) \cdot C_{0k} + \sum\limits_{k=1}^{Q} \bar{n}_k \cdot C_{0k} + \Delta_0 + (n + m - \bar{n}) \cdot C}{(n + m - \bar{n}) \cdot C - \alpha}$$

$$(36)$$

$$V_0 + V = V_0 \cdot \left(-\sum_{k=1}^{P}(n_k - m_k) \cdot C_{0k} - \sum_{k=P+1}^{Q}(n_k + m_k) \cdot C_{0k} + (n + m) \cdot C + \Delta_0\right)$$
$$\cdot \frac{1}{(n + m - \bar{n}) \cdot C - \alpha} + V_0 \cdot \frac{\sum\limits_{k=1}^{Q} \bar{n}_k \cdot C_{0k} - \bar{n} \cdot C}{(n + m - \bar{n}) \cdot C - \alpha}$$

$$(37)$$

Then applying Eqs. 6, 13, 14, 23 and 24 in 37, we have:

$$\frac{dV}{dpH} = \frac{V_0 \cdot \ln 10}{\left(\left(n + m - \sum\limits_{i=1}^{q} i \cdot f_i\right) \cdot C - \alpha\right)^2} \cdot \left(\sum\limits_{k=1}^{P} (n_k - m_k) \cdot C_{0k} + \sum\limits_{k=P+1}^{Q} (n_k + m_k) \cdot C_{0k}\right.$$

$$\left. -(n + m) \cdot C - \Delta_0 - \sum\limits_{k=1}^{Q} C_{0k} \cdot \sum\limits_{i=1}^{q_k} i \cdot f_{ki} + C \cdot \sum\limits_{i=1}^{q} i \cdot f_i\right)$$

$$\cdot \left(C \cdot \sum\limits_{j>i=0}^{q} (j-i)^2 \cdot f_i f_j + [\text{H}] + [\text{OH}]\right)$$

$$- \left(\sum\limits_{k=1}^{Q} C_{0k} \cdot \sum\limits_{j>i=0}^{q_k} (j-i)^2 \cdot f_{ki} f_{kj} - C \cdot \sum\limits_{j>i=0}^{q} (j-i)^2 \cdot f_i f_j\right)$$

$$\times \left((n + m - \sum\limits_{i=1}^{q} i \cdot f_i) \cdot C - \alpha\right) \tag{38}$$

In all cases it is assumed that $\beta_V \geq 0$; for this purpose, the absolute value (modulus) was introduced in Eq. 1. An analogous assumption was made for the static buffer capacity (β).

4 Britton–Robinson Buffers (BRB)

Two buffers proposed by Britton and Robinson [14], marked as BRB-I and BRB-II, are obtained by titration to the desired pH value over the pH range 2–12 [15]. The D ($V = 10$ mL) in BRB-I, consisting of H_3BO_3 (C_{01}) + H_3PO_4 (C_{02}) + CH_3COOH (C_{03}), is titrated to the desired pH with NaOH (C) as T; in this case, $C_{01} = C_{02} = C_{03} = 0.04$ mol·L^{-1}, and $C = 0.2$ mol·L^{-1}. The D in BRB-II, consisting of H_3BO_3 (C_{01}) + KH_2PO_4 (C_{02}) + citric acid $H_3L_{(3)}$ (C_{03}) + veronal $HL_{(4)}$ + HCl (C_{0a}), is titrated to the desired pH with NaOH (C) as T; in this case $C_{01} = C_{02} = C_{03} = C_{04} = C_{0a} = 0.0286$ mol·L^{-1}, and $C = 0.2$ mol·L^{-1}. For BRB-I we have the equation for the titration curve:

$$V = V_0 \cdot \frac{(3 - \bar{n}_1) \cdot C_{01} + (3 - \bar{n}_2) \cdot C_{02} + (1 - \bar{n}_3) \cdot C_{03} - \alpha}{C + \alpha} \tag{39}$$

(see Fig. 1), where:

$$\bar{n}_1 = (3 \times 10^{34.24-3\text{pH}} + 2 \times 10^{25.7-2\text{pH}} + 10^{13.3-\text{pH}})/(10^{34.24-3\cdot\text{pH}} + 10^{25.7-2\text{pH}}$$
$$+ 10^{13.3-\text{pH}} + 1) \tag{40}$$

$$\bar{n}_2 = (3 \times 10^{21-71\text{pH}} + 2 \times 10^{19.59-2\text{pH}} + 10^{12.38-\text{pH}})/(10^{21.71-3\text{pH}} + 10^{19.59-2\text{pH}}$$
$$+ 10^{12.38-\text{pH}} + 1) \tag{41}$$

$$\bar{n}_3 = 10^{4.76-\text{pH}}/(10^{4.76-\text{pH}} + 1) \tag{42}$$

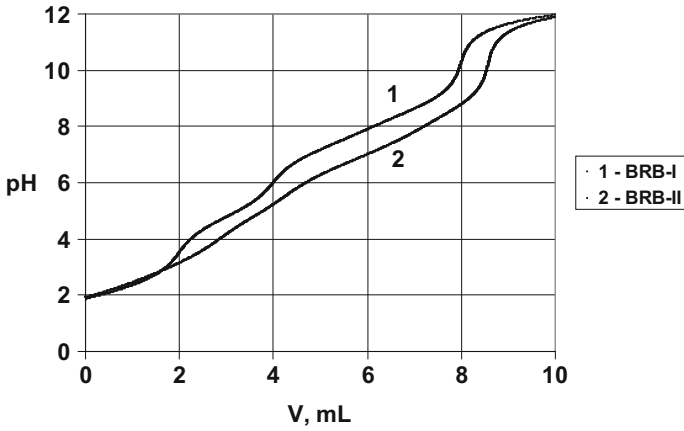For the BRB-II buffer we have the equation for titration curve

Fig. 1 Curves of titration of BRB-I and BRB-II with NaOH. For details see the text
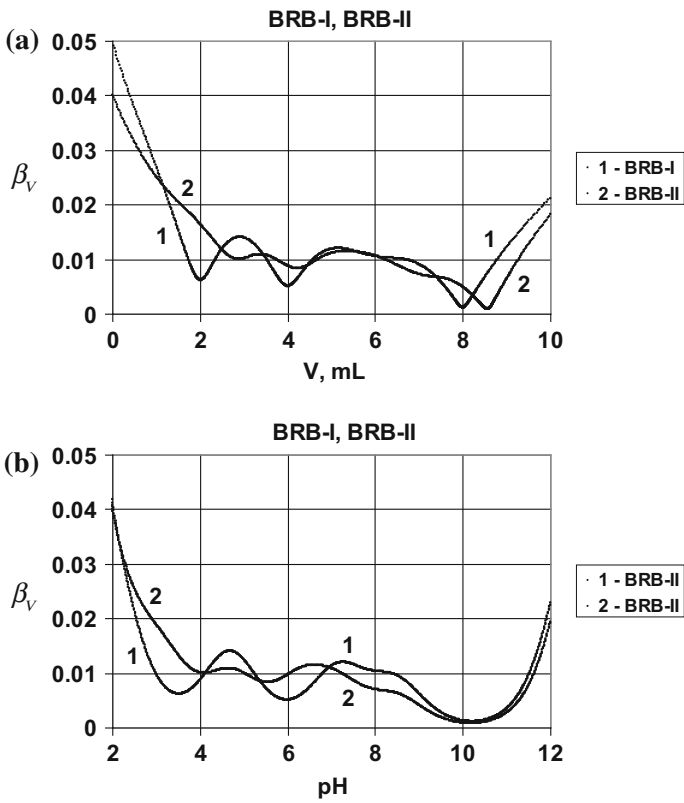

Fig. 2 The plots of **a** β_V vs. V and **b** β_V vs. pH relationships obtained for BRB-I and BRB-II. For details see the text

$$V = V_0 \cdot \frac{(3 - \bar{n}_1) \cdot C_{01} + (2 - \bar{n}_2) \cdot C_{02} + (3 - \bar{n}_3^{\bullet}) \cdot C_{03} + (1 - \bar{n}_4) \cdot C_{04} + C_{0a} - \alpha}{C + \alpha}$$

(43)

(see Figs. 1, 2), where $\bar{n}_1$(Eq. 40) and $\bar{n}_2$(Eq. 41) and:

$$\bar{n}_3^{\bullet} = (3 \times 10^{14.28-3pH} + 2 \times 10^{11.15-2pH} + 10^{6.39-pH})/(10^{14.28-3pH} + 10^{11.15-2\cdot pH} + 10^{6.39-pH} + 1)$$

(44)

$$\bar{n}_4 = 10^{7.43-pH}/(10^{7.43-pH} + 1)$$

(45)

The formulas for $\bar{n}_i$ ($i = 1,...,4$) and $\bar{n}_3^{\bullet}$ in Eqs. 39 and 43 were obtained on the basis of pK_i values found in [16–20].

Note that

$$\sum_{j>i=0}^{3} (j-i)^2 \cdot f_{ki}f_{kj} = f_{k1}f_{k0} + 4f_{k2}f_{k0} + 9f_{k3}f_{k0} + f_{k2}f_{k1} + 4f_{k3}f_{k1} + f_{k3}f_{k2};$$

$$\sum_{j>i=0}^{2} (j-i)^2 \cdot f_{ki}f_{kj} = f_{k1}f_{k0} + 4f_{k2}f_{k0} + f_{k2}f_{k1}; \quad \sum_{j>i=0}^{1} (j-i)^2 \cdot f_{ki}f_{kj} = f_{k1}f_{k0}.$$

(46)

5 Final Comments

The mathematical formulation of the dynamic buffer capacity β_V concept is presented in a general and elegant form, involving all soluble species formed in the system where only acid–base reactions are involved. This approach to buffer capacity is more general than one presented in the earlier study [2] and is correct from a mathematical viewpoint, in contrast to the one presented in [21]. It is also an extension of an earlier approach, presented for less complex acid–base static [8] and dynamic [10, 12] systems. The calculations were exemplified with two complex buffers, proposed by Britton and Robinson [14].

The salts specified in particular systems considered above do not cover all possible types of the salts, e.g. $(NH_4)_2HPO_4$ or potassium sodium tartrate (KNaL) are not examples of the salts of $K_{m_k}H_{n_k-m_k}L_{(k)}$ or $H_{n_k+m_k}L_{(k)}B_{m_k}$ type. However, in D, $(NH_4)_2HPO_4$ (C_{0i}) is equivalent to a mixture of NH_3 ($2C_{0i}$) and H_3PO_4 (C_{0i}), whereas KNaL (C_{0j}) is equivalent to a mixture of NaOH (C_{0j}), KOH (C_{0j}) and H_2L (C_{0j}).

References

1. Albert, A., Serjeant, E.P.: The Determination of Ionisation Constants. Chapman and Hall, London (1984)
2. Asuero, A.G., Michałowski, T.: Comprehensive formulation of titration curves referred to complex acid–base systems and its analytical implications. Crit. Rev. Anal. Chem. **41**, 151–187 (2011)

3. He, J.-L., Li, H.-P., Li, X.-G.: Analysis of prostaglandins in SD rats by capillary zone electrophoresis with undirected UV detection. Talanta **46**, 1–7 (1998)
4. Schneede, J., Ueland, P.M.: The formation in an aqueous matrix, properties and chromatographic behavior of 1-pyrenyldiazomethane derivatives of methylmalonic acid and other short chain dicarboxylic acids. Anal. Chem. **64**, 315–319 (1992)
5. Lagane, B., Treilhou, M., Couderc, F.: Capillary electrophoresis: theory, teaching approach and separation of oligosaccharides using indirect UV detection. Biochem. Mol. Biol. Educ. **28**, 251–255 (2000). http://www.sciencedirect.com/science/article/pii/S147081750000031X
6. Jordan, C.: Ionic strength and buffer capacity of wide-range buffers for polarography. Microchem. J. **25**, 492–499 (1980)
7. Van Slyke, D.D.: On the measurement of buffer values and on the relationship of buffer value to the dissociation constant of the buffer and the concentration and reaction of the buffer solution. J. Biol. Chem. **52**, 525–570 (1922). http://www.jbc.org/content/52/2/525.full.pdf+html. Accessed 24 May 2015
8. Hesse, R., Olin, Å.: A simple expression for the buffer index of a weak polyprotic acid. Talanta **24**, 150 (1977)
9. Butler, J.N.: Solubility and pH Calculations. Addison-Wesley Publishing Company Inc., Reading Mass (1964)
10. Michałowski, T., Parczewski, A.: A new definition of buffer capacity. Chem. Anal. **23**, 959–964 (1978)
11. Moisio, T., Heikonen, M.: A simple method for the titration of multicomponent acid–base mixtures. Fresenius' J. Anal. Chem. **354**, 271–277 (1996)
12. Michalowski, T.: Some remarks on acid–base titration curves. Chem. Anal. **26**, 799–813 (1981)
13. Asuero, A.G., Jiménez-Trillo, J.L., Navas, M.J.: Mathematical treatment of absorbance versus pH graphs of polybasic acids. Talanta **33**, 929–934 (1986)
14. Britton, H.T.K., Robinson, R.A.: Universal buffer solutions and the dissociation constant of veronal. J. Chem. Soc. **10**, 1456–1462 (1931). http://www.oalib.com/references/13396293
15. http://en.wikipedia.org/wiki/Britton-Robinson_buffer. Accessed 24 May 2015
16. http://en.wikipedia.org/wiki/Boric_acid. Accessed 24 May 2015
17. http://en.wikipedia.org/wiki/Phosphoric_acid. Accessed 24 May 2015
18. http://en.wikipedia.org/wiki/Citric_acid. Accessed 24 May 2015
19. http://en.wikipedia.org/wiki/Acetic_acid. Accessed 24 May 2015
20. http://www.zirchrom.com/organic.htm. Accessed 24 May 2015
21. Rojas-Hernández, A., Rodríguez-Laguna, N., Ramírez-Silva, M.T., Moya-Hernández, R.: Distribution diagrams and graphical methods to determine or to use the stoichiometric coefficients of acid–base and complexation reactions. In: Innocenti, A. (ed.) Stoichiometry and Research—The Importance of Quantity in Biomedicine, InTech, Rijeka, Croatia, pp. 287–310. (2012). http://www.intechopen.com/books/stoichiometry-and-research-the-importance-of-quantity-in-biomedicine