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Research Article

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Dynamic Buffer Capacities in Redox Systems

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Abstract

The buffer capacity concept is extended on dynamic redox systems, realized according to titrimetric mode, where changes in pH are accompanied by changes in potential E values; it is the basic novelty of this paper. Two examples of monotonic course of the related curves of potential E vs. Φ and pH vs. Φ relationships were considered. The systems were modeled according to GATES/GEB principles.

Keywords

Thermodynamics of electrolytic redox systems; Buffer capacity; GATES/GEB

Introduction

The buffer capacity concept is usually referred to as a measure of resistance of a solution (D) on pH change, affected by an acid or base, added as a titrant T, i.e., according to titrimetric mode; in this case, D is termed as titrand.

The titration is a dynamic procedure, where V mL of titrant T, containing a reagent B (C mol/L), is added into V_0 mL of titrand D, containing a substance A (C_0 mol/L). The advance of a titration $B(C,V) \Longrightarrow A(C_0,V_0)$, denoted for brevity as $B \Longrightarrow A$, is characterized by the fraction titrated [1-4]

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \tag{1}$$

that introduces a kind of normalization (independence on V_0 value) for titration curves, expressed by pH = pH(Φ), and E = E(Φ) for potential E [V] expressed in SHE scale. The redox systems with one, two or more electron-active elements are modeled according to principles of Generalized Approach to Electrolytic Systems with Generalized Electron Balance involved (GATES/GEB), described in details in [5-16], and in references to other authors' papers cited therein.

According to earlier conviction expressed by Gran [17], all titration curves: pH = pH(Φ) and E = E(Φ), were perceived as monotonic; that generalizing statement is not true [7], however. According to contemporary knowledge, full diversity in this regard is stated, namely: (1°) monotonic pH = pH(Φ) and monotonic E = E(Φ) [18-20]; (2°) monotonic pH = pH(Φ) and non-monotonic E = E(Φ) [6]; (3°) non-monotonic pH = pH(Φ) and monotonic E = E(Φ) [5]; (4°) non-monotonic pH = pH(Φ), and non-monotonic E = E(Φ) [7].

Examples of titration curves pH = pH(Φ) and E = E(Φ) in redox systems

In this paper, we refer to the disproportionating systems: (S1) NaOH ⟹ HIO and (S2) HCl ⟹ NaIO, characterized by monotonic changes of pH and E values during the related titrations (i.e., the case 1°). In both instances, the values: V_0=100, C_0=0.01, and C=0.1 were assumed. The set of equilibrium data [18-20] applied in calculations, presented in Table 1, is completed by the solubility of solid iodine, $\mathbf{I}_{2(s)}$, in water, equal $1.33 \cdot 10^{-3}$ mol/L. The related algorithms, prepared in MATLAB for S1 (NaOH ⟹ HIO) S2 (HCl ⟹ NaIO) system according to the GATES/GEB principles, are presented in Appendices 1 and 2.

The titration curves: pH = pH(Φ) and E = E(Φ) presented in Figure 1 and Figure 2 are the basis to formulation of dynamic buffer capacities in the systems S1 and S2.

Dynamic acid-base buffer capacities β_V and B_V

Dynamic buffer capacity was referred previously only to acid-base equilibria in non-redox systems [3,21-23]. However, the dynamic (β_V) and windowed (B_V) buffer capacities can be also related to acid-base equilibria in redox systems. The β_V is formulated as follows [3,21]

$$\beta_V = \left|\frac{dc}{dpH}\right| \tag{2}$$

where

$$c = \frac{CV}{V_0 + V} \tag{3}$$

is the current concentration of B in D+T mixture, at any point of the titration. In the simplest case, D is a solution of one substance A (C_0 mol/L), and then equation 3 can be rewritten as follows

$$c = \Phi \cdot \frac{C_0 C}{C + \Phi \cdot C_0} \tag{4}$$

where Φ is the fraction titrated (equation 1). Then we get

$$\beta_V = \frac{dc}{d\Phi} \cdot \left|\frac{d\Phi}{dpH}\right| = \frac{C_0 \cdot C^2}{(C + \Phi \cdot C_0)^2} \cdot \frac{1}{|\eta|} = \frac{c^2}{C_0 \cdot |\eta|} \tag{5}$$

where

$$\eta = \frac{dpH}{d\Phi} \tag{6}$$

is the sharpness index on the titration curve. For comparative purposes, the absolute values, $|\beta_V|$ and $|\eta|$, for β_V (equations 1,5) and η (equation 6) are considered. At $C_0/C \ll 1$ and small Φ value, from equation 3 we get

$$\beta_V = \Phi^2 \cdot C_0 / |\eta|$$

The β_V value is the point–assessment and then cannot be used in the case of finite pH–changes (ΔpH) corresponding to an addition of a finite volume of titrant (β_V is a non–linear function of pH). For this purpose, the 'windowed' buffer capacity, B_V, defined by the formula [3,21]

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Table 1: Physicochemical data related to the systems S1 and S2

No.	**Reaction**	**Equilibrium equation**	**Equilibrium data**
1	$I_2 + 2e^{-1} = 2I^{-1}$ (for dissolved I_2)	$[I^{-1}]^2 = K_{e1}\cdot[I_2][e^{-1}]^2$	$E_{01} = 0.621$ V
2	$I_3^{-1} + 2e^{-1} = 3I^{-1}$	$[I^{-1}]^3 = K_{e2}\cdot[I_3^{-1}][e^{-1}]^2$	$E_{02} = 0.545$ V
3	$IO^{-1} + H_2O + 2e^{-1} = I^{-1} + 2OH^{-1}$	$[I^{-1}][OH^{-1}]^2 = K_{e3}\cdot[IO^{-1}][e^{-1}]^2$	$E_{03} = 0.49$ V
4	$IO_3^{-1} + 6H^{+1} + 6e^{-1} = I^{-1} + 3H_2O$	$[I^{-1}] = K_{e4}\cdot[IO_3^{-1}][H^{+1}]^6[e^{-1}]^6$	$E_{04} = 1.08$ V
5	$H_5IO_6 + 7H^{+1} + 8e^{-1} = I^{-1} + 6H_2O$	$[I^{-1}] = K_{e5}\cdot[H_5IO_6][H^{+1}]^7[e^{-1}]^8$	$E_{05} = 1.24$ V
6	$H_3IO_6^{-2} + 3H_2O + 8e^{-1} = I^{-1} + 9OH^{-1}$	$[I^{-1}][OH^{-1}]^9 = K_{e6}\cdot[H_3IO_6^{-2}][e^{-1}]^8$	$E_{06} = 0.37$ V
7	$HIO = H^{+1} + IO^{-1}$	$[H^{+1}][IO^{-1}] = K_{11I}\cdot[HIO]$	$pK_{11I} = 10.6$
8	$HIO_3 = H^{+1} + IO_3^{-1}$	$[H^{+1}][IO_3^{-1}] = K_{51I}\cdot[HIO_3]$	$pK_{51I} = 0.79$
9	$H_4IO_6^{-1} = H^{+1} + H_3IO_6^{-2}$	$[H^{+1}][H_3IO_6^{-2}] = K_{72}\cdot[H_4IO_6^{-1}]$	$pK_{72} = 3.3$
10	$Cl_2 + 2e^{-1} = 2Cl^{-1}$	$[Cl^{-1}]^2 = K_{e7}\cdot[Cl_2][e^{-1}]^2$	$E_{07} = 1.359$ V
11	$ClO^{-1} + H_2O + 2e^{-1} = Cl^{-1} + 2OH^{-1}$	$[Cl^{-1}][OH^{-1}]^2 = K_{e8}\cdot[ClO^{-1}][e^{-1}]^2$	$E_{08} = 0.88$ V
12	$ClO_2^{-1} + 2H_2O + 4e^{-1} = Cl^{-1} + 4OH^{-1}$	$[Cl^{-1}][OH^{-1}]^4 = K_{e9}\cdot[ClO_2^{-1}][e^{-1}]^4$	$E_{09} = 0.77$ V
13	$HClO = H^{+1}+ ClO^{-1}$	$[H^{+1}][ClO^{-1}] = K_{11Cl}\cdot[HClO]$	$pK_{11Cl} = 7.3$
14	$HClO_2 + 3H^{+1} + 4e^{-1} = Cl^{-1} + 2H_2O$	$[Cl^{-1}] = K_{e10}\cdot[HClO_2][H^{+1}]^3[e^{-1}]^4$	$E_{010} = 1.56$ V
15	$ClO_2 + 4H^{+1} + 5e^{-1} = Cl^{-1} + 4H_2O$	$[Cl^{-1}] = K_{e11}\cdot[ClO_2][H^{+1}]^4[e^{-1}]^5$	$E_{011} = 1.50$ V
16	$ClO_3^{-1} + 6H^{+1} + 6e^{-1} = Cl^{-1} + 3H_2O$	$[Cl^{-1}] = K_{e12}\cdot[ClO_3^{-1}][H^{+1}]^6[e^{-1}]^6$	$E_{012} = 1.45$ V
17	$ClO_4^{-1} + 8H^{+1} + 8e^{-1} = Cl^{-1} + 4H_2O$	$[Cl^{-1}] = K_{e13}\cdot[ClO_4^{-1}][H^{+1}]^8[e^{-1}]^8$	$E_{013} = 1.38$ V
18	$2ICl + 2e^{-1} = I_2 + 2Cl^{-1}$	$[I_2][Cl^{-1}]^2 = K_{e14}\cdot[ICl]^2[e^{-1}]^2$	$E_{014} = 1.105$ V
19	$I_2Cl^{-1} = I_2 + Cl^{-1}$	$[I_2][Cl^{-1}] = K_1\cdot[I_2Cl^{-1}]$	$\log K_1 = 0.2$
20	$ICl_2^{-1} = ICl + Cl^{-1}$	$[ICl][Cl^{-1}] = K_2\cdot[ICl_2^{-1}]$	$\log K_2 = 2.2$
21	$H_2O = H^{+1} + OH^{-1}$	$[H^{+1}][OH^{-1}] = K_W$	$pK_W = 14.0$

$$B_V = \left|\frac{\Delta c}{\Delta pH}\right| \tag{7}$$

where

$$\frac{\Delta c}{\Delta pH} = \frac{1}{\Delta pH}\cdot\int_{pH}^{pH+\Delta pH}\beta_V\cdot dpH = \frac{c(pH+\Delta pH)-c(pH)}{\Delta pH} \tag{8}$$

has been suggested. From extension in Taylor series we have

$$\frac{\Delta c}{\Delta pH} = \beta_V + \frac{d\beta_V}{dpH}\cdot\frac{\Delta pH}{2} + \frac{d^2\beta_V}{dpH^2}\cdot\frac{(\Delta pH)^2}{6} + \ldots = \beta_V + \sum_{k=1}^{\infty}\left(\frac{d^k\beta_V}{dpH^k}\right)_{pH}\cdot\frac{(\Delta pH)^k}{(k+1)!} \tag{9}$$

where

$$\left(\frac{d^k c}{dpH^k}\right)_{pH} = \left(\frac{d^{k-1}\beta_V}{dpH^{k-1}}\right)_{pH} \tag{10}$$

From equations 7 and 9 we see that β_V is the first approximation of B_V. One should take here into account that finite changes (ΔpH) in pH, e.g. $\Delta pH = 1$, are involved with addition of a finite volume of a reagent endowed with acid–base properties, here: base NaOH, of a finite concentration, C.

Dynamic redox buffer capacities β_V^E and B_V^E

In similar manner, one can formulate dynamic buffer capacities β_V^E and B_V^E, involved with infinitesimal and finite changes of potential E values:

$$\beta_V^E = \left|\frac{dc}{dE}\right| \tag{11}$$

$$B_V^E = \left|\frac{\Delta c}{\Delta E}\right| \tag{12}$$

where c is defined by equation 2, and then we have

$$\frac{\Delta c}{\Delta E} = \frac{1}{\Delta E}\cdot\int_{E}^{E+\Delta E}\beta_V^E\cdot dE = \frac{c(E+\Delta E)-c(E)}{\Delta E}$$

$$\frac{\Delta c}{\Delta E} = \beta_V^E + \sum_{k=1}^{\infty}\left(\frac{d^k\beta_V^E}{dE^k}\right)_E\cdot\frac{(\Delta E)^k}{(k+1)!} \tag{13}$$

where

$$\frac{d^k c}{dE^k} = \left(\frac{d^{k-1}\beta_V^E}{dE^{k-1}}\right)_E \tag{14}$$

Graphical presentation of dynamic buffer capacities in redox systems

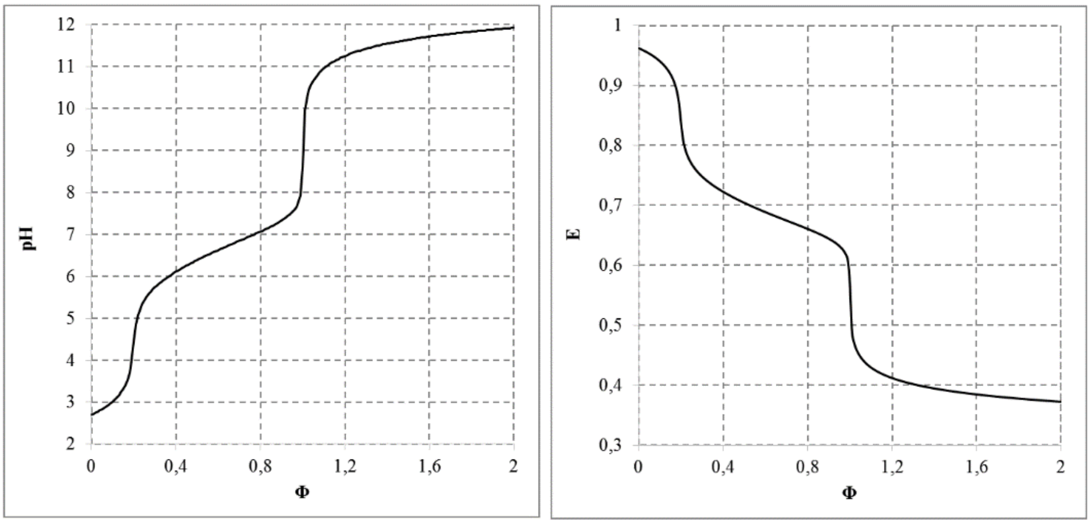
Referring to dynamic redox systems represented by titration curves presented in Figures 1,2, we plot the relationships: β_V vs. Φ, β_V vs. pH, β_V vs. E, and β_V^E vs. Φ, β_V^E vs. pH, β_V^E vs. E for the systems: (S1) NaOH $\Longrightarrow$ HIO; (S2) HCl $\Longrightarrow$ NaIO. The relations: (A) β_V vs. Φ, (B) β_V vs. pH, (C) β_V vs. E and (D) β_V^E vs. Φ, (E) β_V^E vs. pH, (F) β_V^E vs. E are plotted in Figures 3,4.

Discussion

Disproportionation of the solutes considered (HIO or NaIO) in D occurs directly after introducing them into pure water. The disproportionation is intensified, by greater pH changes, after addition of the respective titrants: NaOH (in S1) or HCl (in S2), and the monotonic changes of $E = E(\Phi)$ and $pH = pH(\Phi)$ occur in all instances.

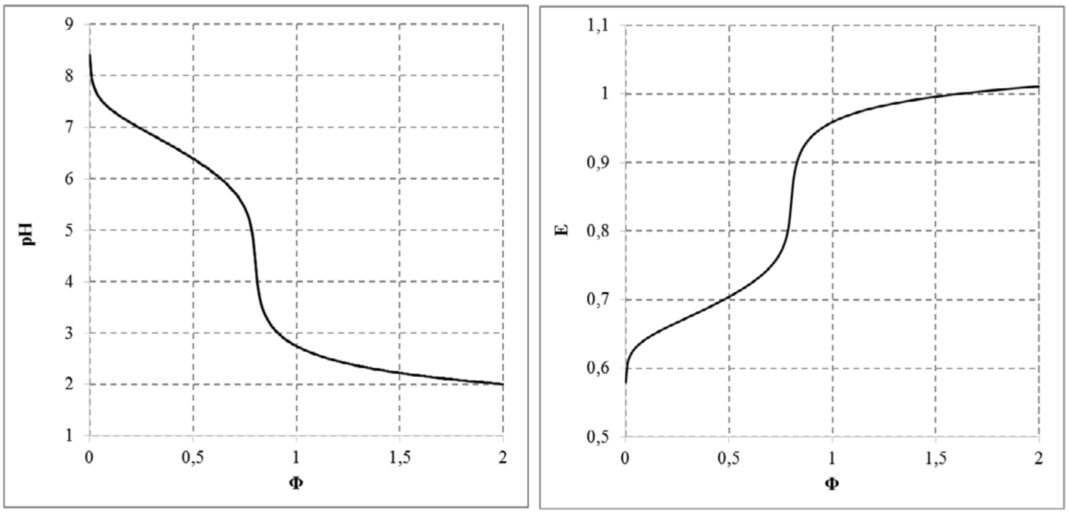
All attainable equilibrium data related to these systems are included in the algorithms implemented in the MATLAB computer program (Appendices 1 and 2). In all instances, the system of equations was composed of: generalized electron balance (GEB), charge balance (ChB) and concentration balances for particular elements ≠ H,O.

In the system S1, the precipitate of solid iodine, $\mathbf{I}_{2(s)}$, is formed (Figure 5). In the (relatively simple) redox system S2, we have all four basic kinds of reactions; except redox and acid-base reactions, the solid iodine ($\mathbf{I}_{2(s)}$) is precipitated and soluble complexes: I_2Cl^{-1}, ICl and ICl_2^{-1} are formed (Figure 6A). Note that $\mathbf{I}_{2(s)} + I^{-1} = I_3^{-1}$ is also the complexation reaction.



(A) **(B)**

Figure 1: (A) pH = pH(Φ) and (B) E = E(Φ) relationships plotted for the system NaOH ⟹ HIO.



(A) **(B)**

Figure 2: (A) pH = pH(Φ) and (B) E = E(Φ) relationships plotted for the system HCl ⟹ NaIO.

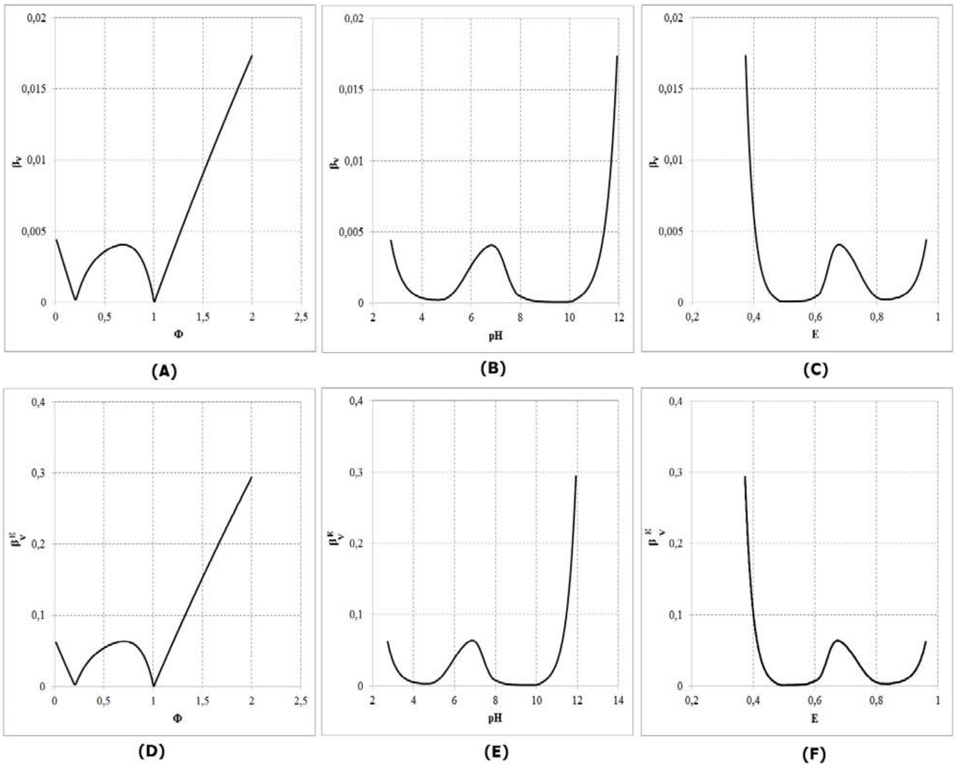
In the system S2, all oxidized forms of Cl^{-1} were involved, i.e. the oxidation of Cl^{-1} ions was thus pre-assumed. This way, full "democracy" was assumed, with no simplifications [18-20]. However, from the calculations we see that HCl acts primarily as a disproportionating, and not as reducing agent. The oxidation of Cl^{-1} occurred here only in an insignificant degree (Figure 6B); the main product of the oxidation was Cl_2, whose concentration was on the level ca. 10^{-16} - 10^{-17} mol/L.

Final comments

The redox buffer capacity concepts: β_V and β_V^E can be principally related to monotonic functions. This concept looks awkwardly for non-monotonic functions pH = pH(Φ) and/or E = E(Φ) specified above (2^o - 4^o) and exemplified in Figures 7,8,9. For comparison, in isohydric (acid-base) systems, the buffer capacity strives for infinity. In particular, it occurs in the titration HB (C,V) ⟹ HL (C_0,V_0), where HB is a strong monoprotic acid HB and HL is a weak monoprotic acid characterized by the dissociation constant $K_1 = [H^{+1}][L^{-1}]/[HL]$; at $4K_W/C^2 \ll 1$, the isohydricity condition is expressed here by the Michałowski formula $C_0 = C + C^2 \cdot 10^{pK_1}$ [24-26].

The formula for the buffer capacity, suggested in [27] after [28], is not correct. Moreover, it involves formal potential value, perceived as a kind of conditional equilibrium constant idea, put in (apparent) analogy with the simplest static acid-base buffer capacity, see criticizing remarks in [29]; it is not adaptable for real redox systems.

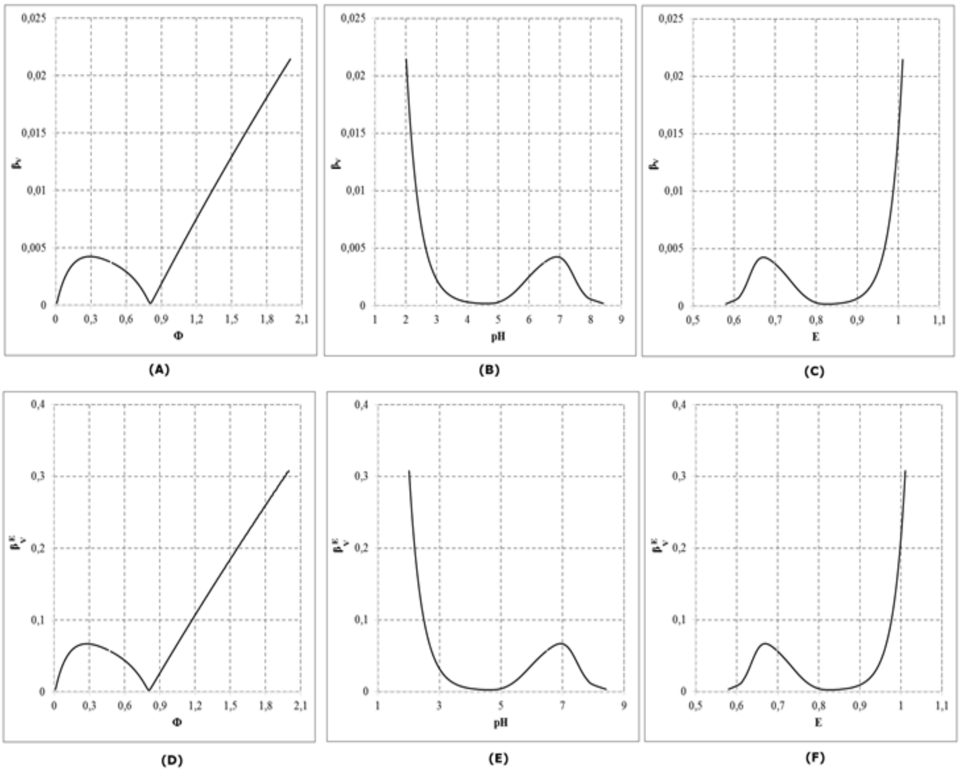
Buffered solutions are commonly applied in different procedures involved with classical (titrimetric, gravimetric) and instrumental analyses [30-33]. There are in close relevance to isohydric solutions



(A) (B) (C)

(D) (E) (F)

Figure 3: The relations: (A) β_V vs. Φ, (B) β_V vs. pH, (C) β_V vs. E and (D) β_V^E vs. Φ, (E) β_V^E vs. pH, (F) β_V^E vs. E for (S1) NaOH ⟹ HIO.



(A) (B) (C)

(D) (E) (F)

Figure 4: The relations: (A) β_V vs. Φ, (B) β_V vs. pH, (C) β_V vs. E and (D) β_V^E vs. Φ, (E) β_V^E vs. pH, (F) β_V^E vs. E for (S2) HCl ⟹ NaIO.

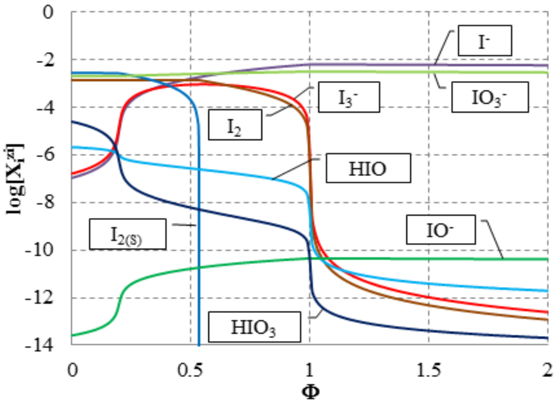


Figure 5: Speciation diagram for the system (S1) NaOH ⟹ HIO.

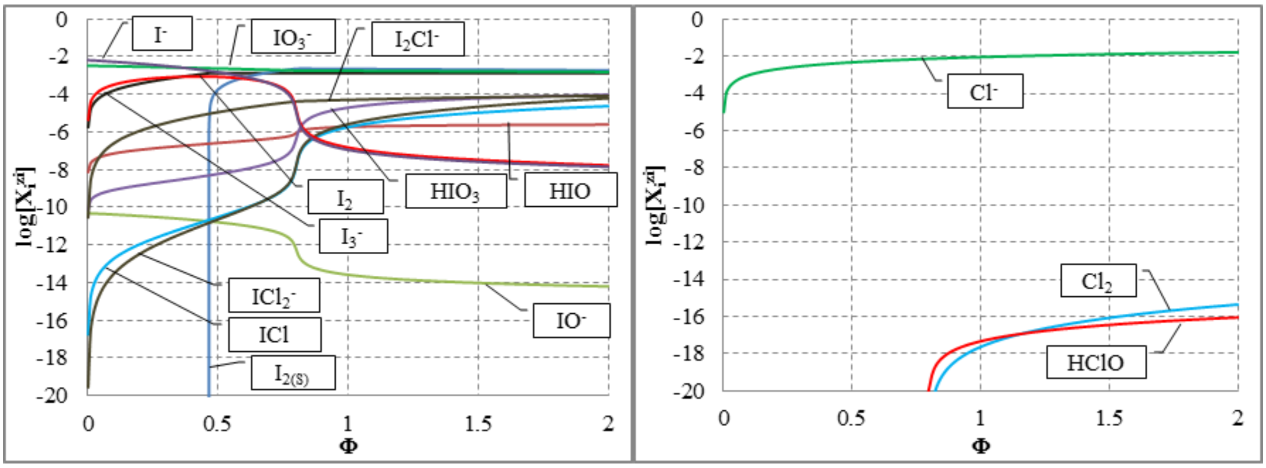


Figure 6: Speciation diagram for the system (S2) HCl ⟹ NaIO: (A) for iodine species; (B) for oxidized forms of chlorine species.

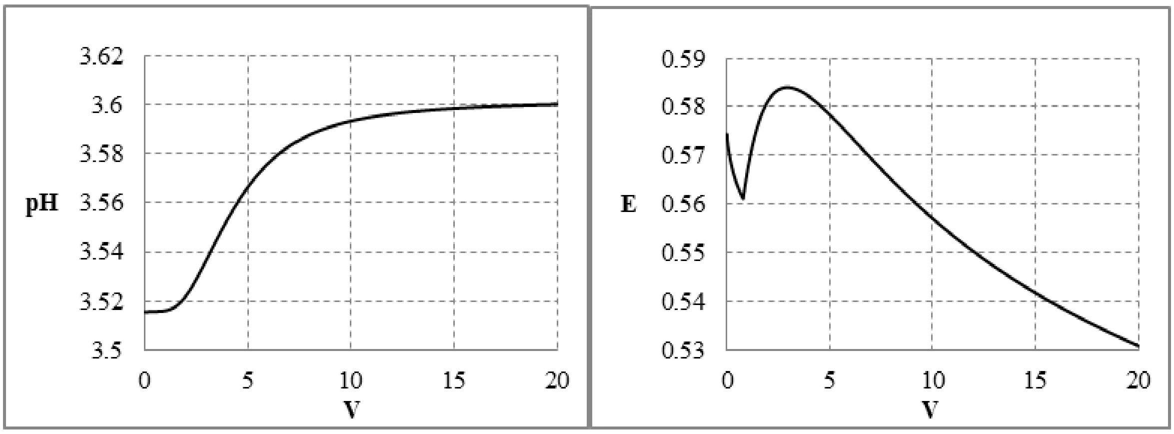


Figure 7: Case (2°): (A) monotonic pH = pH(V) and (B) non-monotonic E = E(V) plots on the step 3 of the process presented in [6].

[24-26] and pH-static titration [4,34], and titration in binary-solvent systems [12,35]. Buffering property is usually referred to an action of an external agent (mainly: strong acid, HB, or strong base, MOH) inducing pH change, ΔpH, of the solution. Redox buffer capacity is also involved with the problem of interfacing in CE-MS analysis, and bubbles formation in reaction $2H_2O = O_{2(g)} + 4H^{+1} + 4e^{-1}$ at the outlet electrode in CE [36-39].

In Baicu et al. [40], a nice proposal of "*slyke*", as the name for (acid-base, pH) buffer capacity unit, has been raised.

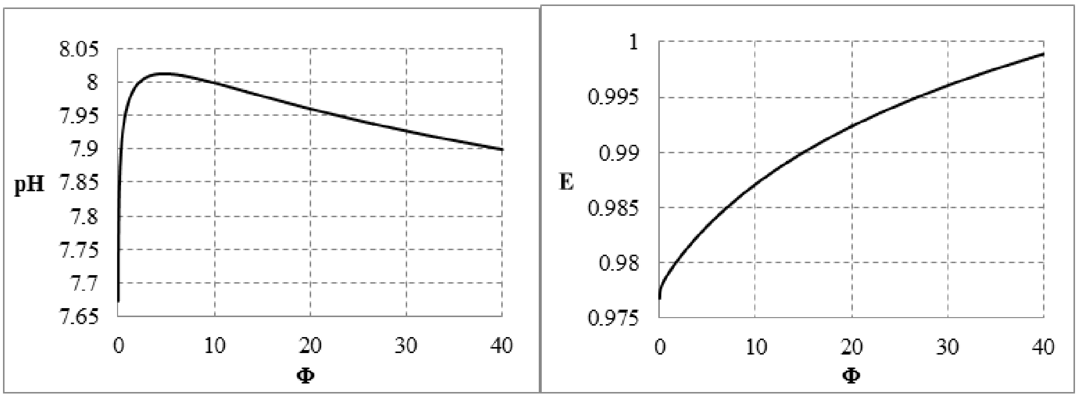


Figure 8: Case (3°): (A) non-monotonic pH = pH(Φ) and (B) monotonic E = E(Φ) functions for the system $KBrO_3 \Rightarrow NaBr$ presented in [5].

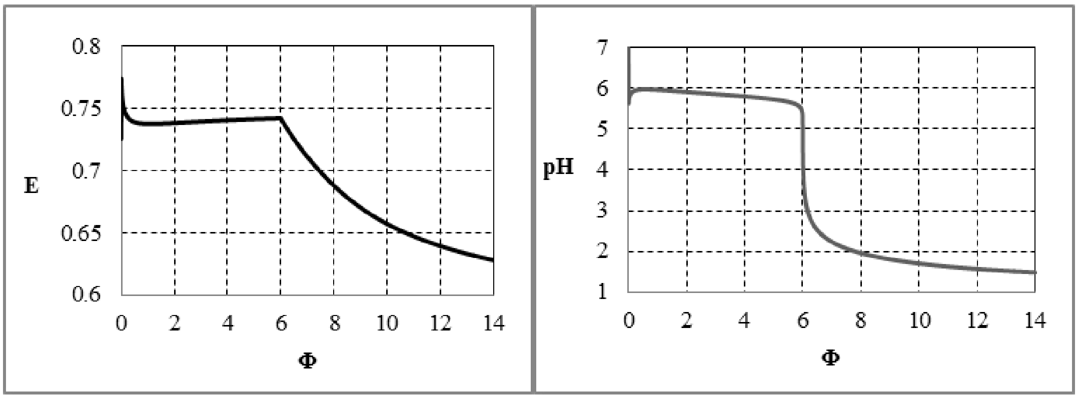


Figure 9: Case (4°): the (A) non-monotonic pH = pH(Φ) and (B) non-monotonic E = E(Φ) functions for the system $HI \Rightarrow KIO_3$ presented in [7].

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