



Research Article

Dynamic Buffer Capacities in Redox Systems

Anna Maria Michałowska-Kaczmarczyk¹, Aneta Spórna-Kucab², Tadeusz Michałowski^{2*}

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 $B(C,V) \Rightarrow A(C_0, V_0)$, denoted for brevity as $B \Rightarrow A$, is characterized by the fraction titrated [1-4]

$$\Phi = \frac{C \cdot V}{C_0 \cdot V_0} \quad (1)$$

that introduces a kind of normalization (independence on V_0 value) for titration curves, expressed by $\text{pH} = \text{pH}(\Phi)$, and $E = E(\Phi)$ 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: $\text{pH} = \text{pH}(\Phi)$ and $E = E(\Phi)$, 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 $\text{pH} = \text{pH}(\Phi)$ and monotonic $E = E(\Phi)$ [18-20]; (2°) monotonic $\text{pH} = \text{pH}(\Phi)$ and

non-monotonic $E = E(\Phi)$ [6]; (3°) non-monotonic $\text{pH} = \text{pH}(\Phi)$ and monotonic $E = E(\Phi)$ [5]; (4°) non-monotonic $\text{pH} = \text{pH}(\Phi)$, and non-monotonic $E = E(\Phi)$ [7].

Examples of titration curves $\text{pH} = \text{pH}(\Phi)$ and $E = E(\Phi)$ in redox systems

In this paper, we refer to the disproportionating systems: (S1) $\text{NaOH} \Rightarrow \text{HIO}$ and (S2) $\text{HCl} \Rightarrow \text{NaIO}$, 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, $\text{I}_{2(s)}$, in water, equal $1.33 \cdot 10^{-3}$ mol/L. The related algorithms, prepared in MATLAB for S1 ($\text{NaOH} \Rightarrow \text{HIO}$) S2 ($\text{HCl} \Rightarrow \text{NaIO}$) system according to the GATES/GEB principles, are presented in Appendices 1 and 2.

The titration curves: $\text{pH} = \text{pH}(\Phi)$ and $E = E(\Phi)$ 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]

$$\beta_V = \left| \frac{dc}{d\text{pH}} \right| \quad (2)$$

where

$$c = \frac{CV}{V_0 + V} \quad (3)$$

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

$$c = \Phi \cdot \frac{C_0 C}{C + \Phi \cdot C_0} \quad (4)$$

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

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

where

$$\eta = \frac{d\text{pH}}{d\Phi} \quad (6)$$

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]

*Corresponding author: Tadeusz Michałowski, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland, Tel: +48126282035; E-mail: michalot@o2.pl

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

No.	Reaction	Equilibrium equation	Equilibrium data
1	$I_2 + 2e^- = 2I^-$ (for dissolved I_2)	$[I^-]^2 = K_{e1} \cdot [I_2][e^-]^2$	$E_{01} = 0.621$ V
2	$I_3^- + 2e^- = 3I^-$	$[I^-]^3 = K_{e2} \cdot [I_3^-][e^-]^2$	$E_{02} = 0.545$ V
3	$IO^- + H_2O + 2e^- = I^- + 2OH^-$	$[I^-][OH^-]^2 = K_{e3} \cdot [IO^-][e^-]^2$	$E_{03} = 0.49$ V
4	$IO_3^- + 6H^+ + 6e^- = I^- + 3H_2O$	$[I^-] = K_{e4} \cdot [IO_3^-][H^+]^6[e^-]^6$	$E_{04} = 1.08$ V
5	$H_5IO_6 + 7H^+ + 8e^- = I^- + 6H_2O$	$[I^-] = K_{e5} \cdot [H_5IO_6][H^+]^7[e^-]^8$	$E_{05} = 1.24$ V
6	$H_3IO_6^{-2} + 3H_2O + 8e^- = I^- + 9OH^-$	$[I^-][OH^-]^9 = K_{e6} \cdot [H_3IO_6^{-2}][e^-]^8$	$E_{06} = 0.37$ V
7	$HIO = H^+ + IO^-$	$[H^+][IO^-] = K_{111} \cdot [HIO]$	$pK_{111} = 10.6$
8	$HIO_3 = H^+ + IO_3^-$	$[H^+][IO_3^-] = K_{511} \cdot [HIO_3]$	$pK_{511} = 0.79$
9	$H_4IO_6^- = H^+ + H_3IO_6^{-2}$	$[H^+][H_3IO_6^{-2}] = K_{72} \cdot [H_4IO_6^-]$	$pK_{72} = 3.3$
10	$Cl_2 + 2e^- = 2Cl^-$	$[Cl^-]^2 = K_{e7} \cdot [Cl_2][e^-]^2$	$E_{07} = 1.359$ V
11	$ClO^- + H_2O + 2e^- = Cl^- + 2OH^-$	$[Cl^-][OH^-]^2 = K_{e8} \cdot [ClO^-][e^-]^2$	$E_{08} = 0.88$ V
12	$ClO_2^- + 2H_2O + 4e^- = Cl^- + 4OH^-$	$[Cl^-][OH^-]^4 = K_{e9} \cdot [ClO_2^-][e^-]^4$	$E_{09} = 0.77$ V
13	$HClO = H^+ + ClO^-$	$[H^+][ClO^-] = K_{11Cl} \cdot [HClO]$	$pK_{11Cl} = 7.3$
14	$HClO_2 + 3H^+ + 4e^- = Cl^- + 2H_2O$	$[Cl^-] = K_{e10} \cdot [HClO_2][H^+]^3[e^-]^4$	$E_{10} = 1.56$ V
15	$ClO_2 + 4H^+ + 5e^- = Cl^- + 4H_2O$	$[Cl^-] = K_{e11} \cdot [ClO_2][H^+]^4[e^-]^5$	$E_{11} = 1.50$ V
16	$ClO_3^- + 6H^+ + 6e^- = Cl^- + 3H_2O$	$[Cl^-] = K_{e12} \cdot [ClO_3^-][H^+]^6[e^-]^6$	$E_{12} = 1.45$ V
17	$ClO_4^- + 8H^+ + 8e^- = Cl^- + 4H_2O$	$[Cl^-] = K_{e13} \cdot [ClO_4^-][H^+]^8[e^-]^8$	$E_{13} = 1.38$ V
18	$2ICl + 2e^- = I_2 + 2Cl^-$	$[I_2][Cl^-]^2 = K_{e14} \cdot [ICl]^2[e^-]^2$	$E_{14} = 1.105$ V
19	$I_2Cl^- = I_2 + Cl^-$	$[I_2][Cl^-] = K_1 \cdot [I_2Cl^-]$	$\log K_1 = 0.2$
20	$ICl_2^- = ICl + Cl^-$	$[ICl][Cl^-] = K_2 \cdot [ICl_2^-]$	$\log K_2 = 2.2$
21	$H_2O = H^+ + OH^-$	$[H^+][OH^-] = K_w$	$pK_w = 14.0$

$$B_V = \left| \frac{\Delta c}{\Delta pH} \right| \quad (7)$$

where

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

has been suggested. From extension in Taylor series we have

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

where

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

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:

$$\beta_V^E = \left| \frac{dc}{dE} \right| \quad (11)$$

$$B_V^E = \left| \frac{\Delta c}{\Delta E} \right| \quad (12)$$

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

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

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

where

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

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 \Rightarrow HIO; (S2) HCl \Rightarrow 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 \neq H,O.

In the system S1, the precipitate of solid iodine, $I_{2(s)}$, 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 ($I_{2(s)}$) is precipitated and soluble complexes: I_2Cl^- , ICl and ICl_2^- are formed (Figure 6A). Note that $I_{2(s)} + I^- = I_3^-$ is also the complexation reaction.

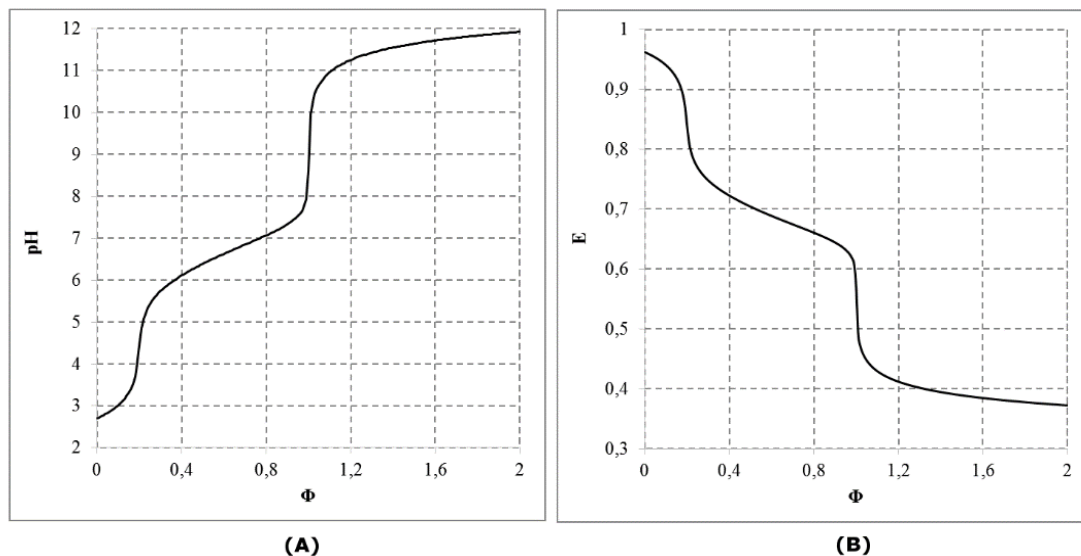


Figure 1: (A) $\text{pH} = \text{pH}(\Phi)$ and (B) $E = E(\Phi)$ relationships plotted for the system $\text{NaOH} \Rightarrow \text{HIO}$.

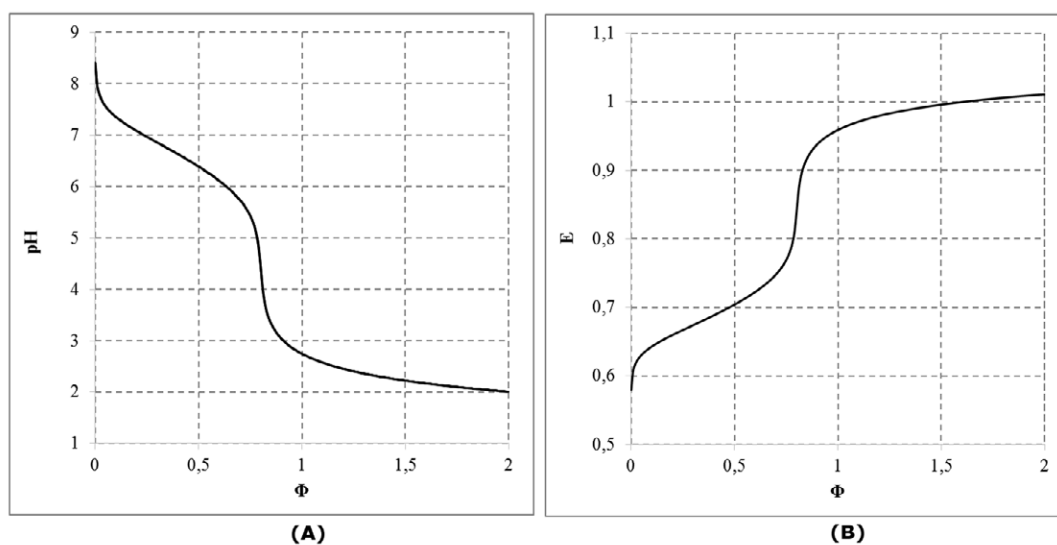


Figure 2: (A) $\text{pH} = \text{pH}(\Phi)$ and (B) $E = E(\Phi)$ relationships plotted for the system $\text{HCl} \Rightarrow \text{NaIO}$.

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 $\text{pH} = \text{pH}(\Phi)$ and/or $E = E(\Phi)$ 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 $\text{HB} (C, V) \Rightarrow \text{HL} (C_0, V_0)$, where HB is a strong monoprotic acid HB and HL is a weak monoprotic acid characterized by the dissociation constant $K_1 = [\text{H}^+][\text{L}^{-1}]/[\text{HL}]$; at $4K_w/C^2 \ll 1$, the isohydricity condition is expressed here by the Michałowski formula $C_0 = C + C^2 \cdot 10^{\text{p}K_1}$ [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

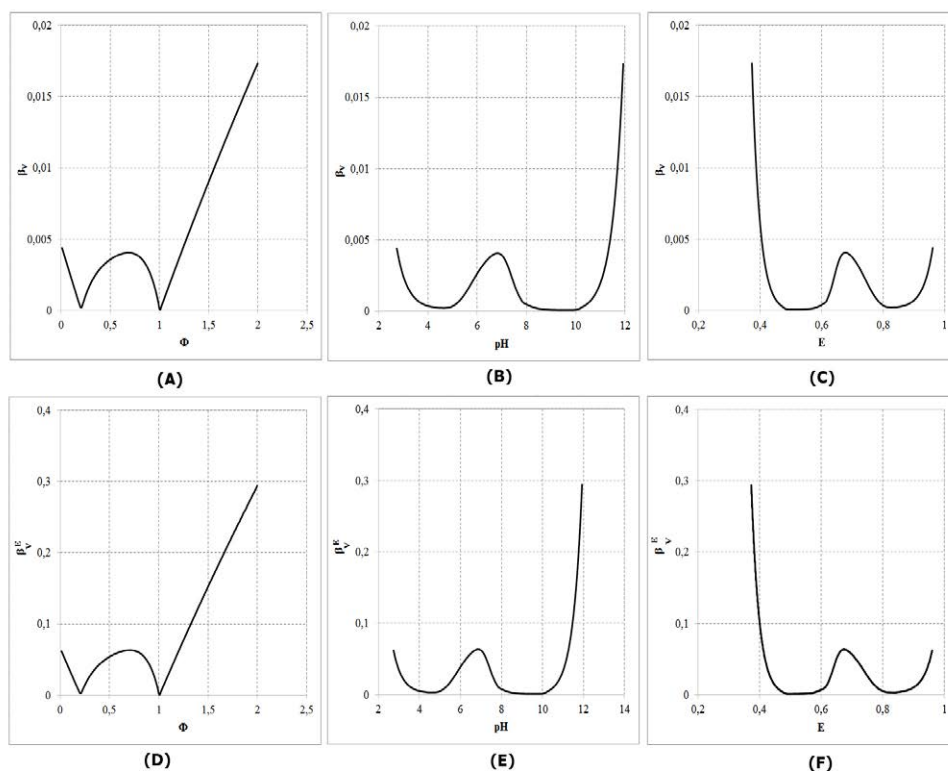


Figure 3: The relations: (A) β_V vs. Φ , (B) β_V vs. pH, (C) β_V vs. E and (D) β_V^E vs. Φ , (E) β_V^E vs. pH, (F) β_V^E vs. E for (S1) $\text{NaOH} \rightleftharpoons \text{HIO}$.

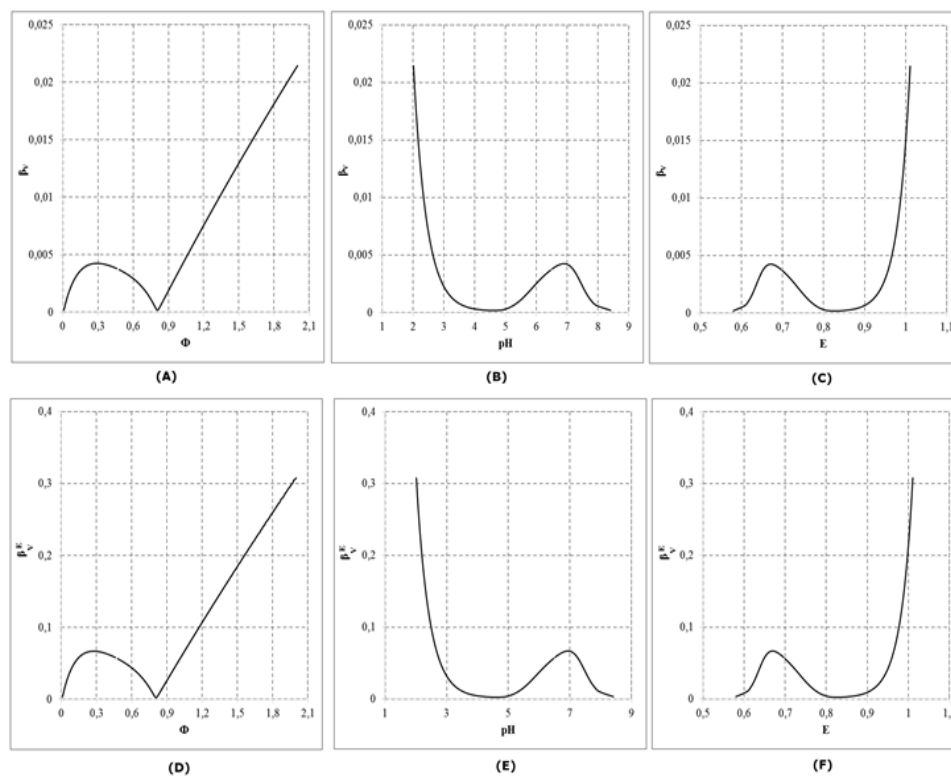


Figure 4: The relations: (A) β_V vs. Φ , (B) β_V vs. pH, (C) β_V vs. E and (D) β_V^E vs. Φ , (E) β_V^E vs. pH, (F) β_V^E vs. E for (S2) $\text{HCl} \rightleftharpoons \text{NaIO}$.

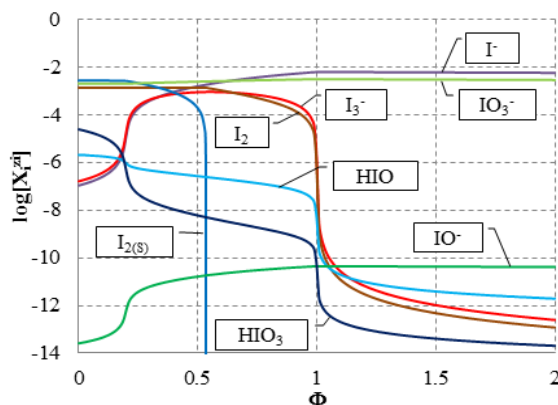


Figure 5: Speciation diagram for the system (S1) NaOH ⇌ HIO.

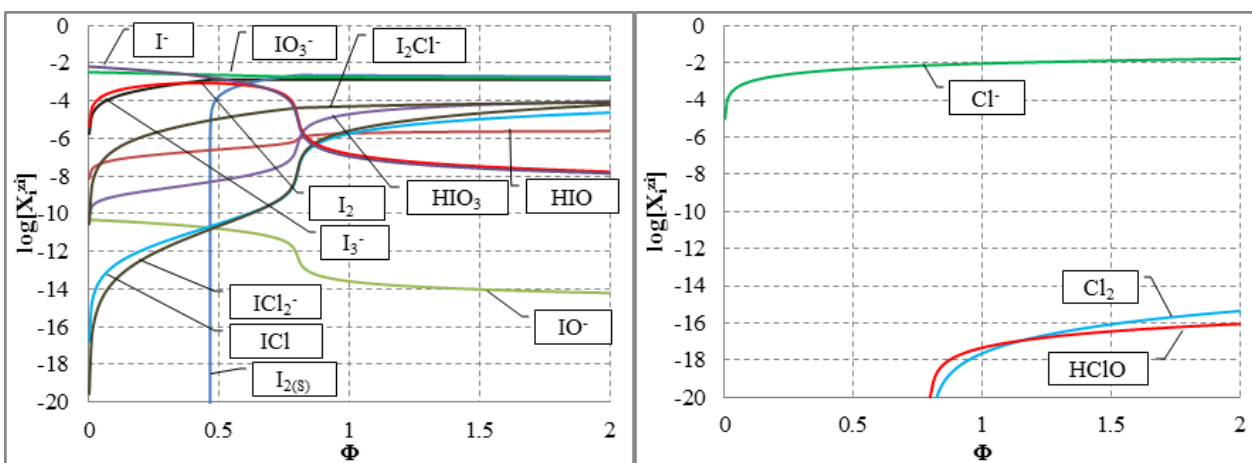


Figure 6: Speciation diagram for the system (S2) HCl ⇌ NaIO: (A) for iodine species; (B) for oxidized forms of chlorine species.

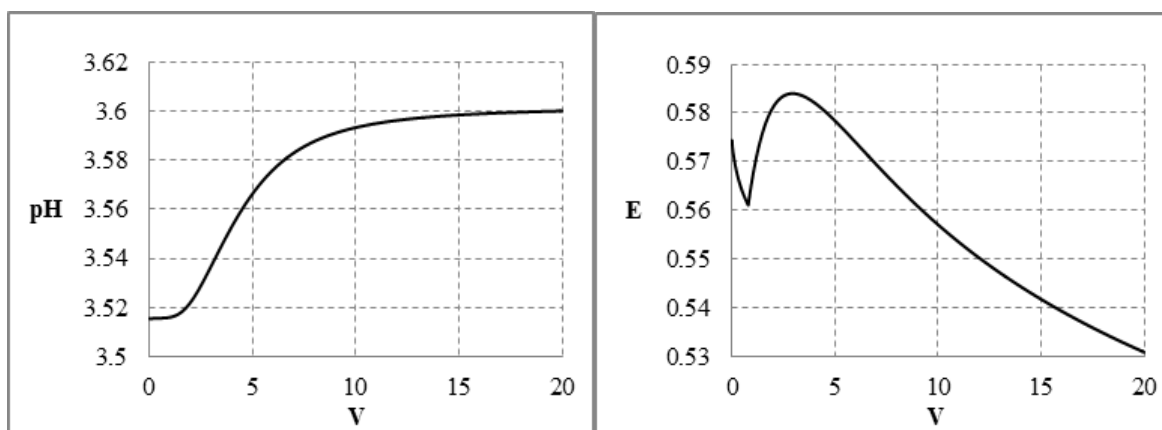


Figure 7: Case (2°): (A) monotonic pH = pH(V) and (B) non-monotonic E = E(V) plots on the step 3 of the process presented in [6].

[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 $2\text{H}_2\text{O} = \text{O}_{2(\text{g})} + 4\text{H}^{+1} + 4\text{e}^{-1}$ 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.

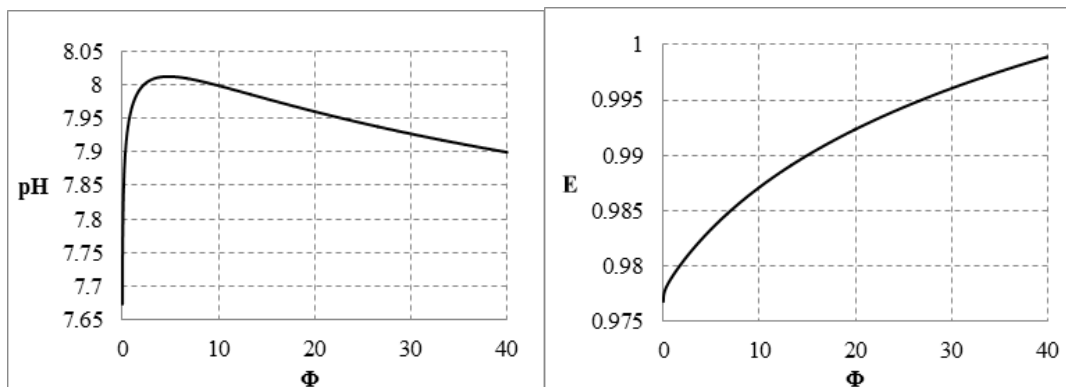


Figure 8: Case (3^o): (A) non-monotonic $pH = pH(\Phi)$ and (B) monotonic $E = E(\Phi)$ functions for the system $KBrO_3 \Rightarrow NaBr$ presented in [5].

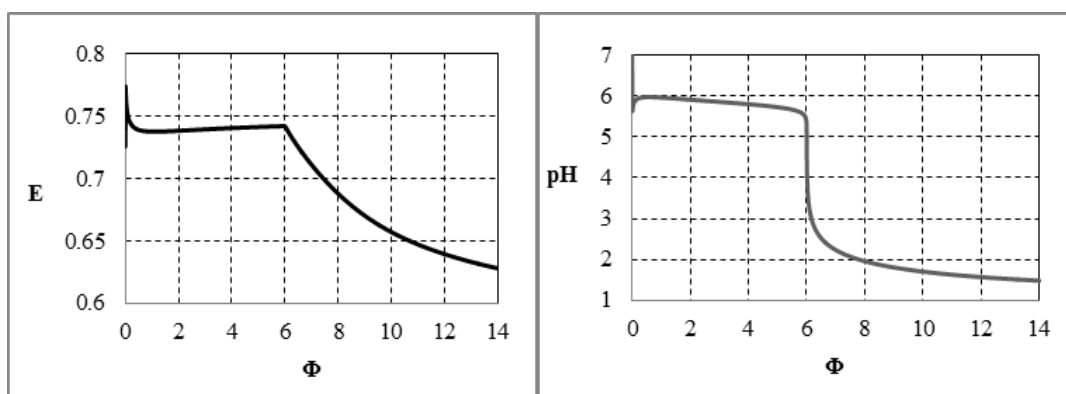


Figure 9: Case (4^o): the (A) non-monotonic $pH = pH(\Phi)$ and (B) non-monotonic $E = E(\Phi)$ functions for the system $HI \Rightarrow KIO_3$ presented in [7].

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Author Affiliation

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¹Department of Oncology, The University Hospital in Cracow, 31-501 Cracow, Poland

²Department of Analytical Chemistry, Technical University of Cracow, 31-155 Cracow, Poland

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