Dynamic Buffer Capacities in Redox Systems

Anna Maria Michałowska-Kaczmarczyk, Aneta Spórn-Kucab, Tadeusz Michałowski*

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 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 V₀ mL of titrand D, containing a substance A (C₀ mol/L). The advance of a titration B(C,V) ⇒ A(C₀,V₀), denoted for brevity as B ⇒ A, is characterized by the fraction titrated [1-4]

\[ Φ = \frac{C \cdot V}{C₀ \cdot V₀} \]  

(1)

that introduces a kind of normalization (independence on V₀ value) for titration curves, expressed by \( \frac{d\Phi}{dpH} \) and \( E(Φ) \) 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: V₀=100, C₀=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, \( I₂ \), in water, equal 1.33∙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]

\[ β_v = \frac{dc}{dpH} \]  

(2)

where

\[ c = \frac{CV}{V₀ + V} \]  

(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 (C₀ mol/L), and then equation 3 can be rewritten as follows

\[ c = \frac{CV}{V₀ + V} \]  

(4)

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

\[ β_v = \frac{dc}{dΦ} \frac{dΦ}{dpH} = \frac{C₀ \cdot C}{(C + Φ \cdot C₀)^2} \]  

(5)

where

\[ η = \frac{dpH}{dΦ} \]  

(6)

is the sharpness index on the titration curve. For comparative purposes, the absolute values, \( |β_v| \) and \( |η| \), for \( β_v \) (equations 1,5) and η (equation 6) are considered. At \( C₀/C << 1 \) and small Φ value, from equation 3 we get

\[ β_v = Φ^2 \cdot C₀ \cdot η \]  

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 (T, is a non–linear function of pH). For this purpose, the ‘windowed’ buffer capacity, \( B_v \), defined by the formula [3,21]

\[ B_v = Φ \cdot C_v \]  

(7)

is considered. The \( B_v \) value is a real–time assessment and then is used in the case of finite pH–changes (ΔpH) corresponding to an addition of a finite volume of titrant (T, is a non–linear function of pH). For this purpose, the ‘windowed’ buffer capacity, \( B_v \), defined by the formula [3,21]
Table 1: Physicochemical data related to the systems S1 and S2

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Equilibrium equation</th>
<th>Equilibrium data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I$_2$ + 2e$^{-}$ = 2I$^{-}$ (for dissolved I$_2$)</td>
<td>[I$^{-}$]$^2$ = $K_e$([I$_2$][e$^{-}$]$^2$)</td>
<td>$E_{1/2}$ = 0.621 V</td>
</tr>
<tr>
<td>2</td>
<td>I$_2$ + 2e$^{-}$ = 3I$^{-}$</td>
<td>[I$^{-}$]$^3$ = $K_e$([I$_2$][e$^{-}$]$^3$)</td>
<td>$E_{1/2}$ = 0.545 V</td>
</tr>
<tr>
<td>3</td>
<td>IO$_3$ + H$_2$O + 2e$^{-}$ = I$^{-}$ + 2OH$^{-}$</td>
<td>[I$^{-}$][OH$^{-}$]$^2$ = $K_e$([IO$_3$][e$^{-}$]$^2$)</td>
<td>$E_{1/2}$ = 0.49 V</td>
</tr>
<tr>
<td>4</td>
<td>IO$_3$ + 6H$^+$ + 6e$^{-}$ = I$^{-}$ + 3H$_2$O</td>
<td>[I$^{-}$]$^3$ = $K_e$([IO$_3$][H$^+$]$^3$)[e$^{-}$]$^3$)</td>
<td>$E_{1/2}$ = 1.08 V</td>
</tr>
<tr>
<td>5</td>
<td>HIO$_2$ + H$^+$ + 8e$^{-}$ = I$^{-}$ + 6H$_2$O</td>
<td>[I$^{-}$]$^3$ = $K_e$([HIO$_2$][H$^+$])[e$^{-}$]$^3$)</td>
<td>$E_{1/2}$ = 1.24 V</td>
</tr>
<tr>
<td>6</td>
<td>HIO$_2$ + 3H$_2$O + 8e$^{-}$ = I$^{-}$ + 9OH$^{-}$</td>
<td>[I$^{-}$][OH$^{-}$]$^2$ = $K_e$([HIO$_2$][H$_2$O])</td>
<td>$E_{1/2}$ = 0.37 V</td>
</tr>
<tr>
<td>7</td>
<td>HIO$^{-}$ + IO$^{-}$</td>
<td>[H$^+$][IO$<em>2$]$^-$ = $K</em>{11}$[HIO$^{-}$][IO$^{-}$]$^-$</td>
<td>p$K_{11}$ = 10.6</td>
</tr>
<tr>
<td>8</td>
<td>HIO$^{-}$ + H$^+$ + IO$^{-}$</td>
<td>[H$^+$][IO$<em>2$]$^-$ = $K</em>{12}$[HIO$^{-}$][IO$^{-}$]$^-$</td>
<td>p$K_{12}$ = 0.79</td>
</tr>
<tr>
<td>9</td>
<td>HIO$_3$ + H$^+$ + IO$_3^-$</td>
<td>[H$^+$][IO$<em>2$]$^-$ = $K</em>{13}$[HIO$^{-}$][IO$^{-}$]$^-$</td>
<td>p$K_{13}$ = 3.3</td>
</tr>
<tr>
<td>10</td>
<td>Cl$_2$ + 2e$^{-}$ = 2Cl$^{-}$</td>
<td>[Cl$^{-}$]$^2$ = $K_e$([Cl$^{-}$][e$^{-}$]$^2$)</td>
<td>$E_{1/2}$ = 1.359 V</td>
</tr>
<tr>
<td>11</td>
<td>ClO$^{-}$ + H$_2$O + 2e$^{-}$ = Cl$^{-}$ + 2OH$^{-}$</td>
<td>[Cl$^{-}$][OH$^{-}$]$^2$ = $K_e$([ClO$^{-}$][e$^{-}$]$^2$)</td>
<td>$E_{1/2}$ = 0.88 V</td>
</tr>
<tr>
<td>12</td>
<td>ClO$_2$ + 2H$^+$ + 4e$^{-}$ = Cl$^{-}$ + 4OH$^{-}$</td>
<td>[Cl$^{-}$]$^4$ = $K_e$([ClO$_2$][H$^+$]$^2$)[e$^{-}$]$^4$)</td>
<td>$E_{1/2}$ = 0.77 V</td>
</tr>
<tr>
<td>13</td>
<td>ClO$^{-}$ + H$^+$ + ClO$^{-}$</td>
<td>[H$^+$][ClO$^{-}$]$^2$ = $K_e$([ClO$^{-}$][ClO$^{-}$])</td>
<td>p$K_{e1}$ = 7.3</td>
</tr>
<tr>
<td>14</td>
<td>HClO + H$^+$ + ClO$^{-}$</td>
<td>[H$^+$][ClO$^{-}$]$^2$ = $K_e$([HClO][ClO$^{-}$])</td>
<td>$E_{1/2}$ = 1.56 V</td>
</tr>
<tr>
<td>15</td>
<td>ClO$_2$ + 4H$^+$ + 5e$^{-}$ = Cl$^{-}$ + 4H$_2$O</td>
<td>[Cl$^{-}$]$^5$ = $K_e$([ClO$_2$][H$^+$]$^2$)[e$^{-}$]$^5$)</td>
<td>$E_{1/2}$ = 1.50 V</td>
</tr>
<tr>
<td>16</td>
<td>ClO$_2$ + 6H$^+$ + 6e$^{-}$ = Cl$^{-}$ + 3H$_2$O</td>
<td>[Cl$^{-}$]$^6$ = $K_e$([ClO$_2$][H$^+$]$^3$)[e$^{-}$]$^6$)</td>
<td>$E_{1/2}$ = 1.45 V</td>
</tr>
<tr>
<td>17</td>
<td>ClO$_2$ + 8H$^+$ + 8e$^{-}$ = Cl$^{-}$ + 4H$_2$O</td>
<td>[Cl$^{-}$]$^8$ = $K_e$([ClO$_2$][H$^+$]$^4$)[e$^{-}$]$^8$)</td>
<td>$E_{1/2}$ = 1.38 V</td>
</tr>
<tr>
<td>18</td>
<td>2Cl$^-$ + 2e$^{-}$ = I$_2$ + 2Cl$^{-}$</td>
<td>[I$<em>2$][Cl$^-$]$^2$ = $K</em>{e2}$[Cl$^-$][I$_2$]</td>
<td>$E_{1/2}$ = 1.105 V</td>
</tr>
<tr>
<td>19</td>
<td>I$^-$(aq) + I$^-$(aq)</td>
<td>[I$<em>2$]$^-$ = $K</em>{e3}$[I$^-$(aq)][I$^-$(aq)]</td>
<td>log$K_{e3}$ = 0.2</td>
</tr>
<tr>
<td>20</td>
<td>ICl$^-$(aq) + Cl$^-$</td>
<td>[ICl$^-$(aq)]$^2$ = $K_{e4}$[ICl$^-$(aq)][Cl$^-$]</td>
<td>log$K_{e4}$ = 2.2</td>
</tr>
<tr>
<td>21</td>
<td>H$_2$O + H$^+$ + OH$^{-}$</td>
<td>[H$^+$][OH$^{-}$]$^2$ = $K_e$</td>
<td>p$K_e$ = 14.0</td>
</tr>
</tbody>
</table>

The dynamic buffer capacities $B^E$ and $B^E_0$ are defined by equations (11) and (12), respectively, and the change of $B^E_0$ is defined by equation (13), where $E$ is expressed as the product of $E$ and pH changes, for example, $E = E_0 - pH_0$.

\[
B^E = \left[ \frac{\Delta c}{\Delta pH} \right]
\]

\[
\Delta E = \frac{\beta^E}{\Delta pH} + \sum_{k=1}^{n} \left( \frac{d\beta^E_k}{dE} \right)^k \cdot \frac{(AE)^k}{E!}
\]

Discussion

The disproportionation of the substances considered (HIO or NaI0) in D occurs directly after introducing them into pure water. The disproportionation is intensified, by greater pH changes, after addition of the respective tautomers: 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 (GB), charge balance (CB) and concentration balances for particular elements = H$_2$O.

In the system S1, the precipitate of solid iodine, I$_{2o}$, 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$_{2o}$) is precipitated and soluble complexes: I$_2$Cl$_2$, ICl and ICl$_4$ are formed (Figure 6A). Note that I$_{2o}$ + I$^-$ = I$_3^-$ is also the complexation reaction.
In the system S2, all oxidized forms of Cl⁻ were involved, i.e. the oxidation of Cl⁻ 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⁻ occurred here only in an insignificant degree (Figure 6B); the main product of the oxidation was Cl₂, whose concentration was on the level ca. 10⁻¹⁶⁻⁻⁻⁻¹⁷ mol/L.

**Final comments**

The redox buffer capacity concepts: \( \beta_V \) and \( \beta_E \) can be principally related to monotonic functions. This concept looks awkwardly for non-monotonic functions \( pH = pH(\Phi) \) and/or \( E = E(\Phi) \) specified above \( 2^\circ - 4^\circ \) 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 \( HB(C,V) \Rightarrow HL(C_0,V_0) \), 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 \( 4K_1/C^2 \ll 1 \), the isohydricity condition is expressed here by the Michałowski formula:

\[
1pK_2^{0}C = C + C^2 \cdot 10^{pK_2}\]

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) $\beta_V$ vs. $\Phi$, (B) $\beta_V$ vs. pH, (C) $\beta_V$ vs. E and (D) $\beta_V^V$ vs. $\Phi$, (E) $\beta_V^V$ vs. pH, (F) $\beta_V^V$ vs. E for (S1) NaOH $\Rightarrow$ HIO.

Figure 4: The relations: (A) $\beta_V$ vs. $\Phi$, (B) $\beta_V$ vs. pH, (C) $\beta_V$ vs. E and (D) $\beta_V^V$ vs. $\Phi$, (E) $\beta_V^V$ vs. pH, (F) $\beta_V^V$ vs. E for (S2) HCl $\Rightarrow$ NaIO.
Buffering property is usually referred to an action of an external agent (mainly: strong acid, HB, or strong base, MOH) inducing pH change, $\Delta$pH, of the solution. Redox buffer capacity is also involved with the problem of interfacing in CE-MS analysis, and bubbles formation in reaction $2H_2O = O_{2(g)} + 4H^+ + 4e^-$ 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 (3o): (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 (4o): 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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