A New Approach to Carbonate Alkalinity

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Abstract

The article provides experimental data applied to the determination of carbonate alkalinity (CAM) according to modified Gran II functions. CAM is related to the mixtures NaHCO₃ + Na₂CO₃ and Na₂CO₃ + NaOH. In addition to the determination of equivalence volumes, one of the main novelties of the proposed method is the possibility of determining the activity coefficient of hydrogen ions (γ). Moreover, CAM can be used to calculate the dissociation constants (K₁, K₂) for carbonic acid and the ionic product of water (K_W) from a single pH titration curve. The parameters of the related functions are calculated according to the least squares method.

Keywords

Carbonate Alkalinity, pH Titration, Mathematical Modelling

1. Introduction

In the papers [1] [2] published recently, the new approaches to the measurement of total alkalinity (TAL) and carbonate alkalinity (CAM) were presented. In particular, CAM refers to titrimetric analysis of two systems (V₀ mL): NaHCO₃ (C₀₁) + Na₂CO₃ (C₀₂) (System I), and Na₂CO₃ (C₀₂) + NaOH (C₀₃) (System II). The results {(Vⱼ, pHⱼ)│j = 1, ..., N} obtained from pH titration of the corresponding systems with C mol/L HCl, undertaken under isothermal conditions, are presented according to a modified Gran II method. The CAM concept is fully compatible with the TAL concept, in which other species with acid-base properties are also included.

The equivalence volumes Vᵦᵢ (i = 1, 2, 3) referring to the corresponding components in Systems I and II are involved in the following relationships:

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\[ \text{C} \cdot \text{V}_{eq1} = \text{C}_{01} \cdot \text{V}_0, \quad \text{C} \cdot \text{V}_{eq2} = 2\text{C}_{02} \cdot \text{V}_0 \quad \text{for System I and} \]
\[ \text{C} \cdot \text{V}_{eq2} = 2\text{C}_{02} \cdot \text{V}_0, \quad \text{C} \cdot \text{V}_{eq3} = \text{C}_b \cdot \text{V}_0 \quad \text{for System II} \]

Subsequently, the carbonate alkalinities (CAM, mmol/L) are calculated from the formulae: CAM(I) = 10^3(C_{01} + 2C_{02}) or CAM(II) = 10^3(2C_{02} + C_b), i.e.,

\[ \text{CAM} \text{(I)} = 10^3 \cdot \frac{\text{C}(\text{V}_{eq1} + \text{V}_{eq2})}{\text{V}_0} \quad \text{for System I} \]
\[ \text{CAM} \text{(II)} = 10^3 \cdot \frac{\text{C}(\text{V}_{eq2} + \text{V}_{eq3})}{\text{V}_0} \quad \text{for System II} \]

The present paper provides a new approach to the problem in question. This approach enables equivalence volumes (\(V_{eqi}\)) to be calculated and the following physicochemical data to be evaluated: dissociation constants \((K_1\) and \(K_2\)) of \(\text{H}_2\text{CO}_3\), the ionic product of water \((K_W)\), and the activity coefficient \((\gamma)\) of hydrogen ions—not only in aqueous media, but also in binary-solvent systems [3]. The functions derived for this purpose have a form similar to those ascribed to Gran II method. The validity of the models proposed was confirmed experimentally by pH titration of synthetic samples referring to Systems I and II.

2. The Gran-Type Functions

The Gran functions applicable for determination of CAM(I) (Equation (3)) and CAM(II) (Equation (4)) are detailed in Table 1 [2]. The notations applied there are as follows: \(\text{ph} = -\log h\), \(h = \gamma[H^+]\) - activity, and \(\gamma\) - the activity coefficient of hydrogen ions; \(K_1^* = \gamma \cdot K_1\), \(K_2^* = \gamma \cdot K_2\), \(K_W^* = \gamma \cdot K_W\) - hybrid values for \(K_1 = [H^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]\), \(K_2 = [H^+]^[\text{CO}_3^-][\text{HCO}_3^-]\), and \(K_W = [H^+][\text{OH}^-]\). The pH intervals, in which the corresponding Gran-like functions are valid, are denoted by b, c, d for System I, and by a, b, c, d for System II.

Interval a is not included in System I in Table 1; simply because the data \{(\text{V}_j, \text{pH}_j) | j = 1, ..., N\} do not cover this pH range in System I. Regarding System II, the experimental points may not cover interval a at lower \(C_b\) values.

The case where \(V_0\) mL of \(C_{02}\) mol/L \(\text{Na}_2\text{CO}_3\) is titrated with \(V\) mL of \(C\) mol/L \(\text{HCl}\) is a particular case of System I (at \(C_{01} = 0\)) or System II (at \(C_b = 0\)). Note that the formulae related to Systems I and II are identical in pH intervals d and c (see Table 1), but the formulae are different in interval b. However, at \(V_b = V_{eq1} = 0\) and \(V_a = V_{eq3} = 0\), both formulae are simplified into the following form:

\[ V \cdot 10^{\text{ph}} = \left(K_2^*\right)^{-1} \cdot \left(V_{eq2} / 2 - V\right) \]

In the data handling step referring to simulated or experimental data \{(\text{V}_j, \text{pH}_j) | j = 1, ..., N\}, the Gran functions are applied to the sequences of pH intervals, such as those specified in Table 1. The use of other possible sequences is not advised.

The parameters:
- \(V_{eq1}, V_{eq2}, K_1^*, K_2^*, \gamma\) (and then \(K_1 = K_1^*/\gamma, K_2 = K_2^*/\gamma\)) for the modified Gran functions referring to System I, or
- \(V_{eq2}, V_{eq3}, K_1^*, K_2^*, \gamma\) (and then \(K_1 = K_1^*/\gamma, K_2 = K_2^*/\gamma\)) for the modified Gran functions referring to System II,

can be found according to the least squares method (LSM) [4] [5] applied to the experimental points:

\[ \left\{\left(V^*, \text{pH}^*_j\right) | j = 1, ..., N_x\right\} \]

referring separately to particular x intervals: \(x = b, c, d\) (System I), or \(x = a, b, c, d\) (System II) in Table 1, with the set of \(N_x\) points, related to the x-th pH interval. It is worth noting that the \(\text{ph}\), referring to activity \(h\) of \(H^+\) ions, is measured in experimental titrations. The \(\text{ph} = -\log h\) as variable (not \(\text{pH} = -\log[H^+]\)) is involved in all relationships specified in Table 1.

3. Calculation Procedure

The functions in Table 1 can be presented in a unified form of the linear regression equation:
Table 1. The Gran functions related to Systems I and II.

<table>
<thead>
<tr>
<th>No.</th>
<th>pH interval</th>
<th>System I</th>
<th>System II</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>pH &gt; pK₂ + ∆</td>
<td>(Vᵢ + V)⋅10ⁿ = C/Kᵢ₋₋⋅(Vᵢ − V)</td>
<td>(Vᵢ + V)⋅10ⁿ = C/Kᵢ₋₋⋅(Vᵢ − V)</td>
</tr>
<tr>
<td>b</td>
<td>pK₂ − ∆ &lt; pH = pK₂</td>
<td>(Vᵢ − V)⋅10ⁿ = Kᵢ₋₋⋅(Vᵢ − V)</td>
<td>(Vᵢ − V)⋅10ⁿ = Kᵢ₋₋⋅(Vᵢ − V)</td>
</tr>
<tr>
<td>c</td>
<td>pKᵡ ≤ pH ≤ pKᵢ + ∆</td>
<td>(Vᵢ + V)⋅10ⁿ = γ⋅C⋅(Vᵢ − V)</td>
<td>(Vᵢ + V)⋅10ⁿ = γ⋅C⋅(Vᵢ − V)</td>
</tr>
<tr>
<td>d</td>
<td>pH &lt; pKᵢ − ∆</td>
<td>(Vᵢ + V)⋅10ⁿ = γ⋅C⋅(Vᵢ − V)</td>
<td>(Vᵢ + V)⋅10ⁿ = γ⋅C⋅(Vᵢ − V)</td>
</tr>
</tbody>
</table>

Sequence of operations

Relationships

\[ y_j = A_x \cdot V_j^x + B_x + ε_j \quad (j = 1, \ldots, N_x; x = a, b, c, d) \]  \hspace{1cm} (6)

Subsequently, applying LSM to the sum of squares

\[ SS(x) = \sum_{j=1}^{N_x} (ε_j)^2 \]  \hspace{1cm} (7)

where \( j \) refers to the points \( \{(V_j^x, ph_j^x)\}\) related to x-th subset (x = a, b, c, d), we obtain the formulæ:

\[ A_x = \frac{N_x \cdot \sum_j V_j^x \cdot y_j^x - \sum_j V_j^x \cdot \sum_j y_j^x}{N_x \cdot \sum_j (V_j^x)^2 - (\sum_j V_j^x)^2}, \quad B_x = \frac{\sum_j (V_j^x)^2 \cdot \sum_j y_j^x - \sum_j V_j^x \cdot \sum_j V_j^x \cdot y_j^x}{N_x \cdot \sum_j (V_j^x)^2 - (\sum_j V_j^x)^2} \]  \hspace{1cm} (8)

where the sum \( Σ_{x} \) covers the points taken from the x-th interval, \( V_j^x \) is the j-th V-value taken from the x-th interval.

As stated above, calculation of the parameters is possible in a defined sequence of operations. For example, the sequence \( d \rightarrow c \) applied in Table 1 for System I means that \( V_d \) value, obtained according to LSM for the data \( \{(V_j^d, ph_j^d)\}\) composing the subset of the points taken from interval d (Figure 1), is inserted on the left side of the relationship referring to interval c and LSM is applied to the data \( \{(V_j^c, ph_j^c)\}\) taken from interval c; in this way, the \( V_c \) value is obtained. From \( V_d \) and \( V_c \), one can calculate:

\[ V_{eq1} = V_d - 2V_c = 2 \cdot B_x - \frac{B_x}{A_x} \quad \text{and} \quad V_{eq2} = 2 \cdot B_x - \frac{B_x}{A_x} \]  \hspace{1cm} (9)

\[ V_{eq2} = 2 \cdot (V_d - V_c) \]  \hspace{1cm} (10)

Moreover, we obtain:

\[ γ = \frac{A_x}{C}, \quad pKᵡ^* = -\log A_x, \quad pKᵢ = \log \frac{A_x}{A_i} - \log C \]  \hspace{1cm} (11)

From Table 1, System I, no. b, for the point \( \{(V_j^b, ph_j^b)\} \) we get
Figure 1. Plots related to NaHCO₃ (C₁) + Na₂CO₃ (C₂) system: y (Table 1, System I) vs V relationships in (a) d interval; (b) c interval; (c) pK₂* vs. V, and (d) pK₂* vs. ph plots.

\[
pK_{2j}^* = p\log h_j + \frac{V_b + V_j^b}{V - V_j} = p\log h_j + \log \frac{V_{eq1} + V_j^b}{V_{eq2}/2 - V_j^b}
\]

(12)

where \(V_{eq1}\) and \(V_{eq2}\) are expressed by Equation (1). Similarly, from Table 1, System II, no. b and a, we get

\[
pK_{2j}^* = p\log h_j + \frac{V_j^b - V_j}{V_b - V_j} = p\log h_j + \log \frac{V_j - V_{eq3}}{V_{eq2}/2 + V_{eq3} - V_j^b}
\]

(13)

\[
pK_{3j}^* = p\log h_j + \frac{V_0 + V_j^a}{V_a - V_j} - \log C = p\log h_j + \log \frac{V_0 + V_j^a}{V_{eq3} - V_j}
\]

(14)

respectively, where \(V_{eq2}\) and \(V_{eq3}\) are expressed by Equation (2). On the basis of Equation (5), we obtain the relationship:
\[ pK_{2j}^* = \phi_j^b + \log \frac{V_j^b}{V_j^{eq2}/2 - V_j^b} \]  

(15)

We then calculate:

\[ pK_2^* = \frac{1}{N_b} \sum_{j=1}^{N_b} pK_{2j}^* \quad \text{and} \quad pK_2 = pK_2^* + \log \gamma \]  

(16)

\[ pK_w^* = \frac{1}{N_a} \sum_{j=1}^{N_a} pK_{wj}^* \quad \text{and} \quad pK_w = pK_w^* + \log \gamma \]  

(17)

and

\[ pK_i = pK_i^* + \log \gamma \]  

(18)

where \( \gamma \) is defined in Equation (11). The nearly constant ionic strength value, required during the titration, can be secured by the addition of a basal electrolyte on the stage of D and T preparation.

As revealed from Equations (3), (4), it is necessary to know the sum of equivalence volumes: \( V_{eq1} + V_{eq2} \) or \( V_{eq2} + V_{eq3} \) to calculate CAM(I) or CAM(II) value. However, determination of \( V_{eqi} \) values (\( i = 1, 2 \) or 2, 3) from a single pH titration curve is also possible.

4. Experimental Part

4.1. Apparatus and Solutions

The pH titrations were carried out in a 30 mL thermostated, self-made measuring cell, equipped with magnetic stirrer and PT 1000 temperature sensor. The pH measurements and titrations were taken at 22°C with a Cerko Lab System microtitrator, equipped with 5 mL syringe pump, 3-way valve, and pH electrode (Hydromet, type ERH-13-6). The electrode was standardized with aqueous standard buffers of pH 5.00, 7.00 and 10.00, purchased from the Chempur Company. When not in use, the electrode was stored in 3 mol/L KCl solution. Titrant was added into \( V_0 = 4.00 \) mL of D stepwise, in aliquots of 0.01 mL, with 6-8-sec. pauses, and the experimental points \( \left\{ V_j, \phi_j \right\} j = 1, \ldots, N \) were recorded.

The reagents: HCl, Na\(_2\)CO\(_3\), NaHCO\(_3\), NaOH of p.a. grade, purchased from Chempur Company, were used for the preparation of stock and diluted solutions in doubly distilled (freshly prepared, with conductivity of approx. 0.18 \( \mu \)S/cm) water. Stock solution of hydrochloric acid (HCl) as T, was standardized against Na\(_2\)CO\(_3\), obtained after prior calcination (220°C, 5 hrs) of commercial disodium carbonate. The NaOH solution was standardized against potassium hydrogen phthalate (p.a., from Merck). Methanol (p.a. grade, 99.5%, supplied by POCH S.A.) was applied for titrations made in binary-solvent media.

Stock titrands were prepared by dilution of weighed portions of Na\(_2\)CO\(_3\) and NaHCO\(_3\) in water, or by addition of a weighed portion of Na\(_2\)CO\(_3\) into a standardized NaOH solution. In other titrations, mixed solvent was prepared from appropriate volumes of water and CH\(_3\)OH, and cooled before preparation of HCl and Na\(_2\)CO\(_3\) solutions. The HCl solution (10% v/v CH\(_3\)OH) was standardized as described previously. Concentrations of HCl, NaHCO\(_3\), Na\(_2\)CO\(_3\) and NaOH in the corresponding solutions are specified below.

4.2. Results and Discussion

The approach was applied first to the results of titrations of Systems I and II, with HCl solution as the titrant, T. Titration in System I was carried out at pre-assumed values \( (V_0, C_{01}, C_{02}, C) = (4.000, 0.01012, 0.02011, 0.10078); V_{eq1} = 0.01012\times4/0.10078 = 0.4017; V_{eq2} = 2\times0.02011\times4/0.10078 = 1.5963 \) The results of exemplary titration are graphically presented in Figure 1. The data obtained for \( V_d = 2.0122, V_c = 0.8017 \) (Figure 1(a), Figure 1(b)) are in good agreement with the expected values: 1.9980 and 0.7982 (see Table 2). Moreover, we get here: \( \gamma = 0.9283 \) and \( pK_1^* = 6.379 \). The pK\(_{2j}^*\) values, calculated on the basis of Equation (13), are plotted in Figure 1(c), Figure 1(d), with V and ph as the variables on the abscissa, respectively. Some discrepancies in \( V_{eqi} \) value can result from the poor knowledge of NaHCO\(_3\) concentration, which is not a primary standard.

Titration in System II was carried out at pre-assumed values \( (V_0, C_{02}, C_{b}, C) = (4.000, 0.0200, 0.0209, \ldots) \)
0.10078). The results obtained from repeated titrations are detailed in Table 3; $2 \cdot 0.0200 \cdot 4/0.10078 = 1.5876$ and $0.0209 \cdot 4/0.10078 = 0.08295$ are the expected values for $V_{eq2}$ and $V_{eq3}$, respectively. Exemplary data are plotted in Figure 2. As can be seen, the sum $V_d = V_{eq2} + V_{eq3}$ is very well reproducible in repeated titrations and is in good agreement with the expected value of 2.4171 (Figure 2(a)). The values for $V_{eq2}$ are slightly smaller than 1.5876, while the values for $V_{eq3}$ are slightly greater than 0.08295. The repeatability of values for $\gamma$ and $pK_1^*$ is lower. The $pK_{w2}^*$ (Figure 2(c)) and $pK_{w3}^*$ (Figure 2(d)) values vary regularly (not stochastically) from point-to-point, although the range of pH values covered by the points close to pH ≈ $pK_2 = 10.1$ is narrow (but in a wider pH range than in Figure 1(c), Figure 1(d)); also $pK_{w2}^*$ (and $pK_2 = pK_{w2}^* + \log \gamma$ values are close to 6.3). The $pK_{w2}^*$ values are distinctly higher than 14.0; this may be ascribed to the non-linear characteristics of the glass electrode in alkaline media. Smaller $pK_{w2}^*$ values at lower pH support this opinion.

Another option for System II is also possible a priori and starts from equation a in Table 1 (System II) and finds $V_a (=V_{eq3})$ and $K_{w2}^*$ on the basis of the points $\{ (V_j^*, \mathrm{ph}_j^*) | j = 1, \ldots, N_a \}$. The $V_a$ value is then inserted in equation b in Table 1 (System II) and $V_b (=V_{eq2}/2 + V_{eq3})$ and $K_{w2}^*$ values are determined on the basis of the

Figure 2. Plots related to Na$_2$CO$_3$ (C$_2$) + NaOH (C$_b$) system: $y$ (Table 3) vs. $V$ relationships in (a) d interval; (b) c interval; (c) $pK_{w2}^*$ vs. $V$, (d) $pK_{w2}^*$ vs. $V$ plots.
points \( \left\{ (V_i^b, \text{pH}_i^b) \right\}_{i=1, \cdots, N_b} \) \}. The \( V_{eq2} = 2(V_b - V_d) \) and \( V_{eq3} \) values can be compared with those obtained on the basis of the experimental points in intervals d and c. This procedure could be regarded as a kind of internal validation of the results. However, it should be borne in mind that the results of \( \text{pH} \) measurements obtained in alkaline media could be loaded by systematic error resulting from the alkaline error of the glass electrode. The errors involved with \( \text{pH} \) measurements in the \( a \) range affect the \( V_a \) value, subsequently applied in the \( (V - V_a) \cdot 10^{\text{pH}} \) vs. \( V \) relationship related to interval b; an improper \( V_a \) value causes this relationship to be a nonlinear one. Therefore, it is advisable to use the experimental points from interval b (for System I) or from intervals a and b (for System II) only for the determination of the related equilibrium parameters, see Equations (12)-(18).

On the basis of known values for \( V_d \) found in interval d for Systems I and II (see Table 1), the alkalinities: CAM(I) (Equation (3)), and CAM(II) (Equation (4)) can be calculated; obtaining:

- CAM(I) = 0.10078·2.0122/4 = 0.0507 (from Table 2, no. 1),
- CAM(II) = 0.10078·2.4123/4 = 0.0608 (from Table 3, no. 3).

5. Final Comments

This article provides the new consistent formulation for alkalinities referring to NaHCO\(_3\) + Na\(_2\)CO\(_3\) (System I) and Na\(_2\)CO\(_3\) + NaOH (System II) solutions, titrated with HCl. The related formulae, specified in Table 2, are valid in defined \( \text{pH} \) intervals, denoted as b, c, d or a, b, c, d. The approach based on these new formulae has been called “carbonate alkalinity in a modified version” (CAM). All the formulae are closely relevant to the recently formulated total alkalinity (TAL) \cite{1} \cite{2}. The formulae for CAM are valid within defined \( \text{pH} \) ranges, in which the relationships between variables are expressed by the functions specified in Table 1.

The CAM approach enables equivalence volumes to be calculated, as well as the following physicochemical data: the activity coefficient \( \gamma \) of hydrogen ions; the hybrid values for dissociation constants: \( K_1^*, K_2^*, K_\mu^* \) for H\(_2\)CO\(_3\), and \( K_W^* \) for the ionic product of water. One of the main novelties of the method is the possibility of determining \( \gamma \). Moreover, the common equilibrium constants: \( K_1, K_2 \) and \( K_W \) are also calculated. The possibility of calculating \( \gamma \) is also inherent in the TAL method \cite{1} \cite{2}. Another interesting option is the determination of the related parameters in binary solvent media \cite{6}.

The \( \text{pH} \)-intervals assumed for calculation of the analytical and physicochemical data are confined (see \cite{2}, p. 229) in comparison with the ones pre-assumed with use of the \( \Delta = 1.9 \) value. The narrowing of the \( \text{pH} \)-range taken for calculations results from the scale of \( (C_{01}, C_{02}, C) \) or \( (C_{02}, C_{03}, C) \) values applied in the experiments.

The procedure applied here can also be extended to salts other than carbonates. To extend the \( \text{pH} \) range covered by \( \text{pH} \) titration, it is suggested that the option involving the addition of a pre-dose is used \cite{2}. When weak acid is considered, the strong base solution can be used as titrant or, after addition of the base as the pre-dose, the mixture can be titrated with a strong acid, as above.

The CAM method was tested experimentally. The results for the dissociation constants of H\(_2\)CO\(_3\) are close to those found in literature \cite{7}. The values for \( \gamma \) are more scattered.

This article attempts to provide an introductory step for further studies about the determination of alkalinity.

<table>
<thead>
<tr>
<th>No.</th>
<th>( V_d )</th>
<th>( V_a )</th>
<th>( V_{eq1} )</th>
<th>( V_{eq2} )</th>
<th>( \gamma )</th>
<th>( pK_1^* )</th>
<th>( pK_2^* )</th>
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<tr>
<td>1</td>
<td>2.0122</td>
<td>0.8017</td>
<td>0.4088</td>
<td>1.6034</td>
<td>0.928</td>
<td>6.379</td>
<td>6.351</td>
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<tr>
<td>2</td>
<td>2.0152</td>
<td>0.8043</td>
<td>0.4066</td>
<td>1.6086</td>
<td>0.874</td>
<td>6.427</td>
<td>6.369</td>
</tr>
<tr>
<td>3</td>
<td>2.0167</td>
<td>0.8046</td>
<td>0.4075</td>
<td>1.6092</td>
<td>0.891</td>
<td>6.453</td>
<td>6.403</td>
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</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>( V_{eq2} = V_{eq1} + V_{eq2} )</th>
<th>( V_{eq2} )</th>
<th>( V_{eq1} )</th>
<th>( \gamma )</th>
<th>( pK_1^* )</th>
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</tr>
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<td>2</td>
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<td>1.5703</td>
<td>0.8402</td>
<td>0.7978</td>
<td>6.459</td>
<td>6.361</td>
</tr>
<tr>
<td>3</td>
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<td>1.5789</td>
<td>0.8334</td>
<td>0.7635</td>
<td>6.467</td>
<td>6.350</td>
</tr>
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</table>
according to the proposed TAL method [1] [2] for examination of natural, municipal and industrial waters, carbonated soft drinks and wines, as well as different biological systems.

The CAM presented here completes the list of modifications of the Gran methods presented in previously published articles [8]-[12], referring to different areas of titrimetric analysis.

References


Symbols Used

CAM—carbonate alkalinity [mmol/L] in modified version;
D—titrand (solution titrated);
\( \gamma = h/[H^+] \)—activity coefficient for H\(^+\) ions;
h—activity of H\(^+\) ions;
LSM—least squares method;
pH = −log[H\(^+\)];
ph = −log(h);
T—titrant;
TAL—total alkalinity;
V—volume [mL] of T;
\( V_0 \)—volume [mL] of D;
\( V_{eqi} \)—volume [mL] of titrant, referring to the equivalence point (\( V_{eqi}, \text{pH}_{eqi} \));
\([X]\)—concentration [mol/L] of the species \( X \).
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