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Research Article

The Simms Constants as Parameters in Hyperbolic Functions Related to Acid-Base Titration Curves

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Abstract

The Simms constants (g_i) are parameters of transformed equations for acid-base titration curves, obtained from rational functions of the Padé type. The relationships between g_i and successive dissociation constants K_i values for polyprotic acids are formulated. The models related to acid-base titration curves are expressed in terms of hyperbolic functions. Some relations of g_i to the Fermi-Dirac distribution function are indicated.

Keywords

Acid-base equilibria; Titration curves; Hyperbolic functions

Notations: D – titrand, gi – Simms constant; T – titrant

Introduction

The term 'Simms constants' is an eponym related to virtual equilibrium constants (g_i) suggested by Simms [1-5], known also as 'titration indices' or 'titration constants' [6,7]. The g_i were considered first in biological context [8-10], and later in a series of papers involved with titrimetric methods of analysis [11-15]. In particular, the g_i concept can be applied in modeling the equilibria occurred in complex acid-base systems, where the isomolarity condition was fulfilled [16,17]. Later on, the Simms constants were applied to modeling of titration curves perceived from the viewpoint of total alkalinity (TAL) [18-20], also with fulvic acids (FA) involved [19]. The Simms can be considered [16-24] in context of rational functions of the Padé type [25], with activity h of H^{+1} ions as the variable.

Application of the Simms constants enables any q-protic acid H_nL (C_0 mol/L), characterized by successive dissociation constants (K_i) values [10,16], to be considered as a mixture of q weak monoprotic acids $HL_{(k)}$ (k = 1, …,q) of the same concentration, i.e., C_0 mol/L; the Simms constants g_i are ascribed to these acids as (virtual) dissociation constants. The relations between g_i and K_i values were formulated. Mathematical transformations made for this purpose resemble the technique called as decomposition of rational functions into a sum of partial fractions, well-known to students during the course in mathematical analysis (integral calculus), see e.g. [26]. The Simms constants are involved in the partial fractions of this kind.

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In this paper, the Simms constants (g_i) will be referred to D+T systems, with $M_mH_{n-m}L$ (C_0) + HB (C_a) + MOH (C_b) solution, called as the sample tested (ST), see Table 1. Depending on the pre-assumed composition of the species formed in a system, we consider first the more general case where complexes of $M_aH_iB_bL^{+a+i-b-n}$ type are formed; a, b = 0,1,…, i.e., the species H_iL^{+i-n} (i=0,…,q) are also admitted here (at a=b=0). The D+T system where only the species H_iL^{+i-n} (i=0,…, q) are formed, is considered as a particular case of the more complex system of the species. The interrelations where hyperbolic functions are involved with parameters of this simpler system, with dissociation constants (K_i) or stability constants of proto-complexes (K_i^H), known from tables of equilibrium data, are presented here. Stability constants of the mixed complexes are rarely met in literature; see e.g. [27-30].

Composition of titrand (D) and titrant (T)

The D and T are prepared in volumetric flasks: F1 and F2, each with a volume of V_f mL. First, equal volumes V_{ST} of a sample tested composed of $M_mH_{n-m}L$ (C_0) + HB (C_a) + MOH (C_b) are introduced into F1 and F2. In turn, V_B mL of HB (C) or V_M mL of MOH (C) is added into F1. Then V^*_{MB} mL of MB (C_{MB}) is introduced into F1, and V_{MB} mL of MB (C_{MB}) is introduced into F2. The volumes V^*_{MB} and V_{MB} of MB fulfill the optional relations:

$$C_{MB} \cdot V_{MB} = C_{MB} \cdot V^*_{MB} + C_B \cdot V_B \text{ or } C_{MB} \cdot V_{MB} = C_{MB} \cdot V^*_{MB} + C_M \cdot V_M \qquad (1)$$

(see Table 1). Both flasks are then supplemented with distilled water to the mark, and mixed thoroughly.

The volume V_0 mL ($V_0 \leq V_f$) is taken for analysis and titrated as D with T, added in portions; V mL is the total volume of T added from the beginning of the titration to a given point of the titration. The value

$$W = V_0 + V \qquad (2)$$

is the total volume of D+T system, at a given point of titration.

Formulation of D+T system

Denoting $[M_aH_iB_bL^{+a+i-b-n}] = c_{aib}$ for brevity, and applying the notations:

$$d = \frac{V_{ST}}{V_f} \; ; b_B = \frac{CV_BV_o}{V_f} \; ; \; \Delta = C_b - C_a \; ; J_{ab} = d \cdot ((n-m) \cdot C_0 - \Delta) \qquad (3)$$

$$\alpha = [H^{+1}] - [OH^{-1}] \qquad (4)$$

$$\overline{n} = \frac{\sum_{a,i,b} i \cdot c_{aib}}{d \cdot C_0} \qquad (5)$$

from addition of balances:

$$\alpha + [M^{+1}] - [B^{-1}] + \sum_{a,i,b} (a+i-b-n) \cdot c_{aib} = 0$$

$$\sum_{a,i,b} n \cdot c_{aib} = d \cdot nC_0$$

$$[B^{-1}] + \sum_{a,i,b} b \cdot c_{aib} = d \cdot C_a + \frac{C_{MB}V_{MB}}{V_f}$$

$$d \cdot (mC_0 + C_b) + \frac{C_{MB} \cdot V_{MB}}{V_f} - \frac{b_B}{V_0} + \frac{b_B}{W} = [M^{+1}] + \sum_{a,i,b} a \cdot c_{aib}$$

Table 1: Composition of titrand (D) and titrant (T) for different isomolar systems and the related expressions for F (Eq. 6); $W = V_0+V$.

System no.	ST		HB (C_B)		MOH (C_M)		MB (C_{MB})		F
	D	T	D	T	D	T	D	T	
1	V_{ST}	V_{ST}	–	V_B	–	–	V_{MB}	V^*_{MB}	$d \cdot J_{ab} + \dfrac{b_B}{V_0} - \dfrac{b_B}{W}$
2	V_{ST}	V_{ST}	V_B	–	–	–	V^*_{MB}	V_{MB}	$d \cdot J_{ab} + \dfrac{b_B}{W}$
3	V_{ST}	V_{ST}	–	–	–	V_M	V_{MB}	V^*_{MB}	$d \cdot J_{ab} - \dfrac{b_M}{V_0} + \dfrac{b_M}{W}$
4	V_{ST}	V_{ST}	–	–	V_M	–	V^*_{MB}	V^*_{MB}	$d \cdot J_{ab} - \dfrac{b_M}{W}$

we get the relation

$$F = \alpha + \overline{n} \cdot d \cdot C_0 = d \cdot ((n-m)C_0 - \Delta) + \frac{b_B}{V_0} - \frac{b_B}{W} \quad (6)$$

(see Table 1). The relations for F in the systems 2 – 4 are obtained similarly. (Equation 6) can be transformed into the form

$$\frac{b_B}{W} = \frac{b_B}{W} + d \cdot ((n-m-\overline{n}) \cdot C_0 - \Delta) - \alpha \quad (7)$$

Note that

$$n - m - \overline{n} = -(\overline{n} + m - n) = (q - \overline{n}) - (q - n + m) \quad (8)$$

where :

$$\overline{n} = \frac{\sum\limits_{a,i,b} i \cdot [M_a H_i B_b L^{+a+i-b-n}]}{\sum\limits_{a,i,b} [M_a H_i B_b L^{+a+i-b-n}]} = \frac{\sum_{i=1}^{q} k \cdot R_i \cdot [H^{+1}]^i}{\sum_{i=0}^{q} R_i \cdot [H^{+1}]^i} \quad (9)$$

$$R_i = \sum_{a,b} K_{aib} \cdot [M^{+1}]^a [B^{-1}]^b \quad (10)$$

$$c_{aib} = [M_a H_i B_b L^{+a+i-b-n}] = K_{aib} \cdot [M^{+1}]^a [H^{+1}]^i [B^{-1}]^b [L^{-n}] \quad (11)$$
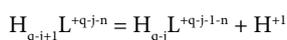
Applying (8) in (7), we have

$$\frac{b_B}{W} = \frac{b_B}{V_0} + d \cdot ((q-\overline{n}) - (q-n+m+\Delta) \cdot C_0 - \alpha \quad (12)$$

where [18-20,30,31]

$$q - \overline{n} = \sum_{k=1}^{q} \frac{g_k}{[H^{+1}] + g_k} = \sum_{k=1}^{q} \frac{g_k^*}{h + g_k^*} = \sum_{k=1}^{q} \left(10^{pg_k^* - ph} + 1 \right)^{-1} \quad (13)$$
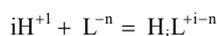
A Simpler System

The simpler case is the system, where the species $H_i L^{+i-n}$ (i=0,…,q) are formed in the D+T mixture. These species can be characterized, optionally, by (successive) dissociation constants, K_j (j = 1,…,q):

$$H_{q-j+1} L^{+q-j-n} = H_{q-j} L^{+q-j-1-n} + H^{+1}$$

$$K_j = \frac{[H^{+1}][H_{q-j} L^{+q-j-l-n}]}{[H_{q-j+1} L^{+q-j-n}]} \quad (14)$$

or by stability constants K_i^H of the related proto-complexes, $H_i L^{+i-n}$,

$$iH^{+1} + L^{-n} = H_i L^{+i-n}$$

$$K_i^H = \frac{[H_i L^{+i-n}]}{[H^{+1}]^i [L^{-n}]} \quad (i = 1,...,q) \quad (15)$$

Then we get the relations

$$K_i^H = \frac{1}{\prod_{j=q-i+1}^{q} K_i} \quad (i = 1,...,q) \quad (16)$$

Applying (15) in the relation

$$\overline{n} = \frac{\sum\limits_{i=1}^{n} i \cdot [H_i L^{+i-n}]}{\sum\limits_{i=0}^{n} [H_i L^{+i-n}]} \quad (17)$$

we have

$$\overline{n} = \frac{\sum\limits_{i=1}^{q} i \cdot K_i^H [H^{+1}]^i}{\sum\limits_{i=0}^{q} K_i^H [H^{+1}]^i} \quad (18)$$

The Simms constants g_k are interrelated with successive dissociation constants K_j (Equation 14) of the acid $H_n L$ considered; we have a set of interrelations:

$$K_1 = \sum_{i=1}^{q} g_i ; \quad K_1 \cdot K_2 = \sum_{i=1}^{q-1} \sum_{j=i+1}^{q} g_i \cdot g_j ; \quad K_1 \cdot K_2 \cdot K_3 = \sum_{i=1}^{q-2} \sum_{j=i+1}^{q-1} \sum_{k=j+1}^{q} g_i \cdot g_j \cdot g_k ; \dots ;$$

$$K_1 \cdot K_2 \cdot ... \cdot K_q = g_1 \cdot g_2 \cdot ... \cdot g_q \quad (19)$$

The expression for $\prod_{i=1}^{k} K_i$ (in Equations 19), formulated for q-protic acid, is a sum involving

$$\binom{q}{k} = \frac{q!}{k!(q-k)!} \quad (20)$$

components [19] formed from k different g_i values. In particular, for $H_3 PO_4$ (acid of $H_3 L$ type, q=n=3):

at k=1 we have $\binom{3}{1} = 3$, $K_1 = g_1 + g_2 + g_3$;

at k=2 we have $\binom{3}{2} = 3$, $K_1 \cdot K_2 = g_1 \cdot g_2 + g_1 \cdot g_3 + g_2 \cdot g_3$;

at k=3 we have $\binom{3}{3} = 1$, $K_1 \cdot K_2 \cdot K_3 = g_1 \cdot g_2 \cdot g_3$.

Generalizing, the binomial coefficient $\begin{pmatrix} q \\ k \end{pmatrix}$ [31] (Equation 20) expresses the number of distinct k-element subsets, formed from a set containing q different elements [32], as in the Pascal's triangle [33].

The g_i values can be calculated, provided that K_i^H (Equation 16) or K_i (Equation 14) values are known beforehand. Such calculations can be done with use of the iterative computer programs [34], as one specified in [19]. In particular,

- for H_2CO_3 (q = 2): pK_1 = 6.3, pK_2 = 10.1, we have: pg_1 = 6.300069, pg_2 = 10.099931;

- for H_3PO_4 (q = 3): pK_1 = 2.1, pK_2 = 7.2, pK_3 = 12.3, we have: pg_1 = 2.100003, pg_2 = 7.200000, pg_3 = 12.299997.

As we see, $pg_i \approx pK_i$ values are here not distant from values. The differences $\mid pg_i - pK_i \mid$ are greater when pK_i values for a polyprotic acid are closer to each other.

For comparative purposes, we consider V_0 mL of titrand D containing a mixture of q weak monoprotic ($q_k = n_k = 1$) acids $HL_{(k)}$ (C_{0k}; k=1,…,q), titrated with V mL of (a) HB (C) or (b) MOH (C) as T, we get the equations:

$$1 - \bar{n}_k = \frac{[L_{(k)}^{-1}]}{[HL_{(k)}] + [L_{(k)}^{-1}]} = \frac{K_{1(k)}}{[H^{+1}] + K_{1(k)}} \qquad (21)$$

and then

$$\sum_{k=1}^{q}(1 - \bar{n}_k) = \sum_{k=1}^{q} \frac{K_{1(k)}}{[H^{+1}] + K_{1(k)}} = \sum_{k=1}^{q} \frac{K_{1(k)}^*}{h + K_{1(k)}^*} = \sum_{k=1}^{q}\left(10^{pK_{1(k)} - pH} + 1\right)^{-1} = \sum_{k=1}^{q}\left(10^{pK_{1(k)}^* - ph} + 1\right)^{-1} \qquad (22)$$

where: $[H^{+1}][L_{(k)}^{-1}] = K_{1(k)} \cdot [HL_{(k)}]$; $K_{1(k)}^* = \gamma \cdot K_{1(k)}$ – the related hybrid dissociation constants, $pK_{1(k)} = -\log K_{1(k)}$, $pK_{1(k)}^* = -\log K_{1(k)}^*$. Then we have

$$\bar{n} = q - \sum_{k=1}^{q} \frac{g_k}{[H^{+1}] + g_k} = \sum_{k=1}^{q} \frac{[H^{+1}]}{[H^{+1}] + g_k} = \sum_{k=1}^{q} \frac{h}{h + g_k^*} = \sum_{k=1}^{q}\left(10^{ph - pg_k^*} + 1\right)^{-1} \qquad (23)$$

The Relative Contents of the Components Constituting D and T

The D and T include sample tested, ST (Table 1). If $C_{MB} \gg \sum_{a,i,b} c_{aib}$ then $[M^{+1}]$ and $[B^{-1}]$ values are practically constant during the titration. Moreover, we assume $C_B \cdot V_B \ll C_{MB} \cdot V_{MB}$. Similar composition of D and T guarantees the stability of ionic strength of the solution. The relative permittivity ε is also kept constant if the D and T compositions are similar; it makes also the volumes additivity more accurate than when mixing various aqueous solutions. Then the isomolarity condition (Equation 1) enables to keep approximately constant values of the equilibrium constants, under isothermal conditions.

Therefore, the values of R_i (in Equation 10) or K_i (in Equation 18) are practically constant during the titration carried out under such conditions. The hydrogen ion activity coefficient $\gamma = \gamma_{H^{+1}}$ has also a stable value. The titration in isomolar systems makes it possible to determine $\gamma_{H^{+1}}$ as one of the physicochemical parameters of the system, along with other equilibrium constants values [17].

Formulation in terms of Hyperbolic Functions

The related formulas can be expressed in terms of hyperbolic functions [35]. For this purpose, we denote: z = ln10·pH, w = ln10·pK_W, s_k = log10·pg_k. Then applying the identity

$$\frac{1}{2}\cdot\left(1 + \frac{e^t - e^{-t}}{e^t + e^{-t}}\right) = \frac{e^t}{e^t + e^{-t}} = \frac{1}{1 + e^{-2t}} \qquad (24)$$

we get:

$$\alpha = 2 \cdot e^{-\frac{w}{2}} \cdot sinh\left(\frac{w}{2} - z\right) \qquad (25)$$

$$\frac{g_k}{[H^{+1}] + g_k} = \frac{1}{2}\cdot\left(1 + tanh\left(\frac{z - s_k}{2}\right)\right) \qquad (26)$$

From Equation 8, 13, 26 we have

$$n - m - \bar{n} = \frac{1}{2}\cdot\sum_{k=1}^{q} tanh\left(\frac{z - s_k}{2}\right) - \left(m + \frac{q}{2} - n\right) \qquad (27)$$

The formulas involved with ph and g_k^* look alike. From Equations: 12, 13, 25 and 26, for $C_{0k} = C_0$, we get

$$\frac{b_B}{W} = \frac{b_B}{V_0} + d\cdot\left(\frac{C_0}{2}\cdot\sum_{k=1}^{q} tanh\left(\frac{z - s_k}{2}\right) - \left(m + \frac{q}{2} - n\right)\cdot C_0 - \Delta\right) - 2\cdot e^{-\frac{w}{2}}\cdot sinh\left(\frac{w}{2} - z\right) \qquad (28)$$

The hyperbolic functions can also be applied to more complex acid-base systems, discussed in [18-20,37].

Rational Functions

The general form of a rational function of variable x [37], y = y(x), is the quotient of polynomials p(x) and q(x), i.e.

$$y = y(x; n, m) = \frac{p(x)}{q(x)} = \frac{\sum_{i=0}^{n} a_i x^i}{\sum_{j=0}^{m} b_j x^j} \qquad (29)$$

where m ≥ 1, i.e., the denominator q(x) involves explicitly the variable x.

The titration curves related to isomolar systems can be presented in the form of rational functions of the Padé type [16,17, 20-24]. For example, for the mixture HL (C_0) + HB (C_a) applied as ST in the system 3, we obtain the function

$$W = -\frac{A_2 \cdot h + A_4 \cdot h^2}{A_1 + A_3 \cdot h + A_5 \cdot h^2 - h^3} \qquad (30)$$

where: A_1 = · $K_W \cdot x_0 \gamma^3$; A_2 = $b_M \cdot x_0 \cdot \gamma^2$; A_3 = (K_W + d·(C_0 + C_a – a_M/V_0)·x_0)·γ^2; A_4 = $b_M \cdot \gamma$; A_5 = (d·(C_a – a_M/V_0) – x_0)·γ, a_M = b_M/d; x_0 = 1/K_1, where $[H^{+1}][L^{-1}]$ = $K_1 \cdot [HL]$; the activity of hydrogen ions, x = h, is the variable in Eq. 30.

Special cases of rational functions are Möbius transformations [38]. The rational functions were also applied in different methods of chemical analysis, namely: in modified Gran methods of titrimetric analyses [39-43], for calibration curve, and standard addition methods [44-47].

Acid-base Micro-Equilibria as Emanation of Stochastic Processes

On the basis of formulation with the Simms constants involved one can state that the dissociation of H^{+1} from different protonation sites/centers proceeds independently, and the proton uptake/dissociation from/to these sites (basicity centers) can be perceived as a stochastic process, categorized in terms of a success/failure. The degree of dissociation $HL_{(k)} = H^{+1} + L_{(k)}^{-1}$ from the k-th site is

$$\alpha_k = \alpha_k(pH) = \frac{1}{10^{pg_k - pH} + 1} = \frac{1}{e^{\beta\cdot(pg_k - pH)} + 1} \qquad (31)$$

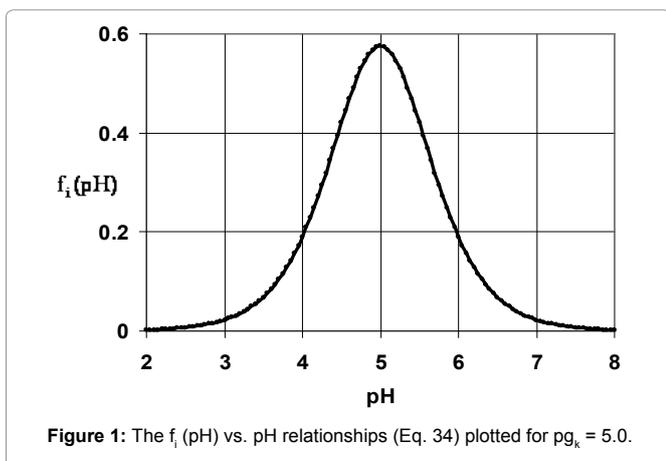where β = ln10. The $\alpha_i = \alpha_i(pH)$ fulfills the properties of cumulative distribution function

Figure 1: The f_i (pH) vs. pH relationships (Eq. 34) plotted for pg_k = 5.0.

$$\lim_{pH \to -\infty} \alpha_i(pH) = 0, \quad \lim_{pH \to \infty} \alpha_i(pH) = 1, \quad \alpha_i(pH) = \int_{-\infty}^{pH} f_i(x) \cdot dx \quad (32)$$

where $y = f_i(pH)$ is the probability density function

$$f_i(pH) = \frac{d\alpha_i(pH)}{dpH} \quad (33)$$

It implies that [19]

$$f_i(pH) = \beta \cdot \frac{10^{pg_i - pH}}{(10^{pg_i - pH} + 1)^2} = \beta \cdot \alpha_i(pH) \cdot (1 - \alpha_i(pH)) \quad (34)$$

The function (34) plotted in Figure 1 appears some similarities with the Fermi-Dirac distribution function [48].

Final Comments

The paper presents formulation of acid-base titration curves of different degree of complexity, for the D+T systems prepared according to unconventional mode, where D and T are prepared in accordance with the principle of isomolar solutions, suggested and formulated first time in the papers [16,17,21-24]. This procedure, where D and T have similar composition, secures constancy of equilibrium constants, activity coefficient of H^{+1} ions, and relative permittivity of D+T system during the titration performed under isothermal conditions.

Assuming formation of the species of (i) H_iL^{+i-n} or (ii) $M_aH_iB_bL^{+a+i-b-n}$ type (i = 0,…,q) formed by an acid H_nL in the system where the species M^{+1} and B^{-1} are also involved, the relations involving the mean number of protons, $\overline{n}$ (Eq. 9 or 18) attached to the basic form L^{-n} and the Simms constants g_k were formulated. The partial ratios involved with g_k were expressed in terms of the hyperbolic tangent (*tanh*) functions. The α (Eq. 4) was expressed in terms of hyperbolic sine (*sinh*). The partial ratios (Eq. 26) have the form (Eq. 34) similar to the one related to the density function in the Fermi-Dirac distribution function. Moreover, in [49], the inverse hyperbolic function *argsinh* [50] was applied for titration curve related to argentometric titration, and inverse hyperbolic function *argcosh* [50] as applied [28-30,52] for other titrations.

It were also proved that the titration of H_nL (C_0) with MOH is equivalent to titration of the mixture of q monoprotic acids, $HL_{(i)}$ (C_0), with the related dissociation constants $g_k = K_{1k} = [H][L_{(k)}]/[HL_{(k)}]$. In other words, application of Simms constants principle provides a kind of 'homogenization', where polyprotic acids are transformed into the mixture of monoprotic acids. It is a very important property, especially advantageous when considered in context with titration of solutions whose composition and then acid-base properties are unknown *a priori*, e.g., fulvic acids. It particularly refers to determination of total alkalinity of natural (e.g. marine) waters, wastes and different beverages, made according to titrimetric mode (pH titration).

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