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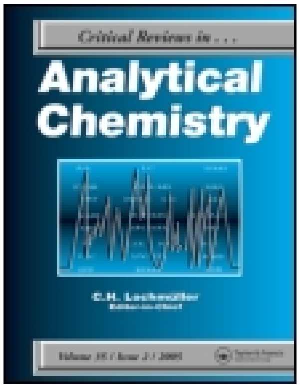

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New Approaches in Modeling Carbonate Alkalinity and Total Alkalinity

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Alkaline measurements (carbonate alkalinity and total alkalinity) are of great importance in analyses of ocean, marine, lake and river waters, and other samples. Carbonate alkalinity (CA) refers to the cases in which only bicarbonate and carbonate species are considered. Total alkalinity (Alk) implies additional species having acid-base properties. Biochemical processes give rise to the organic alkalinity (OA) in natural waters. The value of these topics is obvious if we refer to the plethora of publications in this field. As a matter of fact, the approaches towards Alk provide ambiguous results and those for CA arouse some reservations as well. Having this in mind, a new approach for alkalinity determination, presented in recent review paper published in this journal (*Crit. Rev. Anal. Chem.* 2011, *41*, 151), was developed in a more systematic and complete way, and new acronyms, TAL for total alkalinity and CAM for carbonate alkalinity, were introduced in that article. The methods proposed there and here are based on potentiometric pH titration, as the most common method applied for studying acid-base properties of humic substances (humic and fulvic acids). The parameters involved with CAM are resolved with the use of an Excel spreadsheet for the resolution of linear equations, whereas the parameters of a nonlinear regression equation referring to the TAL method are obtainable according to a more advanced, iterative computer program. A compact approach to CAM, based on the modified Gran II method, is carried out, but in a manner quite different and more thorough than the ones presented hitherto. Except for equivalence volumes, the CAM method enables evaluating the activity coefficient of hydrogen ions and values for (hybrid and concentration) dissociation constants of carbonic acid and ionic product of water. The possibilities and limitations of this method are tested by using a simulation procedure. The results obtained from simulated titrations provide the reference level related to error-free V and pH values at the points of titration curve ph = ph(V), ph = – log h, h – activity of hydrogen ions. The TAL model with Simms constants involved allows "homogenizing" the treatment of mono- and polyprotic acids and bases, especially those of undefined composition, i.e., carbonate species, fulvic acids, and their soluble complexes with metal ions. The TAL model may also be extended to the option where an approach based on a pre-dose addition is applied. pH and acid-base equilibria are very important topics and some aspects of them have been treated in this journal. Alkalinity determinations are of value in anaerobic digesters and anaerobic wastewater treatment, mine drainage and associated water, coastal seawater, marine aquaculture, estuarine water, and food and beverages, to point out a few recent examples.

Keywords Acid-base titration, carbonate alkalinity, total alkalinity, pH titration

INTRODUCTION

Alkalinity measurements are routinely conducted as a part of standard water quality determination; they are used mainly for ocean, marine, lake and river waters, and different beverages. The alkalinity concept appeared the first time in the context of marine chemistry and the *Challenger* expedition of 1872–1876, as noted in Dickson's review article (Dickson, 1992).

Almost the entire alkalinity of such waters is attributed to bicarbonate and carbonate (Wolf-Gladrow, et al., 2007; Wetzel and Likens, 2000); this pair is also the main buffering agent in natural waters. Two different alkalinity concepts, carbonate alkalinity (CA) and total alkalinity (Alk) (Dickson, 1981, 1992; Zhu and Anderson, 2002), are known from the literature. CA refers to the solutions where bicarbonate and carbonate are the only species considered, whereas Alk also involves other species endowed

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with acid-base properties (Emerson and Hedges, 2008). The concept of organic alkalinity (OA) is also in use (Muller and Bleie, 2008); it arises from the fact that the composition of natural waters is controlled by a combination of geochemical and biological processes. These processes are, to some extent, affected by the composition of the water. In aquatic systems, CO_2 is transformed by phytoplankton and macrophytes into organic carbon in the photosynthesis process (Inverznizzi and Terpin, 1997); CO_2 can also be deposited as $CaCO_3$. Such processes lead to increasing pH values. An adverse effect, i.e., respiration, where CO_2 is released, decreases pH value. The complementary processes of photosynthesis and respiration drive a global cycle in which carbon passes slowly between the atmosphere and the lithosphere and between the atmosphere and the oceans. Free strong bases are seldom observed at significant concentrations in natural waters.

Alkalinity (Alk) is distinguished from the acid-neutralizing capacity (ANC) (Stumm and Morgan, 1996) attributed to unfiltered (raw) water samples. Thus, the alkalinity measurement is made by pH titration of the solution obtained after passing the raw sample through a 0.45 μm (or smaller pore) membrane. The ANC is a measure of the overall buffering capacity of the water against acidification. The alkalinities (CA, Alk, and ANC) are measured by titration with a standardized strong acid (mainly HCl or H_2SO_4). However, the plethora of confusing approaches that have been used for Alk for the data-handling step provide ambiguous results (Neal, 2001; Zeebe and Wolf-Gladrow, 2001). Moreover, CA also arouses some reservations.

Total alkalinity and carbonate alkalinity reflect, respectively, the effects of partial and total oxidation of organic matter, as a proton source in waters and soils (Keller et al., 1987). Thus, alkalinity determinations are of value in anaerobic digesters and anaerobic wastewater treatment (Ward and Hobbs, 2011; Lahav and Morgan, 2004; Damasceno et al., 2007), mine drainage and associated waters (Kirby and Cravotta, 2005a, 2005b; McAllan et al., 2009), coastal seawaters (Muller and Bleie, 2008; Watanabe et al., 2004), marine aquaculture (Pfeiffer et al., 2011), estuarine waters (Gray et al., 2008), groundwater (Mapherson, 2009), geothermal waters (Verma, 2004), foods and beverages (Wen et al., 2004), and hydrogen carbonate in the presence of carboxylic acids, i.e., river water and wastewater from a paper-production plant (Gross and Nemarnik, 2007), as examples of recent applications. A more extended review of applications of alkalinity measurements is presented in Table 1.

Carbonate alkalinity and total alkalinity are of highest relevance to acid-base equilibria; pH and acid-base equilibria and related topics (Michalowski et al., 2005, 2010a,b,c; Pilarski et al., 2010; Asuero et al., 1986) were raised also in this journal (Asuero and Michalowski, 2011; Asuero, 2007; Michalowski, 2010; Michałowski et al., 2010a, 2010c; Casado-Riobó, 2005, 2008; de Levie, 1997; Kubista et al., 1999; Norman and Maeder, 2006; Esteban et al., 2006).

This article is organized as follows. First, the new models referring to CA, suggested by Michałowski and presented for first time in this article, will be considered in details. Within the framework of this article, the new approach to total alkalinity (Asuero and Michałowski, 2011) will be considered in a more extensive manner.

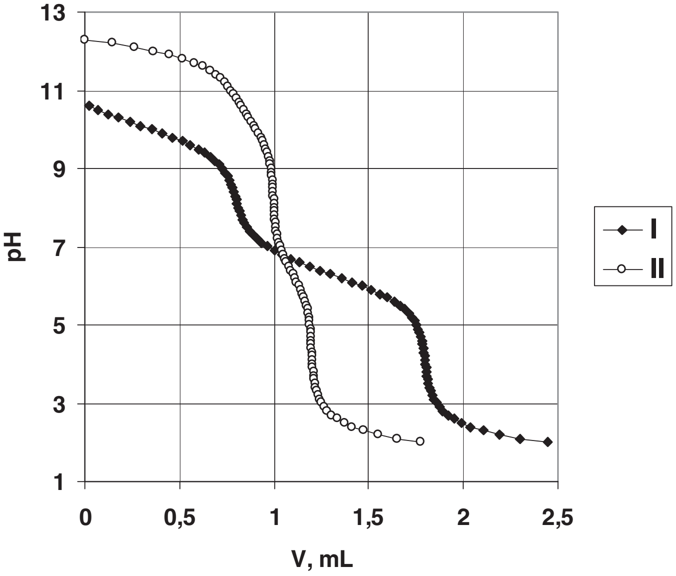


FIG. 1. Simulated titration curves for V_0 mL of: (I) System I ($NaHCO_3$ (C_1) + Na_2CO_3 (C_2)); (II) System II (Na_2CO_3 (C_2) + NaOH (C_3)) titrated with V mL of C mol/L HCl; (V_0, C_1, C_2, C) = (4, 0.005, 0.02, 0.1) for System I; (V_0, C_2, C_3, C) = (4, 0.005, 0.02, 0.1) for System II.

In order to distinguish the new concepts from previous ones, new acronyms were introduced (Asuero and Michałowski, 2011): TAL for total alkalinity and TAC for total acidity. The new approach to carbonate alkalinity is denoted CAM.

CLASSICAL ALKALINITY MEASUREMENTS

pH titrations carried out for carbonate alkalinity and total alkalinity measurements are usually made with HCl as titrant added until the pre-assumed (preset) end pH value, defined by an inflection point on the related pH titration curve, is attained. However, the inflection points, clearly visible in CA measurements (see Figure 1), are frequently difficult/impossible to identify in Alk measurements. In another option, the end point in CA is defined by the color change of an indicator (methyl orange) (Greenberg et al., 1932); in this case, at pH < 4.4, the color orange appears on the yellow background of the basic form of this indicator. At this point, one can approximately state that the carbonate and bicarbonate ions are quantitatively transferred into H_2CO_3. Such an approach to alkalinity seems to be pertinent and comprehensible. The results for Alk are usually reported in milliequivalents of the acid per liter [meq L^{-1}] of the solution tested.

Taking the matter from Greenberg et al., (1932) viewpoint, one can define the reference (zero level) (Kramer, 1982) point. For this purpose, one can consider the following solution:

TABLE 1
Selected applications of alkalinity measurements

Comment	Reference
Infrared gas analyzer was compared with other methods of dissolved carbon dioxide measurement, i.e., standard methods of titration, nomographic, and calculation, use of the portable CO_2 meter by OxiGuard, and an indirect method using pH and pCO_2 correlation curve.	Pfeiffer et al., 2011
Two approaches were used to predict the total alkalinity expressed as mg L^{-1} HCO_3^-, of an anaerobic digester, i.e., software sensors based on multiple linear regression algorithms using data from pH, redox potential, and electrical conductivity data, and near-infrared reflectance spectroscopy.	Ward and Hobbs, 2011
AquaEnv provides a routine to simulate and investigate titrations of water samples with strong acid or base, as well as a routine that allows for a determination of total alkalinity and total carbonate values from recorded titration curves using nonlinear curve fitting.	Hofmann et al., 2010
Calculated pCO_2 values in seawater carbonate chemistry matched measured pCO_2 values if pH and total alkalinity (TA) or pH and dissolved inorganic carbon (DIC) were chosen as input parameters, whereas pCO_2 calculated from TA and DIC was considerably lower than pCO_2 measured values.	Hoppe et al., 2010
Accurate measurements of pH in conjunction with either TA or DIC in open ocean waters can be used to accurately calculate both $pCO_2(aq)$ and concentration of carbonate species. Calculation of the carbonate system was supported by three main software packages.	Hydes et al., 2010
Titration procedures for the determination of carbonate species in rainwater, groundwater, geothermal water, and water samples derived from a petroleum reservoir are presented.	Verma et al., 2010p
Dissolved organic matter produced by marine phytoplankton during photosynthesis is another buffering component in the ocean, and indicates that the contribution of dissolved organic matter to seawater alkalinity can be significant in the biologically productive upper ocean layer.	Kim and Lee, 2009
Chemical changes involved in two basic approaches for carbonate chemistry manipulations, i.e., changing dissolved inorganic carbon at constant total alkalinity and changing total alkalinity at constant dissolved inorganic carbon, are described and analyzed, the chemical background of ocean acidification being provided.	Schulz et al., 2009
Parametric and nonparametric statistical regression methods were implemented to model the removal of natural organic matter as measured by total organic carbon from raw water by conventional surface treatment and to track the behavior of pH and alkalinity.	Towler et al., 2009
Data on carbon and carbon-relevant hydrographic and hydrochemical parameters from previously non-publicly available cruise data sets in the Arctic, Atlantic, and Southern oceans were retrieved and merged into a new database: CARINA (CARbon IN the Atlantic).	Velo et al., 2009
Low-turbidity surface waters and groundwaters were analyzed. The effects of filtering, refrigeration, and sample storage prior to potentiometric titration according to Gran method were considered.	Williams et al., 2009
The development and application of a portable, hybrid reagent-injection gas diffusion flow analysis technique for the underway measurement of total alkalinity in estuarine waters is described	Gray et al., 2008

Potentiometric titration was applied to samples of fjord surface waters of unusually high organic matter content. Some correlations between results obtained for TA and OA (organic alkalinity) were tested.	Muller and Bleie, 2008
Intercalibration of the total alkalinity measurements in seawater according to the Bruevich method, with use of certified reference materials.	Pawlova et al., 2008
An assessment was made of the effect of sodium bicarbonate addition on the determination of solids concentration in samples containing cheese whey and volatile acids to simulate anaerobic reactor effluents.	Damasceno et al., 2007
Ion exclusion chromatography was recognized as the method of choice for reliable determination of the concentration of HCO_3^- in water samples containing anions of carboxylic acid; the method was applied to the analysis of Slovenian river waters and wastewater from a paper production plant.	Gross and Nemarnik, 2007
The potential contribution of organic bases to the alkalinity of seawater samples was assessed, being significant in cultures of the marine microalgae *Rhodomonas* sp. and *Isochrysis aff Galbana* and in three marine environments.	Hernández-Ayon et al., 2007
An overview of alkalinity determination methods available for seawater is given.	Millero, 2007
An expression for TA in terms of the total concentration of certain major ions (Na^+, Cl^-, Ca^{2+}, etc.) and the total concentrations of various acid-base species (total phosphate, etc.) was derived from Dickson's original definition of total alkalinity under the constraint of electroneutrality.	Wolf-Gladrow et al., 2007
The first direct measurements of the contribution of phytoplankton and bacterial cells to the measured alkalinity of unfiltered seawater are reported.	Kim et al., 2006
A new titration methodology, tracer monitored titration, based on spectrophotometric monitoring of titrant dilution, is introduced. It is free of volumetric and gravimetric measurements and insensitive to pump precision and reproducibility; the performance achieved was excellent.	Martz et al., 2006
Synthetic and fields samples of mine drainage having various initial pH values and concentrations of dissolved metals and alkalinity were titrated by several methods and the results compared to alkalinity and acidity calculated on dissolved solutes.	Kirby and Cravotta, 2005a
The authors explain theoretical expressions of three types of alkalinity (caustic, phenolphthalein, and total) and acidity (mineral, CO_2, and total). For most mine-drainage solutions a useful alkaline value can be derived from alkalinity and acidity values based on speciation.	Kirby and Cravotta, 2005b
Review of the methods published in the past four decades for on-site titration measurements of volatile fatty acids and carbonate alkalinity concentrations.	Lahav and Morgan, 2004
The analytical method used by chemists and hydrologists works well for waters containing carbonic alkalinity, whereas the method used by geochemists is conceptually incorrect.	Verma, 2004
A flow-through analyzer was developed for the rapid potentiometric determination of total alkalinity (TA) in small amounts of seawater, in order to capture large temporal and spatial variations of the CO_2 system in coastal zones.	Watanabe et al., 2004

(Continued on next page)

TABLE 1
Selected applications of alkalinity measurements *(Continued)*

Comment	Reference
A new technique (Flash Titration) for the determination of total acidity and total alkalinity, which no requires liquid titrants (they are generated electrochemically), was applied to food and beverage analysis (juices, soft drinks, wines, and food products).	Wen et al., 2004
A method used to certify reference materials based on seawater for total alkalinity is described. The equivalence point is evaluated from titration points in the pH region 3.0–3.5 using a least squares procedure that corrects for the reactions with sulfate and fluoride ions.	Dickson et al., 2003
Alkalinity titrations in combination with theoretical calculations offer a simple and inexpensive method to experiment with carbonate equilibria using both known standards and surface water samples.	Andersen, 2002
A new simple, rapid, and accurate method for on-site measurement of volatile acids (VFA) and carbonate alkalinity in anaerobic reactors is presented, involving eight pH observations and taking approximately 15 min.	Lahav and Morgan, 2002
A discussion on the measurement of alkalinity in bicarbonate-bearing acidic water is presented as a move towards developing a standardized approach within the aquatic sciences. Practical illustrations are provided.	Neal, 2001
An evaluation is made of the modified Gran functions and derivative methods for assessing the concentration of inorganic carbon species, CO_2, HCO_3^-, and CO_3^{2-}, in the cultivation medium of the marine microalgae *Tetraselmis gracilis*.	Rigobello-Masini and Masini, 2001
The partial pressure of carbon dioxide in the ocean's surface waters is determined from dissolved inorganic carbon (DIC) and total alkalinity (TA) and the first and second dissociation constant of carbonic acid.	Lueker et al., 2000
Analysis of seawater sampled from different depths in the North Atlantic Ocean (Canary Islands region) was performed by potentiometric methods involving titration in a closed cell and a two end-point acid addition method.	Mintrop et al., 2000
An algorithm based on alkalinity conservation is presented in order to calculate natural water pH, incorporating the effects of heating, boiling, dilution, and mixing of different types of fluids.	Verma, 2000

H_2CO_3 (C_0) + HCl (C_a) + NaOH (C_b). From the combination of charge

$$[H^+] - [OH^-] + [Na^+] - [Cl^-] = \left[HCO_3^-\right] + 2\left[CO_3^{-2}\right] \quad [1]$$

and concentration balances $[Na^+] = C_b$, $[Cl^-] = C_a$, $[H_2CO_3] + [HCO_3^-] + [CO_3^{-2}] = C_0$, we get the relation

$$\Delta = C_b - C_a = \left[HCO_3^-\right] + 2\left[CO_3^{-2}\right] + [OH^-] - [H^+] \quad [2]$$

At $C_b - C_a \geq 0$, the term carbonate alkalinity (CA) equation (Jensen, 2003) is formulated as

$$CA = \Delta = C_b - C_a = \left[HCO_3^-\right] + 2\left[CO_3^{-2}\right] + [OH^-] - [H^+] \quad [3]$$

At $\Delta = 0$ (and, particularly, at $C_b = C_a = 0$), from Equation [2] we get the relation

$$[H^+] = [HCO_3^-] + 2\left[CO_3^{-2}\right] + [OH^-] \quad [4]$$

This is identical with the charge balance referring to C_0 mol/L H_2CO_3, i.e., CO_2 dissolved in pure water or aqueous NaCl solution (Zeebe and Wolf-Gladrow, 2001); the difference lies in ionic strength and resulting activity coefficient values. A pure solution of CO_2, with CA = 0, is the reference system for calculation of CA. The pH value for C_0 mol/L H_2CO_3 is calculated from the formula $[H^+] = ((4C_0/K_1+1)^{1/2} - 1)\cdot K_1/2$, resulting from the approximation $[H^+] = [HCO_3^-]$ of Equation [4]; at $C_0 = 2\cdot10^{-3}$ mol/L we have pH = pH_0 = 4.5. The value pH = 4.5 (at 20°C and zero ionic strength value) has been recommended as the preset pH value in pH-metric titration (Dickson, 1981; American Public Health Association, 1985; Millero et al. 1998). Other pH values, namely 4.7 (Loewenthal et al, 1989, 1991), 4.3 (Ripley et al., 1986), 4.0 (McCarthy, 1964), 3.3 (DiLallo and Albertson, 1961), and even 2.2 (Powell and Archer, 1989), were applied as the preset pH values for titrands D containing non-carbonate contributors, e.g., carboxylic acids involved with volatile fatty acids (VFAs). An extraordinary proposal is the choice of pH = 5.75 (the midpoint, used to determine partial alkalinity, PA) (Jenkins et al., 1983, 1991). Other authors prefer to use four (Moosbrugger et al., 1993a, 1993b) or five (Moosbrugger et al., 1993c, 1993d; Lahav and Loewenthal, 2000) pH values. Some authors have applied the least squares method (Bisogni, 1994; Bisogni et al., 1998). Comparative studies between the different methods can be found in the literature (e.g., Buchauer, 1998). The addition of neutral salt, e.g., NaCl, shifts pH to lower values (Glaster, 1991). For comparison, the solubility of CO_2 in water at 25°C and 100 kPa CO_2 equals 1.45 g/L, i.e., 0.033 mol/L. One should note that at $pH_0 = 4.5$ we have $[CO_3^{-2}]/[HCO_3^-] = 10^{pH-10.1} = 10^{-5.6}$. The solubility of CO_2 in aqueous media rises with increase of pH value; the relatively high solubilities of $NaHCO_3$ and Na_2CO_3 in water testify to this. The pH value for C_1 mol/L $NaHCO_3$ is calculated from the formula $[H^+] = K_1^{1/2}\cdot(K_2+K_w/C_1)^{1/2}$; at $C_1 = 2\cdot10^{-3}$ mol/L, we get pH = pH_1 = 8.2. The pH_1 value is relevant to acidity measurements done by titration of the sample to be tested, e.g., mine water, with standard NaOH solution, added up to pH_1 = 8.3. In this case, the following options are considered: (1) hot acidity (after boiling the sample), with prior addition of H_2O_2; and (2) cold acidity (a) with or (b) without prior addition of H_2O_2 (Green et al., 2006). The addition of H_2O_2 (30%) promotes oxidation of reduced forms of such cations as Fe^{+2} and Mn^{+2}. Boiling the sample accelerates this process.

POTENTIOMETRIC MEASUREMENTS OF ALKALINITY

In potentiometric Alk measurements, such as the analysis of seawater, a known volume of a sample to be tested is placed in a closed cell and titrated with a HCl + NaCl solution. The contents of NaCl as the basal electrolyte in the titrant approximates the ionic strength of the seawater to be tested (compare with Figure 2). This way, the activity coefficient of hydrogen ions is maintained approximately constant during the pH titration, carried out with a combined glass electrode, as a rule. The data $\{(V_j, pH_j) \mid j = 1, \ldots, N\}$ thus obtained are handled according to two alternative approaches. The first approach is the Gran method (Gran, 1952), applied also in its extended/modified versions (Dyrssen, 1965; Dyrssen and Sillén, 1967; Edmond, 1970; Kozarek and Fernando, 1972; Hansson and Jagner, 1973; Bradshaw et al., 1981; Bos and Williams, 1982; Brewer et al., 1986; Millero et al., 1993). The second approach is based on the curve fitting, realized according to the non linear least-squares method, elaborated by Johansson and Wedborg (1982). Nonlinear curve fitting was also used by the AquaEnv program (Hofmann et al., 2010). A detailed computer program, SOP 3, is presented by U. S. Department of Energy (1994–1997). Both approaches were discussed in a huge number of articles and handbooks in relation to the problem in question, e.g., Stumm and Morgan (1996), Lewenthall and Marais (1976), Holland (1978), Snoeyink and Jenkins (1980), and Morel and Hering (1993).

In the Alk concept it is assumed that all the species are known beforehand. The following expression for alkalinity

$$\begin{aligned} Alk = {} & \left[HCO_3^-\right] + 2\left[CO_3^{-2}\right] + \left[B(OH)_4^-\right] + [OH^-] \\ & + \left[HPO_4^{-2}\right] + 2\left[PO_4^{-3}\right] + \left[SiO(OH)_3^-\right] + [NH_3] \\ & + [HS^-] - [H^+]_T - \left[HSO_4^-\right] - [H_3PO_4] - \ldots \quad [5] \end{aligned}$$

is in common use (U.S. Department of Energy, 1994–1997), where $[H^+]_T$ is the concentration of free hydrogen ions. As we see, the carbonate, phosphate, borate, and other species are specified explicitly in the expression for Alk. Generally, the approach to Alk is repeated, *ad nauseam*, in the same manner, in other articles and handbooks devoted to the subject in question.

Potentiometric pH titration is also the most common method applied for studying acid-base properties of humic substances.

SOME PROPERTIES OF HUMIC SUBSTANCES

Humic substances (humics, HSs) are composed of natural (polydispersed, polyelectrolytic) biopolymers (Pompe et al., 1996; Marinsky et al., 1995; Milne et al., 1995; Koopal et al.,

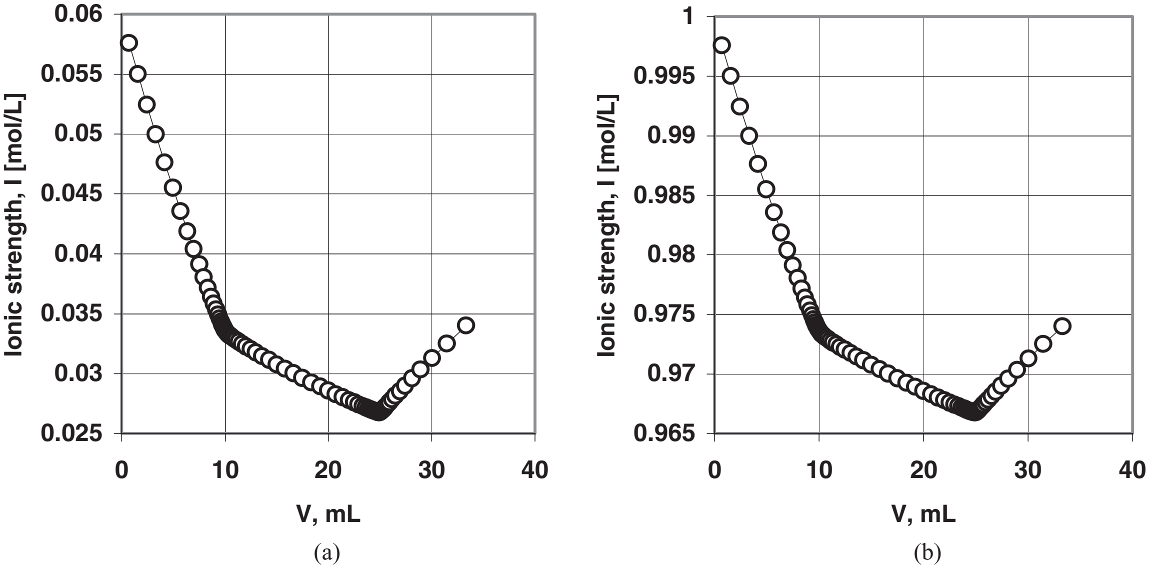


FIG. 2. Changes in ionic strength (I, mol/L) during the titration of V_0 mL of titrand D with V mL of titrant T. Composition of D: $NaHCO_3$ (C_1) + Na_2CO_3 (C_2) + NaCl (C_{NaClD}); composition of T: HCl (C) + NaCl (C_{NaClT}); (V_0, C_1, C_2, C, C_{NaClD}, C_{NaClT}) = (50, 0.01, 0.02, 0.1, 0, 0) (Figure a); and (V_0, C_1, C_2, C, C_{NaClD}, C_{NaClT}) = (50, 0.01, 0.02, 0.1, 0.98, 0.90) (Figure b).

2001; Davies et al., 2001; Hessen and Tranvik, 2010; Steelink, 2002; Drever, 2005; Bratskaya et al., 2008) occurring in water as dissolved organic matter (DOM) or in sediments and soils on the earth's surface (Drever, 2005). Operationally, soluble HSs are classified as humic acids (HAs) or fulvic acids (FAs) (de Souza Sierra et al., 2001), considered as products of more advanced diagenesis (Novotny et al., 1999) (i.e., oxidative decomposition) of complex organic molecules originating from plant and animal tissues (Gaffney et al., 1996; Rouhi, 2000). In contrast to HSs, FAs are soluble within the whole pH range of aqueous solutions. FAs are the major contributor of dissolved organic carbon in water (Suffet and MacCarthy, 1989; Schnitzer and Khan, 1972; Hayes et al., 1989; Aiken et al., 1985), owing to the presence of the highest (among HSs) content of acidic (benzenecarboxylic and phenolic) groups (Hayes et al., 1989; Aiken et al., 1985; Stevenson, 1982; Thurman, 1985; Massini et al., 1998) within molecules of relatively low masses, approximately 500–2000 Da (Lakshman et al., 1993) or 400–1000 Da for groundwater FAs (McIntyre et al., 1997). On the basis of elemental composition, a hypothetical structure for marine FAs has been derived (Woolard and Linder, 1999).

FAs are soluble in water, in the whole pH range, and affect pH of natural waters. Moreover, they are able to form chelate complexes, e.g., with Hg(II), Pb(II), Cu(II), and Al(III) ions leached in the environment (Thurman, 1985; Woolard and Linder, 1999; Reuter and Perdue, 1977; Duursma and Dawson, 1981; Elkins and Nelson, 2001). Conditional stability constants of Cu^{+2} and Pb^{+2} complexes with FAs were cited in Wu and al. (2003). Complexation of toxic metal ions by HAs and FAs plays a major role in maintaining them in a bioavailable state (Buffle, 1988) in environmental waters. It also plays a prominent role in controlling metal speciation and influences the mobility of metal ions in soil and aqueous environments (Sposito, 2008) and hence plays a vital function in the environmental fate, bioavailability, toxicity, and mobility of heavy metals in the biosphere (Oden et al., 1993; Dumat et al., 2000; Pinheiro et al., 2000). Liu and Gonzalez (2000) and Jin et al. (1996) demonstrated that pH and ionic strength are the most important variables controlling metal complexation with HAs.

The presence of carboxylic and phenolic groups, involved in different molecules of different acidic strengths, provides the titration curves with no abrupt inflection points; it is then necessary to employ more advanced programs to resolve titration data (de Souza Sierra et al., 2001). Many computer programs were applied for this purpose (Martell and Motekaitis, 1992; Follows and Oguz, 2002), e.g., the software prepared by Lewis and Wallace (1998).

Potentiometric titrations of HAs were made by Aleixo et al. (1992) and Massini (1993, 1995). On the basis of IR and ^{13}C NMR spectra, Paxéus and Wedborg (1985) stated that an FA sample tested by them behaved as a mixture of six monoprotic acids. Dzombak et al. (1986) and Fish et al. (1986) reviewed discrete and continuous distribution models, applied to describe metal-humate interactions.

In later parts of the article we refer to the new, modified method of carbonate alkalinity (CAM) determination. The approach according to CAM is made with use of Gran II functions (Gran transformation), but the manner applied for this purpose is quite different and more thorough than the ones presented in earlier studies (Stumm and Morgan, 1996; Pankow, 1991; Sigg et al., 1992; Jansen, 2003).

MODIFIED METHOD OF CARBONATE ALKALINITY DETERMINATION

Basic Relationships

Let as consider first the titration of V_0 mL of titrand (D), containing $NaHCO_3$ (C_1) + Na_2CO_3 (C_2) + NaOH (C_3), with V mL of C mol/L HB as titrant (T). The function V = V(pH) for the titration curve can be written as follows:

$$V = V_0 \cdot \frac{(\bar{n} - 1) \cdot C_1 + \bar{n} \cdot C_2 + C_3 + \alpha}{C - \alpha} \qquad [6]$$

where

$$\bar{n} = \frac{2[H_2L] + [HL^-]}{[H_2L] + [HL^-] + [L^{-2}]} = \frac{2[H^+]^2 + K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2}$$
$$= \frac{2 \cdot 10^{16.4-2pH} + 10^{10.1-pH}}{10^{16.4-2pH} + 10^{10.1-pH} + 1} \qquad [7]$$

$$K_1 = [H^+][HL^-]/[H_2L], \;\; K_2 = [H^+][L^{-2}]/[HL^-] \qquad [8]$$

$$\alpha = [H^+] - [OH^-] = 10^{-pH} - 10^{pH-14.0} \qquad [9]$$

The variable $\bar{n}$ (known as the formation function) denotes the mean number of protons attached to the basic form $L^{-2} = CO_3^{-2}$. After transformation of Equation [6] into the form

$$(C - \alpha) \cdot (V_0 + V)/V_0 = (\bar{n} - 1) \cdot C_1 + \bar{n} \cdot C_2 + C_3 + C \qquad [10]$$

the following systems should be considered:

(1) System I: $NaHCO_3$ (C_1) + Na_2CO_3 (C_2), described by the equation ($C_3 = 0$ in Equation [10]):

$$(C - \alpha) \cdot (V_0 + V)/V_0 = (\bar{n} - 1) \cdot C_1 + \bar{n} \cdot C_2 + C \qquad [11]$$

or

(2) System II: Na_2CO_3 (C_2) + NaOH (C_3), described by the equation ($C_1 = 0$ in Equation [10]):

$$(C - \alpha) \cdot (V_0 + V)/V_0 = \bar{n} \cdot C_2 + C_3 + C \qquad [12]$$

(See Figure 1.) Setting $C_1V_0 = CV_{eq1}$ and $2C_2V_0 = CV_{eq2}$ in Equation [11], after transformation we get

$$(V_0 + V) \cdot \alpha/C = V + V_{eq1} - \bar{n} \cdot (V_{eq1} + V_{eq2}/2) \qquad [13]$$

Similarly, setting $2C_2V_0 = CV_{eq2}$ and $C_3V_0 = CV_{eq3}$ in Equation [12], after transformation we get

$$(V_0 + V) \cdot \alpha/C = V - V_{eq3} - \bar{n} \cdot V_{eq2}/2 \qquad [14]$$

All the species, i.e., $NaHCO_3$ (C_1), Na_2CO_3 (C_2), and NaOH (C_3), involved in relation [10], cannot be determined simultaneously in pH titration. To prove it, let us apply the identity $0 \equiv -\bar{n}C_3 + \bar{n}C_3$ in the right side of Equation [10]; we get

$$(\bar{n} - 1) \cdot C_1 + \bar{n}C_2 + C_3 + C \equiv \bar{n} \cdot (C_1 + C_2) + (C_3 - C_1)$$
$$+ C \equiv (\bar{n} - 1) \cdot (C_1 - C_3) + \bar{n} \cdot (C_2 + C_3) + C \qquad [15]$$

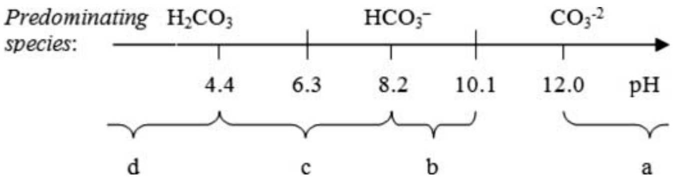


FIG. 3. Predominance diagram for H_2CO_3; $pK_1 = 6.3$ and $pK_2 = 10.1$ taken from Inczédy (1976).

i.e., the presupposed mixture is equivalent to one composed of Na_2CO_3 ($C_2' = C_1+C_2$) and NaOH ($C_3' = C_3–C_1$) if $C_3 > C_1$, or to one composed of $NaHCO_3$ ($C_1' = C_1–C_3$) and Na_2CO_3 ($C_2' = C_2+C_3$) if $C_1 > C_3$. For $C_3 = C_1$, the system is equivalent to Na_2CO_3 ($C_2' = C_1+C_2$) solution.

In a similar way, one can state that the solution of $NaHCO_3$ (C_1) + NaOH (C_3) is equivalent to Na_2CO_3 ($C_2' = C_1$) + NaOH ($C_3' = C_3–C_1$) for $C_3 > C_1$, or to $NaHCO_3$ ($C_1' = C_1–C_3$) + Na_2CO_3 ($C_2' = C_3$) for $C_1 > C_3$. At $C_3 = C_1$, the system is equivalent to the solution of Na_2CO_3 ($C_2 = C_1$).

The system D = $NaHCO_3$ (C_1) + Na_2CO_3 (C_2) and HCl (C) as T, called System I, is characterized by the set of (V_0, C_1, C_2, C) values, whereas the system D = Na_2CO_3 (C_2) + NaOH (C_3) and HCl (C) as T, called System II, is characterized by the set of (V_0, C_2, C_3, C) values (see Figure 1). System III, composed of $NaHCO_3$ (C_1) + NaOH (C_3) at $C_3 > C_1$, and System IV, composed of Na_2CO_3 (C_2') + HCl (C_a) at $C_2' > C_a$ and then equivalent to System II, can also be considered.

Some Simplifications and Approximations

Let us take $\Delta = (pK_2 - pK_1)/2 = (10.1 - 6.3)/2 = 1.9$ and divide the whole pH scale on the pH intervals, denoted in Figure 3 as d, c, b, and a. Within the intervals, we will formulate simplified forms of Equations [13] and [14]. Then we confine the pH ranges of their applicability, resulting from conjunction of the simplifying assumptions applied for $\bar{n}$ (Equation [7]) and α (Equation [9]), within defined criteria formulated for this purpose. One can recall first that pH measurements are made with limited accuracy, expressed by indefinity δpH in pH values. One can do some simplifications/omissions in some formulas applied for particular needs, e.g., in Equation [7]. For this purpose, we assume that the concentrations $[H^+]'$ and $[H^+]$ of hydrogen ions are indistinguishable if the value

$$\xi = \frac{[H^+]' - [H^+]}{[H^+]} = \frac{[H^+]'}{[H^+]} - 1 = 10^{\delta pH} - 1 \qquad [16]$$

does not cross a limiting ξ-value, whose value depends on the δpH value. Taking the limiting value $\xi = 10^{-1.9} \approx 1/80$, from Equation [16] we have

$$\delta pH = \log(1 + \xi) = \frac{\ln(1 + \xi)}{\ln 10} \cong \frac{\xi}{2.303} = \frac{10^{-1.9}}{2.303} \approx 0.005 \qquad [17]$$

This δpH value is related to pH meters of higher quality. Applying this criterion, one can omit some components in the

TABLE 2
Approximate forms for n̄and α, obtained from Equations [7] and [9], for the pH intervals indicated in Figure 1

No.	pH interval	n̄≅	$\alpha\cong$
a	$pH > pK_2 + \Delta$	$\bar{n}_a = 0$	$-\dfrac{K_W}{[H^+]}$
b	$pK_2 - \Delta < pH \approx pK_2$	$\bar{n}_b = \dfrac{[H^+]}{[H^+] + K_2}$	0
c	$pK_1 - \Delta < pH < pK_1 + \Delta$	$\bar{n}_c = \dfrac{2[H^+] + K_1}{[H^+] + K_1}$	0
d	$pH < pK_1 - \Delta$	$\bar{n}_d = 2$	$[H^+]$

numerator and denominator of Equation [7]. Within the pH intervals in Figure 3, the simplified forms for $\bar{n}$ and α, obtained from Equations [7] and [9], can be applied, as presented in Table 2. As results from Table 2, the points (V_j, pH_j) in pH intervals b and c are collected not far from pK_2 and pK_1 values for H_2CO_3. At $pH = pK_1$ and $pH = pK_2$ we have

$$\bar{n}_1 = \bar{n}(pK_1) = \frac{3}{2 + K_2/K_1} \cong 1.5 \text{ and } \bar{n}_2 = \bar{n}(pK_2) = \frac{1 + 2K_2/K_1}{2 + K_2/K_1} \cong 0.5$$

respectively.

From Figure 4 we see that $\bar{n}_b$ (Table 2) approximates $\bar{n}$ (Equation [7]) within the range of higher pH values, whereas $\bar{n}_c$(Table 2) approximates $\bar{n}$ at lower pH values. Moreover, the relationship

$$1/\bar{n}_c = 1/\bar{n} - (10^{16.7-2pH} + 10^{10.1-pH})^{-1}$$

is valid. Note that

$$\log\left(\frac{\bar{n}_x}{\bar{n}}\right) \equiv \log e \cdot \ln\left(1 - \frac{\bar{n} - \bar{n}_x}{\bar{n}}\right) \cong \log e \cdot \left(\frac{\bar{n}_x - \bar{n}}{\bar{n}}\right); \quad \text{i.e., } \frac{\bar{n}_x}{\bar{n}} \cong 1 + \ln 10 \cdot z\,(x = b, c)$$

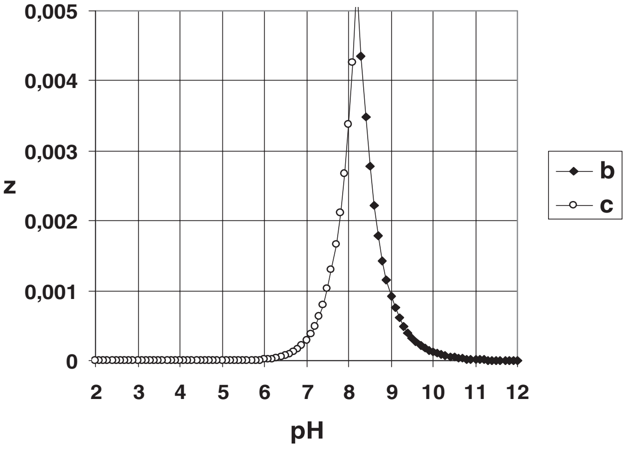


FIG. 4. Plots for: $z = -\log(\bar{n}_b/\bar{n})$ vs. pH (curve b), and $z = \log(\bar{n}_c/\bar{n})$ (curve c) vs. pH relationships.

In the transitory pH interval (pH about 8), the fit of $\bar{n}_x$ (x = b, c) is less expressed.

The approximation also relates α value (Equation [9], Table 2). Omission of the term $(V_0+V)\cdot\alpha/C$ on the left sides of Equations [13] and [14], expressed in volume units, is justifiable within the intervals b and c—provided that the volume corrections resulting from these omissions fall within the tolerance DV pre-assumed for titrant volume increments. In order to define the pH intervals where this correction is valid, for the set (V_0, C_1, C_2, C) for System I, one can plot the DV versus pH relationships (Figure 5) on the basis of relations:

$$DV = V + V_{eq1} - \bar{n}_c \cdot (V_{eq1} + V_{eq2}/2) \qquad [18]$$

and

$$DV = V + V_{eq1} - \bar{n}_b \cdot (V_{eq1} + V_{eq2}/2) \qquad [19]$$

(See Table 2 and Equations [13] and [14]), where V = V(pH) values are calculated from the formula

$$V = V_0 \cdot \frac{(\bar{n} - 1) \cdot C_1 + \bar{n} \cdot C_2 + \alpha}{C - \alpha} \qquad [20]$$

obtained after setting $C_3 = 0$ in Equation [6], see curve I in Figure 1. An analogous relationship (Figure 6) obtained for the set (V_0, C_2, C_3, C) for System II is applied to equations:

$$DV = V - V_{eq3} - \bar{n}_c \cdot V_{eq2}/2 \qquad [21]$$

and

$$DV = V - V_{eq3} - \bar{n}_b \cdot V_{eq2}/2 \qquad [22]$$

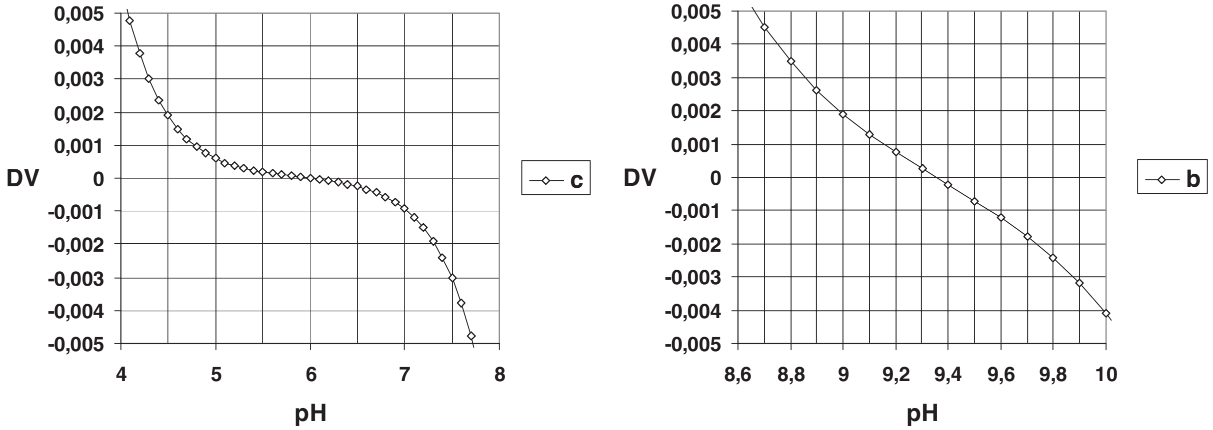
where V = V(pH) is calculated from the formula ($C_1 = 0$ in Equation [6]):

$$V = V_0 \cdot \frac{\bar{n} \cdot C_2 + C_3 + \alpha}{C - \alpha} \qquad [23]$$

(See curve II in Figure 1.) Comparing the related plots in Figures 5 and 6, we see that the pH intervals, where DV assumes low values, are nearly identical for Systems I and II.

Effect of CO_2 from Air

Systems I and II can be prepared from water and commercial preparations of $NaHCO_3$, Na_2CO_3, and NaOH solution. In all



(a) (b)

FIG. 5. DV vs. pH relationships found on the basis of Equation [20] and: (a) Equation [18]; (b) Equation [19] for System I (with $NaHCO_3 + Na_2CO_3$ as D), at $(V_0, C_1, C_2, C) = (4, 0.01, 0.02, 0.1)$; $V_{eq1} = 0.4$, $V_{eq2} = 1.6$.

instances, one should take into account possible effects of CO_2 on the composition of chemicals taken for analysis and the related solutions. The presence of CO_2 in NaOH can strongly affect the results of titrimetric acid-base analyses (Asuero and Michałowski, 2011).

For the D+T system, where V_0 mL of C_1 mol/L $NaHCO_3$ + C_2 mol/L Na_2CO_3 + C_0 mol/L H_2CO_3 as D is titrated with V mL of HCl (C mol/L) as T, we get the relation

$$(V_0 + V) \cdot \alpha/C = V + V_{eq1} + 2 \cdot (C_0/C) \cdot V_0 - \bar{n} \cdot (V_{eq1} + V_{eq2}/2 + (C_0/C) \cdot V_0) \quad [24]$$

Analogously, for the D+T system, where V_0 mL of C_2 mol/L Na_2CO_3 + C_3 mol/L NaOH + C_0 mol/L H_2CO_3 as D is titrated with V mL of HCl (C mol/L) as T, we have

$$(V_0 + V) \cdot \alpha/C = V - V_{eq3} + 2 \cdot (C_0/C) \cdot V_0 - \bar{n} \cdot (V_{eq2}/2 + (C_0/C) \cdot V_0) \quad [25]$$

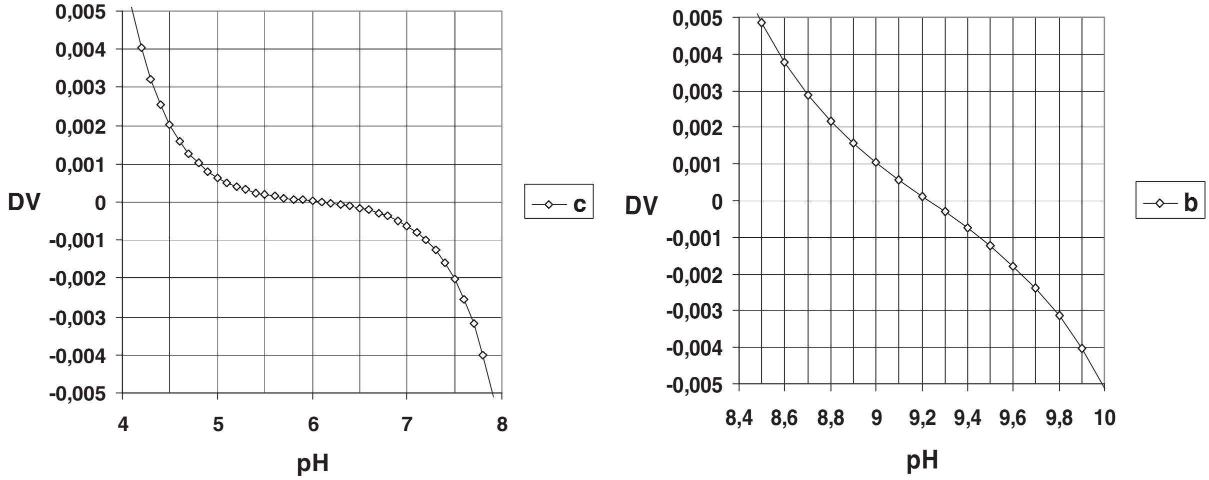
Formulation of Functions of the Gran Type

Setting the simplified expressions for $\bar{n}$ and α (Table 2) into the formulas:

$$V + V_{eq1} - \bar{n}_c \cdot (V_{eq1} + V_{eq2}/2) = 0 \quad [26]$$

and

$$V + V_{eq1} - \bar{n}_b \cdot (V_{eq1} + V_{eq2}/2) = 0 \quad [27]$$



(a) (b)

FIG. 6. DV vs. pH relationships found on the basis of Equation [23] and: (a) Equation [21]; (b) Equation [22] for System II (with $Na_2CO_3 + NaOH$ as D), at $(V_0, C_2, C_3, C) = (4, 0.02, 0.02, 0.1)$; $V_{eq2} = 0.8$, $V_{eq3} = 1.6$.

TABLE 3
Gran functions related to System I (see Appendix A) at $C_0 = 0$ in Equation [24]

Sequence of operations $d \rightarrow c \rightarrow b$		
No.	pH interval (presupposed)	Function of Gran type
a	$pH > pK_2+\Delta$	—
b	$pK_2 - \Delta < pH \approx pK_2$	$(V_b + V) \cdot 10^{ph} = (K_2^*)^{-1} \cdot (V_c - V)$
c	$pK_1 - \Delta \leq pH \leq pK_1+\Delta$	$(V_d - V) \cdot 10^{-ph} = K_1^* \cdot (V - V_c)$
d	$pH < pK_1-\Delta$	$(V_0 + V) \cdot 10^{-ph} = \gamma \cdot C \cdot (V - V_d)$
Relations		$V_d = V_{eq1} + V_{eq2}$, $V_c = V_{eq2}/2$, $V_b = V_{eq1}$

or

$$V - V_{eq3} - \bar{n}_c \cdot V_{eq2}/2 = 0 \qquad [28]$$

and

$$V - V_{eq3} - \bar{n}_b \cdot V_{eq2}/2 = 0 \qquad [29]$$

(See Equations [18], [19] and [21], [22].) Rearranging the terms in the manner specified in Appendixes A and B,we get the formulas for the modified Gran II functions as presented in Tables 3 and 4. The interval *a* is not included in Table 3. Simply, the data $\{(V_j, pH_j) \mid j = 1, \dots, N\}$ do not cover this pH range for System I (see Figure 1, curve I). Also, for System II, the experimental points may not cover the interval *a* at lower C_3 values.

In Tables 3 and 4, the following notations were applied:

- $ph = -\log h$ for activity $h = \gamma \cdot [H^+]$, γ for activity coefficient of hydrogen ions,
- $K_1^* = \gamma \cdot K_1$, $K_2^* = \gamma \cdot K_2$, $K_W^* = \gamma \cdot K_W$ are hybrid values for K_1, K_2 (Equation [7]) and $K_W = [H^+][OH^-]$.

On the data handling step, with simulated $\{(V_j, pH_j) \mid j = 1, \dots, N\}$ or experimental $\{(V_j, ph_j) \mid j = 1, \dots, N\}$ data, the Gran functions are applied in the sequences of pH intervals, specified in headings for the corresponding columns in Tables 3 and 4. Other possible sequences are not advised.

The parameters:

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

can be found according to the least squares (LS) method (Sayago et al., 2004; Asuero et al., 2006), applied to experimental points

$$\{(V_j^x, ph_j^x) \mid j = 1, \dots, N_x\}$$

referring separately to particular x intervals; x = b, c, d in Table 3, and x = a, b, c, d in Table 4. The set of N_x points related to x-th interval does not cover the whole pH intervals indicated in Tables 3 and 4. This confinement is the result of compromises assumed in the simplifications made for $\bar{n}$ and α.

It is noteworthy that ph, referring to activity h of H^+ ions, is measured in experimental titrations. The $ph = -\log h$ as variable (not $pH = -\log[H^+]$) is involved in all the relationships specified in Tables 3 and 4. Nearly constant ionic strength value, needed during titration, is secured by addition of a basal electrolyte; see Figure 2.

One can also refer to the formulas [23] and [24]. From Equation [23], within the intervals d, c, and b (Table 2) one obtains the relations:

$$(V_b^\bullet + V) \cdot 10^{ph} = (K_2^*)^{-1} \cdot (V_c^\bullet - V) \qquad [30b]$$

TABLE 4
Gran functions related to System II (see Appendix B) at $C_0 = 0$ in Equation [25]

Sequence of operations $a \rightarrow b$ and $d \rightarrow c$		
No.	pH interval (presupposed)	Function of Gran type
a	$pH > pK_2+\Delta$	$(V_0 + V) \cdot 10^{ph} = C/K_W^* \cdot (V_a - V)$
b	$pK_2 - \Delta < pH \approx pK_2$	$(V - V_a) \cdot 10^{ph} = (K_2^*)^{-1} \cdot (V_b - V)$
c	$pK_1 - \Delta \leq pH \leq pK_1+\Delta$	$(V_d - V) \cdot 10^{-ph} = K_1^* \cdot (V - V_c)$
d	$pH < pK_1-\Delta$	$(V_0 + V) \cdot 10^{-ph} = \gamma \cdot C \cdot (V - V_d)$
Relations		$V_d = V_{eq2} + V_{eq3}$, $V_c = V_b = V_{eq2}/2 + V_{eq3}$, $V_a = V_{eq3}$

$$(V_d^{\bullet} - V) \cdot 10^{-ph} = K_1^* \cdot (V - V_c^{\bullet}) \qquad [30c]$$

$$(V_0 + V) \cdot 10^{-ph} = \gamma \cdot C \cdot (V - V_d^{\bullet}) \qquad [30d]$$

where:

$$V_d^{\bullet} = V_d = V_{eq1} + V_{eq2},\ V_c^{\bullet} = V_{eq2}/2 - (C_0/C) \cdot V_0,$$
$$V_b^{\bullet} = V_{eq1} + 2 \cdot (C_0/C) \cdot V_0 \qquad [31]$$

(Compare with Table 3). The values for V_{eq1}, V_{eq2}, and $(C_0/C){\cdot}V_0$ (and then C_0) cannot be determined simultaneously, owing to the fact that the corresponding determinant equals zero, i.e.,

$$\begin{vmatrix} 1 & 1 & 0 \\ 0 & 0.5 & -1 \\ 1 & 0 & 2 \end{vmatrix} = 0$$

From Equation [23], within the intervals a, b, c, and d (Table 2), one obtains the relations:

$$(V_0 + V) \cdot 10^{ph} = \frac{C}{K_W^*} \cdot (V_a^{\bullet} - V) \qquad [32a]$$

$$(V - V_a^{\bullet}) \cdot 10^{ph} = (K_2^*)^{-1} \cdot (V_b^{\bullet} - V) \qquad [32b]$$

$$(V_d^{\bullet} - V) \cdot 10^{-ph} = K_1^* \cdot (V - V_c^{\bullet}) \qquad [32c]$$

$$(V_0 + V) \cdot 10^{-ph} = \gamma \cdot C \cdot (V - V_d^{\bullet}) \qquad [32d]$$

where:

$$V_a^{\bullet} = V_{eq3} - 2 \cdot (C_0/C) \cdot V_0;\ V_b^{\bullet} = V_c^{\bullet} = V_{eq2}/2 + V_{eq3}$$
$$- (C_0/C) \cdot V_0;\ V_d^{\bullet} = V_d = V_{eq2} + V_{eq3} \qquad [33]$$

The related determinant also equals zero

$$\begin{vmatrix} 0 & 1 & -2 \\ 0.5 & 1 & -1 \\ 1 & 1 & 0 \end{vmatrix} = 0$$

i.e., V_{eq2}, V_{eq3}, and $(C_0/C){\cdot}V_0$ cannot be determined simultaneously, as well.

Comparison of the formulas [31] and [33] with the relationships given at the bottom of Tables 3 and 4 leads to the expected conclusion that $V_x^{\bullet} = V_x$ (x = d, c, b or d, c, b, a) at $C_0 = 0$, i.e., in the absence of CO_2 in D. Moreover, the presence of free CO_2 in D does not affect the results of analyses made in the interval d, i.e., $V_d^{\bullet} = V_d$ at $C_0 \geq 0$ in d – for both Systems I and II.

As results from Figure 2(a), ionic strength value

$$I = 0.5 \cdot ([H^+] + [OH^-] + [Na^+] + \left[HCO_3^-\right]$$
$$+ 4 \cdot [CO_3^{-2}] + [Cl^-]) \qquad [34]$$

varies significantly during the titration of System I with HCl (see Equation [20]). In order to flatten relative changes in I values, addition of a basal electrolyte (NaCl or KCl) is required (Figure 2(b)). One can note that the curves I = I(V) consist of rectilinear segments intersecting at $V(1) = C_2V_0/C$, and $V(2) = (C_1 + 2C_2)V_0/C$. Similar remarks apply to System II titrated with HCl.

TABLE 5
Formulas for V_{eq1}, V_{eq2}, K_1*, K_2*, γ found for the sequence d → c → b for System I; see Table 3

x	V_x	V_{eq1}	V_{eq2}	K_1*	K_2*	γ
b	V_b	—	$-2B_b/A_b$	—	$-1/A_b$	—
c	V_c	$-B_d/A_d + 2B_c/A_c$	$-2B_c/A_c$	A_c	—	—
d	V_d	—	—	—	—	A_d/C

Calculation Procedure

The functions in Tables 3 and 4 can be presented in unified form of the linear regression equation

$$y_j^x = A_x \cdot V_j^x + B_x + \varepsilon_j^x (j = 1, \ldots, N_x; x = a, b, c, d) \quad [35]$$

Then applying the LS principle to the sum of squares

$$SS(x) = \sum_{j=1}^{N_x} \left(\varepsilon_j^x\right)^2 \qquad [36]$$

where j covers the points $\{(V_j^x, ph_j^x) \mid j = 1, \ldots, N_x\}$ related to x-th subset (x = a, b, c, d), we get the formulas:

$$A_x = \frac{N_x \cdot \sum_x V_j^x y_j^x - \sum_x V_j^x \cdot \sum_x y_j^x}{N_x \cdot \sum_x (V_j^x)^2 - (\sum_x V_j^x)^2},$$
$$B_x = \frac{\sum_x (V_j^x)^2 \cdot \sum_x y_j^x - \sum_x V_j^x \cdot \sum_x V_j^x y_j^x}{N_x \cdot \sum_x (V_j^x)^2 - (\sum_x V_j^x)^2} \qquad [37]$$

where the sum Σ_x covers the points taken from x-th interval, V_j^x is the j-th V value taken from the x-th interval.

As stated above, the calculation of the parameters is possible in a defined sequence of operations. For example, the sequence d → c → b applied in Table 3 means that V_d value, obtained according to LS for the data $\{(V_j^d, ph_j^d) \mid j = 1, \ldots, N_d\}$ composing the subset of the points taken from interval d (Figure 1), is inserted into the left side of the relation referring to interval c and LS is applied to the data $\{(V_j^c, ph_j^c) \mid j = 1, \ldots, N_c\}$ from interval c. Numerical values for $V_d = -B_d/A_d$ and $V_c = -B_c/A_c$ enable calculating $V_b = 2B_c/A_c - B_b/A_d$ value, inserted in the left side of the relation referring to interval b. Applying LS again to the data $\{(V_j^b, ph_j^b) \mid j = 1, \ldots, N_b\}$ from interval b, one can calculate V_b for comparative purposes. All the formulas referring to parameters for Systems I and II are presented in Tables 5 and 6, respectively.

Another approach is also possible. In order to avoid diversities in the equivalence volumes thus obtained, one could insert the V_{eq1} and V_{eq2} values into the relation for K_2^* :

$$pK_{2j}^* = ph_j^b + \log \frac{V_b + V_j^b}{V_c - V_j^b} \qquad [38]$$

TABLE 6
Formulas for V_{eq2}, V_{eq3}, $K_1{}^*$, $K_2{}^*$, $K_W{}^*$, γ for sequences a → b and d → c, for System II; see Table 4

x	V_x	V_{eq2}	V_{eq3}	$K_1{}^*$	$K_2{}^*$	γ	$K_W{}^*$
a	V_a	—	$-B_a/A_a$	—	—	—	$-C/A_a$
b	V_b	$2B_a/A_a - 2B_b/A_b$	—	—	$-1/A_b$	—	—
c	V_c	$-B_d/A_d + 2B_c/A_c$	$-2B_c/A_c + B_d/A_d$	A_c	—	—	—
d	V_d	—	—	—	—	A_d/C	—

obtained from Table 3, no. b; then we get $pK_2^* = (N_b)^{-1} \cdot \sum_{j=1}^{N_b} pK_{2j}^*$ and $pK_2 = pK_2^* + \log\gamma$. Similarly, referring to System II, one can evaluate $pK_{1j}{}^*$ at j-th point $\{(V_j^c, ph_j^c) \mid j = 1, \ldots, N_c\}$ of the interval c, applying the formula

$$pK_{1j}^* = ph_j^c + \log\frac{V_j^c - V_c}{V_d - V_j^c} \tag{39}$$

obtained on the basis of the relation in Table 4, no. c. On the same principle, from Table 4, no. a we get

$$pK_{Wj}^* = ph_j^a + \log\frac{V_0 + V_j^a}{V_a - V_j^a} - \log C \tag{40}$$

SIMULATED DATA

In order to evaluate the errors involved with this method and choose the best a priori set of points $\{(V_j^x, ph_j^x) \mid j = 1, \ldots, N_x\}$ that enables getting the V_{eq1} and V_{eq2} values with highest accuracy possible, one can use the simulation procedure applied to the corresponding x-intervals x = a, b, c, d (see Table 4), based on Equations [18] or [20] and $\gamma = 1$ is assumed, i.e., under the simplifying assumption ph ≅ pH. The linearizing approaches used in the Gran method are valid only for the data distant from the equivalence points (Pankow, 1991).

For comparative purposes, all numerical data in this section were obtained at $(V_0, C_1, C_2, C) = (4, 0.005, 0.02, 0.1)$ for System I and $(V_0, C_2, C_3, C) = (4, 0.005, 0.02, 0.1)$ for System II; $pK_1 = 6.3$, $pK_2 = 10.1$ for H_2CO_3, $pK_W = 14.0$ for water. Then the theoretical values referring to equivalence volumes are:

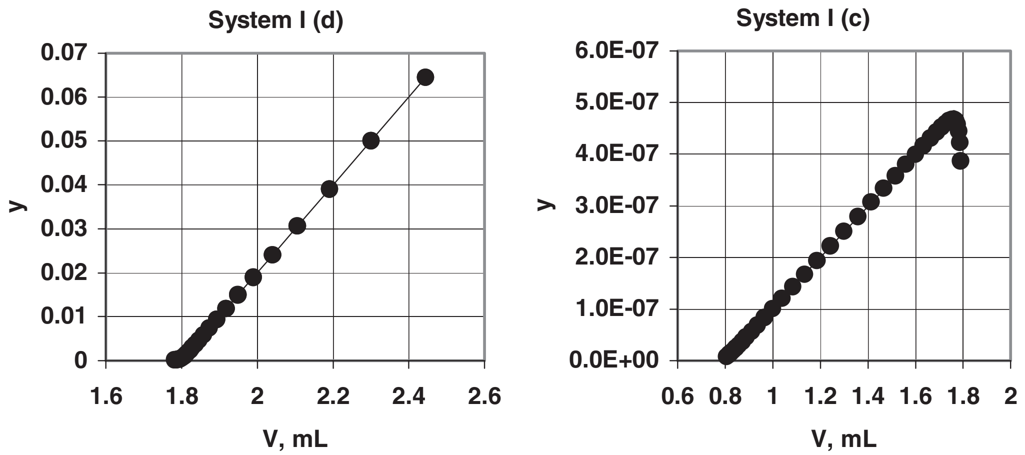
- $V_{eq1} = 0.005 \cdot 4/0.1 = 0.2$, $V_{eq2} = 2 \cdot 0.02 \cdot 4/0.1 = 1.6$, $V_{eq1} + V_{eq2} = 0.2 + 1.6 = 1.8$, $V_{eq2}/2 = 0.8$ for System I
- $V_{eq2} = 2 \cdot 0.005 \cdot 4/0.1 = 0.4$, $V_{eq3} = 0.02 \cdot 4/0.1 = 0.8$, $V_{eq2} + V_{eq3} = 0.4 + 0.8 = 1.2$, $V_{eq2}/2 + V_{eq3} = 0.2 + 0.8 = 1.0$ for System II

The simulated titration curves, obtained on the basis of Equations [20] (for System I) and [23] (for System II) are then the same as in Figure 1. For both curves, the step $\Delta pH = pH^x{}_{j+1} - pH^x{}_j = 0.1$ was applied. The analytical (V_{eq1}, V_{eq2}) (for System I) or (V_{eq2}, V_{eq3}) (for System II) and physicochemical $(\gamma, K_1{}^*, K_2{}^*, K_W{}^*)$ data are obtained on the basis of preselected points $\{(V_j^x, ph_j^x) \mid j = 1, \ldots, N_x\}$ chosen from x-th interval. The pH intervals chosen for calculations are denoted as $<pH^x_{\min}, pH^x_{\max}>$, where $pH^x_{\min}$ and $pH^x_{\max}$ are lower and upper pH limits referring to the x-th interval.

The calculations in System I started from the interval d. The $V_d = V_{eq1} + V_{eq2}$ value, obtained within the most favorable pH interval $<ph^d_{\min}, ph^d_{\max}>$ in d, is recommended to calculate the y_j^c-values for pH_j taken from interval c (Table 3), $y_j^c = (V_d - V_j^c) \cdot 10^{-ph_j^c}$. As results from the data in Table 7 (no. 4), the most favorable (from analytical viewpoint) is the value $V_d = 1.7996$ (closest to 1.8). On the basis of calculations made for different pH intervals $<ph^c_{\min}, ph^c_{\max}>$, the values for $V_c = V_{eq2}/2$ are obtained. The V_d and V_c values are the basis for calculation of V_{eq1} and V_{eq2}. For example, from $V_d = 1.7996$

TABLE 7
Results obtained for System I, intervals d, c

No.	$<pH^x_{\min}, pH^x_{\max}>$	N_x	V_x	γ	$pK_1{}^*$	A_x	B_x
			$x = d$, $V_d = V_{eq1} + V_{eq2}$				
1	< 2.0, 4.6 >	27	1,7949	0,9861	—	0,09861	−0.17905
2	< 2.0, 4.0 >	21	1,7982	0,9957	—	0,09957	−0.17700
3	< 2.0, 3.6 >	17	1,7991	0,9980	—	0,09980	−0.17955
4	< 2.0, 3.1 >	12	1,7996	0,9992	—	0,09992	−0.17982
			$x = c$, $V_c = V_{eq2}/2$				
5	< 4.4, 8.1 >	38	0.7833	—	6.3279	4.6995×10^{-7}	-3.6811×10^{-7}
6	< 4.4, 8.6 >	43	0.7819	—	6.3287	4.6915×10^{-7}	-3.6685×10^{-7}
7	< 4.1, 8.1 >	41	0.7500	—	6.3843	4.1279×10^{-7}	-3.0961×10^{-7}
8	< 4.9, 7.6 >	28	0.7949	—	6.3069	4.9332×10^{-7}	-3.9214×10^{-7}
9	< 4.9, 9.6 >	48	0.7451	—	6.3402	4.5693×10^{-7}	-3.4044×10^{-7}



(a) (b)

FIG. 7. Some points $\{(V^x_j, ph^x_j)\ |j = 1, \ldots, N_x\}$ (x = d, c) and the lines (Equation [35]) drawn for System I in pH intervals taken from Table 7: (a) no. 4, line $y^d = 0.09992 \cdot V^d - 0.17982$; (b) no. 9, line $y^c = (4.9253 \cdot V - 3.9091) \times 10^{-7}$. The value $V_d = 1{,}7996$ was taken (Table 7, no. 4) to calculate y^c values in interval c.

and $V_c = 0.7947$ (Table 7, nos. 4 and 10) we calculate $V_{eq2} = 2V_c = 1.5894$ and $V_{eq1} = V_d - 2V_c = 0.2102$; see also Table 5. Both values should be compared with the expected ones, 1.6 and 0.2, respectively; for V_{eq1}, this is an error of around 5%.

From an experimental viewpoint, the "most favorable" values and the set of experimental points applied to get them are unknown, of course. However, inspection of tables and figures obtained from simulated titrations enables to us to formulate some hints for securing the best possible experimental results (optimization a priori) for the analytical and physicochemical data. In particular, the data specified in Table 7 enable stating that ph^d_j in the set $\{(V^d_j, ph^d_j)\ |j = 1, \ldots, N_d\}$ should be distant from the pK_1 value; it enables getting accurate values for V_d and γ. Accurate values for V_c and $pK_1{}^*$ are obtainable when ph^c_j in the set $\{(V^c_j, ph^c_j)\ |j = 1, \ldots, N_c\}$ is within the interval $pK_1 - \Delta \le pH \le pK_1 + \Delta$ indicated in Table 3.

In Figure 7, some points not belonging to the intervals required are also applied. This way, the course of the lines outside the linear range is also marked; this refers to lower V^d_j values in Figure 7(a) and higher V^c_j values in Figure 7(b). Of course, such points should not be taken into account for the needs of Equation [35].

$V_b = V_{eq1} = V_d - 2V_c$ (see above) could be applied in Table 3 (no. b) in order to find V_c, and thus check (indirectly) the validity of V_{eq1} and V_{eq2} obtained in the intervals d and c. Instead, one can apply another option, expressed by Equation [38], i.e., to find $pK_2{}^*$ on the basis of the points $\{(V^b_j, ph^b_j)\ |j = 1, \ldots, N_b\}$. This option is presented in Figure 8. Mean value for $pK_2{}^* = 10.1031$, taken from V interval $< 0.0, 0.6 >$, corresponding to pH interval $< 9.5, 10.6 >$, is very close to the expected value 10.1.

The $pK_1{}^*$ values found in interval c (Table 7, nos. 5–10) are close to the expected value, 6.3. As regards γ, worse (more distant from 1) values are obtained for the set of points with pH^d values approaching the pK_1 value (Table 7, no. 1).

The exemplary results obtained from simulations done on System II are presented in Tables 8 and 9 and Figure 9. Inspection of the results collected in Table 7 leads to the following conclusions.

The points (V_j, pH_j) drawn on Figure 9(a), refer to pH interval $< 12.3, 10.5 >$. From inspection of Table 8 we see that the $V_a = V_{eq3}$ values exceed the expected value 0.8 mL by approximately 0.4–0.9%. The V_a value, when applied in the formula related to interval b (see Table 8) affects, to some extent, the error in determination of V_b value, although the reverse effect is observed, i.e., the errors in interval b are smaller than ones in interval a. The error in V_a decreases with growth of the $pH^a_{inf} - pK_2$ value. From Table 8 we see that the change in

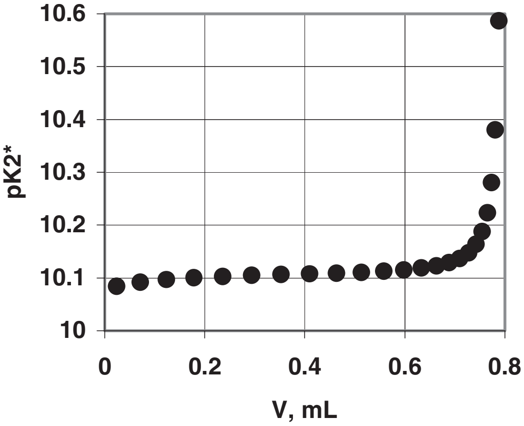
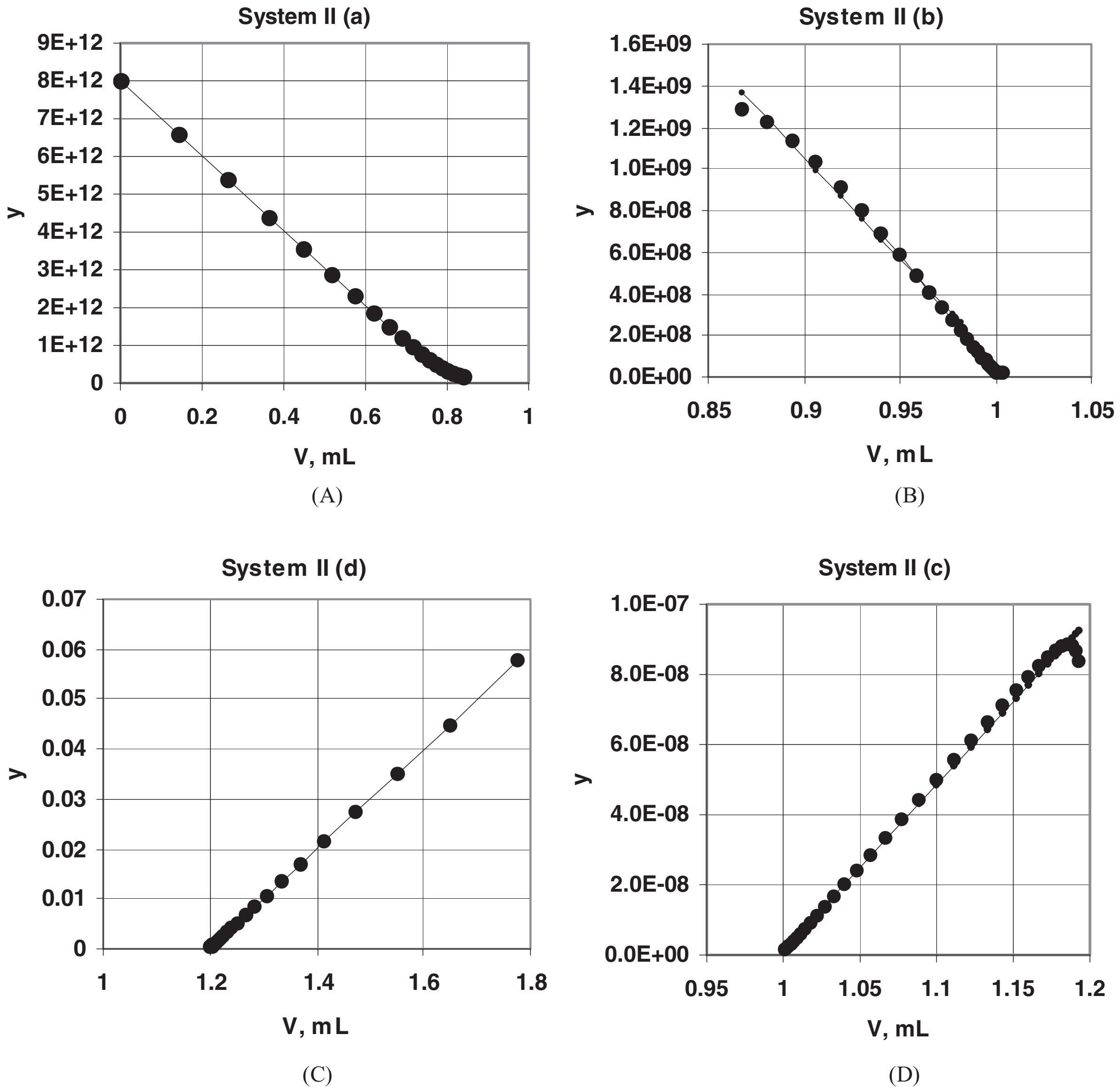


FIG. 8. $pK_2{}^*$ vs. V relationship, formulated in the basis of Equation [38] and the data specified in Table 8 (nos. 4, 10).



(A) (B)

(C) (D)

FIG. 9. Points and the lines plotted for pH intervals specified in Table 9 and referring principally to pH intervals: (A) System II, a; (B) System II, b; (C) System II, d; (D) System II, c.

pH interval affects only to a small degree the pK_W value, which is very close to 14.0. As regards the pK_2* value, it differs by approximately 0.5 unit from 10.1, except the case where $ph^b_{sup}$is close to 10.1. Analysis of the points $\{(V^a_j, ph^a_j)\ |j = 1, \ldots, N_a\}$ and $\{(V^b_j, pH^b_j)\ |j = 1, \ldots, N_b\}$ related to pH intervals a and b may provide accurate values only for pK_W (under the assumption that C_3 significantly exceeds the C_2 value). However, one should take into account that high pH values refer to the nonlinear part of the characteristics of the glass electrode and the results obtained in experimental pH titration should be considered with greater care, especially when the electrode is calibrated beforehand against buffers not spanning the pH range covered by the experimental points from intervals a and b.

In Figures 9(b) and 9(d) the points that do not belong to the (recti)linear parts of the related curves were intentionally included. As we see, even in the case represented by Figure 9(d) (Table 8, no. 16), the line including such points does not represent a dramatic deterioration of the results obtained for V_c and pK_1*; see also Table 8 (no. 15) and Table 9, although the results significantly fall behind the residual results in this group, particularly those based on the points belonging to the rectilinear part of the curve. This regularity results from the fact that the points with small(er) y-values are "concurrent" on the related plots.

The points from interval d should be distant from pK_1. The pH interval b chosen for calculations affects the sum $V_{eq1}+V_{eq2}$

TABLE 8
Results obtained for System II, intervals: a, b and d, c

No.	$<pH^x_{min}, pH^x_{max}>$	N_x	V_x	γ	$pK_1{}^*$	$pK_2{}^*$	$pK_W{}^*$
			$x = a, V_a = V_{eq3}$				
1	< 11.5, 12.3 >	9	0.8072	—	—	—	13.9962
2	< 11.7, 12.3 >	7	0.8056	—	—	—	13.9974
3	< 11.9, 12.3 >	5	0.8044	—	—	—	13.9982
4	< 12.1, 12.3 >	3	0.8034	—	—	—	13.9988
			$x = b, V_b = V_{eq2}/2 + V_{eq3}$				
5	< 9.1, 9.9 >	9	1.0022	—	—	10.0447	—
6	< 9.1, 9.7 >	7	1.0014	—	—	10.0554	—
7	< 9.1, 10.1 >	11	1.0041	—	—	10.0250	—
8	< 9.1, 10.3 >	13	1.0085	—	—	9.9877	—
9	< 8.1, 9.7 >	17	1.0019	—	—	10.0492	—
10	< 8.5, 9.7 >	13	1.0013	—	—	10.0561	—
			$x = d, V_{eq2} + V_{eq3}$				
11	< 2.0, 4.0 >	21	1.1997	0.9990	—	—	—
12	< 2.0, 4.6 >	27	1.1990	0.9970	—	—	—
13	< 2.0, 5.1 >	32	1.1975	0.9921	—	—	—
14	< 2.0, 5.5 >	36	1.1947	0.9823	—	—	—
			$x = c, V_c = V_{eq2}/2 + V_{eq3}$				
15	< 4.4, 8.1 >	38	0.9843	—	6.4318	—	—
16	< 4.9, 8.1 >	33	0.9972	—	6.3256	—	—
17	< 4.9, 8.6 >	38	0.9967	—	6.3270	—	
18	< 4.9, 7.6 >	28	0.9965	—	6.3276	—	—
19	< 4.9, 7.2 >	24	0.9949	—	6.3322	—	—
20	< 7.1, 7.8 >	8	0.9989	—	6.3163	—	—

to a lesser extent; this sum can be determined with a good accuracy. More accurate γ, $pK_1{}^*$, and $pK_2{}^*$ values correlate with more accurate V_{eq1} and V_{eq2} values.

The sequence a → b in Table 8 could provide a reasonable value for V_{eq3} only when the inequality $pH > pK_2 + \Delta$ is represented by a sound number N_a of experimental points $\{(V_j^a, ph_j^a)\ j = 1, \dots, N_a\}$ from the a-th interval. This condition is fulfilled only when the initial solution is sufficiently basic, i.e., it involves a great excess of NaOH. However, the pH measurements in this interval are affected by systematic errors, provided that the electrode was standardized only within a region of lower pH values. Moreover, the error in V_{eq3} brought from interval a unfavorably affects the result for V_{eq2} (the sum $V_b = V_{eq2}/2 + V_{eq3}$ is obtained in interval b). Moreover, more basic solution has higher ionic strength, which makes further, essential troubles concerning uncertainty in the activity coefficient (γ) value, if ionic strength values differ within particular pH intervals.

TABLE 9
Some details for Figure 9

Fig.	Interval	pH interval for points	pH interval for lines	A_x	B_x	Line no.
9(a)	a	< 10.5, 12.3 >	< 11.5, 12.3 >	$A_a = -0.99124 \times 10^{12}$	$B_a = 0.80016 \times 10^{12}$	
9(b)	b	< 7.9, 10.3 >	< 8.7, 9.7 >	$A_b = -1.14071 \times 10^{10}$	$B_b = 1.14208 \times 10^{10}$	1
			< 9.1, 10.3 >	$A_b = -0.97197 \times 10^{10}$	$B_b = 0.98020 \times 10^{10}$	2
9(c)	d	< 2.0, 4.4 >	< 2.0, 4.0 >	$A_d = 0.099904$	$B_d = -0.119849$	
9(d)	c	< 4.4, 8.1 >	< 4.9, 7.2 >	$A_c = 4.65318 \times 10^{-7}$	$B_c = -4.62928 \times 10^{-7}$	1
			< 4.4, 8.1 >	$A_c = 3.69978 \times 10^{-7}$	$B_c = -3.64177 \times 10^{-7}$	2

The V_{eq2} value obtained from interval b for System I (Table 4) can be compared with the value found from the data for intervals d and c. Moreover, it enables evaluating K_2^* and then K_2.

All the data presented in Tables 7–9 were obtained at error-free values for V and ph. Then they can be perceived as an approximation of results $\{(V_j^x, ph_j^x) \mid j = 1, \ldots, N_x\}$ obtained from experimental titrations. As we see, error-free V and pH measurements do not assure error-free values of the parameters determined. There is an impassable boundary inherent in the model applied. Nonetheless, the model is the best of all possible models in this respect.

TOTAL ALKALINITY

Alkalinity is involved with inorganic and organic species, e.g., humic and fulvic acids. The latter acids are gradually degraded, with formation of CO_2 as one of the final products. The new concept of total alkalinity (TAL), presented recently in this journal (Asuero and Michałowski, 2011), refers to monophase (liquid) acid-base systems. In order to "homogenize" mono- and polyprotic acids and bases, particularly ones with undefined composition, carbonate species, particularly fulvic acids and their soluble complexes with metal ions, the Simms constants were introduced.

The TAL concept was introduced by consideration of the monophase D+T system with $M_{m_k}H_{n_k-m_k}L_{(k)}(C_{0k},\ k = 1,\ldots,\ P)$ + $H_{n_k+m_k}L_{(k)}B_{m_k}$ $(C_{0k},\ k = P+1,\ldots,R)$ + $Me_{(k)}(OH)_{u_k-m_k}B_{m_k}(C_{0k},\ k = R+1, \ldots, Q)$ + HB (C_a) + MOH (C_b) solution as D (V_0 mL) titrated with V mL of C mol/L HB as T. Assuming that no (soluble and/or insoluble) complexes are formed between $Me_{(k)}^{+u_k}$ and $H_jL_{(k)}^{+j-n_k}$ species, and the species do not participate except in acid-base reactions the quantity denoted as A and expressed as follows

$$A = \sum_{k=1}^{P} (q_k + m_k - n_k) \cdot C_{0k} + \sum_{k=P+1}^{R} (q_k - m_k - n_k) \cdot C_{0k} + \sum_{k=R+1}^{Q} (u_k - m_k) \cdot C_{0k} + \Delta \qquad [41]$$

$$\Omega = \sum_{k=1}^{Q} q_k \qquad [42]$$

has been introduced; q_k denotes maximal number of protons attached to $L_{(k)}^{-n_k}(k = 1,\ldots, R)$ or maximal number of OH^- ions attached to $Me_{(k)}^{+u_k}(k = R + 1, \ldots, Q)$. The parameters: A (Equation [41]) and Ω (Equation [42]) are involved in the relation

$$CV/V_0 = A + (1 + V/V_0) \cdot \alpha - \sum_{i=1}^{\Omega} C_{0i} \cdot (1 + 10^{-ph}/g_i^*)^{-1} \qquad [43]$$

obtained from juxtaposition of charge and concentration balances related to the system in question.

Within the pH range covered by the points $\{(V_j, ph_j) \mid j = 1, \ldots, N\}$ obtained from pH titration carried out with the use of HCl (C) as T, only a limited part of acid-base species exists in the system at measurable concentrations; other species can be then omitted in quantitative considerations. It is the basis for further simplifications made in the related formulas.

Parameter A (Equation [41]) in Equation [43] involving initial concentrations as constant parameters referring to the composition of D (before titration with T) will be called total alkalinity, A = TAL; Ω (Equation [42]) is the pre-assumed number of all proto- and hydroxo-complexes in the system considered. However, within the pH range covered by titration points $\{(V_j, ph_j) \mid j = 1, \ldots, N\}$, only a part of them participate in acid-base equilibria to a measurable degree. In this case, only a limited part of the components is involved in the sum on the right side of Equation [41]. Then putting Λ for Ω (where $\Lambda \leq \Omega$) in Equation [43], we get

$$CV/V_0 = A + (1 + V/V_0) \cdot \alpha - \sum_{i=1}^{\Lambda} C_{0i} \cdot (1 + 10^{-ph}/g_i^*)^{-1} \qquad [44]$$

The approach to total alkalinity based on Equation [44] (A = TAL) is dissimilar to any other known from the literature. The related model involves $1 + 2 \cdot \Lambda$ parameters: A and the set of pairs $\{(C_{0i}, g_i^*) \mid i = 1, \ldots, \Lambda\}$. The parameters involved in Equation [44] are found according to the curve-fitting method, applied to the set of experimental points $\{(V_j, ph_j) \mid j = 1, \ldots, N\}$, and realizable with the use of an iterative computer program. It should necessarily be noted again (compare with Tables 3 and 4) that activity, h (not concentration, $[H^+]$), of hydrogen ions is involved in Equation [44]; it is one of the advantages of the method proposed. It should also be noted that the component $(1+V/V_0) \cdot \alpha$ on the left side of Equation [44] is not significant at the beginning of the titration; its significance grows at the end of the titration.

The iteration procedure should start with smaller number of $C_{0i} \cdot (1 + 10^{-ph}/g_i^*)^{-1}$ terms in Equation [44]. For example, we start with Λ = 2, referring to carbonate species (q = n = 2) only. To improve the fitting, next terms of this kind are added subsequently. Note that the sum in Equation [44] consists of positive components, in principle. After subsequent additions, the A approximates its real value. The approximation is terminated when, e.g., $C_{0,i+1} < 0$ appears in the subsequent iterative model. In the iteration procedure, minimal value for the sum of squares

$$SS = \sum_{j=1}^{N} \varepsilon_j^2 \qquad [45]$$

referring to the regression equation

$$CV_j/V_0 - (1 + V_j/V_0) \cdot \alpha_j = A - \sum_{i=1}^{\Lambda} C_{0i} \cdot (1 + 10^{-ph_j}/g_i^*)^{-1} + \varepsilon_j \qquad [46]$$

is searched. Subsequent additions of the terms having similar mathematical form are very advantageous from the viewpoint of the iteration procedure.

APPLICATION OF PRE-DOSE IN TAL

In order to cover a wider range of pH values during the titration with HB (C), one can apply a pre-dose of MOH in the stage of titrand (D) preparation.

Let the sample tested, of volume V_0, with $M_{m_k}H_{n_k-m_k}L_{(k)}(C_{0k},\ k = 1, \dots, P) + H_{n_k+m_k}L_{(k)}B_{m_k}(C_{0k}, k = P + 1, \dots, R) + Me_{(k)}(OH)_{n_k-m_k}B_{m_k}(C_{0k}, k = R + 1, \dots, Q)$ + HB (C_a) + MOH (C_b) be treated with a pre-dose V_p of MOH (C_p) and then the volume V_0+V_p of the mixture, considered as titrand D, be titrated with V mL HB (C) as T added in increments ΔV during pH titration, and the points $\{(V_j, ph_j) \mid j = 1, \dots, N\}$ are registered; $V_j = (j–1)\cdot\Delta V$. Applying the derivation procedure (Appendix C) similar to the one presented in (Asuero and Michałowski, 2011), we get the relation

$$(C \cdot V - C_p \cdot V_p)/V_0 = A + (V_0 + V_p + V) \cdot \alpha/V_0 - \sum_{i=1}^{\Lambda} C_{0i} \cdot (1 + 10^{-ph}/g_i^*)^{-1} \quad [47]$$

Referring to the case where V_0 mL of $NaHCO_3$ (C_1) + Na_2CO_3 (C_2) is treated with V_p mL of MOH (C_p) as pre-dose and then titrated with V mL of HB (C), we get the relation

$$(CV - C_pV_p)/V_0 = A + (V_0 + V_p + V) \cdot \alpha/V_0 - (2 - \bar{n}) \cdot (C_1 + C_2) \quad [48]$$

where $A = CA = C_1 + 2C_2$.

CAM VERSUS TAL

Let us consider the titration of V_0 mL of D containing H_2CO_3 (C_0) + $NaHCO_3$ (C_1) + Na_2CO_3 (C_2) + NaOH (C_3) with V mL of C mol/L HCl. The related titration curve can be rearranged into the form

$$CV/V_0 - (1 + V/V_0) \cdot \alpha = A - (2 - \bar{n})(C_0 + C_1 + C_2) \quad [49]$$

where $A = C_1 + 2C_2 + C_3 \equiv 0\cdot C_0 + 1\cdot C_1 + 2\cdot C_2 + 1\cdot C_3$. Then one can consider particular cases of D systems: (a) H_2CO_3 (C_0) + $NaHCO_3$ (C_1); (b) $NaHCO_3$ (C_1) + Na_2CO_3 (C_2) (see Figure 10); (c) Na_2CO_3 (C_2) + NaOH (C_3).

System (a) refers to the case $C_2 = C_3 = 0$, $A = C_1 = 0\cdot C_0 + 1\cdot C_1 + 2\cdot 0 + 1\cdot 0$. For systems (b) and (c) we have: $A = 0\cdot C_0 + 1\cdot C_1 + 2\cdot C_2 + 1\cdot 0$, and $A = 0\cdot C_0 + 0\cdot C_1 + 2\cdot C_2 + 1\cdot C_3$. Comparing it with Equation [41], we have: Q = P = 3, $q_k = n_k = 2$ (k = 1,2,3), $m_1 = 0$, $m_2 = 1$, $m_3 = 2$, i.e., again $A = 0\cdot C_0 + 1\cdot C_1 + 2\cdot C_2 + 1\cdot C_b$, where $C_b = C_3$ ($C_a = 0$). The expression for $\bar{n}$ is the same for k = 1, 2, 3. The compatibility of the generalized formulation (for TAL) with its particular case (for CAM) is proven this way.

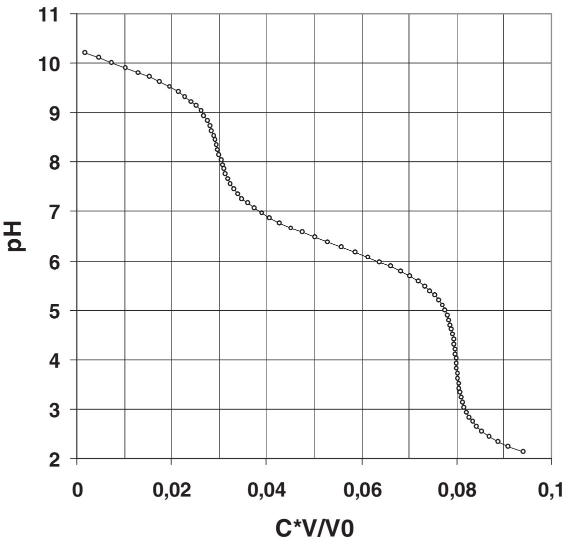


FIG. 10. pH vs. $C\cdot V/V_0$ relationship plotted for System I at (V_0, C_1, C_2, C) = (3, 0.02, 0.03, 0.1).

PROBABILISTIC APPROACH TO ACID-BASE EQUILIBRIA

Referring to the approach based on Simms constants one can consider, at first approximation, that the dissociation of H^+ ions from different protonation centers proceeds independently of each other and the dissociation from these sites can be perceived as a stochastic (random) process (proton uptake or release), categorized in terms of success/failure phenomenon/experiment. As such, it can be characterized by the probability distribution (compare with Onufriev et al., 2001). The degree of dissociation from the i-th site is

$$\alpha_i = \alpha_i(pH) = \frac{[L_{(i)}]}{C_i} = \frac{1}{[H^+]/g_i + 1} = \frac{1}{10^{pg_i - pH} + 1} = \frac{1}{e^{a\cdot(pg_i - pH)} + 1} \quad [50]$$

where $a = \ln 10$, and $\alpha_i = \alpha_i(pH)$ fulfils the properties of the (cumulative) distribution function:

$$\lim_{pH\to-\infty} \alpha_i(pH) = 0,\ \lim_{pH\to\infty} \alpha_i(pH) = 1,\ \alpha_i(pH) = \int_{-\infty}^{pH} f_i(x) \cdot dx \quad [51]$$

where $f_i(pH)$, x = pH, is the probability density function:

$$f_i(pH) = \frac{d\alpha_i(pH)}{dpH} \quad [52]$$

It implies that

$$f_i(pH) = a \cdot \frac{e^{a\cdot(pg_i - pH)}}{(e^{a\cdot(pg_i - pH)} + 1)^2} = a \cdot \alpha_i(pH) \cdot (1 - \alpha_i(pH)) \quad [53]$$

This model appears to have some similarities with the Fermi-Dirac distribution function (Van Zeghbroeck, 1996).

When individual titratable sites in a molecule interact with each other, their pH titration can be considerably more complex than that of an independent site described by the classical Henderson-Hasselbalch (H-H) equation, with sigmoidal shape of the related fragment of titration curve (see, e.g., Michałowski et al., 2010b). For more complex compounds, there are microscopic (intrinsic) dissociation constants, referring to a set of parallel reactions. For titration curve modeling, only "apparent" or "macroscopic" constants could be experimentally measured (Stoyanov and Righetti, 1999; Cohn and Edsall, 1943; Adair, 1925).

As was pertinently stated above, the approach with Simms constants involved (Equation [38]) is applicable to systems where the complexes were omitted or neglected. Inclusion of the complexes in considerations implies some disturbances in the model applied. In such instances, application of an approach with Hill empirical coefficient b (Weiss, 1997; Goutelle et al., 2008) involved in the term

$$\frac{e^{b(pK-pH)}}{e^{b(pK-pH)}+1} \qquad [54]$$

appears to be a reasonable choice in this matter. The b coefficient reflects the extent of co-operativity among multiple ligand binding sites and is appropriately sited in modeling ligand-receptor interactions (Søndergaard et al., 2008). The titration curves of individual sites in biomolecules, exemplified by fulvic acid, often have nonsigmoidal shapes due to interactions between sites within the molecule. The term "co-operativity" refers also to absorption phenomena (van Holde, 1985; Koopal et al., 2005).

OBJECTIONS ON ACCURACY

Errors involved with the Gran method applied to CA and Alk measurements were considered in different articles (Edmond, 1970; Hansson and Jagner, 1973). For example, the errors in accuracy of measurements made according to the Dyrssen approach (1965) reported by Edmond (1970) were ± 0·17% for Alk and ± 0·68% for CA, at 95% confidence limit. In Hansson and Jagner (1973), a modified approach has been applied. In Gieskes and Rogers (1973), accuracy of the method was estimated to be 0.5%. As stated in Bradshaw and Brewer (1988), the CA measurements were evaluated with an accuracy of approximately ± 0.1%. In the Gran methods for carbonate alkalinity measurements, good precision, e.g., 0.05–0.1% (Haraldsson et al., 1997) was usually attained, whereas the accuracy was usually not considered. The standard deviations within the range 1.45–6.7%, stated in Lahav et al. (2002), distinctly exceeded the errors in accuracy of 1–2% evidenced in a series of measurements.

Suspiciously good results for CA, measured according to the Gran method, do not withstand the possibilities resulting from simulated data, obtained at error-free values for V and pH values at each point (V_j, pH_j) of the pH titration curve. Note that an effect of ionic strength on the equilibrium constant values does not occur in simulated titrations either. It is obvious that the experimental results involving both variables should inevitably worsen the results for the parameters V_{eq1}, V_{eq2}, $K_1{}^*$ (K_1), $K_2{}^*$ (K_2), and γ or V_{eq2}, V_{eq3}, $K_1{}^*$ (K_1), $K_2{}^*$ (K_2), $K_W{}^*$ (K_W), and γ, obtained from real titrations. The parameters were calculated with use of the LS method. It should be noted that the least median squares was also applied for the Gran method (Ortiz-Fernández and Herrero-Gutiérrez, 1995).

FINAL COMMENTS

Carbon dioxide plays a fundamental role in governing the environmental processes on Earth. Environmental problems associated with emission of CO_2 due to burning of fossil fuel have been well recognized since the late 1960s. It justifies the examination of CO_2 exchange between atmosphere and water, in aerobic and anaerobic systems (Damasceno et al., 2007), and in close connection with geological and geothermal (Verma et al., 2010) phenomena.

An overview of a huge number of issues involved with the alkalinity concept in recent years testifies to the importance of the problem of alkalinity measurements and analysis of natural (lake, river, and sea) waters and soils. The simple and accurate determination of carbonate species is an important requirement in water purification, diagenetic modeling, oil field inorganic scale precipitation estimations, predicting the extent of acidification of lakes and rivers, as well as environmental and biological research (Gros and Nemarnik, 2007).

Different phytoplanktonic species may behave in diverse ways through variations in inorganic carbon levels, leading to different growth rates; this can have consequences for the structure of communities in marine ecosystems. Accurate measurements of the concentrations of inorganic carbon species in marine or other aquatic environments, e.g., coral reefs (Martz et al., 2006), can support a better understanding of these processes, especially at the enzymological level (Rigobello-Masini and Masini, 2001).

Acidic, metal-laden drainage from active and abandoned mines causes significant environmental and economic problems in coal and metal-mining districts worldwide. The alkalinity and acidity of the mine effluent and receiving water bodies are commonly measured or calculated to identify potential environmental effects and to plan appropriate treatment methods to remove metals and produce near-neutral pH effluents (Kirby and Cravotta, 2005b).

With increasing concerns about climate change and ocean acidification (Lueker et al., 2000; Wolf-Gladrow et al., 2007; Hoppe et al., 2010) there is a strong demand for computational tools that enable a quantitative description of the acid-base properties of natural waters. These tools are needed both from analytical and physicochemical viewpoints. The increased complexity of aquatic ecosystems in comparison with synthetic samples requires increased complexity of models used for the description of biogeochemical systems. The model required for the description of such systems should be sufficiently flexible to possibily examine more complex systems. The model should not be addressed to the analysis of indicated species whose physicochemical properties are more or less defined. It should be addressed to analyses of species with undefined composition and physicochemical acid-base properties, e.g., fulvic acids. Generally, these models are based on fitting the parameters of the related equation (or the set of equations) to experimental pH titration data (Hofmann et al., 2010; Asuero and Michałowski, 2011).

There are several publications that suggest alkalinity as an ideal parameter to monitor the anaerobic digestion process, as total alkalinity, partial alkalinity, the ratio of partial to total alkalinity, or the ratio of volatile fatty acids (VFA) to alkalinity (Ward and Hobbs, 2011). Total alkalinity is an important environmental indicator of the ability of the environment to buffer against acid rain (Andersen, 2002).

The CAM and TAL approaches suggested in this article differ substantially from the ones presented in earlier literature, exemplified by Morel and Hering (1993). The approaches to alkalinity presented hitherto in handbooks and other issues are very opaque and ambiguous; this problem was also raised in Asuero and Michałowski (2011).

The CAM approach was for mixtures $NaHCO_3 + Na_2CO_3$ (System I) and $Na_2CO_3 + NaOH$ (System II) titrated with HCl solution. The parameters of the related systems (and their extensions, also considered in this article) were calculated according to the LS method. The simulations discussed in latter parts of this article were used to determine error-free values for V and pH. On this basis, errors involved with the choice of pH intervals taken for calculations were considered.

The article refers also to total alkalinity, TAL (Asuero and Michałowski, 2011), and provides an extension of this method, based on addition of a pre-dose of standard NaOH solution into the sample tested. The parameters of the related function, where Simms constants are involved, were found according to iterative computer programs, e.g., MATLAB (Michałowski, 2011).

NOMENCLATURE

C_a	concentration of HB
CA	carbonate alkalinity
CAM	modified CA
C_b	concentration of MOH
D	titrand
$\Delta = C_b - C_a$	
LS	least squares method
T	titrant
TAL	total alkalinity
V	volume [mL] of T
V_0	volume [mL] of D

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APPENDIX A: DERIVATION OF FUNCTIONS RELATED TO SYSTEM I

From Equation [13] and Table 2 (no. b, $\bar{n} = \bar{n}_b$) we have, by turns:

$$\begin{aligned}
&0 = V + V_{eq1} - \frac{[H^+]}{[H^+] + K_2} \cdot (V_{eq1} + V_{eq2}/2)\\
&(V + V_{eq1})[H^+] + (V + V_{eq1})K_2 = (V_{eq1} + V_{eq2}/2)[H^+]\\
&(V + V_{eq1})K_2 = (V_{eq1} + V_{eq2}/2 - V - V_{eq1})[H^+]\\
&K_2 \cdot (V_{eq1} + V) = [H^+] \cdot (V_{eq2}/2 - V)\\
&(V_{eq1} + V) \cdot 10^{ph} = (K_2^*)^{-1} \cdot (V_{eq2}/2 - V)
\end{aligned}$$

From Equation [13] and Table 2 (no. c, $\bar{n} = \bar{n}_c$) we have, by turns:

$$\begin{aligned}
&0 = V + V_{eq1} - \frac{2[H^+] + K_1}{[H^+] + K_1} \cdot (V_{eq1} + V_{eq2}/2)\\
&(V + V_{eq1})([H^+] + K_1) = (2[H^+] + K_1) \cdot (V_{eq1} + V_{eq2}/2)\\
&(V_{eq1} + V_{eq2} - V) \cdot 10^{-ph} = K_1^* \cdot (V - V_{eq2}/2)
\end{aligned}$$

From Equation [13] and Table 2 (no. d, $\bar{n} = \bar{n}_d$) we have, by turns:

$$\begin{gathered}
(V_0 + V) \cdot [H^+]/C = V + V_{eq1} - 2 \cdot (V_{eq1} + V_{eq2}/2)\\
(V_0 + V) \cdot [H^+] = C \cdot (V - (V_{eq1} + V_{eq2}))\\
(V_0 + V) \cdot 10^{-ph} = \gamma \cdot C \cdot (V - (V_{eq1} + V_{eq2}))
\end{gathered}$$

APPENDIX B: DERIVATION OF FUNCTIONS RELATED TO SYSTEM II

From Equation [14] and Table 2 (No. a, $\bar{n} = \bar{n}_a$) we have, by turns:

$$\begin{gathered}
-\frac{K_W}{[H^+]} \cdot (V_0 + V) = C \cdot (V - V_{eq3})\\
\frac{K_W^*}{h} \cdot (V_0 + V) = C \cdot (V_{eq3} - V)\\
(V_0 + V) \cdot 10^{ph} = \frac{C}{K_W^*} \cdot (V_{eq3} - V)
\end{gathered}$$

From Equation [14] and Table 2 (no. b, $\bar{n} = \bar{n}_b$) we have, by turns:

$$\begin{aligned}
&0 = V - V_{eq3} - \frac{[H^+]}{[H^+] + K_2} \cdot V_{eq2}/2\\
&[H^+] \cdot (V - V_{eq3}) + (V - V_{eq3}) \cdot K_2 = [H^+] \cdot V_{eq2}/2\\
&(V - V_{eq3}) \cdot K_2 = [H^+] \cdot (V_{eq2}/2 + V_{eq3} - V)\\
&(V - V_{eq3}) \cdot 10^{ph} = (K_2^*)^{-1} \cdot (V_{eq2}/2 + V_{eq3} - V)
\end{aligned}$$

From Equation [14] and Table 2 (no. c, $\bar{n} = \bar{n}_c$) we have, by turns:

$$\begin{aligned}
&0 = V - V_{eq3} - \frac{2[H^+] + K_1}{[H^+] + K_1} \cdot V_{eq2}/2\\
&(V - V_{eq3}) \cdot [H^+] + (V - V_{eq3}) \cdot K_1\\
&\quad = V_{eq2} \cdot [H^+] + K_1 \cdot V_{eq2}/2
\end{aligned}$$

$$(V - (V_{eq2}/2 + V_{eq3})) \cdot K_1 = (V_{eq2} + V_{eq3} - V) \cdot [H^+]$$
$$(V_{eq2} + V_{eq3} - V) \cdot 10^{-ph} = K_1^* \cdot (V - (V_{eq2}/2 + V_{eq3}))$$

From Equation [14] and Table 2 (no. d, $\bar{n} = \bar{n}_d$) we have, by turns:

$$(V_0 + V) \cdot [H^+]/C = V - V_{eq3} - 2 \cdot V_{eq2}/2$$
$$(V_0 + V) \cdot 10^{-ph} = \gamma \cdot C \cdot (V - (V_{eq2} + V_{eq3}))$$

APPENDIX C: EQUATION FOR TITRATION CURVE WITH PRE-DOSE IN TAL

The equation for titration curve is obtained by addition the sides of charge balance

$$\alpha + \sum_{k=1}^{R}\sum_{j=0}^{q_k}(j - n_k) \cdot \left[H_jL_{(k)}^{+j-n_k}\right] + \sum_{k=R+1}^{Q}\sum_{j=0}^{q_k}(u_k - j) \times \left[Me_{(u)}(OH)_j^{+u_k-j}\right] + [M^+] - [B^-] = 0$$

and concentration balances

$$\frac{\sum_{k=1}^{P} m_kC_{0k}V_0 + C_bV_0 + C_pV_p}{V_0 + V_p + V} = [M^+]$$

$$[B^-] = \frac{\sum_{k=P+1}^{R} m_kC_{0k}V_0 + \sum_{k=R+1}^{Q} m_kC_{0k}V_0 + C_aV_0 + CV}{V_0 + V_p + V}$$

$$\sum_{k=1}^{P}\sum_{j=0}^{q_k} m_k[H_jL_{(k)}^{+j-n_k}] = \frac{\sum_{k=1}^{P} m_kC_{0k}V_0}{V_0 + V_p + V}$$

$$\frac{\sum_{k=P+1}^{R} m_kC_{0k}V_0}{V_0 + V_p + V} = \sum_{k=P+1}^{R}\sum_{j=0}^{q_k} m_k[H_jL_{(k)}^{+j-n_k}]$$

$$\frac{\sum_{k=R+1}^{Q} m_kC_{0k}V_0}{V_0 + V_p + V} = \sum_{k=R+1}^{Q}\sum_{j=0}^{q_k} m_k[Me_{(k)}(OH)_j^{+u_k-j}]$$

After cancellation of similar terms, we get, by turns,

$$\alpha + \sum_{k=1}^{P}\sum_{j=0}^{q_k}(j - n_k + m_k) \cdot [H_jL_{(k)}^{+j-n_k}] + \sum_{k=p+1}^{R}\sum_{j=0}^{q_k}(j - n_k - m_k) \cdot [H_jL_{(k)}^{+j-n_k}] + \sum_{k=R+1}^{Q}\sum_{j=0}^{q_k}(u_k - j - m_k) \cdot [Me_{(k)}(OH)_j^{+u_k-j}] + \frac{C_bV_0 + C_pV_p}{V_0 + V_p + V} = \frac{C_aV_0 + CV}{V_0 + V_p + V}$$

$$\alpha + \sum_{k=1}^{P}(\bar{n}_k - n_k + m_k) \cdot \frac{C_{0k}V_0}{V_0 + V_p + V} + \sum_{k=P+1}^{R}(\bar{n}_k - n_k - m_k) \cdot \frac{C_{0k}V_0}{V_0 + V_p + V} + \sum_{k=R+1}^{Q}(u_k - m_k - \bar{n}_k^{\bullet}) \cdot \frac{C_{0k}V_0}{V_0 + V_p + V} = \frac{C_aV_0 - C_bV_0 + CV - C_pV_p}{V_0 + V_p + V}$$

where

$$\bar{n}_k = \frac{\sum_{j=0}^{q_k} j \cdot [H_jL_{(k)}^{+j-n_k}]}{\sum_{j=0}^{q_k} [H_jL_{(k)}^{+j-n_k}]}$$

$$\bar{n}_k^{\bullet} = \frac{\sum_{i=0}^{r_k} i \cdot [Me_{(k)}(OH)_i^{+u_k-i}]}{\sum_{j=0}^{r_k} [Me_{(k)}(OH)_j^{+u_k-j}]}$$

Applying the equalities:

$$\bar{n}_k - n_k + m_k = -(q_k - \bar{n}_k) + q_k + m_k - n_k$$
$$\bar{n}_k - n_k - m_k = -(q_k - \bar{n}_k) + q_k - m_k - n_k$$
$$\Delta = C_b - C_a$$

we get, by turns,

$$\alpha - \sum_{k=1}^{P}(q_k - \bar{n}_k) \cdot \frac{C_{0k}V_0}{V_0 + V_p + V} + \sum_{k=1}^{P}(q_k + m_k - n_k) \times \frac{C_{0k}V_0}{V_0 + V_p + V} - \sum_{k=P+1}^{R}(q_k - \bar{n}_k) \cdot \frac{C_{0k}V_0}{V_0 + V_p + V} + \sum_{k=P+1}^{R}(q_k - m_k - n_k) \cdot \frac{C_{0k}V_0}{V_0 + V_p + V} - \sum_{k=R+1}^{Q}\bar{n}_k^{\bullet} \cdot \frac{C_{0k}V_0}{V_0 + V_p + V} + \sum_{k=R+1}^{Q}(u_k - m_k) \times \frac{C_{0k}V_0}{V_0 + V_p + V} = \frac{C \cdot V - \Delta \cdot V_0 - C_pV_p}{V_0 + V_p + V}$$

$$(V_0 + V_p + V) \cdot \alpha + \left(\sum_{k=1}^{P}(q_k + m_k - n_k) \cdot C_{0k} + \sum_{k=1}^{P}(q_k - m_k - n_k) \cdot C_{0k} + \sum_{k=1}^{P}(u_k - m_k) \cdot C_{0k} + \Delta\right) \times V_0 - \left(\sum_{k=1}^{R}(q_k - \bar{n}_k) \cdot C_{0k} + \sum_{k=R+1}^{Q}\bar{n}_k^{\bullet} \cdot C_{0k}\right) \times V_0 = C \cdot V - C_pV_p$$