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Modelling of acid-base titration curves of mineral assemblages

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Abstract: The modelling of acid-base titration curves of mineral assemblages was studied with respect to basic parameters of their surface sites to be obtained. The known modelling approaches, component additivity (CA) and generalized composite (GC), and three types of different assemblages (fucoidic sandstones, sedimentary rock-clay and bentonite-magnetite samples) were used. In contrary to GC-approach, application of which was without difficulties, the problem of CA-one consisted in the credibility and accessibility of the parameters characterizing the individual mineralogical components.

Keywords: Fucoidic sandstones, sedimentary clays, barrier materials, CA-approach, GC-approach

1 Introduction

The modelling of surface complexation sorption on mineral assemblages is often used, especially if the interaction of the radionuclides (RN) with the given minerals has to be described. For example, it is a case of modelling of their migration from a storage facility of radionuclide wastes through the barrier material type of bentonite, or through the rock surrounding this facility and consisting of different mineral assemblages. This process can be, in principle, explored using two methods, namely, by so-called component additivity (CA) and generalized composite (GC) approaches [1,2,3]. The first one (CA) is based on the assumption that the resulting sorption, adsorption or chemical properties of given assemblage are

additive functions of relative amounts or surface areas of all minerals. In a case of the GC-approach, it is supposed that the studied mineral mixture is characterized by the overall surface area value and the averaged sorption properties of all function groups (sites) presented. The modelling by CA-approach requires the constants of reactions (e.g., complexation, ion exchange, protonation and deprotonation) and parameters (e.g., surface area) characterizing the sorption of given components on individual minerals to be available from literature (see, e.g., [4]). In a case of GC-approach, the determination of over-all constants or other parameters, valid for the whole system, must be based on the evaluation of experimental data obtained for the given sample of the assemblage studied. At the first sight, the CA-approach seems to be preferable to the GC one, but it is often not possible to have access to all data needed, or one cannot ascertain whether the mineral components retain original surface chemical properties in a mixture of them.

Up to now, many articles devoted to these problems were published. For example, the modelling by CA-approach of the surface complexation and ion exchange of Pb(II) and Cd(II) was applied on natural soils [5], the comparison of both approaches were performed for the sorption of U(VI) on natural composite materials sampled from Colorado Naturita Site [6] and on sediments from F-Area Savannah River [7], sorption of Cr(VI) on goethite, kaolinite, montmorillonite etc. [8], or uptake of Zn(II) on sediment collected from an aquifer at Cape Cod, MA [1]. Further, it can be mentioned the application of CA-approach to the modelling of Cu(II) sorption on hydrous ferric oxide and kaolinite [9], Cd(II) on soil components [10], and Ni(II) on granitic materials [11]. Generally, the CA-approach seems to be favourable in the case of clays, clay rocks and soils, e.g., for the description of above mentioned sorption of Cu(II) [3], Cd(II) without complexation agent [10], Pb(II) + Cd(II) [1] and U(VI) [6,7]. Some differences between model results and experimental data were found in sorption of Zn(II) [1], Cr(VI) – which probably was concerned with its anionic form [8], and in a case of Ni(II) sorption on granitic materials [11].

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We did not find any article dealing with the application of CA-approach to the modelling of acid-base titration curves of mineral assemblages, which is necessary for the characterization of surface sites. Only the contribution, regarding this problem, was presented in the frame of our paper describing the results of the study addressing the characterization of uranium behaviour in the Ruprechtov Site (CZ) [12].

Therefore, the goals of this study are as follows:

- (i) to investigate the possibilities of the modelling of acid-base titration curves by CA-approach based on the mineralogical analyses of given assemblages and on the known parameter values characterizing the individual mineral components (e.g. taken from the RES³T database [4]);
- (ii) to compare the CA-approach results with experimental data;
- (iii) to use the CA-approach results as input data into the modelling using GC-approach with the aim to obtain the overall values of equilibrium constants and total concentrations of surface edge and/or layer sites, characterizing the given assemblage;
- (iv) to use the experimental data as input into the GC-approach code and to compare the obtained parameter values with those obtained above.

2 Theory

At first, it has to be mentioned that the mineral components contain at least two types of surface groups. The first type includes permanently charged functional groups created by ionic substitution within the crystal structure, namely, by isomorphic substitution of, e.g., Al^{3+} for Si^{4+} , creating a permanent negative charge on the mineral surface, which is compensated externally by cations. These sites are denoted as layer-sites (with symbol $\equiv\text{X}$). The second type, so called edge-sites, is formed on the edges of the surface structure (with symbol $\equiv\text{SOH}$). They have a pH-dependent charge which arises due to the “adsorption” of H^+ ions (the protonation proceeds approx. at $\text{pH} < 7$: $\equiv\text{SOH}^0 \rightarrow \equiv\text{SOH}_2^+$) or “desorption” of H^+ ions (the deprotonation proceeds approx. at $\text{pH} > 7$: $\equiv\text{SOH}^0 \rightarrow \equiv\text{SO}^-$). Again, the charge is compensated by anions in a case of $\equiv\text{SOH}_2^+$, or by cations in a case of $\equiv\text{SO}^-$. In principle, these surface anionic groups can enter into the coordination sphere of the adsorbed metal ions. The mechanism of this reaction is so called surface complexation in consequence of which the sorption of many species proceeds. At least, there are three basic surface complexation models at hand [2,13,15,17], namely, non-electrostatic chemical equilibrium model

(CEM), constant capacitance model (CCM), and double layer diffusion model (DLM).

In principle, a titration curve of mineralogical component type of montmorillonite, kaolinite, magnetite, etc., can be described by means of two protonation, (1) and (2), and one ion exchange, (3), reactions. As it was mentioned above, the first two reactions proceed on the edge-sites and the third one on the layer-sites:



For these reactions, the equations of equilibrium constants (K_1 , K_2 or K_3) can be written, e. g., using CEM + IExM (chemical equilibrium model, i.e., non-electrostatic model, and ion exchange model), as follows:

$$K_1 = [\text{SOH}^0]/([\text{SO}^-] \cdot [\text{H}^+]) \quad (4)$$

$$K_2 = [\text{SOH}_2^+]/([\text{SOH}^0] \cdot [\text{H}^+]) \quad (5)$$

$$K_3 = ([\text{XH}] \cdot [\text{Na}^+])/([\text{XNa}] \cdot [\text{H}^+]) \quad (6)$$

Three balance equations, (7) – (9), are in need of the complete description of this system:

$$\sum\text{SOH} = [\text{SOH}_2^+] + [\text{SOH}^0] + [\text{SO}^-] \quad (7)$$

$$\sum\text{X} = [\text{XNa}] + [\text{XH}] \approx [\text{X}] + [\text{XH}] \quad (8)$$

$$\sum\text{Na} = m \cdot [\text{XNa}_0] + V_0 \cdot [\text{Na}_0] + v_{\text{OH}} \cdot c_{\text{OH}} = m \cdot [\text{XNa}] + V_{\Sigma} \cdot [\text{Na}^+] \quad (9)$$

Where: V_{Σ} ($=V_0 + v_{\text{H}} + v_{\text{OH}}$) is the total volume and V_0 is the starting volume of the aqueous phase [dm^3], v_{OH} and v_{H} are the consumptions [dm^3] of sodium hydroxide, NaOH, and hydrochloric acid, HCl, respectively, in the course of titration; m is the mass of solid phase [kg], and c_{OH} is the concentration of NaOH solution [mol dm^{-3}] used in the titration procedure; $[\text{XNa}_0]$ and $[\text{Na}_0]$ are the starting concentrations of sodium in solid [mol kg^{-1}] and in liquid [mol dm^{-3}] phases, respectively.

The modelling of the titration system, characterized by reactions (1) – (3), is described in detail elsewhere [13]. In short, the goal of the modelling is to construct the relations (equations) for the calculation of the surface charge [mol kg^{-1}], $Q_{\text{cal}} (=Q_{\text{ES}} + Q_{\text{LS}})$, consisting of the charge of the edge-sites, $Q_{\text{ES}} (= [\text{SOH}_2^+] - [\text{SO}^-])$, and of the charge

of the layer-sites, $Q_{LS} (= -[X^-])$. Then, it is necessary to be derived the function $(Q_{cal})_i = (Q_{ES})_i + (Q_{LS})_i = f([H^+]_i)$ (see Eqs (10) and (11)), applicable for the fitting of experimental data evaluated as $(Q_{exp})_i = f([H^+]_i)$, $i = 1, 2, 3, \dots, np$, where np is the number of experimental points of the given titration curve (see Eq. (12)), and for the determination of the values of $K_1, K_2, K_3, \Sigma SOH$ and ΣX .

$$(Q_{ES})_i = \sum \{SOH \cdot (K_1 \cdot K_2 \cdot [H^+]_i^2 + 1)\} / (1 + K_1 \cdot [H^+]_i + K_1 \cdot K_2 \cdot [H^+]_i^2) \quad [\text{mol kg}^{-1}] \quad (10)$$

$$(Q_{LS})_i = \sum (X \cdot [Na^+]) / ([Na^+] + K_3 \cdot [H^+]_i) \quad [\text{mol kg}^{-1}] \quad (11)$$

$$(Q_{exp})_i = (V_\Sigma / m) \cdot ([C_a] - [C_b] + [OH^-] - [H^+]) \quad [\text{mol kg}^{-1}] \quad (12)$$

Where $C_a = (v_H \cdot c_H) / V_\Sigma$ and $C_b = (v_{OH} \cdot c_{OH}) / V_\Sigma$, c_H [mol dm⁻³] is the concentration of HCl solution used in the titration procedure.

In the case of GC-approach, the acid-base experimental titration data are fitted with $(Q_{cal})_i$, in our case by the Newton-Raphson multidimensional non-linear regression method, and the quantity $WSOS/DF$ (weighted sum of squares of differences divided by degrees of freedom) is used as a criterion of the goodness-of-fit (the agreement of calculated and experimental data) – if $0.1 < WSOS/DF < 20$, then there is a acceptable agreement between the experimental and calculated data [14]. Its calculation is based on the χ^2 – test, calculated according to Eq. (13), and then the $WSOS/DF$ is obtained by means of Eq. (14):

$$\chi^2 = \sum \{(SSx)_i / (s_q)_i^2\}, \quad i = 1, 2, 3, \dots, n_p \quad (13)$$

$$WSOS / DF = (\chi^2 / n_d) \quad n_d = n_p - n \quad (14)$$

Where, $(SSx)_i$ is the i -th square of the deviation of i -the experimental value from the corresponding calculated value, $(s_q)_i$ is the estimate of standard deviation (uncertainty) of the i -th experimental point, n_p is the number of experimental points, n_d is the number of degrees of freedom, and n is the number of model parameters sought during the regression procedure, i.e., $n = 5$ ($K_1, K_2, K_3, \Sigma SOH$ and ΣX) or, if only edge-sites are present, $n = 3$ ($K_1, K_2, \Sigma SOH$).

If it deals with the mineral assemblage consisting of J mineral components, each component takes part individually in the reactions (1) – (3), as it is supposed in a case of CA approach modelling. Of course, the above mentioned model parameters of the j -th mineral component ($K_{1j}, K_{2j}, K_{3j}, \Sigma SOH_j$ and ΣX_j), the values of which are inserted into the Eqs (10) and (11), have to be known, including the percentage by weight of the j -th mineral

component (mP_j , $j = 1, 2, 3, \dots, J$) in an assemblage studied. Then, the calculation algorithm of the corresponding CA-code proceeds according to Eq. (15) as follows:

- At first, for $i = 1$, the surface charges of individual mineral components, $(Q_{ES})_{ij}$ (Eq. (10)), and $(Q_{LS})_{ij}$ (Eq. (11)), for $j = 1, 2, \dots, J$, are calculated for the given value of concentration $[H^+]_i$ or $-\log(pH)_i$, and, the value of $((Q_{cal})_{total})_1$ is obtained.
- This is repeated in an iteration loop for $i = 2, 3, \dots, n_p$.
- In the end, altogether there are n_p values of $((Q_{cal})_{total})_i = f([H^+]_i)$, that is, n_p points modelling the titration curve of the given mineral assemblage.

$$((Q_{cal})_{total})_i = \sum_j \{ (mP_j / 100) \cdot [(Q_{ES})_{ij} + (Q_{LS})_{ij}] \} \quad i = 1, 2, 3, \dots, n_p; \quad j = 1, 2, 3, \dots, J \quad (15)$$

As the goal of the study is the comparison of the calculated (by GC- or CA-code) and experimental titration curves, i.e. of the calculated and experimental surface charges, in such a case, the experimental values $[H^+]_i$ have to be inserted into Eqs (10) and (11) or in Eq. (15). Also in this case, the quantity $WSOS/DF$ can be used as a criterion of the agreement of the modelled and the experimental titration curve.

As it was mentioned above, the CA-approach results, $((Q_{cal})_{total})_i$, can be used as input data into the GC-approach code, and the obtained overall values of $K_1, K_2, K_3, \Sigma SOH$ and ΣX can be compared with the values of the same parameters resulting from the evaluation of experimental data, $(Q_{exp})_i$ (by GC-approach code). If the acceptable agreement exists, this implies that the parameters of mineral assemblage can be obtained on the basis of the knowledge of mP_j and $K_{1j}, K_{2j}, K_{3j}, \Sigma SOH_j$ and ΣX_j values, without experimental determination of the corresponding titration curve.

3 Experimental

3.1 Characteristics of mineral assemblage (MA) samples

Three types of mineral assemblages (**F**, **R** and **B/M**), having different mineralogical composition and origin, were studied:

- **MA-F**: fucoidic sandstone sampled from Cenomenian age deposit in the Stráž pod Ralskem site (Northern Bohemia, CZ). The following samples taken from borehole VP SC 7095 (in the given horizon (depth)) were used: No 48544 (143.5 m), No 48547 (144.65 m)

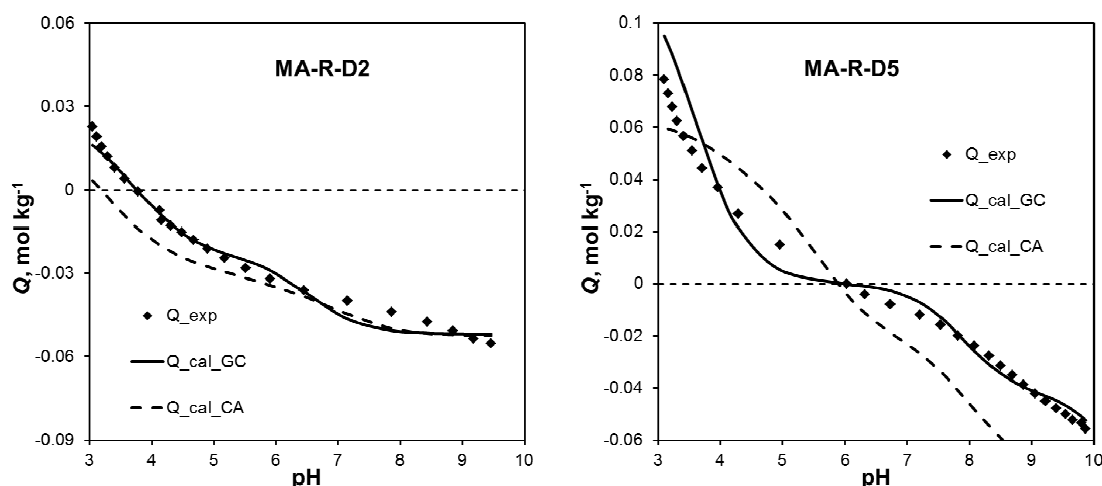


Figure 1: MA – Ruprechtov site samples (D2, D5) – titration curves evaluated using GC- and CA-approach method.

and No 48555 (147.8 m). Their mineralogical composition and the values of parameters of individual mineral components [4] are summarized in Table 1 and Table 2.

- **MA-R**: sedimentary rock-clay formation sampled in the Ruprechtov site (West Bohemia, CZ). The samples from borehole NAR 2 (in the given horizon (depth)) are as follows: No D1 (25.7 m), No D2 (29.86 m), No D3 (32.4 m), and No D5 (23.4 m). Again, their mineralogical composition and the values of parameters of selected mineral components [4] are summarized in Tables 1 and 2 (the samples of **MA-R** are described in detail in [12]).
- **MA-B/M**: bentonite + magnetite mixture with mass ratio 2:1 prepared from Czech bentonite Sabenyl (KERAMOST, Obrnice, CZ) and magnetite (inorganic pigment Bayferrox 318M, from Bayer Chemicals, with following characteristics: 92% Fe_3O_4 , 3% $\text{SiO}_2 + \text{Al}_2\text{O}_3$, granulometry $\approx 0.2 \mu\text{m}$). Magnetite was explored as a representative of corrosion products of storage containers. In this case, bentonite was regarded as one “component” and magnetite as the second one. As for the bentonite and magnetite, their mineralogical composition is presented in Table 1, the values of characteristic parameters of both “components” taken from [15] and [17] can be found in Table 2.

3.2 Acid-base titration of MA-samples F, R and B/M

Before the titration procedure, the given sample was pre-treated in order to remove carbonates and other impurities

using the procedure described in [16]. Then 0.5 g of the pre-treated and dried (under ambient temperature) sample was mixed with 0.1 M NaNO_3 (50 ml) (applied to maintain the ionic strength at almost constant value), and the potentiometric titration using 0.1 M HNO_3 and 0.1 M NaOH was performed under N_2 atmosphere on automatic titrator 845 TIM with a combined electrode pHC2001-8 (Radiometer Analytical). The detailed description of this procedure can be found in [16].

4 Results and discussion

At first, the modelling of titration curves of mineral assemblages, i.e. of **MA F**, **R** and **B/M**, by means of CA-approach code, using the input parameter values summarized in Table 1 and 2, was accomplished. The code based on the Eqs (15), (10) and (11) was constructed and verified in software product Famulus [18] (the principle of the algorithm of the codes used in this contribution can be found in [19]).

The results are demonstrated in Figures 1-3. In each figure, the results of evaluation of experimental data by GC-approach code can be found, and the corresponding resulting values of titration curve overall parameters are collected in Table 3.

Not only experimental data, but also the CA-approach data (results), i.e. the dependences of $((Q_{\text{cal}})_{\text{total}})_i = f[\text{H}^+]_i$, were evaluated by the GC-approach code, in the course of which the values of overall parameters were sought - these are in Table 4.

The first interesting question can be conceived as follows: is it possible to apply the CA- approach to the

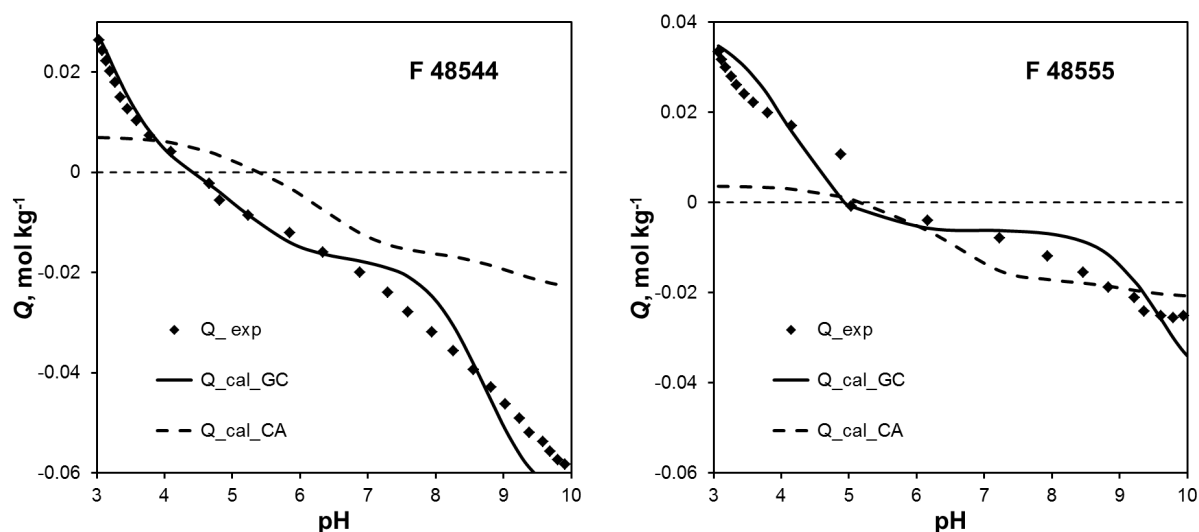


Figure 2: MA - Fucoidic sandstone samples (48544, 48555) – titration curves evaluated using GC- and CA-approach method.

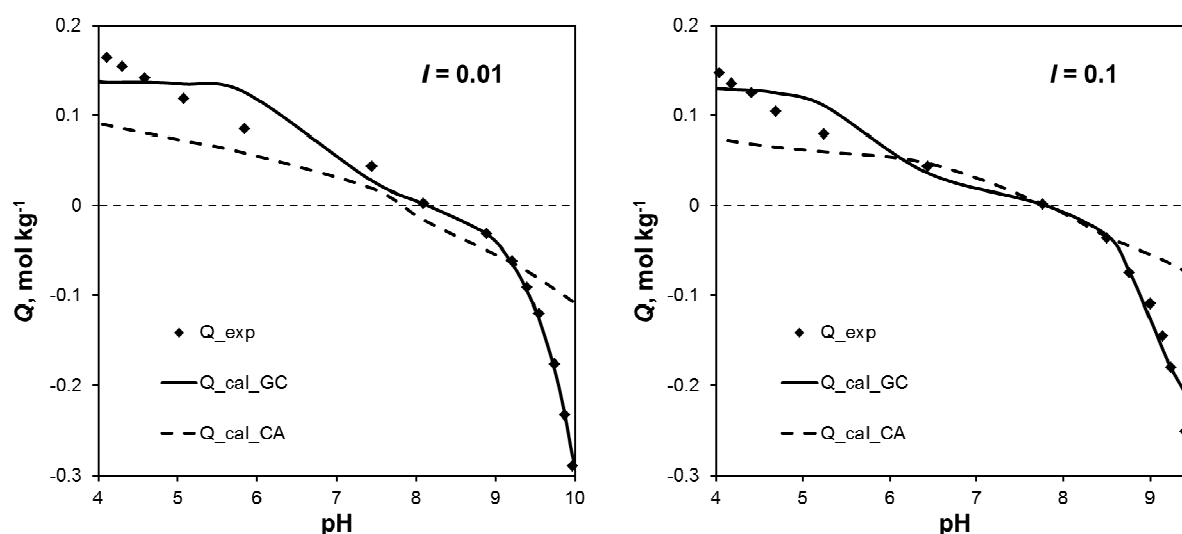


Figure 3: MA - Bentonite/magnetite (B:M = 2:1) sample – titration curves evaluated using GC- and CA-approach method.

modelling of titration curves of mineral assemblages? If we take into account the depicted results in Figures 1-3, especially if we judge the most interesting pH interval from 5 to 8, we can reply positively with a few exceptions. In particular, there are only two titration curves, namely of **MA-R-D5** (Fig. 1) and **MA-F-48544** (Fig. 2), having the criterion ($WSOS/DF$) of the agreement between Q_{exp} and Q_{cal_CA} evidently greater than 20. Of course, the comparison of the results of modelling depends at first on the credibility and applicability of above mentioned input parameters (see Table 2). It seems that the effective way to determine the values of the parameters mentioned, is

their laboratory determination. However, in such case, the individual minerals need to be separated from the given mineral assemblage or such minerals to be used, the properties of which are similar with the minerals present in the given **MA**.

In any case, the realization of it is a difficult task. Then, there is the second way, used in this study, namely the application of the RES³T database [4], in which the parameters available from the literature are summarized. Unfortunately, it is necessary to state that the application of some data from this database is not without difficulties, too. Namely, there is in many cases a sufficient spread

Table 1: Mineralogical composition of mineral assemblages (MA).

MA	Sample No	Mineral components [% by weight]					
		Quartz	Kaolinite	Muscovite	Pyrite	K-feldspar	-
F	48544	81.80	16.00	0.50	0.40	1.30	-
	48547	85.10	11.50	1.90	0.90	-	-
	48550	90.50	8.00	0.50	0.40	0.50	-
R	Sample No	Montmorillonite	Kaolinite	Anatase	Illite	Quartz	Pyrite
	D1	44.90	30.60	2.70	5.60	5.70	4.50
	D2	26.40	36.30	4.10	7.60	15.00	2.80
	D3	17.20	71.00	1.80	3.70	2.90	0.00
	D5	40.60	28.80	4.40	7.20	7.70	0.80
B/M (= 2:1)	Mineral comp.	Montmorillonite + nontronite	Quartz	Muscovite + illite	Goethite	Feldspar	Anatas
	B	70.00	7.90	6.90	6.60	5.00	4.00
	Mineral Comp.	Fe ₃ O ₄	SiO ₂ + Al ₂ O ₃	Residue	-	-	-
	M	92.00	3.00	5.00	-	-	-

Table 2: Parameters of surface sites of selected components (average values $\pm$ standard uncertainties) (the values of equilibrium constants were extrapolated to $I = 0$ by means of Davies equation) (there are input data for CA-approach code in this table).

j-th mineral component	$\log K_{ij}$ $\pm \log \sigma_j$ [log mol ⁻¹]	$\log K_{2j}$ $\pm \log \sigma_j$ [log mol ⁻¹]	ΣSOH_j $\pm \sigma_j$ [mol kg ⁻¹]	$\log K_{3j}$ $\pm \log \sigma_j$ [-]	ΣX_j $\pm \sigma_j$ [mol kg ⁻¹]	Refer.
Anatas	8.16 $\pm$ 0.90	3.98 $\pm$ 1.23	2.53E-04 $\pm$ 5.11E-05	-	-	[4]
Illite	7.62 $\pm$ 4.07	5.66 $\pm$ 3.22	2.98E-04 $\pm$ 7.45E-05	-	-	“-
Kaolinite	9.13 $\pm$ 2.79	4.94 $\pm$ 2.32	4.71E-05 $\pm$ 4.23E-05	2.89 $\pm$ 0.01	3.23E-05 $\pm$ 1.22E-06	“-
K-feldspar	2.12 $\pm$ 0.00	$\approx$ 1.88 $\pm$ 0.00	4.82E-05 $\pm$ 4.85E-05	-	-	“-
Montmorillonite	8.29 $\pm$ 1.49	5.70 $\pm$ 1.34	4.09E-05 $\pm$ 2.05E-05	4.60 $\pm$ 0.00	2.20E-05 $\pm$ 0.00E-05	“-
Muscovite	7.81 $\pm$ 0.00	6.06 $\pm$ 0.00	1.43E-05 $\pm$ 1.16E-05	-	-	“-
Pyrite	4.33	-0.93	2.45E-05 $\pm$ 5.54E-06	-	-	“-
Quartz	6.41 $\pm$ 1.12	-1.05 $\pm$ 1.99	1.88E-05 $\pm$ 1.51E-05	-	-	“-
Bentonite	9.81 $\pm$ 0.11	7.79 $\pm$ 0.29	1.10E-01 $\pm$ 5.90E-04	$\approx$ 2.03	4.02E-02 $\pm$ 6.06E-04	[15,17]
Magnetite	9.70 $\pm$ 0.02	6.07 $\pm$ 0.17	3.80E-02 $\pm$ 1.1E-04	$\approx$ 3.29	5.62E-02 $\pm$ 8.10E-04	[15,17]

in parameter values characterizing selected mineral components, and the choice of the best one can be difficult. In such case it remains to compute, e.g., the arithmetic mean of the values of each parameter of interest and to assess the standard deviation by a conventional statistical procedure.

This way we used, and the results, i.e., the arithmetic means $\pm \sigma_j$ mentioned above, can be found in Table 2 (however if in the database [4] only one parameter value exists, the deviation value equals zero, as it is in the case

of pyrite). It is evident, that the “ σ -values”, as a result of above mentioned spread of parameters, amount to 50% or more in some cases. The arithmetic mean has not then to be the best applicable value, and the better one can be chosen in the range given by the spread (using σ -values) of data in the database.

The second interesting question relates to the substitution of experimental titration curve for its calculation by CA-approach and successive evaluation of $((Q_{\text{cal}})_{\text{total}})_i = f[H^+]_i$ by the GC-approach code. Such procedure

Table 3: Titration curve overall parameters of **MA** samples **F**, **R** and **B/M** obtained by GC-approach code used to the evaluation of the experimental data (CEM + IExM models were applied; the values of equilibrium constants were extrapolated to $I = 0$ by means of Davies equation).

Mineral assemblage sample	$\log K_{1j}$ $\pm \log \sigma_j$ [log mol ⁻¹]	$\log K_{2j}$ $\pm \log \sigma_j$ [log mol ⁻¹]	ΣSOH_j $\pm \sigma_j$ [mol kg ⁻¹]	$\log K_{3j}$ $\pm \log \sigma_j$ [-]	ΣX_j $\pm \sigma_j$ [mol kg ⁻¹]	WSOS/DF
F – 48544	8.81 ± 6.94	3.21 ± 0.53	5.03E-02 ± 7.79E-05	4.21 ± 1.96	1.73E-02 ± 5.58E-05	2.81
F – 48547	10.43 ± 8.41	7.15 ± 4.95	3.32E-02 ± 4.39E-05	2.19 ± 0.45	3.68E-02 ± 4.32E-05	4.48
F – 48555	9.74 ± 7.63	4.32 ± 1.91	4.04E-02 ± 6.94E-05	2.19 ± 0.61	6.13E-03 ± 2.12E-05	9.46
R – D1	9.11 ± 7.70	5.97 ± 4.20	1.55E-01 ± 1E-03	1.89 ± 0.30	1.77E-01 ± 1E-03	3.39
R – D2	10.30 ± 8.30	2.81 ± 0.53	1.31E-01 ± 5.72E-04	4.86 ± 2.65	3.13E-02 ± 8.42E-05	5.16
R – D3	10.95 ± 8.50	3.08 ± 0.53	7.03E-02 ± 1.42E-04	6.68 ± 4.40	1.09E-02 ± 1.93E-05	3.74
R – D5	12.01 ± 9.52	3.71 ± 1.94	1.25E-01 ± 8.57E-04	6.90 ± 5.15	4.25E-02 ± 3.15E-04	7.01
B/M (=2:1)	9.57 ± 8.34	7.51 ± 6.45	1.39E-01 ± 1.69E-03	2.84 ± 2.25	2.42E-02 ± 2.17E-03	12.6

Table 4: Titration curve overall parameters of **MA** samples **F**, **R** and **B/M** obtained by GC-approach code used to the evaluation of the (($Q_{\text{cal}}/Q_{\text{total}}\rangle = f[H^+]_i$) data, i.e., of the CA-approach results. (CEM + IExM models were applied; the values of equilibrium constants were extrapolated to $I = 0$ by means of Davies equation).

Mineral assemblage sample	$\log K_{1j}$ $\pm \log \sigma_j$ [log mol ⁻¹]	$\log K_{2j}$ $\pm \log \sigma_j$ [log mol ⁻¹]	ΣSOH_j $\pm \sigma_j$ [mol kg ⁻¹]	$\log K_{3j}$ $\pm \log \sigma_j$ [-]	ΣX_j $\pm \sigma_j$ [mol kg ⁻¹]	WSOS/DF
F – 48544	6.82 ± 4.11	5.06 ± 2.17	7.55E-03 ± 2.03E-06	3.96 ± 1.35	4.76E-03 ± 3.95E-06	5.97
F – 48547	7.14 ± 4.50	3.43 ± 0.01	1.90E-02 ± 2.19E-05	-0.88 ± 0.64	9.02E-04 ± 1.98E-06	39.00
F – 48555	7.85 ± 6.26	3.95 ± 1.76	5.73E-03 ± 2.02E-05	5.04 ± 2.52	1.36E-02 ± 3.03E-05	7.20
R – D2	9.15 ± 7.84	6.03 ± 4.50	1.87E-02 ± 1.24E-04	2.33 ± 0.28	4.47E-02 ± 9.89E-05	0.33
R – D3	8.81 ± 7.83	4.63 ± 2.50	5.18E-02 ± 1.03E-04	4.77 ± 2.96	3.01E-02 ± 1.74E-04	0.19
R – D5	8.25 ± 6.44	5.74 ± 3.79	5.88E-02 ± 1.51E-04	3.23 ± 4.87	2.09E-02 ± 1.67E-04	0.13
B/M (=2:1) I=0.1	9.58 ± 8.08	7.67 ± 5.68	8.92E-02 ± 6.46E-04	3.19 ± 2.00	3.49E-02 ± 5.36E-04	0.06
B/M (=2:1) I=0.01	9.37 ± 7.82	6.06 ± 4.72	1.11E-01 ± 1.11E-03	0.80 ± 1.09	1.62E-02 ± 2.97E-04	1.60

makes possible, as was mentioned above, that the overall parameters of given **MA**, required for the evaluation of sorption or interaction dependences, are obtained without the experimental determination of its titration curve. The real possibility of the evaluation of CA-approach data by GC-approach code is corroborated in the Table 4.

At first, the attention has to be drawn to the values of *WSOS/DF*. It is evident, that – apart from **MA-F-48547** – their values reflect the goodness-of-fit of these evaluations. Then, it follows from the comparison of the individual parameters ($\log K_{1j}$, $\log K_{2j}$, $\log K_{3j}$, ΣSOH_j and ΣX_j) summarized in Table 3 with the corresponding values in Table 4, that the substitution above mentioned is real. In our opinion, it can be used, because these parameter values differ in the range “ $\pm \sigma$ -value”, and can be regarded as comparable.

The presented results of evaluation of titration curves by GC-approach code with incorporated CEM + IExM models (Figures 1-3 and Table 3) demonstrated good application of these models for the description of the systems studied. Actually, it deals with the classical evaluation procedure used especially, and not only for clayey soils and argillaceous rocks, but also for minerals type of goethite, magnesite, boemite, etc. It can be added, that in principal other surface complexation models [13], e.g. CCM (Constant Capacitance Model) or DLM (Diffuse Double Layer Model) etc., can be used to the description of protonation reactions on the edge sites.

5 Conclusions

The modelling of acid-base titration curves of mineral assemblages using the component additivity approach, and sequential GC-one, was studied, and especially, the problem of the substitution of the experimental titration curve by CA-approach method was followed. On the basis of this study, accomplished with three different types of mineral assemblages (samples of: fucoidic sandstones – 5 components; sedimentary rock-clay formation – 6 components; bentonite/magnetite mixture- 2 components) can be stated that the possibility to apply this method for the determination of mineral assemblage parameters, namely the determination of their overall values which characterize the surface sites, the mentioned substitution is under some conditions real. The main problem consists in the credibility, accessibility and applicability of the parameters characterizing the individual mineralogical components, i.e., of the parameters characterizing the protonation and/or ion exchange reactions undergoing on their surface sites. From this point of view, the CA-approach method can be without doubt applied if these parameters are available. The second important advantage of CA-approach consists in the influence of the composition of the given mineral assemblage to be studied by numerical solution relatively quickly by means of the so called parametric studies.

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