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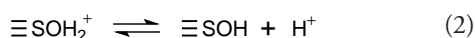
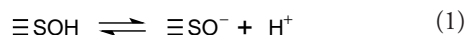
An Easy Determination of the Surface Chemical Properties of Simple and Natural Solids

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A rapid and easy method for the determination of solid surface chemical properties by applying geochemistry principles is described. The surface acidity constants, pK_a^S , and the pH of zero point charge, pH_{zpc} , where the protonic net surface charge is equal to zero, are calculated for solid samples. This methodology is based on potentiometric titrations of the solid surface performed following the protocol of Kummert and Stumm (1) and Sigg and Stumm (2).

Acidity constants and pH_{zpc} are determined according to the surface-complexation model described by Stumm (3, 4). This model shows that surface charges of solids result from acid-base surface reactions. These reactions are described only by the mass-action-law equations of surface hydroxyl groups and are similar to reactions occurring in solution with a simple amphoteric compound. Thus, considering solids as containing functional surface groups expressed as a generic binding site, $\equiv\text{SOH}$, we obtain



and the corresponding acidity constants,

$$K_{a1}^S = \frac{[\text{H}^+]\{\equiv\text{SO}^-\}}{\{\equiv\text{SOH}\}} \quad (3)$$

$$K_{a2}^S = \frac{[\text{H}^+]\{\equiv\text{SOH}\}}{\{\equiv\text{SOH}_2^+\}} \quad (4)$$

where $[\]$ is the solution species concentration in mol L^{-1} and $\{\ \}$ is the solid surface species concentration in mol g^{-1} . These functionally defined parameters, K_{a1}^S and K_{a2}^S , do not describe real protonations of oxygen atoms: they are mathematical simplifications employed to reproduce the amphoteric charge of solids in water. Thus, according to the pH of the solution, the surface is charged differently and could behave as an anion or cation exchanger.

The pH where protonic surface charge is equal to zero is called pH_{zpc} . Considering the solid surface electroneutrality, we obtain from eqs 3 and 4

$$pH_{zpc} = \frac{pK_{a1}^S + pK_{a2}^S}{2} \quad (5)$$

Recently several authors have shown that this surface-complexation model could be applicable to heterogeneous natural solids (5–8). Consequently, the method described in this paper could be applied not only to simple solids such as ox-

ides (or hydroxides) but also to natural solids such as soils or sediments. However, in the case of natural heterogeneous solids, only a general description is obtained.

Experimental Procedure

Students start the experiment with the determination of the total surface reactive-site number, S_{tot} , of the chosen solid (natural or simple). S_{tot} is considered to be equal to the cation exchange capacity (CEC) of the solid. According to method ISO 11260 (9), the ions linked with the solid surface are totally exchanged with cobalthexammine ions. Thus CEC is the concentration of cobalthexammine ions removed from solution (expressed in mol g^{-1}). The solid, 5 g, is mixed with 10 mL of 0.017 M cobalthexammine trichloride solution for 3 h. After centrifugation of the suspension, the concentration of cobalthexammine ions remaining in the solution is measured at 470 nm with an UV spectrophotometer. Experiments are carried out in triplicate.

When the CEC determination is started, students perform potentiometric titrations of the solid sample. Titration can be either carried out with an automatic titrator or a buret. Two experiments are conducted, each with 10 g of solid in 100 mL of 0.1 M NaNO_3 as the supporting electrolyte (1, 2). One suspension is titrated with 0.1 M HNO_3 and the other with 0.1 M NaOH . After waiting 10 min for pH equilibration, titrations are carried out over a pH range of 3 to 11 to avoid any solid solubilization.

Results and Discussion

The surface charge of a solid, Q in units mol g^{-1} , corresponds to

$$Q = \{\text{SOH}_2^+\} - \{\text{SO}^-\} \quad (6)$$

For each point of the titration, we obtain

$$Q = \frac{C_a - C_b + [\text{OH}^-] - [\text{H}^+]}{m} \quad (7)$$

where C_a and C_b are the concentration (mol L^{-1}) of added acid and base, respectively, and m is the solid concentration (g L^{-1}). For a HNO_3 or NaOH addition, Q can be expressed as either

$$Q = \frac{C_a - [\text{H}^+]}{m} \quad (8)$$

or

$$Q = \frac{[\text{OH}^-] - C_b}{m} \quad (9)$$

Using the Microsoft Excel computer program, the solid surface charge as a function of pH is calculated and plotted (Figures 1 and 2). An estimated value of the solid pH_{zpc} , the pH where the curve crosses the x-axis ($Q = 0$), can be obtained from Figure 2.

Since the solid is considered an amphoteric compound, the total concentration of surface species, $\{S\}_{\text{tot}}$, corresponds to

$$\{S\}_{\text{tot}} = \{\equiv\text{SOH}\} + \{\equiv\text{SO}^-\} + \{\equiv\text{SOH}_2^+\} \quad (10)$$

Thus, surface acidity constants and pH_{zpc} of the sample are calculated as follows:

if $\text{pH} < \text{pH}_{\text{zpc}}$, then

$$Q = \{\equiv\text{SOH}_2^+\}, \quad K_{a2}^S = \frac{(\{S\}_{\text{tot}} - Q)[\text{H}^+]}{Q} \quad (11)$$

if $\text{pH} > \text{pH}_{\text{zpc}}$, then

$$Q = \{\equiv\text{SO}^-\}, \quad K_{a1}^S = \frac{Q[\text{H}^+]}{\{S\}_{\text{tot}} - Q} \quad (12)$$

where $\{S\}_{\text{tot}}$ is assumed to be equal to the CEC.¹ The absolute value of Q is used for the calculation of the K_a^S values. Successive $\text{p}K_a^S$ corresponding to each Q value are calculated with the Microsoft Excel spreadsheet (Figure 1) and are plot-

ted (Figure 3). Intrinsic acidity constants are obtained by linear graphic extrapolation to the zero charge (4)

$$\text{p}K_a^S = \text{p}K_{a(\text{int})}^S + \beta Q \quad (13)$$

where β is the slope and $\text{p}K_{a(\text{int})}^S$ (intrinsic acidity constant) is the intercept on the ordinate.^{2,3} Using the intrinsic acidity constants, pH_{zpc} can then be calculated with eq 5.

Students determined by graphical extrapolation the value of each intrinsic surface acidity constant for a river sediment sample (Figure 3): $\text{p}K_{a1}^S = 7.9$, $\text{p}K_{a2}^S = 4.3$. With these data they calculated $\text{pH}_{\text{zpc}} = 6.1$.

Equipment and Chemicals

The reagents used in this experiment are relatively inexpensive and readily available from commercial sources. The solid sample may be natural (e.g., sediment or soil collected anywhere) or simple (e.g., oxide of iron, manganese, or aluminum). Synthetic oxides could be prepared in the laboratory (10). Solid samples must be air-dried and sieved at a maximum of 2 mm (11). The sample should not contain too much organic matter that might interfere in the UV analysis. However, in this case, the cobalthexammine concentration could be analyzed by flame atomic absorption spectroscopy (FAAS).

Standard glassware (buret, beakers, etc.) or an automatic titrator could be used in the laboratory. The experimental data could be directly incorporated into the Microsoft Excel spreadsheet for calculations. This laboratory experiment needs 4 h to be performed by students.

Several parameters such as solid dissolution, presence of solid carbonate (12), precipitation, or reactions with other species in solution might interfere with the acidity constants determination (1, 2).

Figure 1. Typical layout of the Excel spreadsheet for calculation of solid surface chemical properties.

	A	B	C	D	E	F	G	H
1						{S} tot =	1.30E-04	mol.g ⁻¹
2	V (ml)	Ca (mol.L ⁻¹)	pH	[H+] (mol.L ⁻¹)	[OH-] (mol.L ⁻¹)	Q (mol.g ⁻¹)	Ka ^S	pKa ^S
3	0.1 M HNO ₃	(0.1*V)/(100+V)		10 ^{^-(pH)}	10 ^{^(pH-14)}	(Ca-[H ⁺])/10	((S) tot-Q).[H ⁺]/Q	-log (Ka ^S)
4	2	1.96E-03	3.15	7.08E-04	1.41E-11	1.25E-04	2.66E-05	4.574307897
5	1.6	1.57E-03	3.35	4.47E-04	2.24E-11	1.13E-04	6.81E-05	4.16712873
6	1.4	1.38E-03	3.41	3.89E-04	2.57E-11	9.92E-05	1.21E-04	3.917269213
7	1.2	1.19E-03	3.54	2.88E-04	3.47E-11	8.97E-05	1.29E-04	3.88806172
8	1	9.90E-04	3.72	1.91E-04	5.25E-11	8.00E-05	1.19E-04	3.923489154
9	0.8	7.94E-04	4.02	9.55E-05	1.05E-10	6.98E-05	8.23E-05	4.084462681
10	0.6	5.96E-04	4.32	4.79E-05	2.09E-10	5.49E-05	6.56E-05	4.183328007
11	0.5	4.98E-04	4.47	3.39E-05	2.95E-10	4.64E-05	6.11E-05	4.213770633
12	0.2	2.00E-04	4.86	1.38E-05	7.24E-10	1.86E-05	8.28E-05	4.082076229
13	0.1	9.99E-05	5.33	4.68E-06	2.14E-09	9.52E-06	5.92E-05	4.227844476
14	0	0.0E+00	5.7					
15	V (ml)	Cb (mol.L ⁻¹)	pH	[H+] (mol.L ⁻¹)	[OH-] (mol.L ⁻¹)	Q (mol.g ⁻¹)	Ka ^S	pKa ^S
16	0.1 M NaOH	(0.1*V)/(100+V)		10 ^{^-(pH)}	10 ^{^(pH-14)}	(-Cb+[OH ⁻])/10	Q.[H ⁺]/((S) tot-Q)	-log (Ka ^S)
17	0	0.0E+00	5.46					
18	0.1	1.0E-04	6.92	1.20E-07	8.32E-08	-9.99E-06	1.00E-08	8.00
19	0.2	2.0E-04	7.07	8.51E-08	1.17E-07	-2.00E-05	1.54E-08	7.81
20	0.3	3.0E-04	7.2	6.31E-08	1.58E-07	-2.99E-05	1.88E-08	7.72
21	0.4	4.0E-04	7.31	4.90E-08	2.04E-07	-3.98E-05	2.16E-08	7.66
22	0.5	5.0E-04	7.56	2.75E-08	3.63E-07	-4.97E-05	1.71E-08	7.77
23	0.6	6.0E-04	7.66	2.19E-08	4.57E-07	-5.96E-05	1.85E-08	7.73
24	0.7	7.0E-04	7.8	1.58E-08	6.31E-07	-6.95E-05	1.82E-08	7.74
25	0.8	7.9E-04	7.93	1.17E-08	8.51E-07	-7.93E-05	1.84E-08	7.74
26	0.9	8.9E-04	8.06	8.71E-09	1.15E-06	-8.91E-05	1.90E-08	7.72
27	1	9.9E-04	8.13	7.41E-09	1.35E-06	-9.89E-05	2.35E-08	7.63

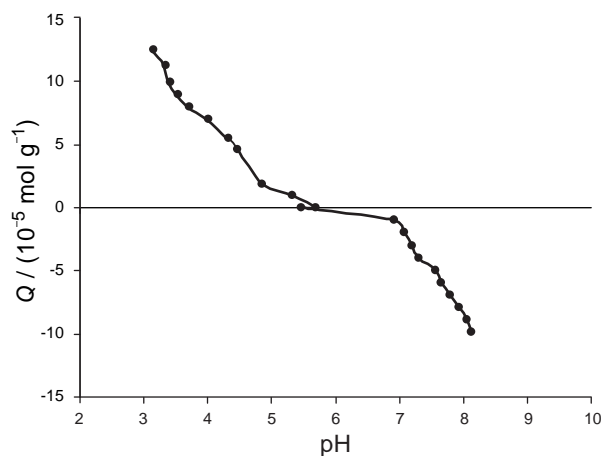


Figure 2. The solid surface charge, Q , as a function of pH.

Hazards

None of the substances used in this activity at the concentrations described pose an unacceptable health hazard for students working safely in an academic laboratory. Cobalt(III) is a heavy metal cation that should be appropriately placed in a specially marked container and not allowed to be disposed of down the drain. The soil reacted with cobalt-hexammine solution should be stored in a specially marked container and then disposed of following local and state laws.

Conclusion

The determination of the surface chemical properties of a solid is an excellent instructive experiment for a geochemistry laboratory. Different analytical techniques can be mastered (acid–base titrations, UV, or FAAS spectrophotometry) and a primary understanding in geochemical modeling can be acquired. Students are also able to use a Microsoft Excel computer program for calculations as well as for the presentation of their results. This tutorial could also be a good alternative to the automatic titration training.

Moreover, the determination of the surface chemical properties of solids by this easy method is of major interest for the study of systems containing a solid phase. Surface acidity constants and pH_{zpc} are major requisite parameters for using the currently available geochemical models.

Acknowledgment

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Notes

1. The value of $\{S\}_{\text{tot}}$ in eqs 11 and 12 represents the total concentration of protonable surface sites, but in practice is often an adjustable parameter. Here, and following previous observations, it is taken as equal to CEC, a very useful approximation (13). $\{S\}_{\text{tot}}$ could be also obtained by spectroscopic techniques (e.g., EXAFS) or from crystal structure; however, each method refers to a specific phenomenon, and thus only approximations are obtained.

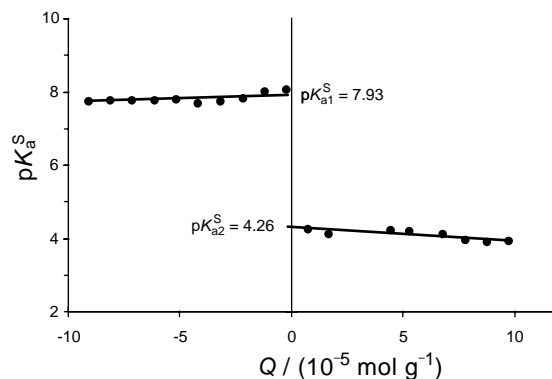


Figure 3. pK_a^S as a function of the solid surface charge, Q , of a river sediment sample.

2. Near the pH_{zpc} , some K_a^S values could be inaccurate because the approximation conditions are not fulfilled: $\text{pH} < \text{pH}_{\text{zpc}}$ or $\text{pH} > \text{pH}_{\text{zpc}}$. In this case, these values do not respect the linear relationship between pK_a^S and Q (Figure 3) and should be deleted.

3. The constant-ionic-medium convention is used here for activities. Thus the values determined (Q , pK_a^S , pH_{zpc}) cannot be extended to other ionic strengths. Further developments incorporating electrostatic (double or triple layer) models allow such an extension (14).

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