

# Effect of the ionic strength on the acid-base titration curves of a soil fulvic acid

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Potentiometric titrations of a soil extracted fulvic acid solutions were carried out varying the initial concentration and the background electrolyte (KNO<sub>3</sub>) concentration in the range from 5 · 10<sup>-3</sup> M to 1.0 M. The mastercurve approach was tried, but the data did not merge into a single curve, so the CA and LOGA-1 methods were applied to the experimental Q(pH) curves to analyse the ionic strength effect over the fulvic acid ionization.

ton concentration but the surface concentration which depends on the surface potential (Eq. 1):

$$H_s = [H^+] \exp\left(-\frac{F\psi_s}{RT}\right) \quad (1)$$

where  $\psi_s$  is the potential of the acidic group site referred to that of the bulk solution. It is assumed that all the functional groups have the same average  $\psi_s$ . In such conditions, the equation obtained for the proton adsorption is mathematically similar to the Langmuir isotherm (Eq. 2):

$$\theta_{i,H} = \frac{K_{i,H}^{int} H_s}{1 + K_{i,H}^{int} H_s} \quad (2)$$

It can be assumed that the electrical double layer around a particle has a behaviour similar to a condenser of capacity  $K$  (Eq. 3).

$$\Psi_s = \frac{\sigma_s}{K} \quad (3)$$

Expressions for  $K$  and  $\psi_s$  can be obtained by solving the Poisson-Boltzman (P-B) equation. For high values of  $\psi_s$  and in the case of spherical or cylindrical geometry, the P-B equation has to be numerically solved [1] or approximated by analytical means [2].

## Introduction

The study of the acid-base properties of humic substances is complex due to their polyelectrolytic nature. Indeed, their acidic constants depend on the saline concentration of the aqueous medium (electrostatic effect). Another important feature of these substances is their heterogeneity due to the presence of functional groups with different acidic character. Only if these two different effects are studied separately will it be possible to quantify the acid-base properties of an humic substance. We have centered the present work in the analysis of the electrostatic effect.

## Electrostatic interactions

The organic matter has a total negative charge due either to the ionization of the functional groups or to the release of protons. This charge produces an electric field which depends on the charge value, on the molecule geometry and on the ionic strength. Using a suitable double layer model, it is possible to remove the ionic strength effect. A set of mastercurves keeping only the heterogeneity effect can be thus obtained.

For a set of organic polyelectrolyte acids with  $n$  different types of functional groups, it is possible to define a protonation equilibrium with an intrinsic constant for each ionizable group,  $i$ . This constant does not include the bulk pro-

## Heterogeneity analysis

Equation (1) applies for the adsorption on an homogeneous surface. For an heterogeneous surface it would be the adsorption on an specific type of surface group and, consequently, a local isotherm. For an heterogeneous particle with a discrete affinity distribution the total degree of protonation  $\theta_{t,H}$  can be expressed as:

$$\theta_{t,H} = \sum_i^n f_i \theta_{i,H}$$

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where  $f_i$  is the fraction of type  $i$  sites compared to the total number of sites. For a continuous affinity distribution:

$$\theta_T[H] = \int_0^{\infty} N(K) \frac{K[H]}{1 + K[H]} dK \quad (4)$$

where  $N(K)$  is the normalized distribution function of the sites concentration depending on their  $K$  value. If the integral equation can be solved it is possible to obtain information about the chemical heterogeneity from the experimental acid-base curves. However, this equation is difficult to solve, both analytically and numerically. Only a small fraction of experimental data are available ("analytical window") and the experimental error is high. For this reason a set of semi-analytical methods have been developed to solve equation (4) without making any assumptions about the nature of the distribution function. The most important methods are Local Isotherm Approximation (LIA), Affinity Spectrum (AS) and Differential Equilibrium Function (DEF).

**Local Isotherm Approximation (LIA)**

These methods [3] are based on the replacement of equation 2 by a function (LIA isotherm) that allows to solve equation (4) analytically. The closer the LIA isotherm ( $\theta_{LIA}$ ) to the true local isotherm, the closer the calculated distribution function ( $f_{LIA}(\log K)$ ) is to the true function. Equation (4) is thus replaced by:

$$\theta_T([H]) = \int_{-\infty}^{+\infty} \theta_{LIA} f_{LIA}(\log K) d \log K.$$

The expressions for the different isotherms are:

$$\theta_{LIA,1} = \alpha_1 (K[H])^{\beta_1} \quad K[H] \leq K^*[H]^* \quad (5)$$

$$\theta_{LIA,2} = 1 - \alpha_2 (K[H])^{\beta_2} \quad K[H] > K^*[H]^* \quad (6)$$

where  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$  and  $\beta_2$  are adjustable parameters and they will determine both the LIA isotherm shape and the intersection point of the isotherm  $K^*[H]^*$ .

Depending on the value of parameters the following local isotherms are obtained:

**(i) Condensation Approximation (CA).**

It is characterized by  $\alpha_1 = \alpha_2 = 0$ , so  $\theta_1 = \theta_2 = 0$  and the integral inversion results in:

$$f_{CA}(\log K) = \frac{d\theta_T}{d \log[H]} \quad \log K = -\log[H] \quad (7)$$

**(ii) Logarithmic symmetrical approximation (LOGA-1).**

The general form of a LOGA isotherm is obtained when  $\alpha_1 = \alpha_2 = \alpha$ ,  $\beta_1 = -\beta_2 = \beta$  and when a Langmuir isotherm (symmetrical in  $\alpha = 0.5$ ) is assumed:

$$f_{LOGA}(\log K) = \frac{d\theta_T}{d \log[H]} - \frac{0.189}{\beta^2} \frac{d^3\theta}{d \log[H]^3} \quad \log K = -\log[H] \quad (8)$$

In this work,  $\beta = 0.7$  has been used.

**Experimental section**

The fulvic acid (FA) studied was isolated from a soil in Galicia (NW of Spain), by the procedure recommended by the IHSS [4]. The characteristics of the sample, such as elemental analysis,  $E_4/E_6$  ratio [5] and estimation of aromaticity and weight-averaged molecular weight using the molar absorptivity at 280 nm [6] are shown in table 1.

0.2 M solutions of HCl and KOH were prepared from commercial HCl 30% and KOH 0.1 M (Merck grade). The KOH solution was titrated against potassic hydrogen phthalate then used to determine the concentration of HCl. The titrant agent was prepared in boiled water to avoid the presence of  $CO_2$ . Finally, Merck grade  $KNO_3$  solutions were used to fix the ionic strength. Bidistilled water was used to prepare all solutions.

The acid-base titrations of the fulvic acids were performed at an ionic strength range from  $5.10^{-3}$  to 1.0 M and at three different initial fulvic acid concentrations (20, 40 and 80 mg/L). A Crison autoburet, Model microBU 2031, a pHmeter Crison micropH 2002 and a combined pH glass electrode Radiometer GK2401 were used. The electrode was calibrated with HCl additions over the background elec-

**Table 1. Characterization of the soil fulvic acid sample.**

Horizon	Soil	Vegetation		Bedrock	Geographic location	
Umbric	Umbric andosol	Heath and ulex		Quartz	Pico Sacro (A Coruña)	
C(%)	O(%)	N(%)	H(%)	O/C	C/N	H/C
47.75	45.52	2.37	4.25	0.72	23.46	1.06
$E_4/E_6$		$\epsilon_{280}$		M(g/mol)	Aromaticity(%)	
4.52		160.31		1130	14.76	

trolyte ( $\text{KNO}_3$ ), at different ionic strengths [7]. The temperature was kept constant with a Haake FE2 thermostat at  $25 \pm 0.1$  °C. During the titrations a stream of  $\text{N}_2$  was blown over the reaction vessel to ensure a  $\text{CO}_2$  free atmosphere.

The titrations were carried out automatically with a programme developed in this laboratory, which controls the work conditions. In this case, the parameters were: maximum addition: 0.010 mL, minimum addition: 0.010 mL (the additions have been setted in such way to avoid any problem if the program controlling the titration break down), stabilization pause: 10 s, pause between two measurements: 5 s, block size: 6 measurements, limit to read block: 0.2 mV, maximum error in the average measurement: 0.2 mV.

### Results and discussion

In studies at different ionic strenghts, Ephraim and coworkers [8] found out that the curves for  $I = 1$  M merge into one curve. This means that at higher values the ionic strenght effect is negligible. For a particular sample, the value at which the electrostatic effect becomes negligible (1 M or less) must be known. In this work, this point has been observed at  $I = 0.1$  M (Fig. 1).

The fulvic molecule was assumed to be rigid and impermeable, meaning that its shape and size do not change with pH and with ionic strength, in order to remove the electro-

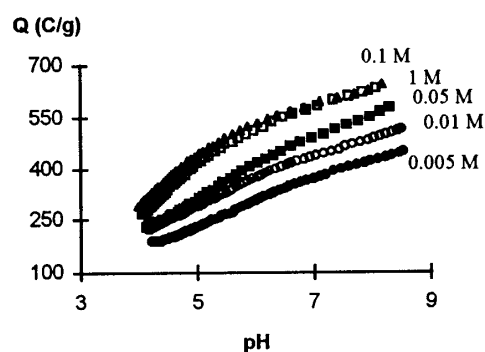


Figure 1. Effect of the ionic strength in the Q-pH curves. Concentration: 40 mg/L.

static effect. With the curve at 1 M as a reference and the surface area as an adjustable parameter, the obtention of a “mastercurve” for Q-pH<sub>s</sub> was tried (radius values in the range 0.1 – 2 nm). The r-S pairs were obtained by interpolation for the estimated molecular mass. Spherical and cylindrical geometries were assumed. Satisfactory results for the same r-S pair and geometry have not been achieved for all ionic strengths. Figure 2 shows the separation in the Q-pH curves, and it is possible to see that this separation still remains in the Q-pH<sub>s</sub> curves.

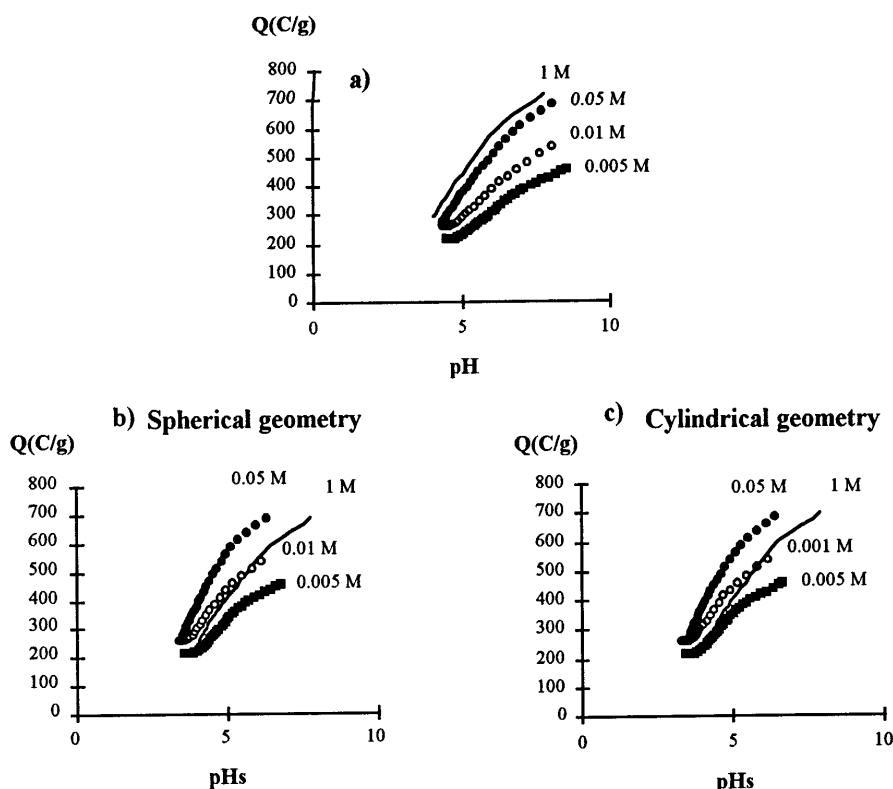


Figure 2. Obtention of the master curve was attempted for spheric (b) and cylindric (c) geometries.

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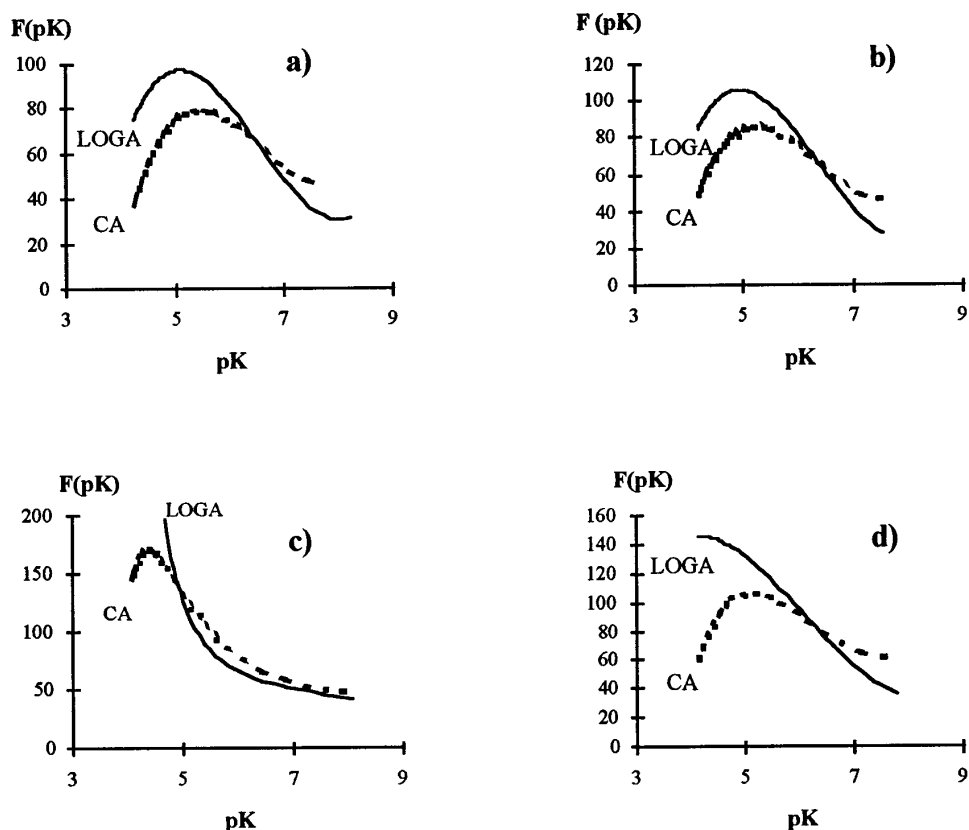


Figure 3. CA and LOGA distribution functions for the different ionic strengths: a)  $I = 0.005$  M, b)  $I = 0.01$  M, c)  $I = 0.1$  M, d)  $I = 0.05$  M.

In the absence of mastercurves the electrostatic and heterogeneity effects cannot be separated. In spite of this, the Q-pH curves were qualitatively analyzed, applying the CA and LOGA-1 methods (Fig. 3). Moreover, figure 3 shows a wide band between 4.5 and 5.5. This band is due to the carboxylic groups distribution and it is displaced to smaller pK values as the ionic strength increases.

### Conclusion

The mastercurve approach do not permit to obtain a single curve. This fact can be attributed to the possibility of a fulvic acid geometry variation with the ionic strength of the solution. The observed distribution functions for the different background concentrations used make it possible to confirm that the ionization pK of the carboxylic groups decreases as the medium ionic strength increases.

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