Ionization constants of a soil fulvic acid

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The ionization constants of a soil extracted fulvic acid were obtained analysing the potentiometric titration curves at different fulvic acid concentrations (20, 40 and 80 mg/L) and different background electrolyte concentrations from 5 10^{-3} M to 1.0 M. The results confirm the presence of two types of acidic groups with ionization constants in the range 4.27 < pK$_1$ < 4.84 and 7.85 < pK$_2$ < 8.81, respectively.

Introduction

Humic substances (humic acids and fulvic acids) are major components of the world´s surface organic matter. Through their weakly acidic character, they buffer soils and account for most of their cation-exchange capacity. Therefore, a deep knowledge of humic substances is of interest to environmental chemistry, biology and geochemistry [1].

In order to understand the role of humic subtances in the environment, one must identify the factors affecting their solution chemistry. Some of these factors are the humic substance concentration and ionic strength effects over their ionization constants. Reported potentiometric studies on humic substances suggest that their deprotonation reflects a polyelectrolyte nature and functional group heterogeneity. This has led to the development of various methods for interpreting the acid-base equilibria of humic substances in the framework of two major types of modelling, namely the discrete ligand approach [2,3] and the continuous distribution approach [4].

Non electrostatic models

In the study of acid-base reactions the non-electrostatic models do not consider the charge over the fulvic acid (FA) molecule. In the present work we used the discrete site model which considers the acidic groups as independent sites without interactions. The effect of the electric charge is assumed negligible or constant. For a simple treatment of these equilibria the Scatchard approximation [2,3] was used. The humic substance is assumed as a finit number of independent ionizable sites, each one with an equilibrium constant and concentration. For the i-th site:

$$H + L_i \leftrightarrow HL_i \qquad K_i = \frac{\left[HL_i\right]}{[H]\left[L_i\right]}$$
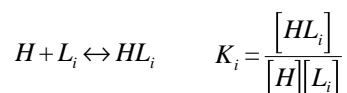
where HL_i stands for the protonated site, L_i for an individual ligand site, H the free H^+ ion and K_i the conditional equilibrium constant, which will depend on the work conditions. For this i-th site, a non-ionized fraction is defined:

$$\theta_i = \frac{\left[HL_i\right]}{c_i} = \frac{K_i[H]}{1 + K_i[H]} \qquad (1)$$

where c_i is the total concentration of the i-th site.

The sum over the total number of sites can be expressed as:

$$\theta_T = \sum_i \theta_i = \frac{c_H - [H]}{c_L} \qquad (2)$$

c_H and c_L being the total concentrations of proton and ionized acidic sites respectively.

The total proton concentration can be estimated by a mass balance:

$$c_H = [H] + \sum_i \frac{K_i[H]c_i}{1 + K_i[H]}. \qquad (3)$$

With these expressions theoretical titration curves can be built and numerical analysis of the data make possible the obtention of proper fitting parameters: K_i, c_i and $i = 1,...., n$.

Gamble [4] proposed a model that assumes the existence of a continuous distribution of different functional groups. K varies continuously and the frequency distributions can be integrated over that variable. An expression for θ_T can be obtained defining a differential ligand concentration:

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

where $N(K)$ is the affinity function which can be written according to different approximations. Posner [5] found that the acid-base titration curves of humic substances could be described with a multisite continuous distribution model, where each site presents a Gaussian distribution around its particular ionization constant, K_i:

$$N(\log K) = \frac{c_i}{c_L} = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{\frac{-1}{2\sqrt{\sigma}}\left(\mu - \log K_i\right)^2\right\} d\log K \qquad (5)$$

where c_i/c_L is the molar fraction of the ionizable site in the $\log K$ interval, σ is the standard deviation of the mean binding constant and μ is the mean $\log K_i$ value of the sites of type i.

Experimental section

The fulvic acid studied was extracted from a soil in Galicia (NW of Spain) by the procedure recommended by the IHSS [6]. Experimental data were obtained from potentiometric titration of FA samples with strong base with a fully automatic system. More experimental details can be found elsewhere [7].

Results and discussion

A common procedure in the study of polyelectrolyte weak acids is to plot the apparent pK *versus* α (degree of dissociation) using the Henderson-Hasselbalch equation:

$$pK^{app} = pH - \log\frac{\alpha}{1-\alpha} \qquad (6)$$

where α = [A$^-$]/[AH].

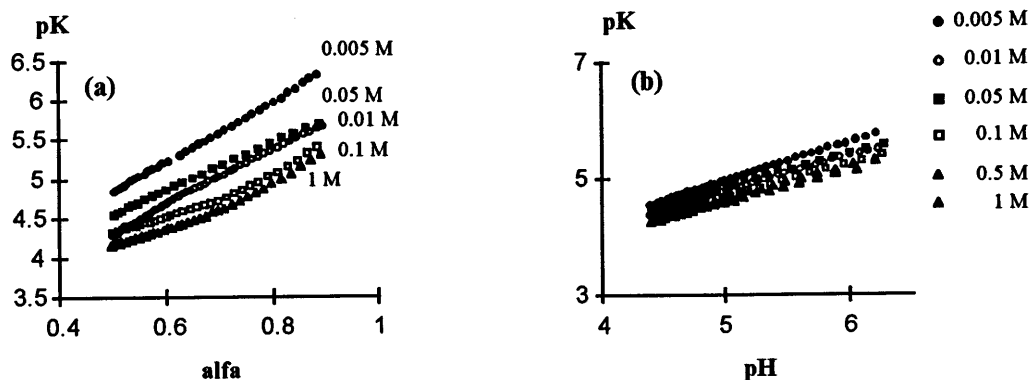From this analysis an increase in the apparent pK as α increases is observed (Fig. 1a). This is characteristic of polyelectrolyte molecules, although the slope is higher due to the typical heterogeneity of fulvic acid. As it can be deduced from figure 1b, the pK^{app} *versus* pH curves merge into one curve which according to Marinsky and coworkers [8], means that the fulvic acid studied is rigid and impermeable.

The simplest situation to begin the study of acid-base reactions according to the discrete ligands model is to assume the existence of only one ionizable site. The aim of the study is to determine the most important characteristics of the fulvic acid from the experimental titration curves using the minimum number of parameters. These parameters are K_a and the total concentration c_T.

Using the one site model theoretical titration curves we observe an abrupt jump of pH. It is typical for simple acids (see Fig. 2a), whereas the experimental curve shows an smooth increase of pH which is typical for weak acidic polyelectrolytes. A better agreement was achieved when the two site model was used (Fig. 2b). In this model the adjustable parameters are the two ionization constants (K_{a1} and K_{a2}) and the total concentration of each site (c_{T1} and c_{T2}).

Conclusion

From figure 3 we can see that the difference between the parameters estimated at 0.1 M and 1 M are quite close. Except for [FA] = 20 mg/L pK$_1$ decreases with ionic strength. This variation is significant only for ionic strength values less than 0.1 M. For the second constant (pK$_2$), a regular behaviour has not been observed. The estimated values of both pKs are in the range 4.27–4.84 and 7.58–8.81 respectively. They are in good agreement with those obtained by Milne et al. [9]. The effect of the fulvic acid concentration is also evident and it has been attributed to aggregation phenomena by Ephraim and Marinsky [10].
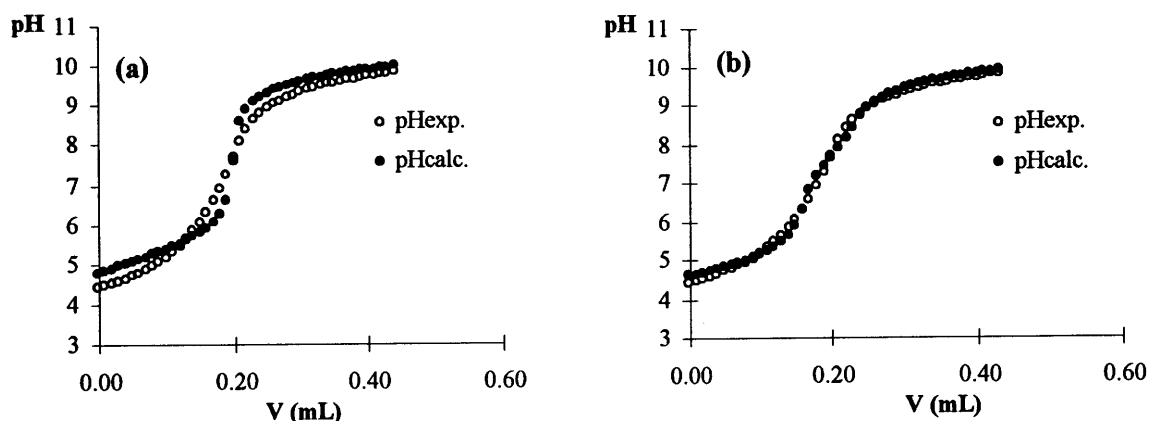

Figure 1. Curves (a) pK^{app} *versus* α and (b) pK^{app} *versus* pH according to the Henderson - Hasselbalch equation. Concentration 40 mg/L.

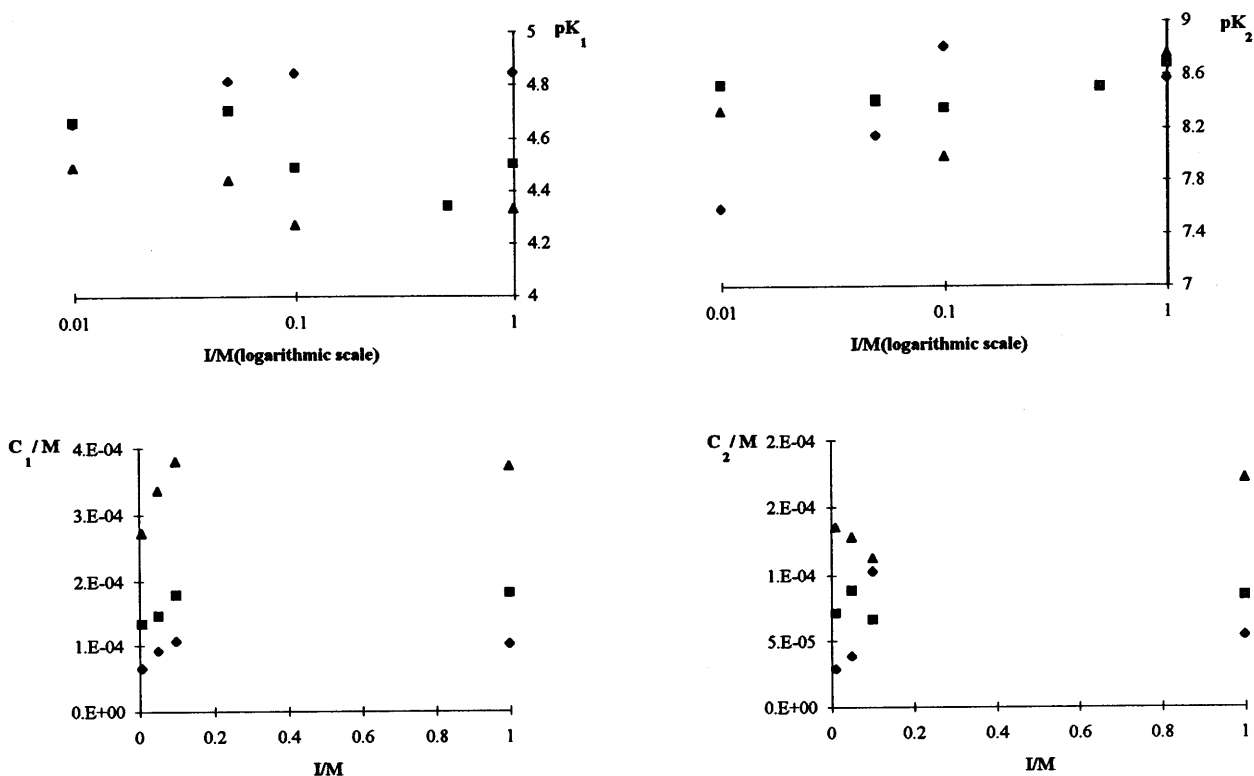Figure 2. Theroetical and experimental titration curves for (a) one site model and (b) two site model.

Figure 3. Effect of ionic strenght on pK and total concentration for the two site model (u 20 mg L^{-1}, n 40 mg L^{-1}, and s 80 mg L^{-1}).

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