

On the dissolution kinetics of humic acid particles. Effect of monocarboxylic acids

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Abstract

The dissolution kinetics of humic acid particles has been studied in batch experiments, and the effects of monocarboxylic (formic, acetic, and propionic) acids are reported. The dissolution rate of the particles is significantly affected by the presence of monocarboxylic acids in the pH range 4–10. At pH 7, for example, propionic acid increases 30 times this dissolution rate. The capacity of increasing the dissolution rate is in the order formic acid < acetic acid < propionic acid, and this dissolving capacity of carboxylics seems to be directly related to their affinity for HA molecules located at the surface of the solid particles. The results indicate that carboxylics and related compounds may affect markedly the mobility and transport of humic substances in the environment.

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1. Introduction

Humic substances (HS) represent a very important and active fraction of the refractory organic matter in soils, sediments and natural waters. They are considered to be a complex mixture of different molecules of amphiphilic nature, containing different functional groups that are very active in binding metal ions, organic contaminants and mineral surfaces (Piccolo, 2001; Sutton and Sposito, 2005). Through this binding, HS play significant roles in the formation of soil aggregates, cycling of nutrients, detoxification of hazardous compounds, and may also affect greatly the distribution and transport of contaminants in the environment (Fortun et al., 1989; Wang et al., 2001; Alvarez-Puebla et al., 2006; Bauer and Blodau, 2006; Durjava et al., 2007).

HS may occur in soils and sediments in several forms: (i) as dissolved molecules in the aqueous phase, (ii) as

adsorbed molecules or adsorbed aggregates at the surface of minerals, or (iii) forming HS particles or solid aggregates (Hayes, 1989; Stevenson, 1989; Oste et al., 2002). Dissolved molecules are mobile and can be readily transported by water flows such as rivers and groundwaters. Adsorbed molecules of HS and particulate HS may be mobile when they are readily dispersed in water, but they may also be retained and immobilized in the soil or sediment matrix. Therefore, the ability of HS to become solubilized may become a key factor that controls the dynamics of HS and attached pollutants. HS that are forming part of the soil or sediment matrix will retain the attached pollutants, limiting their mobility. On the contrary, dissolved HS will tend to mobilize these pollutants, transporting them through different water flows.

Low-molecular mass organic acids are ubiquitous in the soil environment. According to Jones (1998) and Strobel (2001), soil solution concentrations of aliphatic monocarboxylic acids (formic, acetic, propionic, butyric, valeric and lactic) are commonly found in the range 0–1 mM, whereas the di and tricarboxylic acids, including oxalic, citric, malonic, malic, succinic, and tartaric, are usually

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detected between 0 and 50 μM . In soils, organic acids may be derived from vegetal, fungal or microbial sources. They can also be present in soils or natural waters as a result of contamination with industrial wastes, especially from tanning and food processing (Kasemets et al., 2006).

Several reports exist about the effects of monocarboxylic acids on the structure and properties of HS. The works by Piccolo (Piccolo et al., 1996, 1999; Piccolo, 2001) are relevant in this sense. By using high-pressure size-exclusion chromatography, they provided evidence that the apparent size of dissolved humic fragments changes drastically with addition of simple organic acids. These authors concluded that apparent high-molecular-size HS in solution are aggregates or associations of smaller molecules that are held together by hydrophobic forces, and that these forces can be easily disrupted when monocarboxylic acids interact with HS and penetrate the aggregates. This interaction results in the formation of small-molecular-size moieties leading to the disaggregation of HS.

A solid particle of HS can be regarded as a relatively large aggregate of HS molecules (Brigante et al., 2007). Therefore, if monocarboxylic acids are able to disrupt the interaction between these molecules, they may also change significantly the dissolution behavior of HS particles, affecting the environmental mobility of these substances and attached pollutants. The aim of this article is to present a study of the dissolution kinetics of solid particles of a soil HA in order to evaluate the effects of three monocarboxylic (formic, acetic, and propionic) acids on the dissolution rate. The data obtained at different monocarboxylic acids concentrations and different pH are used to quantify the dissolution rates under different conditions, to gain insights into factors that promote or prevent dissolution of HA, and to assess information regarding the mobility of HS and the fate of their attached pollutants.

2. Materials and methods

The HA sample used in this work was taken from an andisol (Boqueixon, A Coruña, Spain). Its elemental composition is N (4.86%), C (52.57%), H (5.06%), O (34.77%), and S (0.33%), and contained some Fe (1.65%) and Al (0.76%) impurities. The solid sample was formed by polyhedral particles whose average size was 250 μm (Brigante et al., 2007). More information about the general characteristics of this humic acid, solid state ^{13}C nuclear magnetic resonance, acid–base potentiometric titrations of the HA in its dissolved state, and binding with an organic pollutant can be found elsewhere (Zanini et al., 2006).

The methodology employed in the dissolution kinetic experiments is very similar to that employed and thoroughly described in a previous publication (Brigante et al., 2007). Briefly, the experiments were performed in a cylindrical, temperature-controlled (25 ± 0.2 °C) reaction vessel covered with a glass cap. 50 ml of a monocarboxylic (formic, acetic, or propionic) acid solution prepared in a 10^{-3} M KCl solution were placed in the

reaction vessel. The monocarboxylic acids were used in their protonated form and the pH of the solution was adjusted to the desired value with KOH and/or HCl solutions. The solution was constantly stirred (450 rpm) and purged with N_2 . The dissolution experiment was started by adding a known weight (around 8 mg) of solid HA to the monocarboxylic acid–KCl solution. At different reaction times, a 5 ml aliquot was withdrawn, the particles were separated from the supernatant and the supernatant was immediately analysed to quantify the concentration of dissolved HA. Separation at the beginning of the dissolution run was done by sedimentation, because HA particles sedimented quickly in a few seconds (Brigante et al., 2007). At long dissolution times, a 3 min centrifugation (1800g) was needed to ensure separation. After the quantification (see below), that took around 30 s, the supernatant and the HA particles were hand shaken to redisperse particles and reintroduced into the reaction vessel. This procedure (aliquot withdrawal, separation, quantification of HA and reintroduction of the aliquot into the reaction vessel) was repeated during several hours in order to achieve complete dissolution of the sample or to gather enough data points. The pH was checked periodically and kept constant by adding minute volumes of concentrated KOH or HCl solutions when necessary. In all experiments, the pH was measured with a Crison GLP 22 pH meter and a Crison 52-02 combined pH electrode. All chemicals were analytical grade.

Quantification of dissolved HA was performed by UV–Vis spectroscopy, using an Agilent 8453 UV–Vis diode array spectrophotometer equipped with a Hellma 1-cm quartz cell. The supernatant of the withdrawn aliquot was placed into the cell and the spectrum was recorded in the 300–900 nm wavelength range. This equipment makes it possible to record a whole spectrum in a few seconds. The concentration of HA, c_{HA} , in the supernatant was then estimated from the absorbance at 400 nm. Calibration curves at the working pH were constructed with several HA solutions having concentrations that ranged between 2 mg l^{-1} and 200 mg l^{-1} . A uniform absorption coefficient was assumed for the different dissolved HA fractions, what gives rather accurate concentration values (Brigante et al., 2007).

The dissolution kinetics of the studied HA was evaluated by plotting c_{HA} as a function of t , or by plotting the degree of progress of the dissolution reaction, α , as a function of t . α is defined as

$$\alpha = \frac{c_{\text{HA}}}{c_{\text{T}}} \quad (1)$$

where c_{T} is the total concentration of HA that would be present in the dissolution vessel after complete dissolution of the solid. The magnitude of c_{T} was calculated from the initial weight of HA and the volume of KCl solution used in the dissolution run. The values $\alpha = 0$ and $\alpha = 1$ mean respectively that 0% and 100% of the solid has been dissolved. A plot α vs. t will be called dissolution curve.

3. Results

The technique employed in this work makes use of the absorptive ability of HA solutions in the UV–Vis region of the electromagnetic spectrum. The concentration of dissolved HA can be estimated from the absorbance in this region, and thus the dissolution kinetics can be easily monitored. As an example, Fig. 1a shows the changes in the UV–Vis spectrum of the supernatant solution during a typical dissolution kinetic experiment in which the studied HA particles are dissolved in a pH = 7 solution containing 10^{-3} M acetic acid and 10^{-3} M KCl. The absorbance (A) at any wavelength increases continuously in time and eventually reaches a constant value after 245 min of reaction. Fig. 1b, on the other hand, shows the dissolution curve obtained by plotting the absorbance at 400 nm as a function of t . The data indicate that under the mentioned conditions, dissolution proceeds continuously in time until it stops after 345 min. It seems that under the given pH and ionic strength conditions the humic acid sample cannot be fully dissolved.

Fig. 2 shows the dissolution curves obtained in 10^{-3} M KCl solutions having constant pH = 7 and different acetic acid concentrations. The dissolution is relatively slow in absence of acetic acid, but becomes faster as the acetic acid concentration increases. In fact, around 300 min are needed to dissolve around 20% of the HA in absence of

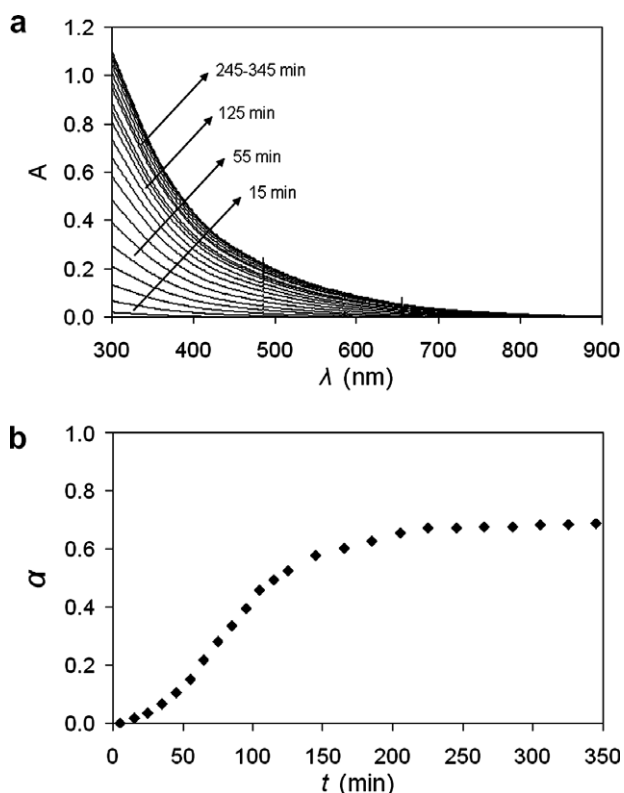


Fig. 1. (a) UV–Vis spectra of the dissolved HA at different dissolution times in a 10^{-3} M acetic acid and 10^{-3} M KCl solution. pH = 7, 25 °C. (b) Dissolution curve obtained from this data.

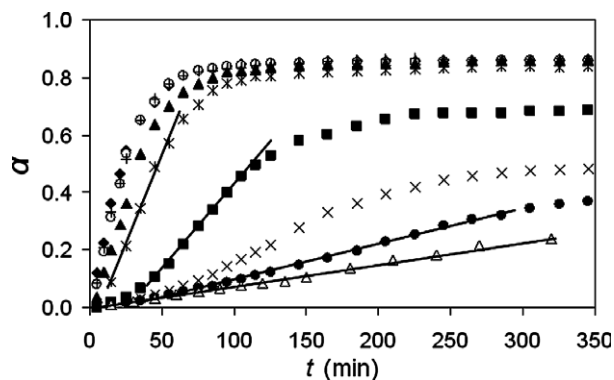


Fig. 2. Effect of acetic acid concentration on the dissolution curves of the studied HA. pH = 7, 10^{-3} M KCl and 25 °C. Acetic acid concentrations: open triangles, 0 M; solid circles, 1×10^{-4} M; crosses, 3×10^{-4} M; solid squares, 1×10^{-3} M; stars, 3×10^{-3} M; solid triangles, 6.5×10^{-3} M; plus signs, 1×10^{-2} M; open circles, 2×10^{-2} M; solid diamonds, 3×10^{-2} M.

acetic acid, whereas less than 100 min are enough to achieve around 80% of dissolution in the presence of 10^{-2} M acetic acid. Although not shown here, studies using formic and propionic acids lead to similar behaviors, i.e., the dissolution becomes faster as the monocarboxylic acid concentration increases.

The promoting effect of monocarboxylic acids on the dissolution kinetics of the studied HA can be better visualized by comparing the dissolution rates at different concentrations for the three acids investigated. The dissolution rate, R , is defined as the slope of the dissolution curve:

$$R = \frac{d\alpha}{dt} \quad (2)$$

The dissolution curves shown in Fig. 2 indicate that in absence of acetic acid or in the presence of 10^{-4} M acetic acid, R is rather constant during the 350 min that the experiment lasted because the curves can be rather well fitted with a straight line. At higher acetic acid concentrations the dissolution curves are S-shaped: R is relatively low at the beginning of the process, acquires its maximum value at intermediate times, and decreases at longer times. As stated previously (Brigante et al., 2007), there is no clear explanation for the shape of the dissolution curve. The relatively low dissolution rate at the beginning of the dissolution run is probably related to some (transient) process that is needed before dissolution takes place, such as surface hydration or perhaps monocarboxylic acid adsorption at the particles surface. After this induction time, the rate acquires its steady state (and maximum) value and then decreases monotonously as time increases, until it becomes zero when dissolution stops. Since factors responsible for the low dissolution rate at the beginning of the process are not well understood, this induction time is not considered to determine the dissolution rate. For comparative purposes, the maximum dissolution rates observed at intermediate times are used in further analyses. For some cases exemplified in Fig. 2, these rates are given by the slopes of the straight lines drawn in the figure.

Fig. 3 shows the effects of concentration of the three investigated monocarboxylic acids on the dissolution rates of HA particles at constant pH = 7. R increases significantly (around 30-fold increase for the cases of propionic and acetic, and around 15-fold increase for the case of formic) by increasing the carboxylic acids concentration up to around 10^{-2} M, and then the curves level off. Formic acid is less efficient than acetic acid in increasing the dissolution rate, and acetic acid is slightly less efficient than propionic acid. The accelerating effect of monocarboxylics cannot be attributed to an increase in the ionic strength. In fact, not shown experiments showed that the dissolution rate in 10^{-2} M KCl solutions is 17 times lower than in 10^{-2} M acetic acid solution (both at pH 7). In order to evaluate if this accelerating effect also takes place at pH values different from 7, experiments at constant carboxylic acid concentration were performed in the pH range 4–11, and the results are shown in Fig. 4. This figure compares R vs. pH curves obtained by dissolving HA particles in absence and presence of monocarboxylic acids. In absence of carboxylic acids (curve a in Fig. 4) the dissolution rate increases markedly as the pH increases: there is a 400-fold increase in the dissolution rate when the pH is changed from 4 to 11. These pH effects were already discussed in a previous publication (Brigante et al., 2007), and were attributed to (i) the breaking of hydrogen bonds that hold HA molecules in the solid phase and (ii) increased electrostatic repulsion among negatively charged molecules. Both effects are a consequence of the progressive deprotonation of carboxylic and phenolic groups of HA molecules as the pH increases, and both effects lead to increased dissolution rates. In presence of carboxylic acids (curves b–d in Fig. 4) the rate increases in almost all the pH range investigated, being the effects more marked at intermediate pH. Between pH 10 and 11, the dissolution rate is already so high in absence of carboxylics that the presence of these acids does not modify significantly the rate. The capacity of increasing the dissolution rate is in the order formic acid < acetic acid < propionic acid under all investigated conditions.

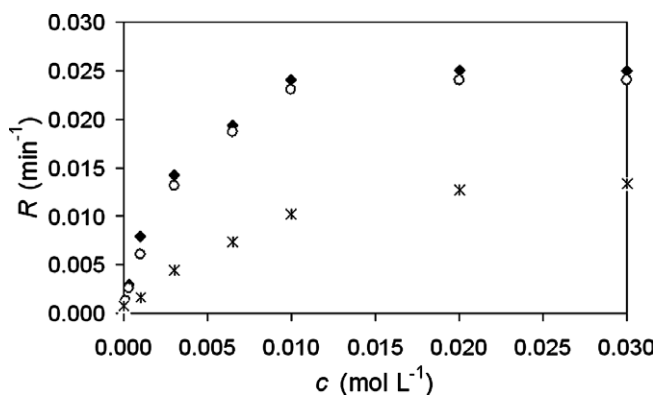


Fig. 3. Effect of monocarboxylic acid concentration on the dissolution rate of the studied sample at 25 °C. Crosses, formic acid; open circles, acetic acid; solid diamonds, propionic acid.

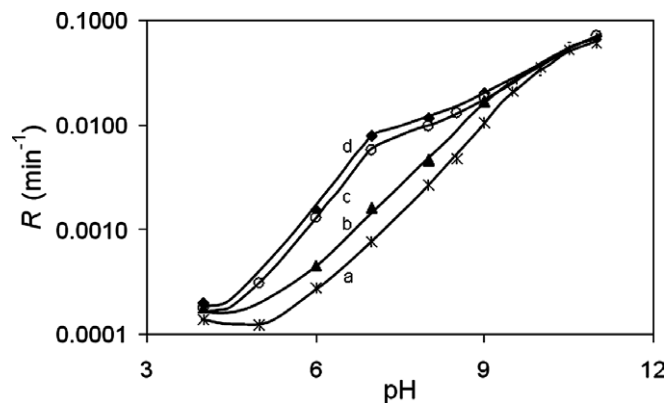


Fig. 4. Effect of pH on the dissolution rate of the studied sample at 25 °C stars, 10^{-3} M KCl; solid triangles, 10^{-3} M formic acid; open circles, 10^{-3} M acetic acid; solid diamonds, 10^{-3} M propionic acid.

4. Discussion

HA particles can be imagined as a solid aggregate of molecules of varying molecular weight and containing a variable amount of different functional groups (carboxylic groups, phenolic groups, aliphatic and aromatic regions, etc.). These molecules are held together in the solid phase by different kinds of interactions such as hydrogen bonds, π -bonds, van der Waals forces and hydrophobic interactions. If some metal ions, such as Fe(III) or Al(III) ions, are within the particles, additional electrostatic interactions and coordinative bonds between the ions and functional groups of HA molecules should be also present. When the solid particles are immersed in a dissolving aqueous solution, their outermost molecules are accessible for water, dissolved ions and molecules, and thus dissolution takes place through the release of molecules to the bulk solution.

The reactivity of a HA particle, i.e., its tendency to dissolve, depends on the type, number and strength of the forces that keep together HA molecules in the solid phase, and on the ability of dissolved ions or molecules to weaken or strengthen those forces. For example, ions or molecules able to establish hydrogen bonds between HA molecules or to decrease electrostatic repulsive forces between them will tend to decrease the dissolution rate. This is the case of H^+ ions (Brigante et al., 2007). At low pH, many phenolic and carboxylic groups of HA molecules are protonated and thus many hydrogen bonds can be established between the molecules. In addition, this protonation weakens the electrostatic repulsion among the molecules. Both effects lead to slow dissolution at low pH. As the pH increases, the deprotonation of the groups results in a decrease in the number of hydrogen bonds and an increase in the electrostatic repulsion, leading to fast dissolution. Another example is represented by divalent cations, such as Ca^{2+} . These ions can block negatively charged groups of HA molecules reducing electrostatic repulsion, and may also act as bridges between functional groups of two adjacent

molecules, increasing attractive intermolecular forces. The dissolution rate is then decreased by increasing the concentration of Ca^{2+} in the aqueous solution (Brigante et al., 2007).

The promoting effect that monocarboxylic acids have on the dissolution rate of HA particles can also be analyzed in terms of the ability of these substances to modify intermolecular forces among HA molecules. Piccolo (Piccolo et al., 1996, 1999; Piccolo, 2002) has proposed that carboxylic acids can interact with HA molecules forming hydrogen bonds between HA and carboxylics. Such interaction modify the previously existing hydrogen bonds between HA molecules and alter the hydrophobic forces that hold the molecules together. The overall result is that carboxylic acids can disrupt the structure of HA aggregates leading to disaggregation. Similar effects seem to occur on the solid HA particles studied in this work: carboxylics interact with HA particles disrupting the interactions among the molecules in the solid phase, favoring their transfer to the solution bulk.

The shape of the curves in Fig. 3 gives some indication about the dissolution mechanism. In dissolution kinetics of solid particles, this shape is typical of sorption-controlled processes (Stumm, 1992; Blesa et al., 2000; Casey, 2002), where there is at least one fast sorption step followed by a slower and rate-determining release of molecules to the bulk solution. In the case of dissolution of solid HA particles promoted by monocarboxylics, the fast sorption process is believed to be the attachment of monocarboxylics to the surface of HA particles. This attachment leads to the formation of surface species that weaken the interactions between HA molecules at the surface of the particles. The following and rate-determining step is the passage of these surface molecules to the solution bulk. In this sorption-controlled process, the dissolution rate results to be proportional to the concentration of surface species (sorbed monocarboxylics in this case). Therefore, R vs. concentration curves should have the shape of an adsorption isotherm, with a leveling off of the curves, in agreement with the shape of the curves in Fig. 3.

Piccolo et al. (1999) have also shown that the extent of conformational changes on HA aggregates is dependent on the hydrophobicity of carboxylic acids. The larger the number of carbon atoms in the acid, the greater is the affinity for the hydrophobic components of HA, and the greater is their capacity to alter the humic associations. Therefore, the disrupting effect of monocarboxylics is generally in the order formic acid < acetic acid < propionic acid (Piccolo et al., 1999). This is in line with the results found here, and thus the dissolving capacity of carboxylics seems to be directly related to their affinity for HA molecules located at the surface of the solid particles. Data in this article, however, suggest that there is a limit to this effect since the capacity to alter the humic association is very similar for acetic acid and propionic acid. Besides this hydrophobic interaction and besides the disrupting effect that carboxylics may have when forming hydrogen bonds with

HA molecules as indicated above, it has to be noted that at slightly acidic or alkaline pH values most of the carboxylics are actually present in solution as carboxylate anions. Although these anions could still attach humics by hydrophobic interactions or hydrogen bonds, they may also coordinate Fe(III) and Al(III) ions that act as bridges between adjacent molecules in the solid phase. In this case, some bonds that the metal ions establish with functional groups of HA molecules will be replaced by bonds with carboxylates, leaving surface HA molecules more susceptible to detachment. This is also in agreement with the trends observed in Figs. 3 and 4, because the complexation constants of carboxylates with Fe(III) and Al(III) increase in the order formic < acetic < propionic (Mantell and Smith, 1997). As an additional effect, it also has to be noted that Fe(III) and Al(III) species in the dissolved state will tend to keep HA in a coagulated or precipitated form. The complexation in solution of these cations by monocarboxylic acids may also contribute to increase the dissolution rate of HA particles.

5. Conclusions and environmental implications of dissolution studies

The dissolution rate of humic acid particles is significantly affected by the presence of monocarboxylic acids in an ample range of pH. Dissolution appears to take place through a sorption-controlled process, which is initiated by the attachment of carboxylic to the surface of the particles, followed by the transfer of HA molecules to the bulk solution. Carboxylics can enhance the dissolution rate of humics because they are able to weaken the attractive forces that maintain HA molecules together in the solid phase. They may also contribute to increase the dissolution rate by complexing iron and aluminum cations in solution.

The results presented here may have significant importance for environmental processes because they imply that under certain conditions (low pH, low carboxylic concentrations, high metal ion concentrations) humic acids molecules that are forming solid aggregates in soils or that are aggregated at the surface of minerals will show a very slow dissolution even though they may be “thermodynamically” soluble. This slow dissolution will limit the mobility of HA molecules and that of the attached pollutants. On the contrary, conditions that enhance the dissolution rate (such as high pH, high carboxylic acids concentrations and low metal ion concentrations) will increase quickly that mobility.

It is rather well accepted at the moment that HA molecules can aggregate or disaggregate depending on the environmental conditions (Avena and Wilkinson, 2002; Sutton and Sposito, 2005). The dynamics of these processes are not well known at the moment, and it is still necessary to investigate the mechanisms and intermolecular interactions that lead to aggregation or disaggregation. Besides carboxylics, many other chemical species such as pesticides, surfactants, anions and cations could also affect this dynamics.

Dissolution kinetic studies, combined with precipitation kinetics, may provide useful information regarding these processes.

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