Environ. Sci. Technol. **1998**, *32,* 3331−3335

An ATR−FTIR Study of Glyphosate and Its Fe(III) Complex in Aqueous Solution

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An ATR−FTIR study of the vibrational spectrum of glyphosate (*N*-phosphonomethylglycine) in aqueous solution 1 M in NaCl is reported. Band assignments are given in the 1800−850 cm^{-1} range based on the analysis of the spectral changes from low to high pH values (2−11). Potentiometric titrations of glyphosate are performed at 0.1, 0.5, and 1 M ionic strengths in NaCl and the pK_{a2}, pK_{a3}, and pK_{a4} values determined. A chemometric analysis of the spectral data has been carried out to support the assignments and reproduce the pK_a values. In addition, the ATR−FTIR spectrum of the 1:1 Fe(III)/glyphosate complex in aqueous solution is analyzed by comparison with that of the free ligand.

Introduction

Glyphosate, *N*-phosphonomethylglycine, is a nonselective and broad spectrum postemergent herbicide characterized by a highly effective herbicidal action on both annual and perennial plants. Due to the different application methods and weather conditions, a significant amount of herbicide reaches the soil. Herbicides that enter the soil may be bound in various ways to soil constituents. They may undergo transport from the contacted area, and they may be degraded by different mechanisms (*1*). In the soil, herbicides are generally adsorbed to constituents such as clay minerals, organic matter, metallic oxides, and humic substances. Since the fate of a herbicide through the soil is generally mediated by water, water-solubility, metal complexation, and adsorption characteristics are of great importance concerning the rate of the transport process. Adsorption mechanisms of glyphosate onto soils and clay minerals (*2*−*6*) as well as metal complexation (*7*) in aqueous solution depend directly on the pH values.

Complete and rapid microbiological degradation of glyphosate occurs in soils and/or water (*8*−*10*). However, the rate of glyphosate degradation in different soils can vary considerably depending on the degree of microbial activity of the soil, and a single factor is not usually involved in the disappearance of the herbicidal activity when glyphosate is applied to the soil. Certainly, inactivation through adsorption onto soils and complexation with dissolved metal ions (i.e., Fe^{3+}, Al^{3+}) reduce the degradation rate as well.

These types of chemical interactions are responsible for the availability of the free herbicide to undergo further biodegradation in natural waters.

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Attenuated Total Reflection (ATR) infrared spectroscopy has become the most powerful method for IR work in aqueous solution. The extremely short path length provided by this technique makes possible the subtraction of the aqueous background (*11*). A detailed knowledge of the vibrational spectrum of glyphosate in aqueous solution is necessary as a first step for the further in situ adsorption studies above-mentioned. To our knowledge, only the infrared spectra of solid glyphosate (*12*) and of its sodium salts obtained by the freeze-dried technique at different pH values were reported (*13*).

In this work an ATR−FTIR study of glyphosate in aqueous solution 1 M in NaCl at different pH values was carried out and used as an aid to the interpretation of the nature of the coordination of the 1:1 Fe(III)/glyphosate complex in aqueous solution.

Experimental Section

Materials. All solutions were prepared using doubly distilled deionized water and reagent grade chemicals. Glyphosate was provided by Sigma Co. and used without further purification. Iron(III) solutions were prepared from $Fe(NO_3)_3 \cdot 9H_2O$ (Anedra). Deuterium oxide, NaOD, and DCl were provided by Aldrich Company.

ATR−FTIR Spectroscopy. The ATR−FTIR spectra were obtained with 4 cm^{-1} resolution on a Nicolet 510P spectrometer equipped with a TGS detector and a Balston H_2O/CO_2 stripper. The ATR accessory consisted of a 10 cm horizontal boat plate (Spectra Tech.) with a 45° ZnSe crystal (range 4000−800 cm^{-1}). Typically, a background spectrum of 500 scans was recorded with the empty sample boat. Reference and sample spectra were recorded, 500 scans each, at the same pH in 1 M NaCl and subtracted to obtain the spectrum of the solute. Due to the low solubility of glyphosate in water a concentration of 0.05 M in 1 M NaCl was used.

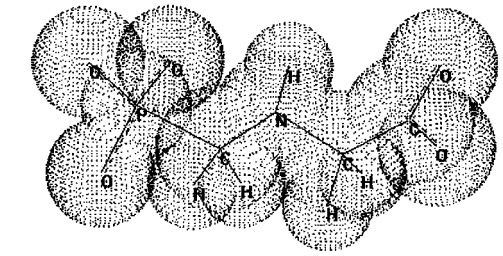
The spectrum of the 1:1 Fe(III)/glyphosate complex was obtained under the same conditions without NaCl addition. The concentration of the complex in water was 1×10^{-4} M, and the resulting pH was 3.65 (sample spectrum). Since $Fe(NO_3)_3 \cdot 9H_2O$ was used to prepare the complex, a reference spectrum of aqueous KNO_3 3×10^{-4} M was subtracted from the sample spectrum in order to avoid the interference of the nitrate ion in the resultant spectra of the Fe(III)/glyphosate complex. Higher concentrations of the complex resulted in solid precipitation.

UV−vis Measurements. The UV−vis spectra were obtained on a Hewlett-Packard HP-8452A diode array spectrophotometer with 10 mm quartz cells. The method of the continuous variations (*14*) was used to determine the stoichiometry of the Fe(III)/glyphosate complex in aqueous solution. The spectra of aqueous solutions of Fe(III)/glyphosate with molar concentration ratios ranging from 1:3 to 3:1 were recorded, keeping the total concentration at 1×10^{-4} M. Formation of a complex was evidenced by the spectral changes observed among the spectra of the ligand and the metal ion with respect to those of the solutions. A new absorption band centered at 255 nm appeared at pH values from 3.9 to 4.1. Plotting the absorbance values of each Fe(III)/glyphosate solution at this wavelength against the mole fraction of glyphosate in the mixtures, a ratio of 1:1 was obtained for the complex.

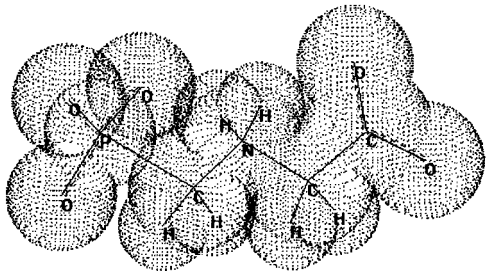
Potentiometric Titration. A 682 automatic titroprocessor with a combined pH microelectrode (Metrohm) was used. All solutions were prepared using water free of CO_2 at ionic strengths of 1, 0.5, and 0.1 M in NaCl. Three NBS buffers were used for calibration at pH 4.01, 6.87, and 9.18 at 25 °C

S0013-936X(98)00038-8 CCC: $15.00
Published on Web 09/12/1998

CHART 1. Two Species with the Angles and Bond Lengths Obtained from a Semiempirical Calculation (AM1) in Vacuum Using Hyperchem Software: (A) Species IV [$-OOCCH_2NHCH_2PO_3^{2-}$] and (B) Species III [$-OOCCH_2(NH_2)^+CH_2PO_3^{2-}$]



A



B

and rechecked after each measurement. The initial volume of glyphosate solution was 20.00 mL in all cases, and the concentrations used were 2.63×10^{-3} M (for $I = 0.1$ M), 5.13×10^{-3} M (for I = 0.5 M), and 1.96×10^{-2} M (for $I = 1$ M). The titration curves were recorded up to pH ≅ 11, and the titrant was added automatically in volumes of 0.008 mL.

Mathematical Treatment. Chemometric analysis of spectroscopic data has been extensively reported elsewhere (*15*−*20*). A very brief description will be given in order to understand the main steps. The experimental spectra data are arranged in a matrix **A**.

According to Beer's Law, matrix **A** for glyphosate is the product of the real molar absorptivities matrix **E** at different wavenumbers and the real molar concentrations matrix **C** of all species at different pH values.

$$\mathbf{A} = \mathbf{E}\cdot\mathbf{C}$$

SVD (single value deconvolution) or NIPALS (non linear iterative partial least squares) algorithms (*19*) allow for decomposition of matrix **A** into two new abstract ones, **P** and **T**, yielding a set of orthogonal vectors. An appropriate conversion matrix **R**, finds the best linear combination of these abstract vectors to reproduce matrix **A**. So, **A** can be written as

$$\mathbf{A} = \mathbf{C}\cdot\mathbf{E} \quad \text{or} \quad \mathbf{A} = \mathbf{P}\cdot\mathbf{T} \quad \text{(NIPALS)}$$

Introducing matrix

$$\mathbf{R,A} = \mathbf{P}\cdot\mathbf{R}\cdot\mathbf{R}^{-1}\cdot\mathbf{T}$$

Now

$$\mathbf{P}\cdot\mathbf{R} = \mathbf{E} \quad \text{and} \quad \mathbf{R}^{-1}\cdot\mathbf{T} = \mathbf{C}$$

Matrix **R** can be found from **T** and **C** matrixes by a least-squares fit, with the pK_a values left as the adjustable parameters. This is calculated minimizing the squared difference between **T** and **C**·**R** matrixes.

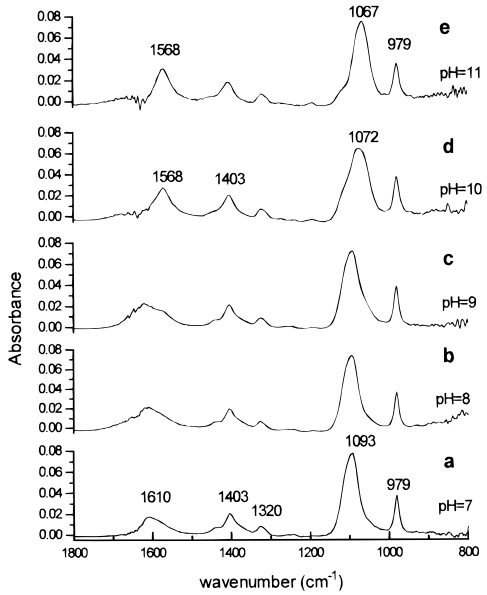


FIGURE 1. ATR−FTIR spectra of 0.05 M glyphosate in aqueous solution from pH = 7−11 at 1 M ionic strength in NaCl.

Computing the product **P**·**R**, a matrix similar to **E** is obtained which contains the predicted spectral components of the system. If the assumed model is the correct one, the predicted spectral components render the true species of glyphosate as well as the pK_a values.

Plotting the **P**·**R** matrix product ($M^{-1}\cdot cm^{-1}$) against the wavenumbers (cm^{-1}), the calculated spectral components are obtained which are the basis to reproduce the whole set of spectroscopic data.

Results and Discussion

ATR−FTIR Spectra. Glyphosate is a weak acid with four acidity constants: two for the phosphonic group (pK_{a1}, pK_{a3}), one for the amino group (pK_{a4}), and one for the carboxylic group (pK_{a2}). However, only three of them can be measured due to the formation of a zwitterion between the amino and the phosphono groups in aqueous solution. The acid-base equilibria of glyphosate are given in Scheme 1.

SCHEME 1

$$HOOCCH_2(NH_2)^+CH_2PO_3H^- \leftrightarrow \underset{\text{Species I}}{}$$
$$^-OOCCH_2(NH_2)^+CH_2PO_3H^- + H^+ \quad pK_{a2}$$
$$\text{Species II}$$

$$^-OOCCH_2(NH_2)^+CH_2PO_3H^- \leftrightarrow$$
$$^-OOCCH_2(NH_2)^+CH_2PO_3^{2-} + H^+ \quad pK_{a3}$$
$$\text{Species III}$$

$$^-OOCCH_2(NH_2)^+CH_2PO_3^{2-} \leftrightarrow$$
$$^-OOCCH_2NHCH_2PO_3^{2-} + H^+ \quad pK_{a4}$$
$$\text{Species IV}$$

The ATR−FTIR spectra of glyphosate at different pH values are shown in Figures 1 and 2. The use of water solutions to study species with oxoanions or amine groups determines that the bands associated with this species, inherently broad in solid state, become much broader in water solutions, and little detailed information is obtained. However, several comments on the assignments in the different regions may be made.

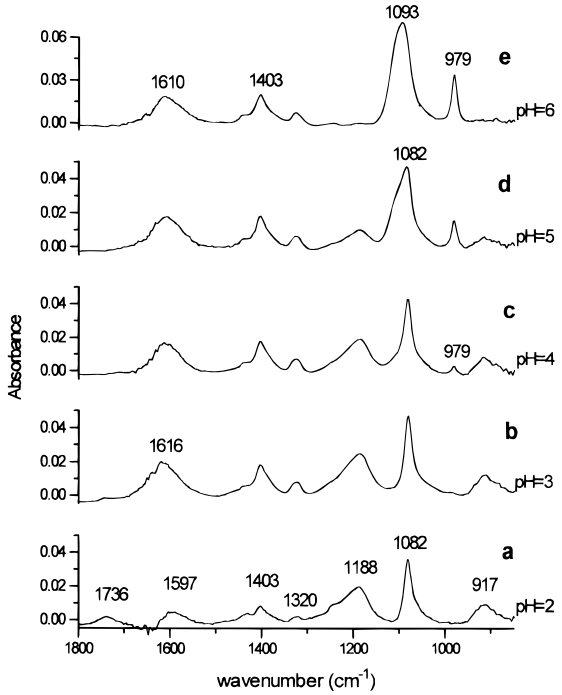


FIGURE 2. ATR−FTIR spectra of 0.05 M glyphosate in aqueous solution from pH = 2−6 at 1 M ionic strength in NaCl.

TABLE 1. Band Assignments for Glyphosate in Aqueous Solution in cm^{-1} [a]

band assignment	species I	species II	species III	species IV[a]
ν_{P-OH}	917	917		
δ_{P-OH}	1250	1250		
ν_{PO_2}	$\nu_a = 1188$	$\nu_a = 1188$		
	$\nu_s = 1082$	$\nu_s = 1082$		
ν_{PO_3}			979 (A_1)	979 (A_1)
			1093 (E)	1067 (E)
ν_{CO}	1736			
ν_{COO}		$\nu_a = 1616$	$\nu_a = 1616$	$\nu_a = 1568$
		$\nu_s = 1403$	$\nu_s = 1403$	$\nu_s = 1403$
δ_{NH_2}	1597	overlapped with $\nu_{a\ COO}$	overlapped with $\nu_{a\ COO}$	

[a] The species refer to Scheme 1.

Frequency Range 1400−850 cm^{-1}. The bands to be considered in this region are those related with the changes in the protonation of the phosphonic group (Table 1).

At 9 > pH ≥ 6, the predominant species for the phosphonic group is the totally deprotonated $R-PO_3^{2-}$ (Figures 1c−2e). Based on frequency values trends for ZXY_3 tetrahedral molecules of C_{3v} symmetry (*21*) and previous vibrational studies of phosphates in aqueous solution (*22*), the following assignment is proposed:

$$\nu_{(PO_3)}(A_1) = 979\ cm^{-1}, \quad \nu_{(PO_3)}(E) = 1093\ cm^{-1}, \quad \text{and} \quad \nu_{(R-P)}(A_1) = 1320\ cm^{-1}$$

For pH > 9, the amino group deprotonates according to its pK_a (Table 2). This is accompanied by a decrease of ~30 cm^{-1} in the frequency value of the $\nu_{(PO_3)}(E)$ from 1093 to 1067 cm^{-1} at pH = 11 which may be attributed to the increase in the total negative charge of the glyphosate unit that accompanies the deprotonation (Figure 1d,e).

At 4 ≥ pH ≥ 2, the prevalent species is likely to be $R-PO_2(OH)^-$ with a lower C_1 symmetry. As the pH is decreased, $\nu_{(PO_3)}(E)$ at 1093 cm^{-1} splits into two new bands

TABLE 2. Acidity Constants of Glyphosate

ionic strength (M)	pK_{a_2}	pK_{a_3}	pK_{a_4}	ref
1	1.77	5.08 (4.91)[a]	9.76 (9.73)[a]	this work
0.5	1.96	5.28	9.98	this work
0.1	2.09	5.52	10.28	this work
0.1	2.27	5.57	10.25	26
0.1	2.23	5.46	10.14	27

[a] Calculated from the chemometric analysis.

at 1188 and 1082 cm^{-1} (Figure 2a). The infrared bands are assigned as follows

$$\nu_{(P-OH)} = 917\ cm^{-1}, \quad \nu_{sym(PO_2)} = 1082\ cm^{-1}, \quad \nu_{asym(PO_2)} = 1188\ cm^{-1}, \quad \text{and} \quad \nu_{(R-P)} = 1320\ cm^{-1}$$

In solid state, previous band assignments were reported for the phosphonate group (*13*).

It is clear from the pH dependence of $\nu_{(P-OH)}$ at 917 cm^{-1} and $\nu_{(PO_3)}(A_1)$ at 979 cm^{-1} above in aqueous solution from pH = 2 to pH = 6 (Figures 2a−e) that these two modes are related to the protonation and deprotonation of the phosphonate group, pK_{a3}.

These assignments are of interest as they are expected to be diagnostic bands in the studies of the interactions of glyphosate with metal ions or sediments in aqueous solutions.

It is worth mentioning that the bands at 917 and 979 cm^{-1} have been previously assigned to skeletal CCNC vibrations and to CH_2 and CH_3 deformations, respectively (*12*, *13*). The weak shoulder at 1250 cm^{-1} may be assigned to the $\delta_{(POH)}$ mode.

Frequency Range 1800−1400 cm^{-1}. The bands to be analyzed in this region are those related with the carboxylic and the amino groups (Table 1).

At pH = 2, both the carboxylate and the carboxylic groups are present together with the amino group totally protonated. Based on amino acids vibrational studies (*23*−*25*) the following assignment is straightforward:

$$\nu_{sym(COO)} = 1403\ cm^{-1}, \quad \delta_{(NH_2)} + \nu_{asym(COO)} = 1597\ cm^{-1}, \quad \text{and} \quad \nu_{(C=O)} = 1736\ cm^{-1}$$

In the range 2 < pH ≤ 5 the carboxylic acid is mostly deprotonated, while the amino group is still protonated. When the pH is increased, the band at 1736 cm^{-1} assigned to the free carbonyl group disappears, while the band centered at 1597 cm^{-1} shifts to a strong and broad band centered at 1616 cm^{-1} (Figure 2a,b). According to the pK_{a2} and the evolution of the spectra with the pH, the band at 1616 cm^{-1} is related with the deprotonation of the carboxylic group. The following assignment is proposed:

$$\nu_{sym(COO)} = 1403\ cm^{-1}, \quad \delta_{(NH_2)} + \nu_{asym(COO)} = 1616\ cm^{-1}$$

At pH = 9, the band at 1616 cm^{-1} appears to split into two (Figure 1c). For higher pH values, the prevalence of the deprotonated amino group is expected. Under these conditions, the asymmetric stretching of the carboxylate anion is observed at 1568 cm^{-1} with a very weak band around 1640 cm^{-1} (Figure 1e), consistent with reported IR studies for α-amino and α-ammonium carboxylates in aqueous solution (*21*).

To confirm the position of the asymmetric stretching of the carboxylate anion we studied the spectral changes of a 0.05 M solution of glyphosate in heavy water at pD = 2, 7, and 11 (Figure 3). No amino bands are present in the range

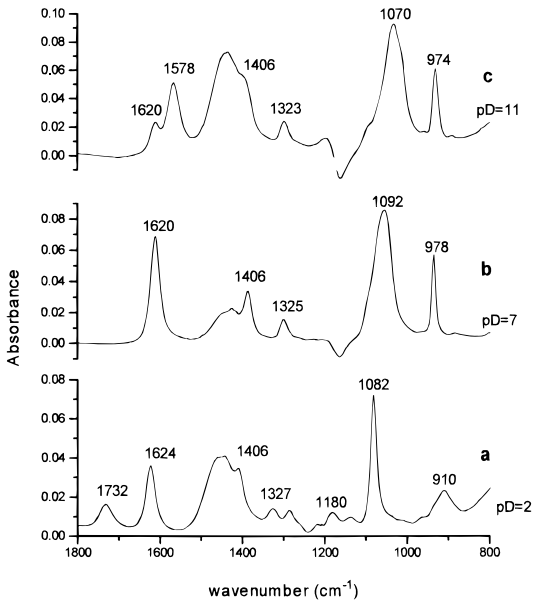


FIGURE 3. ATR−FTIR spectra of glyphosate 0.05 M in D_2O at pD = 2, 7, and 11.

of interes (1800−1400 cm^{-1}) in D_2O solutions. The reported pK_a values for the carboxylic, phosphonic, and amino groups in D_2O are 2.0, 5.5, and 10.5, respectively (*26*).

At pD = 2, the stretching of the carbonyl appears at 1732 cm^{-1}, while the strong band at 1624 cm^{-1} is best assigned to the asymmetric stretching of the carboxylate anion (Figure 3a). This suggests that the band centered at 1597 cm^{-1} in Figure 2a may arise mainly from the deformation modes of the protonated amino group which is overlapped with the strong asymmetric stretching of the carboxylate anion at higher pH values.

At pD = 7, the bands at 1620 and at 1406 cm^{-1} are assigned to the asymmetric and symmetric stretching modes of the carboxylate anion, similar to the above assignments at pH = 7 (Figure 3b).

At pD = 11, the amino group is partially deprotonated. This may determine the presence of two different carboxylate asymmetric stretching vibrations as reported in amino acids (*21*), one arising from the protonated amino at 1620 cm^{-1} and the second from the deprotonated amino at 1578 cm^{-1} (Figure 3c). Thus, it is clear that the frequencies associated with the asymmetric vibrations of the carboxylate anion in glyphosate depend strongly on the pH values in aqueous solution. Asymmetric carboxylate modes may be present at 1616 and/or 1568 cm^{-1}, depending on the charge of the amino group.

These possibilities should be taken into account in studies where complexation between glyphosate and metals are involved, since carboxylate bands are usually diagnostic bands for metal complex formation. Bands or shoulders at 1440 and 1050 cm^{-1} may be assigned to CH_2 deformations coupled with CCNC skeletal vibrations.

In Figure 4, the spectrum of the 1:1 Fe(III)/glyphosate complex is shown together with that of the free glyphosate at similar pH. The shoulder at ca. 1580 cm^{-1} should be assigned to the deformation mode of the protonated amino group in the complex in accordance with the above assignment for the free ligand at pH = 4. Phosphonate coordination is indicated by the very broad and unresolved band in the range 1200−950 cm^{-1} assigned above to the stretching modes of the PO_2^- and PO_3^{2-} units for the free ligand. Despite the complexity of the spectrum in this range, the absence of the characteristic group frequencies for $\nu_{(P=O)}$ in the range 1400−1200 cm^{-1} and for $\nu_{(P-OH)}$ at 917 cm^{-1} in the free ligand above

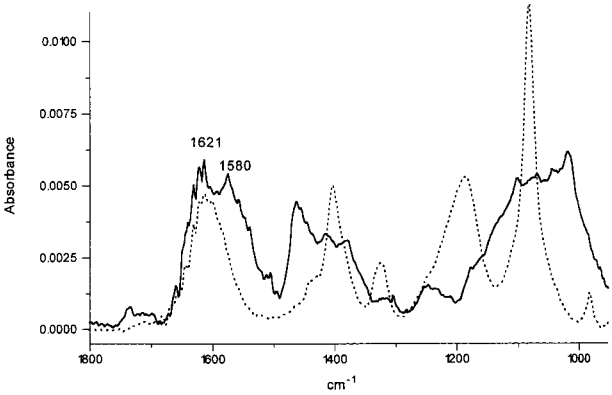


FIGURE 4. ATR−FTIR spectra in aqueous solution of glyphosate (···) and the 1:1 Fe(III)/glyphosate complex (−) at pH = 4 and 3.65, respectively.

suggests that coordination of Fe(III), or more likely $Fe(OH)^{2+}$ species, occurs through the phosphonic group. No further structural information on the nature of the Fe(III) species in solution can be obtained from UV−vis and IR spectroscopic data. This observation is in accordance with reported ESR studies in frozen aqueous 1:1 Fe(III)/glyphosate solutions which show that the phosphonic group is involved in complexation in aqueous solution (*7*).

While in solid state the complexation of Fe(III) with glyphosate through the carboxylate ion and amino groups has been reported (*27*), no shifts are observed for the $\nu_{asym(COO)}$, $\nu_{sym(COO)}$, and $\delta_{(NH_2)}$ modes in aqueous solution at similar pH values for the free ligand. This suggests that the ionic character of these groups remains unchanged when the metal is present. In conclusion, in aqueous solution, glyphosate shows no evidence of coordinating the metal through the carboxylate anion or the amino group; however, significant changes are observed in the range for the phosphonic group vibrations as expected for metal-phosphonate coordination.

Potentiometric Titration. Potentiometric titrations of glyphosate were performed in aqueous solution at 1, 0.5, and 0.1 M ionic strengths in NaCl, and the estimated pK_a values are given in Table 2 together with previously reported values at 0.1 M (*28, 29*).

The titration curves of glyphosate were fitted from the initial to the final experimental pH values (∼2 to 12). From the mass balance equation and the expressions of the acidity constants, the concentrations of all the acid−base species of glyphosate can be expressed in terms of the proton concentration in equilibrium, the total glyphosate concentration, and the volume of NaOH added at each point of the titration curve. Similarly, from the electroneutrality condition, the concentrations of cation Na^+ can be expressed as a function of all the ions present in the solution. Similar considerations to describe the progress of a titration can be found in the literature (*30*).

Thus, it is possible to adjust the volume of titrant coming from the charge balance equation to reproduce the experimental volume by minimization of the total sum of the squared difference of both values, setting the pK_a as adjustable parameters. This least-squares fit generates the pK_a values given in Table 2, that best reproduce the experimental titration curve of Figure 5. The goodness of fit was evaluated by the χ^2 parameter.

Mathematical Treatment. The set of ATR−FTIR spectra of glyphosate in aqueous solution from pH = 3−11 was simultaneously analyzed using NIPALS algorithm and least-squares fit at all wavenumbers. Data were modeled under the assumption that the equilibria given in Scheme 1 were dominant. The results revealed three spectral components and two pK_a values of 4.91 and 9.73, as expected for the

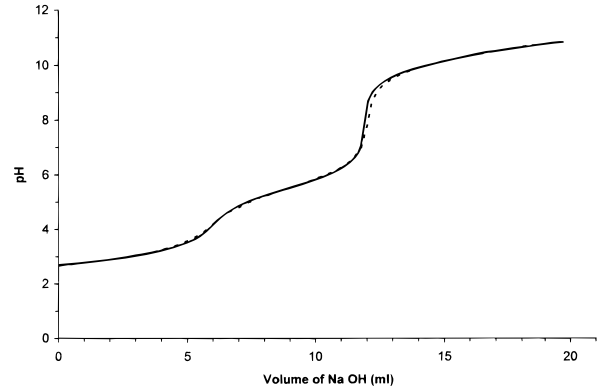


FIGURE 5. Titration curve of 2.63 × 10^{-3} M glyphosate with 8.8 × 10^{-3} M NaOH at 0.1 M ionic strength in NaCl. Points: experimental data. Line: best fit to these data. The χ^2 goodness-of-fit parameter was 0.77 for the volume and 4.6 × 10^{-8} M for the concentration.

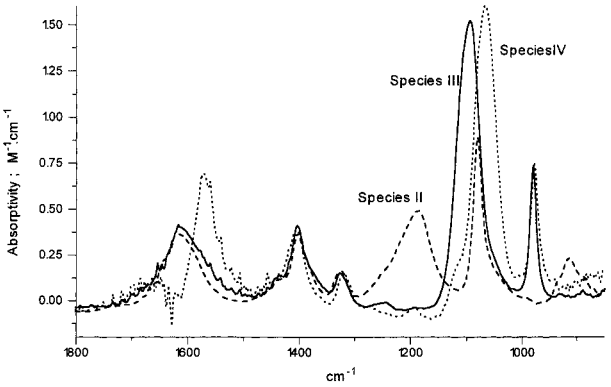


FIGURE 6. Calculated spectral components for glyphosate species in aqueous solution at 1 M ionic strength in NaCl. Spectra are normalized to 1 M in total glyphosate concentration. From the output data of the chemometric analysis, a pK_{a3} = 4.91 and a pK_{a4} = 9.73 correspond to the equilibrium constants between the species III(—)/II(- - -) and IV(···)/III(—), respectively.

measured pH range. The residual value for the least-squares fit was 2.18 × 10^{-2}. The calculated spectral components are shown in Figure 6. An inspection of these three spectral profiles evidence the correlation with the true glyphosate species II, III, and IV of Scheme 1 in aqueous solution from pH = 3 to pH = 11.

The calculated pK_a values are in good agreement with the experimental pK_{a3} and pK_{a4} at 1 M ionic strength (Table 2). The pK_{a2} of the carboxylic group could not be calculated because of the restricted range of pH (higher than 2) imposed by the ZnSe ATR crystal.

In summary, the ATR technique has proved to be very adequate to obtain information from systems in aqueous solution, and the spectra are suitable to be treated mathematically allowing to extract valuable information from the system. This analysis proves to be particularly useful for complex molecules with several acid—base functional groups as is the case of many substances which present environmental impact. While potentiometric methods provide a set of pK_a values, it is not always obvious to find the correspondence among these pK_a values and the different functional groups. Also, when the IR bands of the species at different pH values are overlapped, it is not possible to find the pK_a values directly from the spectra with a simple calculation of absorbance ratios.

The availability of glyphosate in hydrosoils and water for microbial activity is strongly dependent on soil-glyphosate and metal-glyphosate complexes formation. Obviously, the pH, organic matter, and dissolved metals have a strong impact in the movilization of herbicides. The use of this technique made possible the study of a system with environmental interest closer to its natural conditions. In this work we see that the coordination of Fe(III) with glyphosate in aqueous medium can differ from the results obtained in solid state.

Acknowledgments

This work was supported by UBA (UBACyT Ex-158 and Ex-037). The authors wish to thank Dr. M. Perec, L. Baraldo, and Lic. A. Parise for helpful discussions.

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Received for review January 20, 1998. Revised manuscript received June 23, 1998. Accepted July 8, 1998.

ES9800380