**BINDING OF Glyphosate BY OPEN-CHAIN POLYAMMNONIUM CATIONS**

LORENZO ABATE,† CONCETTA DE STEFANO,‡ CLAUDIA FOTI,‡ and SILVIO SAMMARTANO*‡

†Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria, 6, I-95125 Catania, Italy
‡Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone, 31, 1-98166 Messina (Vill. S. Agata), Italy

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**Abstract**—Interaction of glyphosate (N-(phosphonomethyl)-glycine) with six polyamines (ethylenediamine, cadaverine, putrescine, triethylenetetramine, spermine, and tetraethylenepentamine) was studied potentiometrically. Several species of different stoichiometry are formed in the various systems, according to the general formation reaction $\text{AH}_n^{\text{z}+} + \text{H}_n\text{glp}^{n-} \rightarrow \text{A}^{(n-\text{z})} \text{glp}^{n+} + \text{zH}^+$ (where A = amine and glp = glyphosate). The complex species formed are always $\text{A}^{(n-\text{z})} \text{glp}^{n+}$ with $r = 1, \ldots, (n + 2)$ ($n =$ maximum degree of protonation of amines). The stability of various complexes is a linear function of charges involved in the formation reaction, and can be expressed as $\log K_i = 0.9(\pm 0.2)i$ (where $i = [3 - j]$). From the temperature dependence of formation constants, $\Delta H^\circ$ and $\Delta S^\circ$ values have been obtained. Formation percentages of mixed glyphosate–polyammonium cation complexes are relevant also in low concentration conditions, and this means that these species may play a significant role in the speciation of natural fluids containing the reactants.

**Keywords**—Amine–glyphosate complexes Pesticides Amines Anion coordination chemistry Glyphosate speciation

**INTRODUCTION**

Glyphosate (N-(phosphonomethyl)-glycine, (H$_2$PO$_4$)-CH$_2$\text{-}NH-CH$_2$-COOH) is a widely used herbicide. Its generalized use is due to some very interesting biological properties, such as broad-spectrum nonselective activity, very low toxicity for mammals and other animals, and the lack of resistant weed biotypes [1]. Glyphosate is used in more than 119 countries [1]; in a typical year between 1988 and 1991, 13 to 20 $\times 10^6$ acres were treated worldwide with $\sim 19 \times 10^6$ pounds of glyphosate [1]. This commercial success has led to the publication of more than 3,000 papers dealing with the chemistry of this herbicide. Most of these investigations were devoted to preparative methods and structural and spectroscopic properties. In contrast, the ability of glyphosate to interact with different cations, and in general the aqueous chemophysical properties of these complexes, have been rarely studied [2,3]. Although the structure of glyphosate is particularly interesting, with reference to the possibility of forming coordination compounds with metal ions, few papers have dealt with this topic, only partially contributing to the full understanding of the coordination characteristics of glyphosate in solution [4–12]. Some previous literature reports demonstrate a high stability for 1:1 metal to ligand complexes, if compared with that of the corresponding glycine species, and suggest a stronger coordination by glyphosate. Only calcium (II) and copper (II) complexes have been widely investigated [4,6,8,10–12]. Copper complexes have been studied [12] by potentiometry, calorimetry, and visible spectrophotometry, and formation of several quite strong species that can have relevant roles in the speciation of glyphosate has been demonstrated. Also, organic cations (polyammonium cations) may form complexes with glyphosate, such as with other inorganic and organic polyammonics [13–16]. This formation of complexes is very interesting, because polyamines are widely present in natural systems and take part in the speciation of cations and anions. Bearing in mind the wide use of glyphosate, the importance of speciation studies (the toxicity and the bioavailability of a substance depend on its form, that is, free, protonated, complexed, and so on), and the relevance of amines in natural systems, we investigated the interaction of this herbicide with some amines in aqueous solution.

We report here a potentiometric investigation on the binding of glyphosate by diamines (ethylenediamine [1,2-diaminoethane, en], putrescine [1,4-diaminobutane, pbr], and cadaverine [1,5-diaminopentane, cdv]), tetramines (triethylenetetramine [ethylene bis 2’-aminoethylamine, trien], spermine [N-(3-amino propyl)-1,4-diaminobutane, sper]), and pentamine (tetraethylenepentamine [3,6,9-triazatriotane-1,11-diamine, tetren]) at various temperatures between 15 and 45°C.

**MATERIALS AND METHODS**

* N-(Phosphonomethyl)-glycine (96%, Aldrich, Milan, Italy, or 99.8%, Ehrenstorfer, Ausburg, Germany), ethylenediamine dihydrochloride (98%, Aldrich), triethylenetetramine tetrahydrochloride (97%, Aldrich), tetraethylenepentamine pentahydrochloride (98%, Aldrich), spermidine trihydrochloride (99%, Aldrich), spermine tetrahydrochloride (98%, Aldrich), putrescine (tetramethylendiamine dihydrochloride, 98%, Sigma, Milan, Italy), and cadaverine (1,5-diaminopentane dihydrochloride, 99%, Aldrich) were used after recrystallization (final purity ≥99%). Sodium hydroxide and HCl solutions were prepared by diluting concentrated ampoules by Carlo Erba (CE Institute, Milan, Italy) and standardized by potassium hydrogen phthalate (t, minimum purity 99.5%, Sigma) and sodium carbonate (alkalimetric standard, minimum purity 99.95%, Sigma), respectively. Twice-distilled water and grade A glassware were used in preparing solutions.

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* To whom correspondence may be addressed (sammartano@chem.unime.it).
Electromotive force measurements

Potentiometric measurements were performed at 20, 25, 37, and 45°C by a Metrohm 654 potentiometer (Metrohom, Berchem, Belgium) coupled with an Orion 8102 (Ross type) combined pH glass electrode (Orion, Beverly, MA, USA). The accuracy of apparatus was ±0.15 mV (±0.003 units in pH). Titrant was delivered by a Metrohm Dosimat 655 dispenser, with an accuracy of ±0.002 ml in the delivered volume.

Solutions containing various glyphosate (5 × 10⁻³ to 1 × 10⁻² M)-amine (4 × 10⁻³ to 2.5 × 10⁻² M) systems, magnetically stirred and thermostatted at selected temperatures (±0.2°C), were used for the titrations. A stream of purified N₂ was bubbled into the solution to exclude O₂ and CO₂. Standardized NaOH at about 0.5 M was used as titrant solution. The electrode couple was calibrated, before and/or after measurements, by titrating HCl with NaOH (both accurately standardized) in the same ionic strength conditions of the system under study. This allows pH values to be obtained, in concentration scale, over the entire investigated range [17]. Because Na⁺ and Cl⁻ (or other cations and anions) may strongly interfere with the formation of glyphosate–amine complexes, no background salt was added to the solutions. Therefore, the ionic strength of various solutions was quite low; for example no background salt was added to the solutions. Thus, the accuracy of apparatus was

Calculations

The computer program ESAB2M [18] was used to calculate the purity of the reagents and to refine all the parameters related to the calibration of the electrode system. The computer programs BSTAC [19] and STACO [20] were used to calculate the formation constants. The selection of the equilibrium model was tackled on a statistical basis, as recommended by Vacca and Sabatini [21]. The ionic strength (I, in M)-dependence of formation constants was taken into account by using the Debye–Hückel–type equation [22]

\[ \log \beta = \log \beta_0 - z^* \sqrt{I/(2 + 3\sqrt{I})} + CI + DI^{1/2} \]  

\[ C = e_0 p^* + e_1 z^*; \quad D = d_1 z^* \]  

\[ p^* = \sum p_{\text{reactants}} - \sum p_{\text{products}} \]  

\[ z^* = \sum z^*_{\text{reactants}} - \sum z^*_{\text{products}} \]  

where \( \beta \) = formation constants; \( \beta_0 \) = formation constant at zero ionic strength; and \( p \) and \( z \) are the stoichiometric coefficients and the charges, respectively. For the calculations performed in this work, the values of \( c_0 = 0.10, c_1 = 0.23, \) and \( d_1 = -0.1 \) [23]. The computer programs STACO and BSTAC are able to perform calculations in nonconstant ionic strength. The ionic strength is calculated for each titration point and formation constants are adjusted using Equation 1. Distribution diagrams and simulated titration curves were obtained using the computer program ES4ECI [19].

The different equilibria considered in this work are expressed as

\[ \text{AH}^+ + \text{H}(glp)^{z-3} = \text{A}(glp)\text{H}^+_{i+j} \]  

where A = amine and glp = glyphosate. In Figure 1 we report, as an example, one titration curve relative to the system glyphosate–spermine. As one can see, values of pH calculated without considering the formation of glyphosate–amine complexes are very different from experimental values.

![Fig. 1. Titration curve for the system glyphosate–spermine. Initial conditions: glyphosate concentration = 10.13 mM, spermine concentration = 20.28 mM; titrant: NaOH 0.5005 M. • experimental points (the full line represents the fit of the model that includes amine–glyphosate complexes); ○ pH calculated for each point by neglecting the formation of glyphosate–amine complexes.](image)

RESULTS

Protonation constants of glyphosate and amines

Protonation constants of glyphosate and amines have been recently reported at different temperatures [11,15,24]. Glyphosate also forms some weak species with Na⁺ (coming from titrant NaOH) and amines form complexes with Cl⁻ (amines are used as hydrochlorides). The protonation constants of the ligands under study are reported in Table 1, along with the formation constants of Na⁺ and Cl⁻ complexes.

Diamine complexes

For the three diamines considered here, we found the formation of three species according to the reactions

\[ \text{AH}^+ + \text{H}(glp)^{z-3} = \text{A}(glp)\text{H}^+_{i+j} \]  

\[ \text{AH}_2^{2+} + \text{H}(glp)^{z-3} = \text{A}(glp)\text{H}^+_{i+j} \]  

\[ \text{AH}^+ + \text{H}_2(glp)^+ = \text{A}(glp)\text{H}^+_{i+j} \]  

whose equilibrium constants are reported in Table 2. The most important species is \( \text{A}(glp)\text{H}^+ \), which is in accordance with the charge neutralization in the formation reaction (III). The stabilities of the different species are fairly similar (and small differences are observed in the order \( en < ptr < cdv \)) for the different diamines, mean values: \( \log K(\text{II}) = 3.0 \pm 0.5 \), \( \log K(\text{III}) = 3.1 \pm 0.3 \), and \( \log K(\text{IV}) = 2.0 \pm 0.5 \). This stability order is unusual because, in general, the charge separation leads to less stable species, but for amine–glyphosate complexes a favorable fitting might occur between =COO⁻ and negative phosphonic group (separated by two –CH₂ and one NH₃⁺ groups) and the two –NH₂⁺ groups of diamines (for cdv the formal distance between positive charges is about the same as the distance of negative charges in glyphosate). Measurements relative to ethylenediamine were performed at different temperatures. The stability constants (\( K \)) show a minimum at temperature \( T = 25°C \), as shown in Figure 1 (reaction (III)), and can be expressed as

\[ \log K(\text{II}) = 2.41 - 1.1F_1(T) + 24.7F_2(T) \]  

\[ \log K(\text{III}) = 2.75 - 5.4F_1(T) + 110F_2(T) \]  

\[ \log K(\text{IV}) = 1.24 - 3.3F_1(T) + 170F_2(T) \]  

where [25]
Binding of glyphosate by open-chain polyammonium cations

Table 1. Protonation constant and weak complex (Na⁺, Cl⁻) formation constants, at ionic strength I = 0 M and at different temperatures (T)

<table>
<thead>
<tr>
<th>Amine</th>
<th>pq</th>
<th>T (°C)</th>
<th>logβ_{pq}</th>
<th>Polyamine</th>
<th>pq</th>
<th>T (°C)</th>
<th>logβ_{pq}</th>
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<tr>
<td>glp</td>
<td>01</td>
<td>10.85</td>
<td>10.77</td>
<td>10.59</td>
<td>10.49</td>
<td>sper</td>
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<tr>
<td></td>
<td>02</td>
<td>16.83</td>
<td>16.73</td>
<td>16.59</td>
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<td></td>
<td>11</td>
<td>9.36</td>
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<tr>
<td></td>
<td>12</td>
<td>19.32</td>
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<td></td>
<td>14</td>
<td>28.78</td>
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<td></td>
<td></td>
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<td>23</td>
<td>26.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24</td>
</tr>
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</table>

*glp* = Glyphosate; *en* = Ethylenediamine; *ptr* = Putrescine; *cdv* = Cadaverine; *trien* = Triethylentriamine; *sper* = Spermine; *tetren* = Tetraethylenepentamine.

The indexes of logβ_{pq} refer to the reactions: glyphosate, pNa⁺ + (glp)_{i} + qH⁺ = Na_{p} (glp)H_{q}^{i-q}; amines, A_{p} + pCl⁻ + qH⁺ = AH_{q}Cl_{p-q}.

[11], [24], [15].

Unpublished results from this laboratory.

\[ F_{1}(T) = (1/\Theta - 1/T)/(RT \ln 10) \]
\[ F_{2}(T) = (\Theta/T - 1 + \ln T/\Theta) \]

where \( T \) = temperature in K and \( \Theta \) = reference temperature (298.15K).

**Tetramine complexes**

In the systems glyphosate-*trien* and -*sper*, five species are formed, according to the following reactions:

\[ AH^{+} + H(glp)^{2-} = A(glp)H_{2}^{i} \] (V)
\[ AH_{2}^{+} + H(glp)^{2-} = A(glp)H_{4}^{i} \] (VI)
\[ AH_{3}^{+} + H(glp)^{2-} = A(glp)H_{6}^{i} \] (VII)
\[ AH_{4}^{+} + H(glp)^{2-} = A(glp)H_{8}^{i} \] (VIII)
\[ AH_{5}^{+} + H_{2}(glp)^{2-} = A(glp)H_{10}^{i} \] (IX)

whose equilibrium constants are reported in Table 2. As expected, the stability of these species is significantly higher than those of diamine complexes, in particular as regards the species \( A(glp)H_{2}^{i} \). Measurements relative to *sper* were performed at different temperatures. The formation constants markedly increased with the temperature over the whole investigated range, 293 to 318K (Fig. 1, reaction (VIII)), and can be expressed by the equations

\[ \log K(V) = 2.49 + 25.9F_{1}(T) + B \] (7)
\[ \log K(VI) = 2.89 + 30.2F_{1}(T) + B \] (7a)
\[ \log K(VII) = 3.35 + 31.8F_{1}(T) + B \] (7b)
\[ \log K(VIII) = 3.87 + 28.5F_{1}(T) + B \] (7c)
\[ \log K(IX) = 2.25 + 37.2F_{1}(T) + B \] (7d)

where \( B = 183 F_{1}(T) \).

**Pentamine complexes**

The pentamine *tetren* forms six complex species with glyphosate, according to the reactions

\[ AH_{i}^{+} + H(glp)^{2-} = A(glp)H_{i+2}^{i+2} \] for \( i = 1 \ldots 4 \) (X–XIII) and
\[ AH_{i}^{+} + H_{2}(glp)^{2-} = A(glp)H_{i+3}^{i+3} \] for \( i = 4, 5 \) (XIV–XV)

Formation constants (Table 2), obtained at different temperatures, can be expressed by the equations
Table 2. Formation constants for the formation of glyphosate–amine complexes at different temperatures (T) and ionic strength I = 0 M

<table>
<thead>
<tr>
<th>Amine</th>
<th>T (°C)</th>
<th>logK (± SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>en</td>
<td>20</td>
<td>2.42 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>2.41 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>2.42 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>2.45 ± 0.02</td>
</tr>
<tr>
<td>ptr</td>
<td>25</td>
<td>3.12 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>3.47 ± 0.03</td>
</tr>
<tr>
<td>cdv</td>
<td>25</td>
<td>3.72 ± 0.14</td>
</tr>
<tr>
<td>trien</td>
<td>25</td>
<td>6.52 ± 0.14</td>
</tr>
<tr>
<td>sper</td>
<td>20</td>
<td>3.84 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>3.87 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>4.34 ± 0.08</td>
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<tr>
<td></td>
<td>45</td>
<td>4.94 ± 0.02</td>
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<td>tetren</td>
<td>20</td>
<td>2.98 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>2.89 ± 0.13</td>
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<tr>
<td></td>
<td>37</td>
<td>2.70 ± 0.06</td>
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<td></td>
<td>45</td>
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<td>20</td>
<td>4.75 ± 0.02</td>
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<td></td>
<td>25</td>
<td>4.83 ± 0.13</td>
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<td></td>
<td>37</td>
<td>5.02 ± 0.06</td>
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<tr>
<td></td>
<td>45</td>
<td>5.13 ± 0.07</td>
</tr>
</tbody>
</table>

*en = ethylenediamine; ptr = putrescine; cdv = cadaverine; trien = triethylenetetramine; sper = spermine; tetren = tetraethylenepentamine.

The different formation constants have different temperature gradients, which increase with the product of the charges involved in the formation reaction. In Figure 2, log K(XIII) versus temperature is shown.

**Thermodynamic parameters**

The ΔG° values can be calculated for all the systems studied here and, in addition, for the systems investigated at different temperatures, ΔH° and TΔS° values can be obtained. In general the temperature dependence of formation constants is fairly positive, as shown in Figure 2. The thermodynamic parameters are reported in Table 3. For most of the species the entropy term TΔS° is significantly > 0, which means that these complexes are entropically stabilized, as expected for noncovalent interactions.

**Reliability of formation parameters and errors**

Formation constants for all the species found in this work are reported in Table 2 along with their standard deviations. These vary from 0.02 to 0.13 and are consistent with both the experimental apparatus and the complexity of the systems under study.

In Figure 3 we report the error plot (for the titration shown in Fig. 1) in terms of ΔE/mV = E_{expt} – E_{calc}. As can be seen, errors for the model that includes the formation of (sper)glpH complexes are much lower than those for the model that neglects the formation of these species. Mean error in the various measurements is σ_{M} = 0.010. This error can be expressed in terms of different factors: σ_{inv} (instrumental error from electromotive force and titrant volume readings), σ_{con} (error due to uncertainties in analytical concentrations of components), and σ_{model} (error attributed to the speciation model; that is, σ_{M} = σ_{inv} + σ_{con} + σ_{model} = (σ_{pH}σ_{E})^{2} + (σ_{pH}σ_{C})^{2} + (σ_{pH}σ_{E})^{2}). By performing appropriate calculations we obtain σ_{model} = 0.03. This is a value comparable to experimental error and therefore the speciation model can be accepted.

By the error propagation rule, the uncertainties in the formation constants can be determined.

![Fig. 2. Log K values versus temperature T – 298°K. en, reaction III; sper, reaction VIII; tetren, reaction XIII.](image)
tion percentages can be calculated, as reported for the system putrescine–glyphosate in Table 4. As one can see, standard deviations in formation percentages are quite small and allow a correct speciation of the system. As regards $\Delta H^0$ and $T \Delta S^0$ values, we must take into consideration that they are obtained from temperature dependence of formation constants in a narrow temperature range, and therefore they are affected by large errors. Nevertheless, the general considerations reported in the discussion are not invalidated by these errors. Finally, we must consider the correctness of the model proposed for each system. Are the species found to be significant? Do other species occur in the investigated systems? On the basis of our experience in this field we can answer positively. The models proposed are very similar to those of other systems, such as polycation–amino acids or polycation–inorganic and organic polyanions [13–16,20,26]. Moreover, proposed models fit experimental data quite well, using appropriate calculation procedures [20]. As is well known, other species possibly are formed at higher reagent concentrations, but these conditions are not interesting from the natural fluids point of view, because under natural conditions concentrations of glyphosate and amines are lower than those used in this work.

**DISCUSSION**

Significance of amine–glyphosate complexes

Some speciation diagrams are reported in Figures 4 to 6. At a 10 mM glyphosate–putrescine concentration (Fig. 4), a good yield was obtained for all three species formed, with a maximum of $\sim 50\%$ for $(ptr)(glp)H_2^+$, at pH = 7 to 7.5. In all cases it is noteworthy that maximum species yields are obtained in the pH range of interest for natural and biological fluids. Moreover, the presence of these species is highly significant over a large pH range (5–10), as can be seen in Figure 5, where the sum of percentages (curve 6) is reported. In order to ascertain the relevance of these mixed amino–glyphosate species, one must refer to real natural conditions. Under natural conditions, the concentrations of glyphosate and amines are certainly much lower than those used in the experiments, but a generalized concentration cannot be given because of the enormous variability in conditions. If a solution containing only glyphosate $10^{-6} \text{M}$ with pentamine $10^{-4} \text{M}$ is considered, at pH = 7, 27% formation of $(tetren)(glp)H_2^+$ species occurs (and at pH = 8, $\sim 14\%$), which means that the polycation cation also can have a substantial effect on the speciation of glyphosate at low concentrations. Moreover, the interference of Na$^+$ and Cl$^-$ must be considered. Figures 4 to 6 report speciation diagrams for three very different systems with very different formation constants at $I = 0.1 \text{M (NaCl)}$, but the maximum percentages of mixed species are quite similar. This is not a contradiction because the higher stability of mixed species is counterbalanced, to some extent, by the higher Cl$^-$ complex formation constant (see Table 1). Thermodynamic data reported in this work can be included in general databases for the speciation of natural fluids when glyphosate and amines are present simultaneously.

**Generalization of thermodynamic parameters and predictive equations**

The inspection of the data in Tables 2 and 3 reveals that $\log K$, $\Delta G^*$, and $T \Delta S^0$ are increasing functions of charges involved in the formation reaction. In Figure 7 we report mean

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**Table 4. Uncertainties of formation percentages (expressed as standard deviations) for the system H+-glyphosate–putrescine, concentration of glyphosate = concentration of putrescine = 10 mM, ionic strength $I = 0.1 \text{M (NaCl)}$, at 25°C**

<table>
<thead>
<tr>
<th>pH</th>
<th>$(ptr)(glp)H_2^+$</th>
<th>$(ptr)(glp)H_+^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>17.8 ± 2.4</td>
<td>20.6 ± 3.6</td>
</tr>
<tr>
<td>6</td>
<td>42.1 ± 2.9</td>
<td>4.9 ± 1.1</td>
</tr>
<tr>
<td>7</td>
<td>48.6 ± 3.1</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>8</td>
<td>46.3 ± 3.0</td>
<td>—</td>
</tr>
</tbody>
</table>

*ptr = putrescine; glp = glyphosate.*

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**Fig. 4. Distribution of the species versus pH for the system $ptr$-glp 10 mM in NaCl 0.1 M. Species 1, $(ptr)(glp)H_2^+$; 2, $(ptr)(glp)H_+^*$; 3, $(ptr)(glp)H_+^*$; 4, $(ptr)(glp)H_+^*$; 5, $(ptr)(glp)H_+^*$; 6, $\Sigma$$(ptr)(glp)$ $H_+^*$; (remaining %: $ptr$-$H^+$ and $ptr$-$Cl^-$ species; the percentage of the free amine is negligible).**
\( \Delta G^\circ \) and \( T \Delta S^\circ \) values versus \( \zeta \) (where \( \zeta \) is the product of charges of reactant anion and cation, that is, \( \zeta = |\xi| - |\eta| \), see reaction [I]). As can be seen, the dependence of both thermodynamic parameters on \( \zeta \) is fairly linear and can be expressed by the empirical equations (\( \Delta G^\circ \) and \( T \Delta S^\circ \) in kJ/mol):

\[
\begin{align*}
- \Delta G^\circ &= 5(\pm 1)\zeta \\
T \Delta S^\circ &= 7(\pm 3)\zeta
\end{align*}
\]

and for the formation constants we have \( \log K = 0.9(\pm 0.2)\zeta \). By using the rough approximation [14–15] \( n = \zeta/2 \) (\( n \) = number of possible salt bridges) we have

\[
\begin{align*}
- \Delta G^\circ &= 10 \pm 2 \text{ kJ/mol} \\
T \Delta S^\circ &= 14 \pm 6 \text{ kJ/mol}
\end{align*}
\]

These values are comparable to those obtained for some pyrophosphate–open chain polyammonium cations [27], that is, \( \Delta G^\circ = 8.2 \), \( T \Delta S^\circ = 10.4 \) kJ/mol. Predictive equations, such as Equations 9 and 10, for general speciation databases must include as many as possible interactions between a component (in this case glyphosate) and a class of ligands (amines).

**CONCLUSION**

Glyphosate forms quite stable complexes with polyammonium cations (Table 2) with high formation percentages (Figs. 4–6). Also at low concentrations of glyphosate and amines, yields in terms of protonated polyammonium cation–anion of glyphosate complexes are significant, which means that these species must be taken into consideration in speciation studies. A regular trend of thermodynamic parameters

\( \Delta G^\circ \) and \( T \Delta S^\circ \) allows predictive Equations 9 and 10 to be obtained. The temperature dependence of formation constants 6 to 8 can be used for the speciation of systems in the range 15 to 45°C.

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**REFERENCES**

8. Clarke ET, Rudolf PR, Martell AE, Clearfield A. 1989. Structural investigation of the Cu(II) chelate of \( N \)-phosphonomethylglycine. X-ray crystal structure of Cu(II) \([\text{H}_2\text{O}]_{3.5}\text{[Cu} \text{2}\text{O} \text{C} \text{H}\text{N} \text{H} \text{C} \text{H} \text{C} \text{H}_3\text{PO}_3] \text{Na}\) \((\text{H}_2\text{O})_{\text{a}}, \text{Inorg Chim Acta} 164:59–63.


