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COMPLEXING ABILITY OF PESTICIDES AND RELATED COMPOUNDS. FORMATION AND STABILITY IN AQUEOUS SOLUTION OF H^+, Li^+, Na^+, K^+, Mg^{2+} AND Ca^{2+} PHENOXYACETATE COMPLEXES AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

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ABSTRACT

The formation constants of Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} phenoxyacetate complexes were determined potentiometrically using an (H^+)-glass electrode at 10, 25, 37 and 45°C, at several ionic strengths, in the range $0.04 \leqslant I \leqslant 0.9$ mol l^{-1}. Simple empirical equations for the dependence of the formation constants on ionic strength were derived. From the temperature coefficients, estimates of ΔH^0 and ΔS^0 were obtained.

INTRODUCTION

Several groups of compounds which act as pesticides [1] are potential ligands for the cations present in the soil. The use of pesticides (insecticides, fungicides, herbicides, etc.) in agriculture is rapidly increasing (in 1945 less than 10^8 kg of pesticides were manufactured, while in 1975 this quantity was about 20 times higher, and the increase is exponential), whereas the quantitative knowledge of the interactions among these compounds and the cations present, often in great amounts, in the soil is unsatisfactory. We, therefore, thought it would be interesting to start a systematic study of the complexing ability of some pesticides with respect to the most common cations. These studies will be of some interest in the chemical modelling of natural systems in which such types of compounds are involved.

The first contribution in this series deals with a potentiometric study of phenoxyacetate complexes with Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} (phenoxyalkanoic acids, in particular 2,4-dichloro derivatives, are widely used as herbicides) using a glass electrode at 10, 25, 37 and 45°C and at several ionic strengths.

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EXPERIMENTAL

Materials

Phenoxyacetic acid (Fluka purissimum) was used without further purification; from alkalimetric titrations, the purity was found to be > 99.5%. Tetraethylammonium iodide (Et_4NI, Fluka purissimum), was recrystallized from methanol. Lithium, sodium and potassium chloride solutions were prepared from corresponding C. Erba salts, purity > 99.5%, previously dried in a stove at 110°C or in vacuum. Magnesium and calcium chloride solutions were prepared from Fluka purum p.a. reagents and standardized by EDTA titrations [2]. NaOH and HNO_3 stock solutions were prepared by diluting concentrated ampoules, supplied by C. Erba. The solutions were preserved from atmospheric CO_2 by means of soda lime traps. Twice-distilled water and grade A glassware were employed.

Apparatus

The free concentration of hydrogen ion, c_H, was measured by means of a potentiometer (Metrohm Model E 600) coupled with glass-saturated calomel electrodes supplied by the same firm. The titrant solution of NaOH was delivered by an Amel dispenser model 232, having a minimum reading of 0.001 cm^3.

Procedure

The solution under study (25 cm^3) was titrated with NaOH (0.2 mol l^{-1}) up to ~ 90% neutralization. An excess of HNO_3 (15 mmol l^{-1}) was added to every solution in order to complete the protonation of ligand and to calculate directly the internal E^0 values, E^0_{int}. By means of separate titration in the same analytical conditions, but without ligand, we calculated E^0_{ext}. If $|E^0_{ext} - E^0_{int}| > 1.5$ mV, the titration was rejected.

Calculations

The nonlinear least-squares computer programs ACBA [3] and ESAB [4] were used to calculate the protonation constants, the constant E^0 of the electrode couple and the purity of the ligand. The formation constants of weak complexes were calculated graphically (see Results) and by using the nonlinear least-squares computer program WECO [5]. Protonation and formation constants were expressed as

$$K^H = c_{HL}(c_H c_L)^{-1}$$

$$K^M = c_{ML}(c_M c_L)^{-1}$$

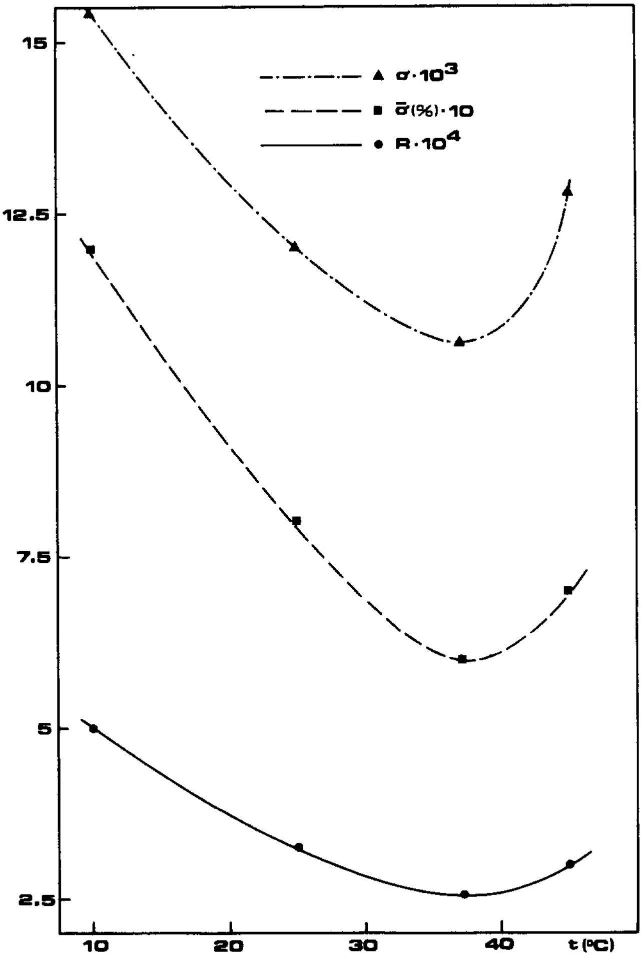

Fig. 1. Statistical parameters relative to the pH-metric measurements at different temperatures.

where c indicates free concentration. All concentrations, and hence all formation constants, are expressed in molar scale. pK_w values used in the calculations were taken from a previous work [5].

The reproducibility of pH ($= -\log c_H$) measurements (deduced from calibration curves) was $\pm 0.003 + 4 \times 10^{-6}(t - 35)^2$ (t, °C), i.e., there is a minimum in the error at 35°C. It is interesting to note that the same behaviour (Fig. 1) is revealed by statistical parameters [6] (reported in Table 1, together with some experimental details) relative to the protonation of phenoxyacetate with different backgrounds.

TABLE 1

Protonation constants of phenoxyacetate with various backgrounds

t (°C)	$\bar{I}$ [a]	log $K^{\mathrm{H}\prime}$ $\mathrm{Et_4N^+}$	$\bar{I}$	log $K^{\mathrm{H}\prime}$ $\mathrm{Li^+}$	$\bar{I}$	log $K^{\mathrm{H}\prime}$ $\mathrm{Na^+}$	$\bar{I}$	log $K^{\mathrm{H}\prime}$ $\mathrm{K^+}$	$\bar{I}$	log $K^{\mathrm{H}\prime}$ $\mathrm{Mg^{2+}}$	$\bar{I}$	log $K^{\mathrm{H}\prime}$ $\mathrm{Ca^{2+}}$
10	0.041	2.929	0.084	2.916	0.038	2.946	0.084	2.901	0.037	2.957	0.125	2.899
	0.096	2.900	0.181	2.868	0.084	2.907	0.129	2.889	0.086	2.892	0.175	2.844
	0.141	2.892	0.43	2.842	0.129	2.891	0.180	2.869	0.126	2.848	0.42	2.787
	0.198	2.911	0.60	2.829	0.180	2.879	0.43	2.861	0.177	2.844	0.57	2.752
	0.47	2.974	0.80	2.823	0.43	2.842	0.60	2.843	0.425	2.787	0.77	2.740
	0.65	3.058			0.60	2.855	0.80	2.868	0.59	2.788		
	0.87	3.115			0.80	2.871			0.80	2.750		
	$\bar{\sigma} = 0.006$ [b]		$\bar{\sigma} = 0.005$		$\bar{\sigma} = 0.004$		$\bar{\sigma} = 0.004$		$\bar{\sigma} = 0.004$		$\bar{\sigma} = 0.008$	
	$R = 0.21\%$ [c]		$R = 0.15\%$		$R = 0.11\%$		$R = 0.11\%$		$R = 0.12\%$		$R = 0.23\%$	
25	0.087	2.964	0.038	3.001	0.087	2.994	0.038	2.981	0.037	2.997	0.037	2.993
	0.129	2.962	0.087	2.943	0.128	2.945	0.087	2.955	0.085	2.943	0.085	2.937
	0.181	2.966	0.128	2.920	0.43	2.860	0.128	2.923	0.125	2.915	0.125	2.919
	0.59	3.060	0.181	2.902	0.60	2.864	0.180	2.907	0.176	2.898	0.175	2.881
	0.79	3.131	0.43	2.869	0.80	2.883	0.43	2.879	0.42	2.837	0.42	2.815
			0.60	2.842			0.60	2.872	0.59	2.805	0.58	2.779
			0.80	2.877			0.79	2.894	0.79	2.795	0.78	2.760
	$\bar{\sigma} = 0.002$		$\bar{\sigma} = 0.004$		$\bar{\sigma} = 0.004$		$\bar{\sigma} = 0.003$		$\bar{\sigma} = 0.003$		$\bar{\sigma} = 0.004$	
	$R = 0.09\%$		$R = 0.14\%$		$R = 0.15\%$		$R = 0.10\%$		$R = 0.10\%$		$R = 0.14\%$	

37	0.038	3.033	0.038	3.035	0.038	3.046	0.038	3.042	0.037	3.031	0.037	3.028
	0.082	3.015	0.087	2.984	0.086	2.982	0.087	2.988	0.079	2.982	0.084	2.991
	0.128	3.010	0.128	2.955	0.128	2.969	0.128	2.973	0.120	2.954	0.135	2.949
	0.180	3.009	0.180	2.931	0.180	2.946	0.180	2.963	0.170	2.938	0.191	2.915
	0.425	3.056	0.43	2.878	0.43	2.917	0.43	2.916	0.42	2.865	0.45	2.814
	0.59	3.107	0.60	2.879	0.59	2.913	0.59	2.914	0.59	2.833	0.63	2.791
	0.79	3.177	0.79	2.893	0.79	2.916			0.80	2.821	0.84	2.774
	$\bar{\sigma} = 0.002$		$\bar{\sigma} = 0.0025$		$\bar{\sigma} = 0.003$		$\bar{\sigma} = 0.003$		$\bar{\sigma} = 0.002$		$\bar{\sigma} = 0.003$	
	$R = 0.08\%$		$R = 0.12\%$		$R = 0.13\%$		$R = 0.11\%$		$R = 0.09\%$		$R = 0.11\%$	
45	0.095	3.020	0.038	3.082	0.038	3.073	0.038	3.074	0.093	3.013	0.040	3.062
	0.140	3.010	0.087	3.016	0.087	3.018	0.087	3.027	0.193	2.942	0.135	2.966
	0.48	3.097	0.128	2.984	0.128	2.990	0.179	2.985	0.46	2.875	0.190	2.940
	0.65	3.127	0.180	2.973	0.179	2.982	0.43	2.945	0.64	2.846	0.45	2.853
	0.86	3.219	0.43	2.923	0.43	2.940	0.59	2.946	0.86	2.812	0.62	2.819
			0.59	2.919	0.59	2.923	0.79	2.953			0.84	2.790
			0.79	2.922	0.79	2.940						
	$\bar{\sigma} = 0.0025$		$\bar{\sigma} = 0.004$		$\bar{\sigma} = 0.003$		$\bar{\sigma} = 0.004$		$\bar{\sigma} = 0.002$		$\bar{\sigma} = 0.0025$	
	$R = 0.11\%$		$R = 0.18\%$		$R = 0.14\%$		$R = 0.15\%$		$R = 0.09\%$		$R = 0.10\%$	

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[a] Mean ionic strength during the titration. Since the ligand concentration and the strong acid concentration were always $C_L = C_{HNO_3} = 0.015$ mol l^{-1}, the concentration of the cation under study can be deduced from the equation $C_M \approx \bar{I} - 0.023$.

[b] Mean standard deviation for each background at each temperature (see also Fig. 1).

[c] R factor (see ref. 6); $R = \Sigma[(v - v_{calc})^2/\Sigma(v)^2]^{1/2}$, where v is the titrant volume.

TABLE 2

Thermodynamic parameters for the protonation of phenoxyacetate, at $I = 0$ mol l^{-1}

t (°C)	$\log {}^{T}K^{H}$	ΔG^{0} [a]	ΔH^{0} [a]	ΔS^{0} [b]	ΔC_{p}^{0} [b]
10	3.095 ± 0.026 [c]	16.8 ± 0.2	3.6 ± 2.0	72 ± 7	
25	3.137 ± 0.012	17.9 ± 0.1	5.5 ± 1.2	78 ± 5	134 ± 46
37	3.180 ± 0.013	18.9 ± 0.1	7.2 ± 1.2	84 ± 5	
45	3.213 ± 0.016	19.5 ± 0.2	8.5 ± 1.6	88 ± 6	

The results reported in this Table can be synthesized by the following equations

$$\log {}^{T}K^{H} = 3.137 + 0.003232(t-25) + 0.000029(t-25)^{2}$$

$$\log K^{H} = \log {}^{T}K^{H} - \frac{2\sqrt{I}}{2+3\sqrt{I}} + [0.65 - 0.004(t-25)]I - [0.15 - 0.0028(t-25)]I^{3/2}$$

$$\Delta H^{0} = 5.5 - 6.8\, I + 4.8\, I^{3/2} \text{ (kJ mol}^{-1}\text{)}$$

[a] ΔG^{0} and ΔH^{0} in kJ mol^{-1}.

[b] ΔS^{0} and ΔC_{p}^{0} in J mol^{-1} K^{-1}.

[c] $\pm 3\sigma$.

RESULTS

Alkalimetric titrations of phenoxyacetic acid performed in the presence of various backgrounds were firstly analysed to obtain conditional protonation constants, which values are reported in Table 1. The extrapolation of all these values to $I = 0$ allowed us to calculate the thermodynamic parameters relative to the protonation of phenoxyacetate, as reported in Table 2.

The trend, for the different salt solutions, is $\log K^{H}$: $EtN_{4}^{+} > K^{+} \gtrsim Na^{+} > Li^{+} > Mg^{2+} > Ca^{2+}$. If we assume that $Et_{4}N^{+}$ does not form complexes with phenoxyacetate * (in Table 1 we use $\log K^{H\prime}$ for the "conditional" protonation constants in Li^{+}, Na^{+}, K^{+}, Mg^{2+} and Ca^{2+}) and that the difference $\Delta \log K^{H} = \log K^{H} - \log K^{H\prime}$ is due to the formation of weak complexes **, we can calculate K^{M} by the equation [5]:

$$\log K^{H} = \log K^{H\prime} + \log(1 + K^{M} c_{M}) \qquad (1)$$

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* The assumption according to which tetralkylammonium cations do not interact significantly with carboxylic ligands and with some inorganic ligands has been widely discussed in previous papers [8–10]. On the other hand, it must be stressed that this assumption cannot be generalized since, in some cases, such as for hexacyanoferrate(II), tetralkylammonium cations form complexes having a stability comparable to that of alkali metal ions [7].

** Differences in protonation constants determined with various backgrounds are often explained in terms of specific changes of activity coefficients. In a series of works dealing with the dependence of formation constants on ionic strength [11–19] we found that the main source of variation in the formation constants, at the same ionic strength, and in different salt solutions, is due to the formation of weak complexes between the ligand and the cations of the background (for $I \leqslant 1$ mol l^{-1}).

TABLE 3

Formation constants together with parameters for their dependence on temperature and ionic strength, at 25°C, calculated graphically (see text)

M	I (mol l^{-1})	log K^{M}	$\frac{\partial \log K^{M}}{\partial T} \times 10^{3}$	C [a]	$\frac{\partial C}{\partial T} \times 10^{3}$
K^{+}	0	0.05 ± 0.07 [b]			
	0.25	-0.15 ± 0.05	0.6	0.44 ± 0.06	-1.0
Na^{+}	0	0.08 ± 0.08			
	0.25	-0.12 ± 0.05	2.5	0.41 ± 0.06	-1.9
Li^{+}	0	0.19 ± 0.09			
	0.25	-0.07 ± 0.06	5.0	0.44 ± 0.06	-10.0
Mg^{2+}	0	0.96 ± 0.06			
	0.25	0.52 ± 0.04	0.6	0.71 ± 0.05	2.6
Ca^{2+}	0	1.00 ± 0.05			
	0.25	0.57 ± 0.04	3.5	$0.73_{5} \pm 0.05$	-5.7

[a] See eqn. (6) with $B = 2.5$.
[b] $\pm 3\sigma$.

or

$$K^{M} = (10^{\Delta \log K^{H}} - 1) c_{M}^{-1} \tag{2}$$

By using this method a value of K^{M} can be obtained at each temperature and ionic strength. Then, the dependence on ionic strength can be calculated by the semiempirical Debye–Hückel type equation

$$\log K^{M}(I) = \log K^{M}(I') - z^{*}G(I, I') + C(I - I') + D(I^{3/2} - I'^{3/2}) \tag{3}$$

with

$$G(I, I') = \left[\sqrt{I}/(2 + B\sqrt{I}) - \sqrt{I'}/(2 + B\sqrt{I'})\right] \tag{4}$$

$$z^{*} = 2z_{M} \tag{5}$$

where I' is a reference ionic strength and z_{M} is the charge of the cation. By using the values $D = 0$ and $B = 2.5$ *, eqn. (3) can be rewritten, when $I' = 0.25$

$$\log K^{M}(I) + z^{*}G(I, 0.25) = \log K^{M}(0.25) + C(I - 0.25) \tag{6}$$

that is the equation of a straight line. The values of log K^{M} and C so obtained are dependent on temperature, and this dependence has been found to be fairly linear. The results of this calculation method (in practice a graphical method) are reported in Table 3. The calculation of K^{M} was also

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* When dealing with log formation data affected by an error of ± 0.05, or higher, and with z^{*} values $\leqslant 4$, D can be kept equal to zero and $B = 2.5$; in other cases it is better to keep $B = 3$ and to find a value not equal to zero for D.

TABLE 4

Formation constants together with parameters for their dependence on temperature and ionic strength, at 25°C, calculated by the computer program WECO

M	I (mol l^{-1})	$\log K^{M}$	$\frac{\partial \log K^{M}}{\partial T}$ $\times 10^{3}$	$\frac{1}{2}\frac{\partial^{2} \log K^{M}}{\partial T}$ $\times 10^{5}$	C [a]	$-\frac{\partial C}{\partial T}$ $\times 10^{3}$
K^{+}	0	-0.01 ± 0.08 [b]	0.85	-1.8	0.60 ± 0.02 [b]	3.0
	0.25	-0.16 ± 0.05				
Na^{+}	0	0.00 ± 0.08	1.5	-4.8	0.595 ± 0.02	3.0
	0.25	-0.15 ± 0.05				
Li^{+}	0	0.07 ± 0.08	1.5	-3.8	0.60 ± 0.03	3.1
	0.25	0.01 ± 0.05				
Mg^{2+}	0	1.00 ± 0.07	-1.0	14	0.77 ± 0.06	1.6
	0.25	0.58 ± 0.05				
Ca^{2+}	0	1.04 ± 0.08	3.4	1.0	0.83 ± 0.05	6.4
	0.25	0.64 ± 0.05				

[a] See eqn. (3): $B = 3$; $D = -0.075z^{*}$; $\partial D/\partial T = 0.0014z^{*}$.
[b] $\pm 3\sigma$.

TABLE 5

Thermodynamic parameters for the formation of Li^{+}, Na^{+}, K^{+}, Mg^{2+} and Ca^{2+}-phen-

t (°C)	I [b]	$\log K^{M}$	ΔG^{0} [c]	ΔH^{0} [c]	ΔS^{0} [d]	$\log K^{M}$	ΔG^{0}	ΔH^{0}	ΔS^{0}	$\log K^{M}$
		Li^{+}				Na^{+}				K^{+}
10	0.0	0.06	-0.32	7.8	29	0.00	0.00	4.5	16	0.01
	0.1	-0.10	0.56	6.9	22	-0.17	0.91	4.2	12	-0.16
	0.25	-0.10	0.52	5.6	18	-0.17	0.93	3.7	10	-0.16
	0.5	-0.03	0.16	3.5	12	-0.12	0.68	3.4	10	-0.11
	1.0	0.16	-0.86	-0.3	2	0.02	-0.13	2.9	11	0.04
25	0.0	0.13	-0.75	7.7	28	0.04	0.23	4.1	14	0.02
	0.1	-0.04	0.23	6.7	22	-0.13	0.76	3.5	9	-0.15
	0.25	-0.05	0.26	5.2	16	-0.14	0.80	3.1	8	-0.15
	0.5	0.00	-0.01	3.0	10	-0.10	0.55	2.6	7	-0.11
	1.0	0.15	-0.86	-1.3	-2	0.05	-0.27	2.0	8	0.05
37	0.0	0.18	-1.09	7.5	28	0.06	0.38	3.1	11	0.03
	0.1	0.00	-0.03	6.4	21	-0.11	0.66	2.7	7	-0.15
	0.25	-0.01	0.07	4.8	15	-0.12	0.73	2.3	5	-0.15
	0.5	0.02	-0.12	2.4	8	-0.08	0.48	1.7	4	-0.11
	1.0	0.14	-0.83	-2.2	-5	0.06	-0.35	1.1	5	0.04
45	0.0	0.21	-1.31	7.3	27	0.08	0.46	2.5	9	0.03
	0.1	0.03	-0.19	6.1	20	-0.10	0.62	2.1	5	-0.15
	0.25	0.00	-0.05	4.4	14	-0.11	0.69	1.6	3	-0.15
	0.5	0.03	-0.18	1.9	7	-0.08	0.46	1.1	2	-0.11
	1.0	0.13	-0.78	-3.0	-7	0.06	-0.38	0.4	3	0.04

[a] On average the errors (3σ) are: $\log \beta \pm 0.05$–0.1; $\Delta G^{0} \pm 0.3$–0.5; $\Delta H^{0} \pm 1$–2; $\Delta S^{0} \pm 4$–8.
[b] Ionic strength in mol l^{-1}.
[c] ΔG^{0} and ΔH^{0} in kJ mol^{-1}.
[d] ΔS^{0} in J K^{-1} mol^{-1}.

performed by the least-squares computer program WECO [5] and the results are reported in Table 4.

DISCUSSION

The formation constants calculated by the two methods agree satisfactorily (within 3σ for alkali metals and 2σ for alkaline earth metals). From the dependence on temperature, estimates of ΔH^0 and ΔS^0 have been derived. In Table 5 mean values of all thermodynamic parameters at different temperatures and ionic strengths are reported. The stability of various complexes follows the usual trend for carboxylate ligands [20]: $Ca^{2+} > Mg^{2+} > Li^+ > Na^+ \gtrsim K^+$. It is interesting to note that, though the protonation constant of phenoxyacetate is significantly lower than that of acetate, the formation constants of M^+– and M^{2+}–phenoxyacetate complexes are very similar to those of acetate complexes [21].

This confirms our previous hypothesis about the independence of substrates when only a carboxylate group binds to an alkali or an alkaline earth

oxyacetate complexes at several temperatures and ionic strengths [a]

ΔG^0	ΔH^0	ΔS^0	$\log K^M$	$-\Delta G^0$	ΔH^0	ΔS^0	$\log K^M$	$-\Delta G^0$	ΔH^0	ΔS^0
			Mg^{2+}				Ca^{2+}			
−0.06	1.3	5	1.00	5.43	−4.0	5	0.96	5.19	6.2	40
0.86	1.1	1	0.63	3.41	−3.8	−1	0.60	3.24	5.4	30
0.87	0.8	0	0.57	3.08	−3.3	−1	0.56	3.02	4.4	26
0.60	0.5	0	0.58	3.15	−2.2	4	0.60	3.28	3.1	23
−0.24	0.4	2	0.70	3.78	1.1	17	0.79	4.30	1.2	19
−0.12	1.0	4	0.98	5.59	−0.9	16	1.02	5.82	7.1	43
0.86	0.7	0	0.61	3.46	−0.6	10	0.65	3.72	6.2	33
0.88	0.4	−1	0.55	3.15	−0.1	10	0.60	3.43	5.1	29
0.61	0.1	−2	0.58	3.29	1.2	15	0.63	3.63	3.7	25
−0.26	0.0	1	0.72	4.13	4.7	30	0.81	4.60	1.6	21
−0.16	0.7	3	0.98	5.84	2.2	26	1.07	6.35	7.9	46
0.86	0.4	−2	0.61	3.64	2.4	20	0.70	4.11	6.9	36
0.91	0.1	−3	0.56	3.33	3.0	20	0.64	3.80	5.7	31
0.64	−0.2	−3	0.60	3.53	4.4	25	0.66	3.94	4.2	26
−0.26	−0.4	0	0.77	4.56	8.2	41	0.82	4.86	1.9	22
−0.18	0.4	2	1.00	6.07	4.4	33	1.10	6.72	8.4	48
0.88	0.1	−2	0.63	3.83	4.7	27	0.73	4.42	7.5	37
0.94	−0.2	−4	0.58	3.52	5.4	28	0.66	4.04	6.2	32
0.67	−0.5	−4	0.62	3.76	6.8	33	0.68	4.15	4.6	27
−0.25	−0.7	−1	0.81	4.92	10.8	50	0.83	5.03	2.2	23

metal ion [22]. In the literature, only a few papers can be found dealing with phenoxyacetate complexes. Ramamoorthy and Santappa [23] studied UO_2^{2+} complexes, Suzuki and Yamasaki [24] reported the formation constants of Cd^{2+}, Ca^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} complexes, and Pettit et al. [25,26] investigated Ag^{+} complexes. The values reported for the conditional protonation constants are in good agreement with those of this work: log $K^{H} =$ 2.96 at 31°C and $I = 0.1$ mol l^{-1} [23] (our value 2.97); log $K^{H} = 2.93$ at 25°C and $I = 0.1$ mol l^{-1} (our value 2.95). No other comparison can be made.

As regards the dependence on ionic strength, the results are in good accordance with our previous findings [11–19]. In fact, we obtain, in this work, for $L(I) = CI + DI^{3/2}$ the mean value at 25°C $L(I) = 0.46 \pm 0.03$ when $z^* = 2$ and $L(I) = 0.51 \pm 0.05$ when $z^* = 4$ (see Tables 2 and 4). The mean values obtained from all previous works [19] are 0.41 and 0.61, respectively (at $I = 1$ mol l^{-1}).

In order to evaluate the significance of the figures obtained we must analyse the errors involved in the measurements so as to see how these errors are reflected in the formation of thermodynamic parameters and in the percentages of species formed. By using equations and methods reported in previous papers [19–21,27] we found that the errors in formation constants should be $\leqslant \pm 0.1$ and $\leqslant \pm 0.05$ (3σ) for alkali and alkaline earth metal complexes, respectively. These errors, calculated a priori, are in accordance with those experimentally obtained, indicating the absence of systematic experimental errors. In Table 6 we report some formation percentages together with their errors; it can be seen that the uncertainties are suffi-

TABLE 6

Some formation percentages of Na^{+} and Ca^{2+} phenoxyacetate complexes, at 25°C [a]

pH	$I = 0.1$ [b]	$I = 0.64$	$I = 1.0$
	$C_{Na} = 0.1$ [b]	$C_{Na} = 0.64$	$C_{Na} = 1$
	% $[Na(L)]^0$		
2.5	1.8 ± 0.4 [c]	9.8 ± 2.1	15 ± 3
3.5	5.4 ± 1.2	28 ± 5	42 ± 6
4.5	6.7 ± 1.4	35 ± 5	51 ± 6
	$C_{Ca} = 0.03$	$C_{Ca} = 0.213$	$C_{Ca} = 0.333$
	% $[Ca(L)]^{+}$		
2.0	1.2 ± 0.2	6.8 ± 0.8	10.5 ± 1.2
3.0	6.3 ± 0.7	31 ± 2	44 ± 3
4.0	10.7 ± 1.1	47 ± 3	65 ± 3

[a] The formation percentages are calculated with respect to the ligand (5 mmol l^{-1}).

[b] Ionic strengths and analytical concentrations in mol l^{-1}.

[c] $\pm 3\sigma$.

ciently low to permit a correct speciation of a fluid containing phenoxyacetate and the cations studied here. As to the significance of the formation of these complexes, more systems must be studied in order to build up model systems of fluids in the soil. This will be done in subsequent papers.

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