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COMPLEXING ABILITY OF PESTICIDES AND RELATED COMPOUNDS. THERMODYNAMIC PARAMETERS FOR THE FORMATION OF H^+, Na^+ AND Ca^{2+} COMPLEXES WITH 2,4-DICHLOROPHENOXYACETATE IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

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ABSTRACT

The formation constants of 2,4-dichlorophenoxyacetate for H^+, Na^+ and Ca^{2+} complexes were determined pH-metrically at 10, 25 and 45 °C in the ionic strength range $0.05 \leqslant I \leqslant 1$ mol l^{-1}. The dependence of formation constants on ionic strength and temperature was taken into account by empirical equations and estimates of $\Delta H^{\ominus}$ were obtained. Comparisons with the stability of similar carboxylate complexes are made.

INTRODUCTION

The use of models in studying the effect of some classes of substances on the ground and in natural waters is growing continuously. For this purpose we need several chemico-physical properties, such as volatility, solubility, partition coefficients, etc., for each class of substances to be studied. In order to understand the behaviour of pesticides (and other organics) in solution it is of great importance to know some thermodynamic parameters for the formation of complexes of these substances with protons and metal ions present in the fluid being considered.

Therefore we undertook a systematic study on the complexing ability of pesticides in solution. In the first contribution [1] we studied alkali and alkaline earth metal complexes of phenoxyacetate. Here, we report a potentiometric study on H^+, Na^+ and Ca^{2+} 2,4-dichlorophenoxyacetate (hereafter 2,4-D) complexes at 10, 25 and 45 °C, at different ionic strengths, $0.05 \leqslant I \leqslant 1$ mol l^{-1}. Comparisons with the thermodynamic parameters for analogous complexes of similar ligands were made in order to assess the possibility of finding empirical relations for classes of ligands.

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EXPERIMENTAL

Materials

The ligand (Janssen Chimica) was purified by dissolution in NaOH and precipitation with diluted HCl [2]; its purity, checked by alkalimetric titrations, was 98 ± 2%. The 2,4-D acid is not very soluble; we performed some solubility measurements at 25 + 0.2 °C in pure water and the mean value (15 determinations) was 2.75 ± 0.15 (3σ) mmol l^{-1} (σ = standard deviation). Stock solutions of NaCl were prepared from C. Erba reagent, purity > 99.5%, previously dried in a stove at 110 °C. $CaCl_2$ stock solutions were prepared from Fluka purum reagent and standardized by EDTA titrations [3]. Tetraethylammonium iodide (Et_4NI, Fluka purissimum) was recrystallized from methanol [2]. Stock solutions of NaOH and HCl were prepared by diluting concentrated ampoules supplied by C. Erba and standardized against potassium hydrogenophthalate and sodium carbonate, respectively. All solutions were prepared with bidistilled water and preserved from atmospheric CO_2 by means of soda-lime traps.

Apparatus

Potentiometric readings were made to measure the free concentration of hydrogen ion using a Metrohm E600 potentiometer coupled with glass-satured calomel electrodes supplied by the same firm. The titrant solution of NaOH was delivered by an AMEL Mod. 232 dispenser readable to 1 μl. The measurement cell was kept at constant temperature within ±0.2 °C and a magnetic stirrer was used. Titrations were carried out under a stream of nitrogen gas.

Procedure

Test solutions (50 ml) were titrated with 0.05 M NaOH up to $\simeq 90\%$ neutralization. Electrodic chain was calibrated by separate titrations of standard HCl under the same experimental conditions. The concentration of 2,4-D was about 2.3 mmol l^{-1} and the ionic strength was adjusted by means of appropriate amounts of electrolyte (NaCl or $CaCl_2$) solution.

Calculations

The non-linear least-squares computer program ACBA [4] and/or ESAB [5] and/or ESAB2M [6] were used to elaborate the potentiometric data in order to refine the protonation constants by assuming no complex formation. Subsequently the formation constants of the weak complexes were calculated by means of non-linear least-squares computer programs WECO

[7] and/or ES2WC [8]. Concentrations and thermodynamic parameters are expressed in the molar scale.

The dependence on ionic strength and on temperature of formation constants was taken into account as previously reported [7,8]. The formation constants are expressed as

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

where M = H^+, Na^+, Ca^{2+}.

RESULTS AND DISCUSSION

The protonation constants, calculated without allowing the formation of Na^+ and Ca^{2+} complexes, are reported in Table 1.

By assuming that Et_4N^+ does not interact with 2,4-D [1], the formation constants for Na^+ and Ca^{2+} complexes can be calculated by the method already proposed for weak species [9], by using the computer program WECO [7] and/or ES2WC [8].

TABLE 1

Protonation constants of 2,4-dichlorophenoxyacetate at different temperatures and ionic strengths, and in different backgrounds (primes indicate conditional protonation constants)

t (°C)	Et_4NI		NaCl		$CaCl_2$	
	I [a]	$\log K^{H}$	I	$\log K^{H\prime}$	I	$\log K^{H\prime}$
10	0.06	2.78 [b]	0.06	2.75	0.07	2.72
	0.12	2.78	0.12	2.75	0.26	2.64
	0.24	2.83	0.24	2.68	0.52	2.67
	0.47	2.85	0.71	2.70		
	0.71	2.94	0.98	2.73		
	0.98	2.99				
25	0.06	2.78	0.06	2.76	0.06	2.77
	0.12	2.76_5	0.12	2.71_5	0.13	2.70
	0.24	2.76	0.24	2.65	0.52	2.65
	0.24	2.78	0.24	2.70	0.78	2.66
	0.47	2.88	0.47	2.73		
	0.71	2.93	0.71	2.71		
	0.98	3.05	0.98	2.74		
45	0.06	2.88	0.06	2.87	0.13	2.78
	0.12	2.87	0.12	2.81	0.26	2.73
	0.23	2.90	0.23	2.79_5	0.51	2.68
	0.47	2.90	0.47	2.75	0.77	2.69
	0.70	2.99	0.70	2.80	0.96	2.67_5
	0.97	3.10_5	0.97	2.79		
	0.98	3.04	0.97	2.79_5		

[a] Ionic strength in mol l^{-1}.

[b] Confidence intervals for $\log K^{H}$ (and $\log K^{H\prime}$) are $\pm 0.01-0.03$ (3σ).

TABLE 2

Thermodynamic parameters for the formation of H^+, Na^+ and Ca^{2+} 2,4-dichlorophenoxyacetate complexes ($\Delta H^\ominus$ values are expressed in kJ mol^{-1})

I	t (°C)	H^+		Na^+		Ca^{2+}	
		log K	$\Delta H^\ominus$	log K	$\Delta H^\ominus$	log K	$\Delta H^\ominus$
0	10	2.900 ± 0.015[a]		-0.08 ± 0.05		0.64 ± 0.08	
0.25		2.772 ± 0.011		-0.21 ± 0.05		0.36 ± 0.07	
1		3.032 ± 0.022		0.05 ± 0.07		0.81 ± 0.09	
0	25	2.913 ± 0.011	4.9 ± 1.1[a]	-0.10 ± 0.04	-2.4[b]	0.66 ± 0.04	2.4[b]
0.25		2.780 ± 0.009	4.3 ± 0.9[c]	-0.24 ± 0.04	-2.9	0.37 ± 0.04	1.0[c]
1		3.023 ± 0.015	2.4 ± 1.5	0.01 ± 0.04	-4.9	0.78 ± 0.05	-2.9
0	45	2.999 ± 0.014		-0.13 ± 0.05		0.69 ± 0.05	
0.25		2.858 ± 0.011		-0.27 ± 0.05		0.38 ± 0.04	
1		3.078 ± 0.018		-0.05 ± 0.06		0.75 ± 0.05	

[a] Value ± standard deviation.

[b] These $\Delta H^\ominus$ values are affected by large errors and are to be considered only as indicative.

[c] $\Delta S^\ominus = 72$ $[HL]^0$, 21 $[CaL]^+$ kJmol^{-1} K^{-1}.

In Table 2 we report the formation constants of H^+, Na^+ and Ca^{2+} 2,4-D complexes at different temperatures and ionic strengths. From the dependence on temperature of the protonation constant it was possible to calculate a reasonable value for $\Delta H^\ominus$ of the protonation reaction whilst, for the formation constants of Na^+ and Ca^{2+} complexes, only indicative values of $\Delta H^\ominus$ can be reported (Table 2). The dependence of the protonation constant on temperature and ionic strength can be expressed by the equation

$$\log K^{H}_{I,T} = 2.193 - 2\sqrt{I}/(2 + 3\sqrt{I}) + \left[0.71 - 1.1 \times 10^{-3}(t - 25)\right] I$$
$$-0.2\ I^{3/2} + 1.9 \times 10^{-3}(t - 25) + 10^{-4}(t - 25)^2$$

which is quite similar to that reported for the protonation of phenoxyacetate. In Fig. 1 we report some distribution diagrams versus pH for the system Na^+–Ca^{2+} 2,4-D. As can be seen, quite significant formation percentages are shown, revealing that in the speciation of natural fluids containing 2,4-D, the formation of these weak species cannot be neglected.

Two points must be discussed about the values obtained. The first one relates to the errors that affect the values; the second implies a comparison with other low molecular weight carboxylate ligands. As regards the errors affecting the thermodynamic parameters for the formation of H^+, Na^+ and Ca^{2+} 2,4-D, we must remember that the standard deviations reported in Table 2 do not take into account the contribution of systematic errors due to the purity of the reagents. In general, when the purity is $> 99.5\%$ this contribution is negligible but, in this case where the purity of 2,4-D acid is $\sim 98\%$, an additional error of ~ 0.05 log units must be added to the formation constants. By performing some calculations with the program

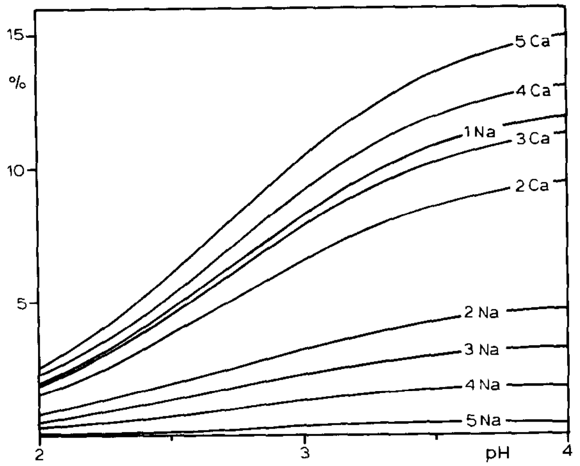

Fig. 1. Distribution diagrams for the system Na^+-2,4-D and Ca^{2+}-2,4-D vs. pH, at 25 ° C. Concentrations in mol l^{-1}: (1) $Na^+ = 0.25$, $Ca^{2+} = 0.00001$, $L = 0.002$; (2) $Na^+ = 0.10$, $Ca^{2+} = 0.05$, $L = 0.002$; (3) $Na^+ = 0.07$, $Ca^{2+} = 0.06$, $L = 0.002$; (4) $Na^+ = 0.04$, $Ca^{2+} = 0.07$, $L = 0.002$; (5) $Na^+ = 0.01$, $Ca^{2+} = 0.08$, $L = 0.002$.

ES4EC [10] we obtained ($c_{Ca} = 0.07$ mol l^{-1}) at $pH = 4$ $c_{CaL} = 13 \pm 4$ ($\pm 3\sigma$), instead of 13 ± 1 (when neglecting additional error). Nevertheless, even with this additional error the figures are quite significant, and can be used in the speciation and in comparison with other thermodynamic parameters for similar ligands.

As regards the comparison with the formation of Na^+ and Ca^{2+} complexes of carboxylate, in Table 3, some formation constant values are reported for ligands where only one carboxylic group is involved. For both Na^+ and Ca^{2+} complexes the differences in the stability among various ligands are fairly small, in particular considering that by allowing for all

TABLE 3

Formation constants of Na^+ and Ca^{2+} complexes of low molecular weight carboxylate ligands at 25 ° C and $I = 0.25$ mol l^{-1}

Ligand	$\log K^{Na}$	$\log K^{Ca}$	Ref.
Phenoxyacetate	−0.12	0.57	1
2,4-Dichlorophenoxyacetate	−0.24	0.37	This work
Acetate	−0.27	0.57	9
Salicylate	−0.5	0.63	9
Malonate[a]	−0.21	0.54	9
L-Histidinate[b]	–	0.33	9
Monocarboxylates[c]	−0.3	–	11

[a] Reaction $M + HL \rightleftharpoons [M(HL)]$.

[b] Reaction $M + H_2L \rightleftharpoons [M(H_2L)]$.

[c] Value deduced by the analysis of literature data.

sources of errors, the error (95% confidence interval) for weak species should be $S_{\log K} = 0.07–0.15$. Although on one hand this fact, already taken into consideration [1,9,11], requires further confirmation, on the other hand it allows us to simplify the calculations for the speciation of natural fluids. Other similarities for other classes of ligand will be studied.

Values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the protonation and Na^+ and Ca^{2+} complex formation show the same pattern [1,9] with respect to monocarboxylates as do the formation constants: once again the dependence on ionic strength of thermodynamic parameters is quite similar to that of analogous complexes of monocarboxylates. This means (apart from the obvious consideration about the similarity of bonding characteristics) that the use of a mean value in modelling natural fluids for ligands with unknown thermodynamic parameters is also permissible for their dependence on temperature and ionic strength.

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