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Polarographic study of the complexes of cadmium(II) and lead(II) with methoxyacetate ions

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Abstract. Reduction of the complexes of cadmium(II) and lead(II) at DME in aqueous and aqueous-methanol media at $\mu = 1{\cdot}0$ M($NaClO_4$) at $15 \pm 0{\cdot}1$ and $25 \pm 0{\cdot}1$°C is reversible and diffusion-controlled. Four complex species are formed in either case. The overall stability constants of 1 : 1, 1 : 2, 1 : 3 and 1 : 4 complexes have been determined. Lead(II) complexes are much stronger than the corresponding cadmium(II) complexes.

Keywords. Polarography; cadmium; lead methoxyacetate.

1. Introduction

Recently, the plant auxins such as 3-indoleacetate, 3-indole-butyrate, and 1-naphthaleneacetate have been reported to form weak complexes with trace elements cadmium(II), zinc(II), manganese(II) and thallium(I) (Parkash *et al* 1981, 1983). Since fungicide action is also an important phenomenon occurring in plants, it was considered worthwhile to study the interaction of methoxyacetate, a fungicide, with trace elements cadmium(II) and lead(II) at DME in aqueous and aqueous-methanol mixture media.

2. Experimental

Cadmium nitrate tetrahydrate (E Merck, AG), lead nitrate (BDH, AnalaR), sodium perchlorate monohydrate (E Merck, GR), perchloric acid (Reidel) and Triton-X-100 (Rohms and Hass Co.) were used. All the other chemicals used were of guaranteed purity. Triple-distilled mercury and double distilled water were used. Methanol was purified and distilled before use (Vogel 1959). Methoxyacetic acid was prepared from sodium methoxide and freshly-distilled chloroacetic acid (Blatt 1946) and purified by distillation under reduced pressure (96·5°C/13 mm) b.p. 203–204°. Structure and purity of the acid was further confirmed by its PMR spectrum.

Stock solutions of cadmium(II) and lead(II) were prepared in water and standardized (Welcher 1959). Sodium salt of methoxyacetic acid was prepared and pH of this stock solution was adjusted using ELICO pH meter model LI-10. Solutions containing metal ions (4×10^{-4} M) and varying concentrations of the complexing agent (0·0–0·9 M) were prepared in water and 10% methanol media at ionic strength 1 M maintained with sodium perchlorate.

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The capillary characteristics measured in 0·1 M sodium perchlorate (open circuit) and at a mercury height of 60 cm were $m = 2{\cdot}012$ mg sec^{-1} and $t = 3{\cdot}9$ sec. Purified N_2 gas presaturated with the background solution to be polarographed, was used for deaeration and an inert atmosphere was maintained over the solution during electrolysis. The electrolysis was carried out in a H-cell in conjunction with an agar-agar plug saturated with sodium chloride. Polarograms of 0·4 mM cadmium(II) and lead(II) solutions were obtained in the presence of different concentrations of methoxyacetate at $15 \pm 0{\cdot}1$ and $25 \pm 0{\cdot}1$°C using REDELKIS polarograph type OH-102 in aqueous and 10% methanol media. Triton-X-100 (0·002% in the final solution) was used as maxima suppressor whenever required. An *iR* compensation was used while working with methanolic solutions. The currents were corrected for residual current. The resulting polarographic data as a function of the ligand concentration (C_x) which was calculated from the pH of the solution and pK_a value of the ligand (3·55 at 15°C, 3·57 at 25°C (King 1960)), are given in table 1.

3. Results and discussion

Both cadmium(II) and lead(II) give single well-defined reversible polarographic reduction wave. Current is directly proportional to $(h_{eff})^{1/2}$ showing that the reduction is diffusion-controlled. Plot of E_{de} vs $\log i/i_d - i$ is a straight line with a slope of 32 ± 1 mV. Cathodic reduction of cadmium(II) and lead(II) in methoxyacetate is, therefore, reversible and involves two electron transfer in either case. That $E_{1/2}$ is

Table 1. Polarographic data of the interaction of cadmium(II) and lead(II) with methoxyacetate ions.

		Cadmium(II)-methoxyacetate system in aqueous medium at		10% methanol medium at				Lead(II) methoxyacetate system in aqueous medium at			
C_X	p^X	25 ± 0·1°C		15 ± 0·1°C		25 ± 0·1°C		25 ± 0·1°C		15 ± 0·1°C	
M		$E_{1/2}$ (−V)	i_d (μA)	$E_{1/2}$ (−V)	i_d (μA)	$E_{1/2}$ (−V)	i_d (μA)	$E_{1/2}$ (−V)	i_d (μA)	$E_{1/2}$ (−V)	i_d (μA)
0·0000	—	0·5800	1·872	0·5865	1·584	0·5695	1·733	0·3755	2·088	0·3810	1·992
0·0200	1·699	0·5810	1·814	0·5885	1·464	0·5725	1·570	0·3855	2·047	0·3905	1·934
0·0500	1·301	0·5825	1·800	0·5920	1·459	0·5770	1·546	0·3965	1·824	0·3985	1·934
0·0999	1·000	0·5860	1·680	0·5970	1·428	0·5838	1·464	0·4025	1·872	0·4100	1·728
0·1499	0·824	0·5895	1·584	0·6010	1·392	0·5890	1·440	0·4145	1·853	0·4160	1·680
0·1999	0·699	0·5945	1·661	0·6045	1·356	0·5943	1·450	0·4210	1·862	0·4215	1·618
0·2499	0·602	0·5980	1·632	0·6080	1·363	0·5985	1·416	0·4250	1·824	0·4250	1·363
0·2998	0·523	0·6015	1·560	0·6108	1·344	0·6025	1·392	0·4290	1·781	0·4280	1·176
0·3498	0·456	0·6050	1·555	0·6130	1·272	0·6060	1·356	0·4330	1·728	0·4345	1·416
0·3998	0·398	0·6080	1·546	0·6160	1·272	0·6100	1·392	0·4360	1·651	0·4380	1·354
0·4497	0·347	0·6115	1·536	0·6183	1·262	0·6135	1·380	0·4400	1·651	0·4405	1·248
0·4997	0·301	0·6148	1·519	0·6205	1·272	0·6155	1·320	0·4425	1·560	0·4430	1·145
0·5996	0·222	0·6205	1·488	0·6250	1·224	0·6213	1·308	0·4485	1·560	0·4485	1·056
0·6996	0·155	0·6255	1·440	0·6298	1·248	0·6265	1·248	0·4540	1·512	0·4540	1·114
0·7995	0·097	0·6300	1·368	0·6325	1·152	0·6310	1·200	0·4588	1·440	0·4595	1·145
0·8995	0·046	0·6335	1·296	0·6355	1·128	—	—	0·4600	1·157	0·4630	0·984

$Cd^{2+} = Pb^{2+} = 0{\cdot}4$ mM; $\mu = 1{\cdot}0$ M($NaClO_4$); pH = $6{\cdot}8 \pm 0{\cdot}1$

independent of the effective height of mercury column (h_{eff}) is in keeping with the reversible character of the electrode process. There is an appreciable cathodic shift in the $E_{1/2}$ with increase in ligand concentration in either case. The diffusion current also decreases with increasing concentration of the complexing agent due to increase in the size of Cd(II) and Pb(II) ions on complex formation.

$F_o(X)$ functions are calculated at different concentrations of the ligand (DeFord and Hume 1951) and then solved for the stability constant by a graphical procedure, depicted for cadmium as a typical example, in figure 1, which confirms the formation of four consecutive complexes, 1 : 1, 1 : 2, 1 : 3 and 1 : 4 in equilibrium with each other in either case, having stabilities for the cadmium-methoxyacetate complexes β_1 = 5, 13, 17; β_2 = 25·5, 29, 67, β_3 = 37, 20·5, 108·5 and β_4 = 63·48, 40·25, 149·4 at 25 ± 0·1, 15 ± 0·1°C (both in aqueous medium) and 25 ± 0·1°C (in 10% methanol) respectively; for lead-methoxyacetate complexes in aqueous medium β_1 = 70, 80; β_2 = 450, 200; β_3 = 210, 900 and β_4 = 1120·96, 861·79 at 25 ± 0·1 and 15 ± 0·1°C respectively. Lead(II) complexes with methoxyacetate could not be studied in methanol medium due to precipitation of the complexes formed. The values of overall stability constants calculated by Mihailov's method (1974) are in close agreement with those calculated by DeFord and Hume's method.

Percentage distribution of cadmium(II) and lead(II) present in various forms in equilibrium as a function of logarithm of ligand concentration has also been calculated and a typical figure (figure 2) for distribution diagrams of this type is given.

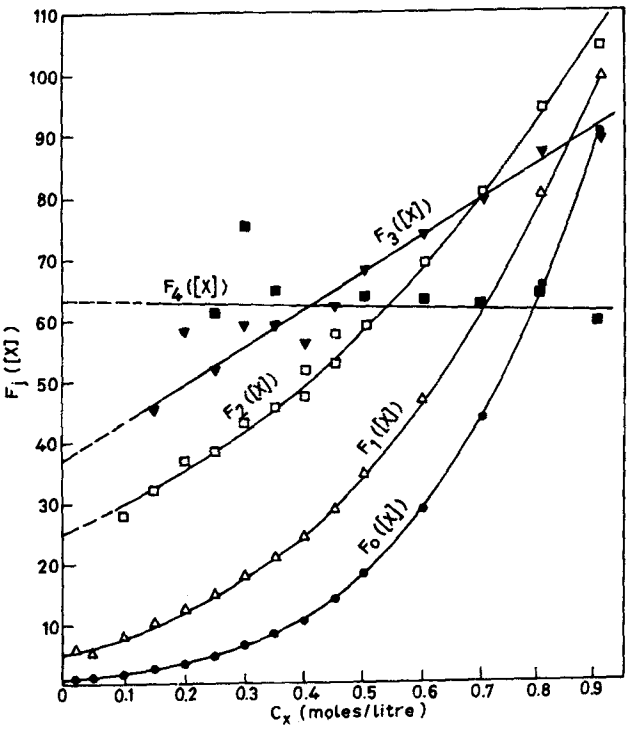

Figure 1. Plot of $F_j(X)$ functions *vs* C_x for cadmium(II) methoxyacetate system in aqueous medium at 25 ± 0·1°C.

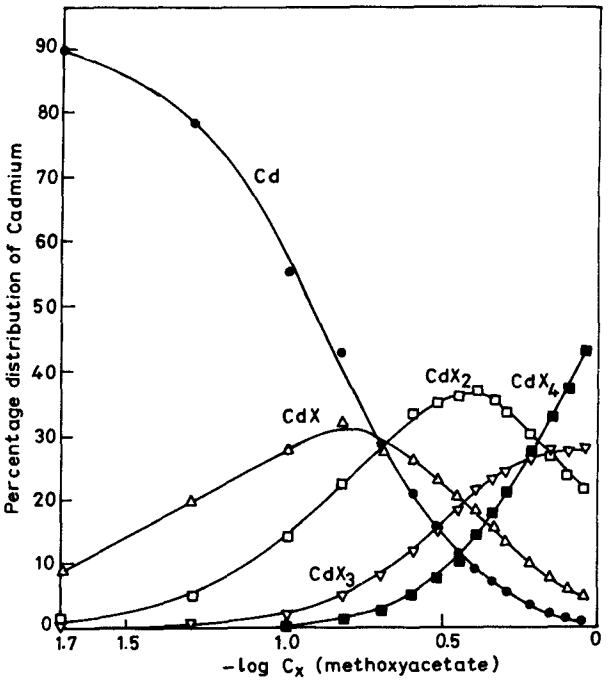

Figure 2. Percentage distribution of cadmium in various forms as a function of $-\log C_x$ in aqueous medium at $25 \pm 0{\cdot}1$°C.

It is evident from the results that the complexes formed are more stable at lower temperatures or in methanol medium. However, the highest complex becomes less stable in both cases on lowering the temperature. The lead(II)-methoxyacetate complexes are, in general, more stable than the corresponding cadmium(II) complexes.

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