Studies on complexes of Cd(II) and Pb(II) with ortho-benzoyl-benzoate at d.m.e.

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For the complexes of Pb^{2+} and Cd^{2+} with ortho-benzoyl-benzoate the electrode reactions were found to be reversible and diffusion controlled. The overall formation constants were calculated by DeFord and Hume's method. In each case three complex species were formed having β_1, β_2, β_3 as 8, 16.5 and 150 for Cd(II) – o-benzoyl-benzoate complexes and 70, 350 and 3650 for Pb(II)-o-benzoyl-benzoate complexes at 25°C. The percentage distribution of metal present in various forms at each ligand concentration has been presented.

The polarographic behaviour of the complexes formed by Cd(II) and Pb(II) with benzoate phthalates, etc have been studied in our laboratories[1–8]. The present studies are devoted to the polarographic behaviour of ortho-benzoyl-benzoate complexes of Pb(II) and Cd(II). The composition and formation constants of the complexes formed have been calculated.

Experimental

Stock solutions of Pb(II) and Cd(II) M/40 each, were prepared from their nitrates. The sodium o-benzoyl-benzoate served as complexing agent. The ionic strength was maintained by $NaClO_4$. Triton X-100 (0.001%) was used as maxima suppressor whenever needed. Solutions containing 1mM of metal ion with varying amounts of ligand were prepared at unit ionic strengths ($\mu = 1$) and polarographed after deaeration for 25 minutes with purified nitrogen. The H-type cell having agar-agar plug saturated with NaCl served as electrolytic cell The d.m.e. had $m = 1.6mg\ sec^{-1}$ & $t = 4.1$ sec (open circuit) with S.C.E. (with NaCl) as reference one. All the measurements were carried out at $30 \pm 0.1°C$. The pH of the solutions was 6.6 ± 0.1.

Results and Discussion

Both Pb(II) and Cd(II) produced well defined current-voltage curves. The $E_{1/2}$ of these solutions shifted to more negative values and i_d decreased as the concentration of the ligand was increased. The plots of i_d vs metal concentration and i_d vs $\sqrt{h}$ (h = height of mercury column) were linear and passed through origin. The plots of log $i/(i_d - i)$ vs $E_{d.e.}$ were linear having the slope of the order of 32 ± 1 mV. These results showed complex formation. The electrode process is diffusion-controlled and reversible for two electron transfer.

The plots of $E_{1/2}$ vs – log C_x (C_x ligand concentration) were smooth curves indicating the formation of more than one complex with metal ions. The composition and the formation constants of the complexes formed have been calculated by DeFord and Hume's method[9]. The polarographic characteristics and $F_0([X])$ values have been summarised in Table, the plots of $F_0([X])$ vs C_x are smooth curves, confirming the formation of two or more complex species which are in equilibrium. The plots of $F_1([X])$ vs C_x are again smooth curves, the extrapolation of these to zero ligand concentration resulted into β_1 The plots of $F_2([X])$ vs C_x are linear and the plots of $F_3([X])$ vs C_x resulted into a straight line parallel to the concentration axis. The extrapolation of $F_2([X])$ and $F_3([X])$ plots to $C_x = 0$ gave the values of β_2 and β_3 respectively. Thus the O-benzoyl-benzoate ion forms three complex species : [M(O-benzoyl benzoate)]*, [M(O-benzoyl benzoate)] and $[M(\text{O-benzoyl benzoate})_3]^-$ with both the metal ions. The formation constants are :

System	β_1	β_2	β_3
Cd(II). O-benzoyl benzoate	8	16.5	150
Pb(II). O-benzoyl-benzoate	70	350	3650

Although the same three complex species are formed with both the metal ions, the complexes formed by Pb(II) are much stronger then those formed by Cd(II).

The percentage distributions of the metal ions and their complexes present at each ligand concentration have been calculated and the results are presented in figure. 1.

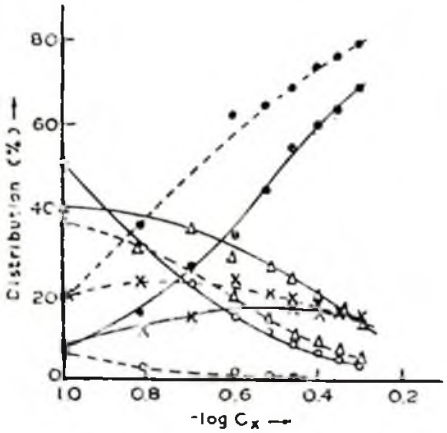


FIG Percentage distribution of Cd (II) (—) & Pb (II) (– – –) in Orthobenzoyl benzoate system
o, M ; Δ, MX_1 ; x, MX_2, •, MX_3

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Table I Polarographic characteristics and $F_o([X])$ Values

Lig-and Conc M	Pb(II)-Ortho Benzoyl Benzoate System $E_{1/2}$ (-V*)	i_d (Divs.)	$F_o([X])$	Cd(II)-Ortho Benzoyl Benzoate System $E_{1/2}$ (-V*)	i_d (Divs)	$F_o([X])$
0.0	0.373	106	—	0.563	86	—
0.05	—	—	—	0.564	81.5	1.139
0.10	0.408	84	18.61	0.570	75.5	1.949
0.15	0.416	83	34 79	0.575	66	3.273
0 20	—	—	—	0 579	66	4.44
0 25	0.428	80	90.67	0.584	61.5	6.149
0 30	0.434	78	151.40	0.587	60.5	8.969
0.35	0.438	77.5	226.3	0.590	58.5	11.680
0.40	0.443	76	313.7	0.594	58.5	15.870
0.45	0.447	74.5	434.9	0.597	54.5	21.450
0.50	0.452	73	651.6	0.600	54.5	27.010

* vs. sce.

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