

Polarographic study of mixed ligand complexes of Pb(II) with ethylenediamine-malonate and propylene-diamine-malonate

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MS received 5 March 1982; revised 27 September 1982

Abstract. Overall stability constants of mixed ligand complexes formed by Pb(II) with ethylenediamine-malonate and propylenediamine-malonate have been determined. The reductions were reversible and diffusion-controlled involving two electrons in both systems. The equilibrium concentration of the ligand is calculated from pH and the total amount present using pK values. The formation constants have been used to discuss the results.

Keywords. Mixed-ligand complexes; lead (II), ethylenediamine; propylenediamine malonate ion.

1. Introduction

Single ligand complexes have been studied by polarographic methods by several workers. However, it has been rarely applied to mixed ligand complexes. It was used to study mixed ligand complexes by Schaap and McMasters (1961) by extending the method of DeFord and Hume (1951) to cases where a metal ion forms complexes with two ligands simultaneously in solution.

Mixed complexes of Pb(II) with various organic ligands have been extensively studied (Gupta and Kaur 1979; Verma and Yadav 1980; Agarwal 1979; Garg *et al* 1982). The present investigation deals with mixed ligand complexes formed by Pb(II) with (i) ethylenediamine-malonate and (ii) propylenediamine-malonate. It was observed that Pb(II) forms 1:3 highest complexes with ethylenediamine (EN), propylenediamine (PN) and malonate ion (MALO).

2. Experimental

The chemicals used were of reagent grade. A manual polarograph was used for this work. Capillary characteristics for the open circuits were: $m = 1.89$ mg/sec and $t = 3.5$ sec. All the measurements were carried out at $298 \pm 0.5^\circ$ K. pH measurement (Toshniwal pH meter) was adjusted with nitric acid solution or CO₂-free potassium hydroxide. Potassium nitrate was added to make the ionic strength equal to 1.5 M. The solution was placed in H-type cell coupled with saturated calomel electrode through an agar-agar saturated with KCl salt bridge. Prior to reduction at DME, oxygen was removed by bubbling pure nitrogen gas through the solution for 20 min. The pk values

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of the ligands were measured by generally accepted procedures and were found to be as follows:

Ligands	pk ₁	pk ₂
Ethylenediamine	6.5	9.48
Propylenediamine	7.0	9.78
Malonic acid	2.85	5.69

3. Results and discussion

3.1 Simple systems

The reduction of Pb(II) was reversible involving two electrons and diffusion-controlled in each case as revealed from the linear plots of i_d vs $h^{1/2}$ of mercury column passing through the origin. The plots of $\log i/i_d - i$ vs E_{de} were linear with a slope of 31 ± 2 mV. No maximum suppressor was needed in these systems. The concentrations of "free" EN, PN and malonate were calculated from the pH and the total amount present using the pk values. The overall formation constants of simple complexes have been evaluated by DeFord and Hume's method and the results are summarized below:

System	Overall formation constants		
	log β_1	log β_2	log β_3
Pb (II) - EN	4.079	7.243	10.099
Pb (II) - PN	5.061	8.204	10.959
Pb (II) - MALO	2.857	3.663	4.268

3.2 Mixed systems

Three different mixed complexes of Pb(II) are possible with two bidentate ligands. These are $[\text{Pb}(\text{EN})(\text{MALO})]$, $[\text{Pb}(\text{EN})(\text{MALO})_2]^{-2}$ and $[\text{Pb}(\text{EN})_2(\text{MALO})]$ for ethylenediamine-malonate system and $[\text{Pb}(\text{PN})(\text{MALO})]$, $[\text{Pb}(\text{PN})(\text{MALO})_2]^{-2}$ and $[\text{Pb}(\text{PN})_2(\text{MALO})]$ for propylenediamine system.

A shift in $E_{1/2}$ to more cathodic potential with increase in EN or PN concentrations was observed in all the cases. The shift is greater in the presence of weaker ligand (MALO) than in its absence signifying mixed ligand formation. The Schaap and McMasters treatment was applied to the half-wave potential data and F_{i0} functions evaluated. Leeden's (1941) graphical extrapolation method was then applied to calculate A, B, C, D and the calculations are given in tables 1 to 4.

Due to experimental advantage, malonate concentrations were held at two different fixed values (0.20 and 0.25 M) allowing the F_{00} functions to be evaluated as function of EN or PN concentration which varied with pH. Under this condition, for the lead systems, the F_{00} functions may be written:

$$F_{00} = A + B[X] + C[X]^2 + D[X]^3,$$

where, $[X] = \text{EN or PN}$,

$$A = 1 + \beta_{01} [\text{MALO}] + \beta_{02} [\text{MALO}]^2 + \beta_{03} [\text{MALO}]^3,$$

$$B = \beta_{10} + \beta_{11} [\text{MALO}] + \beta_{12} [\text{MALO}]^2,$$

$$C = \beta_{20} + \beta_{21} [\text{MALO}], \text{ and } D = \beta_{30}.$$

The values of A and D are known from the studies of the simple systems. However, B values must be evaluated at least at two appropriate malonate ion concentrations, so that the mixed constants β_{11} and β_{12} can be calculated.

Theoretically, $\log C$ must be equal to $\log \beta_{30}$. Our results agree with this postulation. The average $\log D$ values from both the series in the EN-MALO system were 10.040 and 10.056 which agree reasonably well with the value of $\log \beta_{30} = 10.099$. However, in PN-MALO system, the $\log D$ values were 10.932 and 10.945 which also agree with the corresponding value of $\log \beta_{30} = 10.959$.

Table 1. Lead-ethylenediamine-malonate system

$[\text{EN}] \times 10^4$	$\log I_M/I_C$	$\Delta E_{1/2}$	$F_{00}(X)$	$F_{10}(X) \times 10^{-4}$	$F_{20}(X) \times 10^{-8}$	$F_{30}(X) \times 10^{-12}$
6.1485	0.1205	0.0830	849.6107	—	—	—
9.2228	0.1272	0.0863	1115.8145	69.2105	—	—
12.297	0.1339	0.0890	1398.4921	74.8957	0.8860	0.01106
15.371	0.1385	0.0912	1677.6756	78.0805	0.9160	0.01080
18.445	0.1408	0.0933	1986.4241	81.8067	0.9654	0.01168
21.519	0.1455	0.0951	2310.3830	85.1751	0.9840	0.01087
24.594	0.1478	0.0969	2672.3664	89.2440	1.0264	0.01124
27.668	0.1501	0.0985	3043.2666	92.7341	1.0385	0.01043
30.742	0.1525	0.1001	3466.4424	97.2267	1.0808	0.01076

$[\text{Pb}]^{+2} = 0.5\text{mM}$; $\mu = 1.5 \text{ M}$; $\text{pH} = 7.7$; $I_M = 65.0 \text{ divs}$; $E_{1/2} = -0.4150 \text{ volts vs SCE}$; $[\text{malonate}] = 0.20 \text{ M}$

$A_{\text{cal}} = 477.5$ $B = 64 \times 10^4$ $C = 0.75 \times 10^8$ $\log D_{\text{av}} = 10.040$

Table 2. Lead-ethylenediamine-malonate system

$[\text{EN}] \times 10^4$	$\log I_M/I_C$	$\Delta E_{1/2}$	$F_{00}(X)$	$F_{10}(X) \times 10^{-4}$	$F_{20}(X) \times 10^{-8}$	$F_{30}(X) \times 10^{-12}$
6.1485	0.1272	0.0876	1234.7641	—	—	—
9.2228	0.1362	0.0908	1617.6032	93.1391	—	—
12.297	0.1408	0.0932	1971.0062	98.5937	1.0241	0.01091
15.371	0.1501	0.0951	2334.9844	102.5557	1.0771	0.01217
18.445	0.1549	0.0969	2716.4142	106.1433	1.0921	0.01096
21.519	0.1597	0.0986	3135.6240	110.4616	1.1367	0.01147
24.594	0.1670	0.1001	3584.1319	114.8870	1.1746	0.01157
27.668	0.1670	0.1017	4060.0182	119.3226	1.2044	0.01136
30.742	0.1695	0.1031	4554.1150	123.4635	1.2186	0.01069

$[\text{Pb}]^{+2} = 0.5\text{mM}$; $\mu = 1.5 \text{ M}$; $\text{pH} = 7.7$; $I_M = 65.0 \text{ divs}$; $E_{1/2} = -0.4150 \text{ volts vs SCE}$; $[\text{malonate}] = 0.25 \text{ M}$

$A'_{\text{cal}} = 758.6$ $B' = 86 \times 10^4$ $C' = 0.89 \times 10^8$ $\log D_{\text{av}} = 10.056$

Table 3. Lead-propylenediamine-malonate system

$[\text{PN}] \times 10^4$	$\log I_M/I_C$	$\Delta E_{1/2}$	$F_{00}(X)$	$F_{10}(X) \times 10^{-4}$	$F_{20}(X) \times 10^{-8}$	$F_{30}(X) \times 10^{-12}$
2.7536	0.1362	0.0833	901.7615	154.0752	—	—
4.1305	0.1400	0.08695	1208.9365	177.0818	4.1355	0.08123
5.5073	0.1431	0.08953	1488.7676	183.6231	4.2894	0.08887
6.8841	0.1455	0.0918	1786.3736	190.1299	4.3767	0.08378
8.2610	0.1525	0.0937	2105.3786	197.0559	4.4856	0.08300
9.6378	0.1573	0.0955	2449.1461	204.5743	4.6249	0.08556
11.014	0.1645	0.0971	2821.0923	212.7830	4.7924	0.09010
12.391	0.1695	0.0986	3206.8938	220.2723	4.8642	0.08588
13.768	0.1719	0.1001	3625.0934	228.6166	4.9838	0.08598

$[\text{Pb}]^{+2} = 0.5\text{mM}$; $\mu = 1.5\text{ M}$; $\text{pH} = 7.7$; $I_M = 65.0\text{ divs}$; $E_{1/2} = -0.4150\text{ volts vs SCE}$; $[\text{malonate}] = 0.20\text{ M}$

$A_{\text{cal}} = 477.5$; $B = 160 \times 10^4$; $C = 3.8 \times 10^8$; $\log D_{\text{av}} = 10.932$.

Table 4. Lead-propylenediamine malonate system

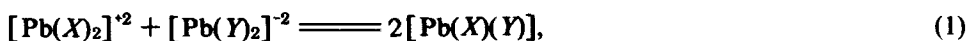
$[\text{PN}] \times 10^4$	$\log I_M/I_C$	$\Delta E_{1/2}$	$F_{00}(X)$	$F_{10}(X) \times 10^{-4}$	$F_{20}(X) \times 10^{-8}$	$F_{30}(X) \times 10^{-12}$
2.7536	0.1455	0.0870	1228.9672	170.819	—	—
4.1305	0.1501	0.0910	1696.4458	227.0538	4.6129	—
5.5073	0.1549	0.0933	2051.9746	234.8473	4.8749	—
6.8841	0.1621	0.0952	2419.1789	241.2195	4.8255	—
8.2610	0.1645	0.0971	2820.7461	249.6243	5.0386	0.08336
9.6378	0.1719	0.0987	3250.1844	258.5221	5.2421	0.09256
11.014	0.1769	0.1002	3695.6870	266.6685	5.3267	0.08868
12.391	0.1820	0.1016	4169.8574	275.3012	5.4315	0.08728
13.768	0.1845	0.1030	4677.8295	284.6622	5.5681	0.08848

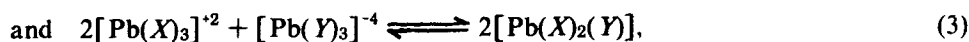
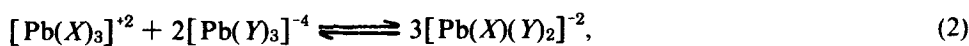
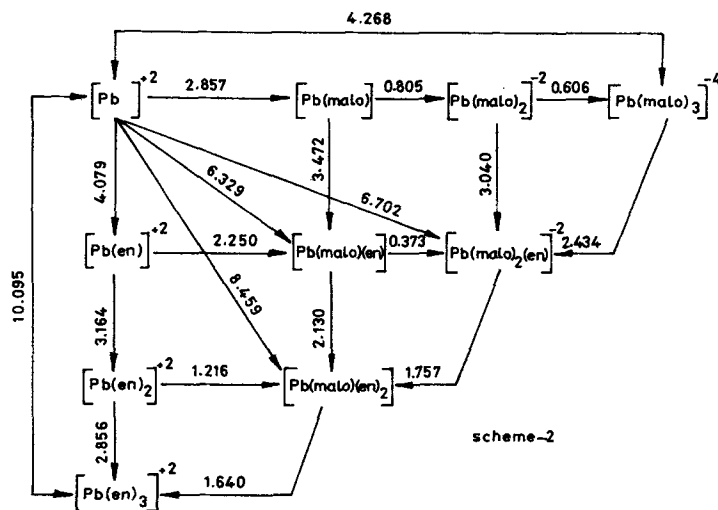
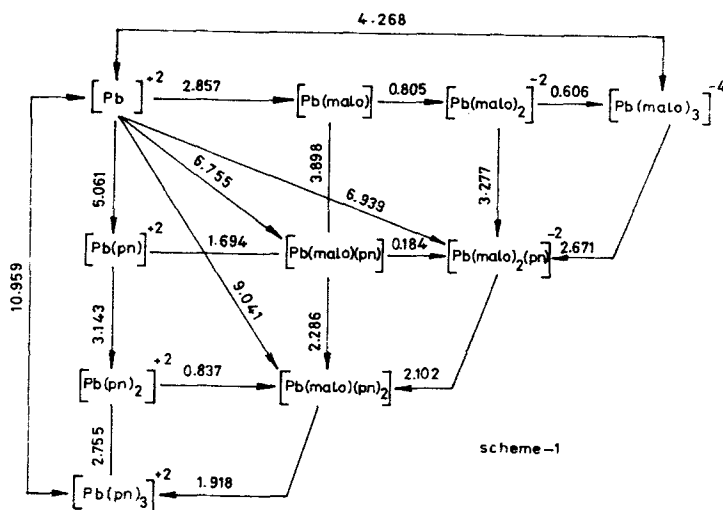
$[\text{Pb}]^{+2} = 0.5\text{mM}$; $\mu = 1.5\text{ M}$; $\text{pH} = 7.7$; $I_M = 65.0\text{ divs}$; $E_{1/2} = -0.4150\text{ volts vs SCE}$; $[\text{malonate}] = 0.20\text{ M}$

$A'_{\text{cal}} = 758.6$ $B' = 208.0 \times 10^4$; $C' = 4.35 \times 10^8$; $\log D'_{\text{av}} = 10.945$.

The results are summarized in schemes 1 and 2 where $\log K$ of the steps is indicated. These trends may be understood if it is assumed in accord with evidence (not cited here) that the $\text{N} \rightarrow$ metal bond is appreciably more covalent than the $\text{O} \rightarrow$ metal bond with these ligands. The ethylenediamine or propylenediamine complexes would then be more strongly influenced by the stereochemistry of the hybridized sp^3 orbitals of lead than the more ionic malonate complexes and have a correspondingly greater tendency to be tetrahedral. Addition of either ethylenediamine/propylenediamine molecule or malonate ion to $[\text{Pb}(\text{EN})_2]^{+2} / [\text{Pb}(\text{PN})_2]^{+2}$ would be hindered, despite the opposite charges of the latter two species, while addition of either ligand to $[\text{Pb}(\text{MALO})_2]^{-2}$ would proceed more readily, offsetting the repulsion of the like charges in the case of malonate addition.

For reactions





where $X = \text{EN}$ or PN and $Y = \text{MALO}$.

The log values of X_{11} , X_{12} and X_{21} for both the systems were calculated and found as follows:

System	log X_{11}	log X_{12}	log X_{21}
Pb(II)-EN-MALO	1.753	1.471	0.911
Pb(II)-PN-MALO	1.644	1.322	0.937

The log X_{11} value on statistical grounds is 0.6, and the observed value of log X_{11} greater than 0.6 indicates favoured formation of mixed complexes. The observed log X_{12} and log X_{21} are also greater than the expected values on statistical basis.

Acknowledgement

Thanks are due to Sri G S Kachhawha for helpful discussion.

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