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Lead(II) Butanedioate–Pentanedioate Mixed Complexes

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Butanedioate and pentanedioate form 1 : 3 highest complexes separately with lead(II) in aqueous medium, three mixed complexes of these two ligands with the metal ion expected in solution being observed. The formation constants of mixed complexes have been evaluated on the basis of polarographic measurements by the method of Schaap and McMasters. The formation constants of the mixed complexes $[Pb(X)(Y)]^{2-}$, $[Pb(X)(Y)_2]^{4-}$, and $[Pb(X)_2(Y)]^{4-}$ are 3.57, 4.22, and 4.49 respectively in their logarithmic form at 303 K, where X^{2-} and Y^{2-} stand for butanedioate and pentanedioate ion, respectively. The statistically calculated values of logarithm of formation constants are 3.43, 4.43, and 4.49 in the above order. The small differences in the observed and calculated values may be due to electrostatic, steric *etc.* factors. The relative probability of the existence of these mixed complexes and also simple complexes has been explained.

When two or more complexing species are added to a solution containing a metal ion, it has been observed that metal ion forms complex with all the ligand molecules simultaneously. The complexes so formed in the solution are called mixed complexes. Such species have been found as components in natural waters and biological fluids.

Many workers have reported the existence of mixed complexes.[1–4] Polarographic measurements have also shown the formation of mixed complexes in solution.[5–8]

Discussion of the Schaap and McMasters method has been given in detail in our previous publication.[5]

Experimental

All the chemicals used were of reagent grade purity. The sodium salts of butanedioic and pentanedioic acids were used as complexing species at pH 6.8±0.1. The capillary of DME had the following characteristics, $m=2.14$ mg s^{-1} and $t=4.65$ s, where m is the mass of mercury in milligram falling from capillary per second and t is the drop life in seconds. Ionic base strength was kept constant at 2.0 mol dm^{-3} using KNO_3 as electrolyte. At 5×10^{-4} mol dm^{-3} metal ion concentration no maximum suppressor was required. Potentials were measured with reference to SCE. All solutions were prepared in twice distilled water. The temperature was maintained constant at 303±0.1 K using a U_3 Ger. Nr. 8954 type thermostat.

Results

Polarographic Behavior. *Simple Systems*: In each case a single well defined reversible and diffusion controlled reduction wave was obtained. Reversibility and the diffusion controlled nature of reduction were revealed from the slope (31±1) mV of the E_{de} *vs.* $\log(i/(i_d-i))$ plots and the i *vs.* $h^{1/2}$ straight line plots, respectively, where E_{de} is applied potential, i_d is diffusion current, i is current at any potential and h, is effective height of mercury head of DME. The method of DeFord and Hume[10] was used to calculate the overall formation constants (β's) of complexes formed by butanedioate and pentanedioate ions individually with lead(II). The results are as follows:

Equilibria with Butanedioate:

$[Pb(H_2O)_6]^{2+} + X^{2-} \rightleftharpoons [Pb(H_2O)_4X]$; β_{10} (230)

$[Pb(H_2O)_6]^{2+} + 2X^{2-} \rightleftharpoons [Pb(H_2O)_2(X)_2]^{2-}$; β_{20} (3250)

$[Pb(H_2O)_6]^{2+} + 3X^{2-} \rightleftharpoons [Pb(X)_3]^{4-}$; β_{30} (11700)

Equilibria with Pentanedioate:

$[Pb(H_2O)_6]^{2+} + Y^{2-} \rightleftharpoons [Pb(H_2O)_4Y]$; β_{01} (200)

$[Pb(H_2O)_6]^{2+} + 2Y^{2-} \rightleftharpoons [Pb(H_2O)_2(Y)_2]^{2-}$; β_{02} (2950)

$[Pb(H_2O)_6]^{2+} + 3Y^{2-} \rightleftharpoons [Pb(Y)_3]^{4-}$; β_{03} (7850)

where the numerals in parentheses are the overall formation constant at 303 K.

Mixed Systems: The lead(II) butanedioate–pentanedioate mixed complexes were found to reduce reversibly at DME with the involvement of two electrons. The ions reaching the electrode were solely due to diffusion. The above conclusions were drawn from the slopes of the log plots (30—32) mV and the constancy of the ratio of diffusion current and square root of the effective height of mercury column.

In the first set of observations the fixed concentration of pentanedioate ion was 0.075 mol dm^{-3} in all the solutions. The varying quantities of butanedioate were added to the solutions. A cathodic shift in the half wave potential was observed as a function of butanedioate concentration. The shift was greater in the presence of pentanedioate than the one obtained for the simple lead(II) butanedioate system. This indicates the mixed ligand complex formation of butanedioate and pentanedioate with lead(II). In the second set of observations the pentanedioate ion concentration was fixed at 0.2 mol dm^{-3}.

The Schaap and McMasters functions F_{10} given in the theory were computed. The graphical extrapolation of the plots of F_{10} *vs.* C_X gave the values of A, B, C, and D; A, B, C, and D are constants and are the intercepts of the plots of F_{00}, F_{10}, F_{20}, and F_{30} *vs.* C_X on the F_{10} axis, respectively. C_X is the butanedioate concentration which is varied. The functions F_{10} and the constants A, B, C, and D have been defined in our previous publication.[5] The values of A, B, C, and D for the two fixed concentrations of pentanedioate are recorded below:

[Pentanedioate] in mol dm^{-3}	Temperature 303 K			
	A	B	C	D_{av}
0.075	35	600	5550	12200
0.20	200	1850	9400	14100

The values of β_{11} and β_{12} were calculated using values of B at two fixed concentrations of pentanedioate by means of the equation

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

Table 1. Polarographic measurements and F_{10} function values of lead(II) butanedioate-pentanedioate system at 303 K[a]

C_X[b]	$-E_{1/2}$[c] (V vs. SCE)	i_d[d] (Divs.)	F_{00}	F_{10}	F_{20}	F_{30}
0.025	0.4215	51.0	53.70	748.0	5920	14800
0.05	0.4265	50.5	80.23	904.6	6092	10840
0.10	0.4355	50.0	161.60	1266.0	6660	11100
0.15	0.4425	48.0	288.00	1686.6	7244	11293
0.20	0.4490	47.5	479.30	2221.5	8107	12787
0.30	0.4585	45.5	1037.00	3340.0	9133	11944
0.40	0.4665	44.0	1983.00	4870.0	10675	12812

$m=2.14\ \mathrm{mg\ s^{-1}}$, $t=4.6\ \mathrm{s}$, and $\mu=2.0\ \mathrm{mol\ dm^{-3}}$.

μ is ionic strength of the electrolyte solution.

a) Concentration of Pentanedioate = 0.075 mol dm^{-3} (fixed). b) C_X = Butanedioate concentration in mol dm^{-3}. c) $-E_{1/2}$ of simple metal ion = 0.3695 volts. d) i_d of simple metal ion = 51 Divisions.

Table 2. Polarographic measurements and F_{10} eunction values of lead(II) butanedioate-pentanedioate system at 303 K[a]

C_X[b]	$-E_{1/2}$[c] (V vs. SCE)	i_d[d] (Divs.)	F_{00}	F_{10}	F_{20}	F_{30}
0.025	0.4400	50.0	228.3	1132	9280	—
0.05	0.4420	49.5	268.7	1374	9480	—
0.10	0.4495	48.0	494.0	2940	10900	15000
0.15	0.4545	47.0	739.1	3594	11626	14840
0.20	0.4590	47.0	1044.0	4220	11850	12250
0.25	0.4635	46.5	1189.0	5156	13224	15296
0.30	0.4670	46.0	1970.0	5900	13500	13666
0.40	0.4735	45.0	3318.0	7795	14862	13656

a) Concentration of Pentanedioate = 0.20 mol dm^{-3} (fixed). b), c), d) See footnotes b), c), d) of Table 1.

from which we get β_{11} and β_{12} to be 3.57 and 4.22, respectively, in their logarithmic form. The β's are overall formation constants of the corresponding simple and mixed complexes.

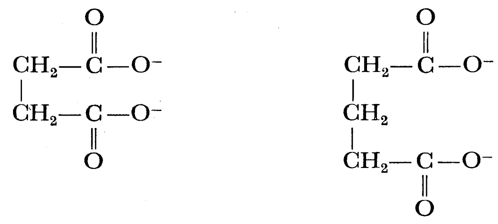
The two values of C gave two values of log β_{21}, both of which are 4.49. The relation between β_{21} and C is given by

$$C = \beta_{20} + \beta_{21}[\mathrm{Y}].$$

The polarographic measurements and the values of F_{10} functions values are given in Tables 1 and 2 at pentanedioate concentrations 0.075 and 0.20 mol dm^{-3}, respectively.

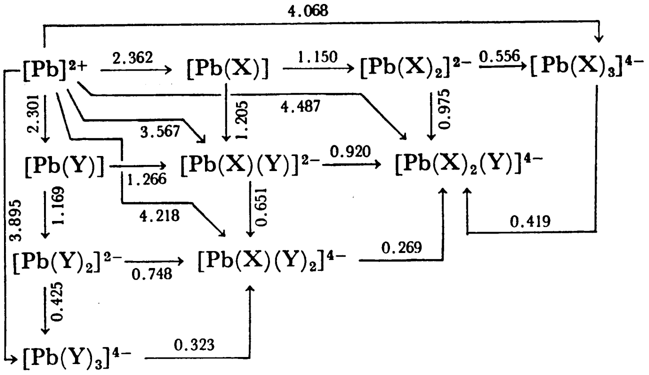
Discussion

The structures of butanedioate and pentanedioate are as follows:



Butanedioate Pentanedioate

As is evident from their structures the butanedioate complexes are more stable than the pentanedioate complexes (see results of the simple complexes). The highest complex formed with lead(II) is 1 : 3 with each ligand which shows the formation of three mixed complexes, *viz.* $[\mathrm{Pb(X)(Y)}]^{2-}$, $[\mathrm{Pb(X)_2(Y)}]^{4-}$, and $[\mathrm{Pb(X)(Y)_2}]^{4-}$, where $\mathrm{X^{2-}}$ and $\mathrm{Y^{2-}}$ stand for butanedioate and pentanedioate ion, respectively. The schematic representation of all the complexes (simple as well as mixed) present in the system and the equlibria between them are:



The numerical values in the scheme above are log K values for the step indicated where K is the equilibrium constant for that step.

Statistical calculations[9] suggest that

$$\beta_{11} = 2.\ 3.\ \beta_{30}{}^{1/3}.\ \beta_{03}{}^{1/3},$$

$$\beta_{12} = 3.\ \beta_{30}{}^{1/3}.\ \beta_{03}{}^{2/3},$$

and $$\beta_{21} = 3.\ \beta_{30}{}^{2/3}.\ \beta_{03}{}^{1/3}.$$

The statistically calculated values of log β_{11}, log β_{12} and log β_{21} are 3.43, 4.43, and 4.49, respectively. The observed and calculated values of log β_{21} agree well, while those of log β_{11} and log β_{12} slightly differ. The deviations in the values of β_{11} and β_{12} may be due to steric or electrostatic factors and also to different approaches for getting these values. From the theory it is seen that log D equals log β_{30} as was observed in our results.

we can compare the tendency of various unsaturated complex species to add another ligand with that of saturated complex species to substitute another ligand. The complexes [Pb(X)] and [Pb(Y)] have a tendency to add $\mathrm{Y^{2-}}$ and $\mathrm{X^{2-}}$, respectively. The equilibrium constants in the logarithmic form for these addition reactions are 1.205 and 1.266, respectively. These values show greater probability of the formation of the mixed complex $[\mathrm{Pb(X)(Y)}]^{2-}$ from [Pb(Y)] than from [Pb(X)] and hence a slightly greater complexing tendency of $\mathrm{X^{2-}}$ than of $\mathrm{Y^{2-}}$. The tendency of [Pb(X)] to add $\mathrm{X^{2-}}$ and $\mathrm{Y^{2-}}$ shows that there is a greater probability of a mixed ligand complex formation than a simple complex formation. The same is also concluded from the relative tendency of $[Pb(Y)]$ to add X^{2-} and Y^{2-}. The equilibrium constants for all the above addition reactions are nearly equal, showing a nearly equal complexing tendency of the two ligands, as seen from their nearly equal size.

The tendency of $[Pb(X)_2]^{2-}$ to add X^{2-} and Y^{2-} favor the formation of mixed complexes. Similarly X^{2-} is more easily added to $[Pb(Y_2)]^{2-}$ than Y^{2-}. It is also seen that $[Pb(X)_3]^{4-}$ has a tendency to substitute Y^{2-} and $[Pb(Y)_3]^{4-}$ to substitute X^{2-}. These substitution reactions prove that formation of mixed complexes is favored.

The unsaturated mixed complex $[Pb(X)(Y)]^{2-}$ has a greater tendency to add X^{2-} than Y^{2-}, which shows that the approach of Y^{2-} to $[Pb(X)(Y)]^{2-}$ is hindered to a greater extent. The saturated mixed complex $[Pb(X)(Y)_2]^{4-}$ can substitute X^{2-} but not Y^{2-}. The saturated mixed complex $[Pb(X)_2(Y)]^{4-}$ can substitute neither X^{2-} nor Y^{2-}.

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