

DCC-25 (Univ. Zagreb)

Croat. Chem. Acta 39 (1967)

**Polarographic Investigations of Complexes of Some Metal Ions
in Solutions of β -Oxybutyric Acid and Sodium β -Oxybutyrate**

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β -Oxybutyrate complexes of Pb, Cd, Cu and In were studied by polarographic method.

Strong influence of β -oxybutyric acid on the electrode processes of Pb, Cd, Cu and In ions was established in preliminary measurements. The necessary β -oxybutyric acid in the buffer was obtained from its sodium salt by adding the equiv. quantity of perchloric acid. Such buffer soln., contg. β -oxybutyric acid at a const. concn. of 0.1 M were used in the present work. All the electrode processes were polarographically reversible. The polarographic potentials of the »free« ions were detd. by graphical extrapolation to zero ligand concn. The stability const. of corresponding complexes of Cd, Cu and Pb were detd. by applying the method of DeFord and Hume.

The results show that the stabilities of β -oxybutyrate complexes increase in the series: Cd, Cu, Pb:

Cd: $\beta_1 = 45$, $\beta_2 = 120$, $\beta_3 = 370$, $\beta_4 = 590$
 Cu: $\beta_1 = 85$, $\beta_2 = 1250$, $\beta_3 = 150$, $\beta_4 = 600$, $\beta_5 = 2900$
 Pb: $\beta_1 = 240$, $\beta_2 = 4300$, $\beta_3 = 1900$, $\beta_4 = 9700$

The order of stability found for the β -oxybutyrate complexes does not conform completely with the analogous series of some other ligands. β -Oxybutyrate ion has two donor groups, but it does not form chelate complexes with the investigated cations. On that score it behaves similarly to the glycolate and lactate ions. β -Oxybutyrate ion is more basic than the glycolate and lactate ions and accordingly, it should form more stable complexes. This has been found with complexes of Cd and Pb, and partly with those of Cu.

Examiners: Prof. I. Filipović, Prof. S. Žilić, and Prof. M. Karšulin

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1. Polarographic Investigations of Complexes of Some Metal Ions in Solutions of β -Oxybutyric Acid and Sodium β -Oxybutyrate
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Cadmium
Copper
Indium
Lead
 β -Oxybutyric acid
Polarography, of metal complexes

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Polarographic Investigations of Metal Complexes in Glycolic Acid Solutions

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Glycolate complexes of Cd, Pb, Cu and In were studied using the polarographic method under identical exptl. conditions, in order to obtain information on the nature of the bond between the central atom and the ligand.

The reversibility of the electrode processes, the shift of the equil., the polarographic maxima and the influence of the compn. of the glycolate buffer on the half-wave potentials were investigated. It was found that the half-wave potential is a function of the concn. of the free glycolic acid in the buffer, and with its increase it is shifted to more positive values probably due to a change in liquid junction potential and a change in viscosity. This shift is opposite to the shift of the half-wave potential caused by complex formation, necessitating experiments in glycolate buffers of a const. glycolic acid concn. In this case, the shift in positive direction is const., and the half-wave potential of the free central ion can be detd. by graphical extrapolation.

In order to det. the stability consts., measurements were made in two series of buffers with a glycolic acid concn. of 0.1 M and 2 M. With indium, only a buffer of 0.1 M in the acid concn. could be used because of the irreversibility of the electrode process at higher acid concns. Results for the first stability consts., obtained for both series, are in good agreement.

The results show that ions of Cd, Pb and Cu form very weak glycolate complexes, but no chelate compounds. Their stabilities increase in the series: Cd, Pb, Cu:

Cadmium: $\beta_1 = 30$, $\beta_2 = 130$, $\beta_3 = 290$, $\beta_4 = 204$
Lead: $\beta_1 = 45$, $\beta_2 = 850$, $\beta_3 = 1650$
Copper: $\beta_1 = 120$, $\beta_2 = 3300$, $\beta_3 = 600$, $\beta_4 = 11,900$.

The glycolate ion in the investigated complexes is a monodentate ligand, whose donor properties are slightly more pronounced than those of the nonsubstituted monocarboxylate ions of the same basicity (the formate ion). The presence of the hydroxilic group probably influences the complex stability, this being demonstrated also by the lactate ion.

Examiners: Prof. I. Filipović, Prof. B. Lovreček, and Prof. S. Žilić

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DCC-26

1. Polarographic Investigations of Metal Complexes in Glycolic Acid Solutions

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Cadmium
Copper
Glycolic acid
Indium
Lead

Polarography, of metal complexes

MCC-30 (Univ. Zagreb)

Master of Science Thesis

Croat. Chem. Acta 39 (1967)

Infrared Spectra of Methyl Mercuric Bromide. Analysis of Normal Vibrations

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The solid state ir. spectra of both methyl mercuric bromide and methyl- d_3 mercuric bromide are recorded in the 4000–250 cm^{-1} region. The Raman spectra of the solid samples are also recorded. The fundamental frequencies and an approx. description of the vibration modes (assignment) are essentially in agreement with those of Goggin and Woodward (C. A. 65, 181b).

A force const. calcn. is carried out using Wilson and Eliashevich's FG matrix method. An approx. force field, for both A_1 and E spp., with several non-zero interaction force consts. is assumed. By following a method developed by Mills, the results are improved using the Jacobian matrix, which relates a change in frequencies to a small change in the F matrix elements.

The calcd. and exptl. fundamental frequencies (in cm^{-1}), and the force const. matrix elements ($\text{md}/\text{\AA}$) are as follows:

Sym. spp.	Fundamental frequency	CH_3HgBr		CD_3HgBr	
		exptl.	calcd.	exptl.	calcd.
A_1	1	2921	2934	2126	2111
	2	1185	1173	916	920
	3	538	547	495	488
	4	202	202	201	201
E	5	3003	3026	2262	2243
	6	1393	1403	1027	1017
	7	783	791	597	589
	8	—	100	—	92

 $F_{11} = 4.95, F_{12} = 0.05, F_{22} = 0.412, F_{23} = 0.13, F_{33} = 2.48, F_{44} = 1.41.$
 $F_{55} = 4.92, F_{56} = -0.10, F_{57} = 0.10, F_{66} = 0.517, F_{67} = -0.015, F_{77} = 0.44,$
 $F_{88} = 0.30.$

The F_{ij} elements not listed are zero.

All the F_{ij} elements assumed zero are found not to affect the calcd. frequencies significantly. The force field obtained is consistent with the hybrid orbital force field model, although such a model has not been assumed.

Due to uncor. anharmonicities, the calcd. CH and CD vibrations show larger deviations from the exptl. values. The L^{-1} matrices, as well as other details of the calcs., are given in the thesis.

Examiners: Prof. M. Randić, Prof. D. Hadži, and Dr. S. Borčić.

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Z. MEIĆ

MCC-30

1. Infrared Spectra of Methyl Mercuric Bromide. Analysis of Normal Vibrations

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Force constant calculation Jacobians

Normal coordinates (L^{-1} matrices)
Solid state ir. and Raman spectra assignment

MCC-31 (Univ. Zagreb)

Master of Science Thesis

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Study of Some Cycloalkanes by the Method of Maximum Overlap

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The hybridization in several cycloalkanes is calcd. by the max. overlap method. The following mols. are considered: cyclopropane, nortricyclene, cyclobutane, bicyclobutane, cubane, bicyclo(1.1.1)pentane, tricyclo(1.1.0.0.^{2,3})butane, tetracyclo(3.3.1.0.^{2,3,0,4,6})nonane and cyclopentane. A large no. of these mols. are characterised by bent bonds. Since CC and CH bonds have different bond energies, the weighting factors $k_{CC} = E^0_{CC}/S^0_{CC}$ and $k_{CH} = E^0_{CH}/S^0_{CH}$ are introduced. These factors are detd. from the standard hybridization and bond energies for ethane and methane. Results show that overlap is a good criterion for the strenght of the CC bond. Overlaps less than 0.60 are characteristic of mols. contg. a C₃-ring ($\delta \sim 20^\circ$), between 0.60 and 0.63 of those contg. a four-membered ring ($\delta \sim 10^\circ$), and above 0.60 of those with normal or very slightly bent bonds ($\delta \sim 5^\circ$), where δ is the bending of the CC bond hybrid. Two kinds of atomic functions, Slater's and Clementi's »double zeta« orbitals are used. The latter give better agreement with exptl. data, and we recommend them for this kind of approx. calcn. The maximum overlap method provides hybrides, interorbital angles, bond overlaps, deviations of the bent bonds and even *e.g.* in bicyclobutane gives information on the twisted bonds. The results of the maximum overlap calcn. are correlated with such exptl. data as spin-spin coupling const. $J_{C^{13},H}$ and stretching frequencies from ir. spectra. We found that the max. overlap calcn. are very useful in describing the bonding in large mols. of low symmetry.

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MCC-31

1. Study of Some Cycloalkanes by the Method of Maximum Overlap

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Bond, bent

—, overlap

—, twisted

Cycloalkanes

Double zeta orbitals

Hybridization

Maximum overlap method

Spin-spin coupling constant