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A Polarographic Study of the Monocarboxylato Complexes of Lead

*V. Klemenčić** and I. Filipović*

Institute of Inorganic Chemistry, Faculty of Technology, University of Zagreb,
Zagreb, Croatia, Yugoslavia

The formation of monocarboxylato complexes of lead has been investigated by polarographic method in aqueous solutions containing excess of sodium formate, acetate, propionate, butyrate, n-valerate, iso-valerate, monochloracetate, and glycollate, respectively. The concentrations of monocarboxylate ions have been ranged from 0 to 3 M. To avoid the hydrolysis of monocarboxylato complexes, the solutions contained a constant concentration (2 M) of the corresponding monocarboxylic acid, and, in the case of less soluble valeric acids, 20% of free acid. The solutions of monocarboxylates ranging from 0 to 1 M were held at a constant ionic strenght of 1.00 with sodium perchlorate. Although no maximum suppressor was found to be necessary, all solutions contained 0.005% gelatin in order to get a better diffusion current. The plots of the potential (corrected for iR drop) vs. log $[(i_d — i)/i]$ gave straight lines whose slope was about 30 mv.

The polarographic results were interpreted by the method of DeFord and Hume[1]. The extropolation of the F(X) curves to zero monocarboxylate ion concentration gave values for the successive »over-all« formation constants which were:

Formiato complexes: $K_1 = 27$, $K_2 = 47$, $K_3 = 42$.

Acetato complexes: $K_1 = 180$, $K_2 = 750$, $K_3 = 1350$.

Propionato complexes: $K_1 = 180$, $K_2 = 1320$, $K_3 = 2220$.

Butyrato complexes: $K_1 = 190$, $K_2 = 1000$, $K_3 = 2000$, $K_4 = 1800$.

n-Valerato complexes: $K_1 = 190$, $K_2 = 1500$, $K_3 = 5000$, ($K_4 = 5000$, $K_5 = 0$, $K_6 = 1400$).

iso-Valerato complexes: $K_1 = 190$, $K_2 = 1500$, $K_3 = 4000$, ($K_4 = 1000$, $K_5 = 1000$, $K_6 = 700$).

Monochloracetato complexes: $K_1 = 22$, $K_2 = 40$, $K_3 = 42$.

Glycollato complexes: $K_1 = 190$, $K_2 = 1300$, $K_3 = 4500$, $K_4 = 7500$, $K_5 = 4500$, $K_3 = 10^4$.

The results of formiato and acetato complexes, respectively, differ from those recently published[2,3]. The linear relationship between the logarithm of complex stability constant (log K_c) and the negative logarithm of acid constant (pK_a) has been found in the series from formic to butyric acid. Thus, with increasing base strength of the corresponding ligand increases the stability of complex.

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* Institute of Technology, Faculty of Economy, University of Zagreb.

The relation between the diffusion current (i_d) and the viscosity coefficient (η) of the medium has been determined. It was found, that the Stokes-Einstein relation combined with Ilkovič equation, i. e. $i_d = K\eta^{-1/2}$ is valid, if the concentration of monocarboxylate ion is greater than $1\,M$. In other words, i_d vs. $\eta^{-1/2}$ — curve has a bend and a linear course in the concentration range, in which the last complex predominates. In the range of lower monocarboxylato complexes the hydration and the formation of higher complexes effect the course of i_d vs. $\eta^{-1/2}$ — curve.

The displacement reactions of monocarboxylato ligands by the other anion ligands (NO^-_3, SO_4^{--}, Cl^-, Br^- I^- and OH^-) have been studied. The displacement power is proportional to the stability of complex, which is formed in displacement reaction ($OH^- > I^- > Br^- > Cl^- > SO_4^{--} > NO_3^-$), i. e. the anion concentration that shifts the half-wave potential ($E_{1/2}$) to more negative values is inversely proportional to the stability of the complex formed. With lead solutions containing iodide the polarogram consists of two waves, a small prewave followed by a normal reduction wave of lead. The total diffusion current corresponds to the concentration of lead in the solution. The lower the concentration of monocarboxylate ion, the lower is the concentration of iodide at which the prewave begins to appear and reaches the maximum height. From the electrocapillary curve in the potential range of the prewave it is evident, that the prewave occurs as a result of an adsorption layer on the surface of the dropping electrode. As the prewave disappears at iodide concentration greater than $1.5\,M$ and as the height of the prewave somewhat rises with decrease of the rate of mercury flow from the dropping electrode, the adsorption layer is probably a monomolecular rather compact layer. Namely, by decrease of the rate of mercury flow from the dropping electrode the adsorption layer may become more compact and in the presence of a high iodide concentration it cannot be formed, as the soluble iodo complexes arise.

The detailed results of this investigation will be published at a later date.

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IZVOD

Polarografska studija monokarboksilato-kompleksa olova

V. Klemenčić i I. Filipović

Nađeno je, da u otopinama olova, koje sadrže različne koncentracije natrijeva formijata, acetata, propionata, butirata, valerata, *iso*-valerata, *m*onokloracetata, odnosno glikolata, postoje odgovarajući monokarboksilato-kompleksi s ovim konstantama kompleksnosti:

formijato-kompleksi $K_1 = 27$, $K_2 = 47$, $K_3 = 42$; acetato-kompleksi $K_1 = 180$, $K_2 = 750$, $K_3 = 1350$; propionato-kompleksi $K_1 = 180$, $K_2 = 1320$, $K_3 = 2220$; butirato-kompleksi $K_1 = 190$, $K_2 = 1000$, $K_3 = 2000$, $K_4 = 1800$; valerato-kompleksi $K_1 = 190$, $K_2 = 1500$, $K_3 = 5000$, $(K_4 = 5000$, $K_5 = 0$, $K_6 = 1400)$; *iso*-valerato-kompleksi $K_1 = 190$, $K_2 = 1500$, $K_3 = 4000$, $(K_4 = 1000$, $K_5 = 1000$, $K_6 = 700)$; monokloracetato-kompleksi $K_1 = 22$, $K_2 = 40$, $K_3 = 42$; glikolato-kompleksi $K_1 = 190$, $K_2 = 1300$, $K_3 = 4500$, $K_4 = 7500$, $K_5 = 4500$, $K_6 = 10^4$.

Ustanovljeno je, da u nizu od mravlje do maslačne kiseline postoji linearni odnos između pK_a i log K_k, t. j. da s porastom bazičnosti liganda raste stabilnost kompleksa. Studirane su i reakcije izmjene liganda. U otopinama olova, koje sadrže jodid-ion, dobivena su na polarogramu dva vala. Po elektrokapilarnoj krivulji moglo se zaključiti, da je prvi val — adsorpcioni val.

ZAVOD ZA ANORGANSKU KEMIJU
TEHNOLOŠKI FAKULTET
ZAGREB