Complexes of Hg(II) with Carboxylic Acids in Water and Water-Methanol Solutions

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The results of studies on complex formation properties of: acetic, hydroxyacetic, propionic and α-hydroxypropionic acids with the Hg(II) ions in aqueous and water-methanol mixed solvent are presented. Literature data on the composition and stability of the tested compounds are incomplete, and the results differ substantially in the reported number of formed complexes and their stability constants (Table 1) [1–8]. Moreover, the reactions of complex formation in these systems were never investigated in mixed water-methanol solvents.

Table 1. Literature data of the dissociation constants of studied ligands and stability constants of their complexes with the Hg(II) ions.

Ligand	pK_{HL}	Stability constants		Ref.
Acetic acid CH_3COOH	$4.42 \div 5.01$	$\log K_1$ $\log K_2$ $\log K_3$ $\log K_4$	$3.32 \div 6.50$ $0.82 \div 4.29$ $0.40 \div 3.98$ 3.78	[1–8]
Hydroxyacetic acid $CH_2(OH)COOH$	$3.35 \div 3.93$	$\log K_1$ $\log K_2$	3.60 3.45	[2,8]
Propionic acid CH_3CH_2COOH	$4.52 \div 5.16$	$\log K_1$ $\log K_2$ $\log K_3$ $\log K_4$	$3.54 \div 4.56$ $2.14 \div 4.47$ $1.44 \div 2.34$ $1.05 \div 2.25$	[1,2,7,8]
α-Hydroxypropionic acid $CH_3CH(OH)COOH$	$3.57 \div 3.86$	—		[8]

If more results are available the values shown are limits for the range of reported results.

Mercury and its compounds are very reactive and are easily introduced into various biological cycles. The high stability of these compounds leads to the accumulation of mercury in ecosystems and therefore their contamination. Toxicity of this metal is due to its particular affinity to $-SH$, $-NH_2$ and $-COOH$ groups of amino acids

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and proteins and results from blocking of biochemical functions of these compounds. The most frequent form of mercury in the natural environment is Hg(II) [9,10]. Specific biological activity is also observed for the carboxylic acids studied, particularly for acetic and propionic acids, which occur as anions in cells and body fluids. Lactic acid in normal metabolism is synthesized in muscles, skin, liver, stomach and intestines. In natural form it can be found in cheese, milk, wine, silage and mead. Glycolic acid is commonly used in dermatology and cosmetic products [11–13].

The potentiometric method, based on changes of activity of hydrogen ions released during the complex formation reaction, was employed to determine the composition and stability constants of complexes of Hg(II) with acidic ligands. The values of stability constants of complexes were determined graphically from the Bjerrum curves, $\bar{n} = f\,(-\log\,[L])$ and then confirmed, using least-square method and complex formation functions [14,15].

All the reagents used were of analytical grade. Because of the average strength of the acids studied and the possibility of dimerization, ligands were used as potassium buffer with the ratio 1:1 of concentrations of the acid to its salt. Potentiometric measurements were performed using the Radiometer PHM-84 and PHM-220 pehameters with a glass–silver chloride electrode system at $20 \pm 1°C$ under nitrogen, keeping a constant ionic strength $\mu = 1$ KNO_3 in water and $\mu = 0.1$ KNO_3 in the water-methanol (1:1 vol.) solutions, due to the limited solubility of the potassium nitrate (V) in the mixed solvent. In order to determine whether the complexes formed are mono- or polynuclear, experiments were conducted with various concentrations of the Hg(II) ions within the range: 3×10^{-3} to 10×10^{-3} M. The ligand concentrations in the titration system varied from 1×10^{-3} to 50×10^{-3} M. The calculation of stability constants was preceded by the determination of dissociation constants of the ligands under investigation, employing also the potentiometric method [16]. Stability constants of the complex formation and dissociation constants of the acids are presented in Table 2.

Studying complex formation properties of the considered acidic it was ascertained that all the ligands form mononuclear complexes with mercury(II) ions. Acetic and glycolic acids each, form three complexes with the Hg(II) ions, both in aqueous and in mixed solvents. For propionic acid in water two complexes: HgL^+ and HgL_2 were found, while in the water-methanol solution the formation of the third complex HgL_3^+ was observed. Lactic acid forms four complex compounds with the mercury cations in both media. For all systems studied the consecutive stability constants decrease in the sequence $K_1, K_2 \ldots K_n$. This means that electrostatic attraction between the positive metal ions and the anion of the acid studied decreases, when the next ligand molecule is added, until it turns into an electrostatic repulsion when the complex becomes negative. Many authors express the opinion that formation constants of complexes increase with the increase in length of the acid carbon chain. The results of our investigation do not confirm that opinion, since it was ascertained that for simple carboxylic acids the stability of formed complexes decreases with the decreasing of the acid strength. Acetate complexes of Hg(II) are more stable than propionic com-

plexes, in spite of the fact that pK_{HL} of acetic acid is lower than pK_{HL} of propionic acid. In the case of the tested hydroxy acids a similar stability of complex compounds was observed (Table 2). Based on the determined values of the formation constants, the following sequence of stability increase of the complexes of Hg(II) studied can be established: acetate > propionate > glycolate ≥ lactate. The presence of substituents, due to steric effects and changes in donor-acceptor properties, is a significant factor, which influences the complex formation ability of the ligand. The investigated hydroxyacids, *i.e*. glycolic and lactic acids form complex compounds with the Hg(II) ions with the stability lower by 0.7 units in the logarithmic scale than complex formation constants of acetates and propionates in water, as well as in the mixed water-methanol environment. This is in accord with the dissociation constants of appropriate acids (Table 2) – simple carboxylic acids dissociate less than their hydroxy derivatives. Moreover, a considerably lower stability of the complexes of Hg(II) with hydroxyacids indicates that the hydroxyl group does not participate in coordination. The results obtained do not allow a decisive determination of the coordination's type of the Hg(II) ions with the acids studied. Only in the case of lactates, for which four stability constants were found, it can be inferred that the carboxyl group is monodentate and bonds through one oxygen atom. It should be emphasized that the system: lactic acid–Hg(II) has never been investigated.

Table 2. Dissociation constants of the studied acids and stability constants of their complexes with the Hg(II) ions in aqueous and water-methanol (50%/50% vol.) solutions ($\mu_{H_2O} = 1$ KNO$_3$, $\mu_{H_2O-CH_3OH} = 0.1$ KNO$_3$, temp. 20°C).

Ligand	Dissociation constants pK_{HL}		Stability constants		
	H$_2$O	H$_2$O-CH$_3$OH	logK	H$_2$O	H$_2$O-CH$_3$OH
Acetate	4.58	5.24	$\log K_1$	4.36 ± 0.03	5.46 ± 0.02
			$\log K_2$	3.61 ± 0.02	4.77 ± 0.03
			$\log K_3$	2.94 ± 0.03	4.21 ± 0.05
Hydroxyacetate (glicolate)	3.68	4.38	$\log K_1$	3.60 ± 0.02	4.72 ± 0.02
			$\log K_2$	2.87 ± 0.02	4.09 ± 0.03
			$\log K_3$	2.13 ± 0.02	3.48 ± 0.03
Propionate	4.73	5.53	$\log K_1$	4.21 ± 0.03	5.44 ± 0.02
			$\log K_2$	3.41 ± 0.03	4.72 ± 0.04
			$\log K_3$	–	2.62 ± 0.08
α-Hydroxypropionate (lactate)	3.52	4.36	$\log K_1$	3.51 ± 0.04	4.77 ± 0.01
			$\log K_2$	2.91 ± 0.05	4.25 ± 0.01
			$\log K_3$	2.37 ± 0.05	3.90 ± 0.02
			$\log K_4$	1.72 ± 0.05	3.48 ± 0.05

Comparing the stability constants of the complexes tested in aqueous solutions with stability constants in mixed environment, we found that in each case the stability of complexes in the water-methanol (50%/50% vol.) solution is significantly greater

than in water (Figs. 1 and 2). The differences between stability constants are between 1.1–1.7 units. It was also observed that the dissociation of the acids studied decreases when water is replaced by the mixed solvent. The change of stability of complex com-
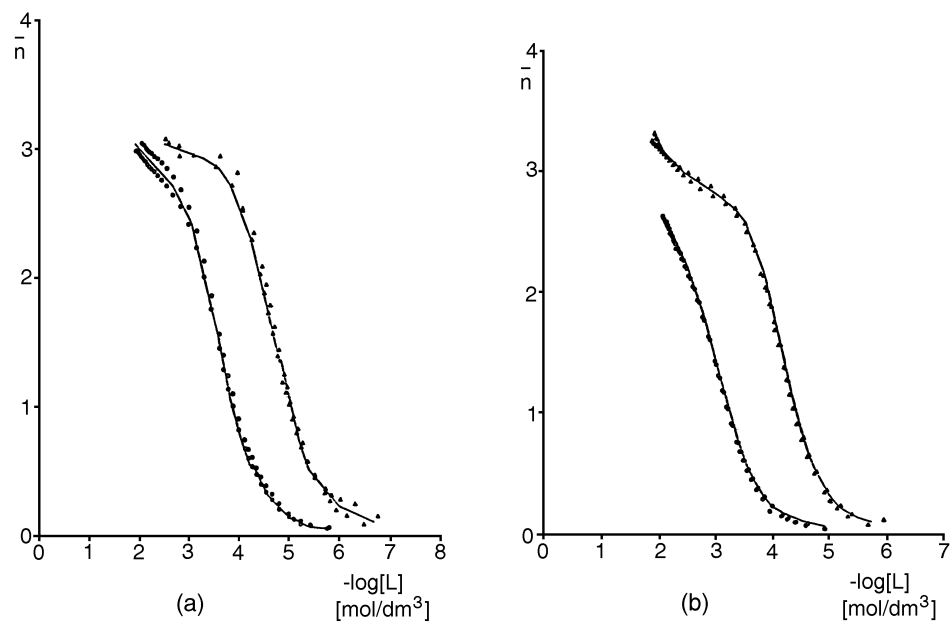

Figure 1. The formation curves of the systems: Hg(II)–acetic acid (a); Hg(II)–hydroxyacetic acid (b) in water (O) and water-methanol solution (▲).
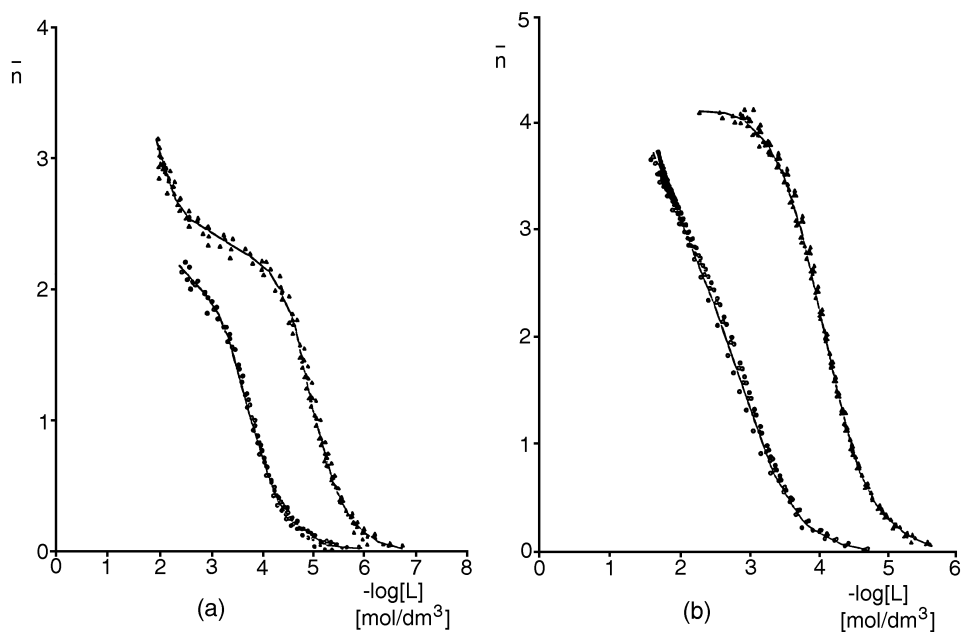

Figure 2. The formation curves of the systems: Hg(II)–propionic acid (a); Hg(II)–hydroxypropionic acid (b) in water (O) and water-methanol solution (▲).

pounds and acid-base equilibrium constants, due to the solvent change, depends on donor-acceptor properties and the dielectric constant of the solvent (ε), as well on the nature of the bond between the central atom and the ligand [17]. For the complex studied forming systems, where the electrostatic attractive forces dominate, the decrease of ε causes an increase of ionic interactions between proton and the oxygen atom of the carboxyl group to a greater degree than the interactions between proton and solvent. Therefore, the change of activity of the solvent causes an increase of metal-ligand atom interactions, and as a consequence, the coordination compounds are more stable.

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