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Precipitation and Complex Formation of Zirconium(IV) with Malonic, Succinic and Adipic Acids at 298 K

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Using the tyndallometric technique, the precipitation of zirconium(IV) from aqueous solution of zirconyl chloride (1 mM) was investigated, in the presence of dicarboxylic acids: malonic, succinic and adipic, at pH 2—10 and 298 K. In the precipitation diagram only one region at $pH < 2$ exists in which zirconium is water-soluble with these acids. Polymeric, insoluble compounds of the composition $Zr(OH)_3HA$ (A = malonate, succinate, adipate ligands) were isolated at $2 < pH < 3$. At $pH > 3$ continuous increase of zirconium percentage in precipitate with pH increasing was observed in all samples, due to zirconium hydroxide coprecipitation.

INTRODUCTION

Complexes of zirconium with dicarboxylic acids have been investigated both in the solid state and in solutions in a limited number of papers. Aggarwal et al.[1] have prepared, by precipitation or by fractional crystallization, a series of compounds: $ZrOC_2O_4 \, 2H_2O$, $ZrOC_3H_2O_4$, $ZrOC_4H_4O_5$, $ZrOC_4H_4O_4$, $ZrOC_6H_8O_4$, $ZrOC_8H_4O_4$, $K_2[ZrO(C_2O_4)_2]$, $K_2[ZrO(C_3H_2O_4)_2]$, $K_2[ZrO(C_4H_4O_5)_2]$.

We have recently[2] prepared, by a precipitation method, compounds with maleic and phthalic acids of the composition $Zr(OH)_3(OOCCH{=}CHCOOH)$ and $Zr(OH)_3(OOCC_6H_4COOH)$.

There is only slight evidence for the existence of soluble complexes by the method of stability constant determination but none of the values cited is included in the Critical Stability Constants.[3]

Upadhya and Mushran[4] have observed, by conductometric and pH measurements, the formation of the 1 : 1 complex in the reaction of zirconium nitrate and sodium succinate.

Yatsimirskii and Raizman[5] have used a kinetic method to study the $Zr(OH)_3C_3H_2O_4^-$ complex. Furthermore, Yatsimirskii and Khukov[6] have determined the constant for the $ZrOHC_4H_4O_4^+$ complex.

Konunova et al.[7] used a spectrophotometric method to study complexes of zirconium and hafnium with malonic, succinic, glutaric, adipic, maleic and fumaric acids at $pH < 1.3$, assuming a MA_2 complex with malonic acid and $M(OH)_3(HA)_2$ with all other acids. The corresponding values for stability constants are given in their paper.

The present investigation represents a continuation of our interest in zirconium hydrolysis[8,9] and zirconium complexes with oxygen donor ligands.[10,2]

The objectives of the work were:

— to find out if malonic, succinic and adipic acids can form water-soluble complexes with zirconium which are stable at high pH, as was found previously for oxalic,[10] phthalic and maleic acids;[2]

— to determine the composition of the precipitated zirconium compounds and to characterize them by IR spectra.

EXPERIMENTAL

Zirconium-oxide-chloride octahydrate, $ZrOCl_2 \cdot 8\,H_2O$ was used to make a stock solution. It was analysed for zirconium by complexometric titration with titriplex III.

Solutions of malonic (0.1 M), succinic (0.5 M), adipic (0.1 M) acids, of sodium malonate (0.2 M), potassium succinate (0.1 M), potassium adipate (0.1 M), hydrochloric acid (1 M) and of sodium and potassium hydroxide (0.5 M) were prepared from reagent grade chemicals (Merck, Darmstadt, Germany).

For determination of the precipitation diagram, the method described earlier by Težak et al.[11] was used. Turbidity measurements, used in precipitation studies, were performed with a Zeiss tyndallometer attached to a Pulfrich photometer.

For quantitative analyses of the solid phases, precipitates were left to settle down, and then filtered, washed with water and dried in a dessicator over calcium chloride. Zirconium was determined as ZrO_2, after thermal decomposition of the complex in a Pt-crucible. Carbon and hydrogen were determined in the Microanalytical Laboratory of the »Ruđer Bošković«, Institute, Zagreb. Infrared spectra were recorded on a Perkin Elmer, Model 257 spectrophotometer (Nujol mulls and KBr pellets). X-ray diffraction patterns were recorded on a Philips X-ray diffractometer with proportional counter, using graphite monochromated CuK_α radiation.

RESULTS AND DISCUSSION

Figure 1 represents the ground plan of the precipitation diagram of zirconium salts in the presence of sodium malonate. The pH was varied by

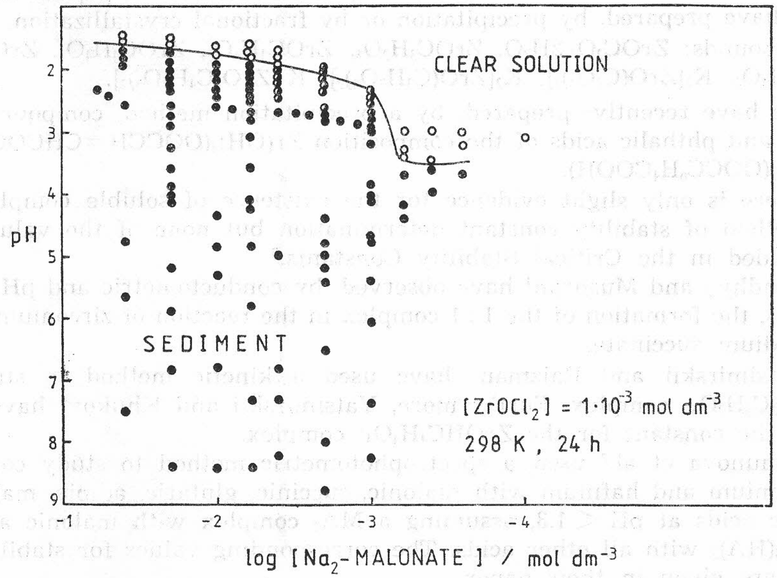

Figure 1. The ground plan of a three dimensional concentration diagram in the system $ZrOCl_2 = 1 \cdot 10^{-3}$ mol dm^{-3} — Na_2 — malonate various — pH various (295 K, 24 h aging). Symbols : circles = clear solution, semi-dots = colloids, dots = precipitate.

adding sodium hydroxide for higher pH values and hydrochloric acid for lower pH values. Turbidity was measured as a function of pH and of sodium malonate for a constant concentration of $ZrOCl_2$ equal to $1 \cdot 10^{-3}$ mol dm^{-3}, 24 h after mixing the reactant components. Precipitates were isolated for characterization in the presence of a large excess of malonic acid ($5 \cdot 10^{-2}$ mol dm^{-3}) at pH 2.4, and then in the presence of a small excess of malonate ($2 \cdot 10^{-3}$ mol dm^{-3}) at $2 < pH < 9$. In the presence of excess malonic acid, and at $pH < 3$, the 1 : 1 complex was isolated. Its analytical data are presented in Table I and infrared spectral data in Tables II and III. Composition of the precipitate varied at $pH > 3.5$, showing an increasing percentage of zirconium, due to $Zr(OH)_4$ formation. Soluble complexes of zirconium were not found when malonic acid was in excess at high pH values.

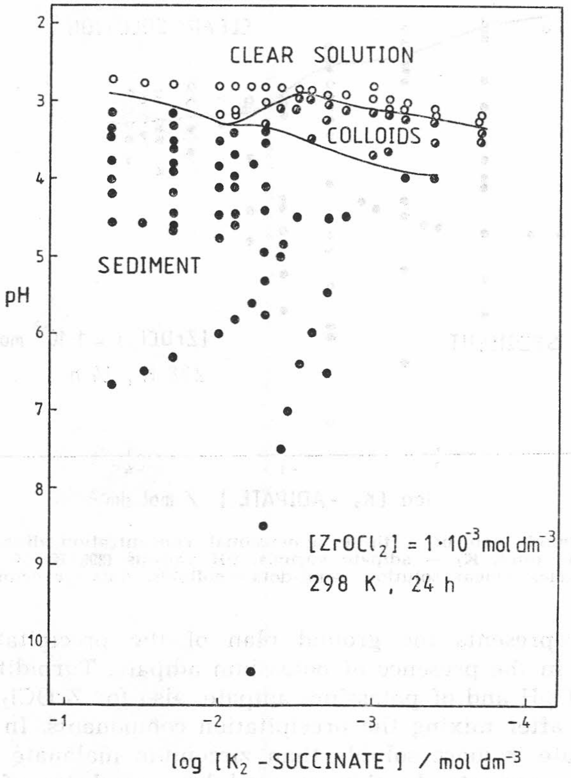

Figure 2. The ground plan of a three dimensional concentration diagram in the system $ZrOCl_2 = 1 \cdot 10^{-3}$ mol dm^{-3} — K_2 — succinate various — pH various (295 K, 24 h aging). Symbols : circles = clear solution, semi-dots = colloids, dots = precipitate.

The ground plan of the precipitation diagram of zirconium salts in the presence of potassium succinate is presented in Figure 2. Turbidity was measured as a function of pH and of potassium succinate, for $ZrOCl_2$ equal to $1 \cdot 10^{-3}$ mol dm^{-3}, 24 h after mixing the precipitation components. Precipitates were isolated for characterization in the presence of a large excess of succinate ($2 \cdot 10^{-2}$ and $3 \cdot 10^{-2}$ mol dm^{-3}) at pH 4.5 and 6.3 respectively. Series of precipitates were also isolated in the presence of a small excess of succinate ($2 \cdot 10^{-3}$ and $4 \cdot 10^{-3}$ mol dm^{-3}) at $2.5 < pH < 6.5$. Analytical data for the complex isolated at $pH < 3$ are presented in Table I and infrared spectral data in Tables II and III. Analogously to what was found for malonic acid, the composition of the precipitate with succinic acid varied at $pH > 3.5$ due to $Zr(OH)_4$ coprecipitation.

In the acid region zirconium succinate is more soluble than zirconium malonate. Also, there exists a rather large region of stable colloids, even after 24 hours. Soluble complexes of zirconium with succinic acid at high pH were likewise not found.

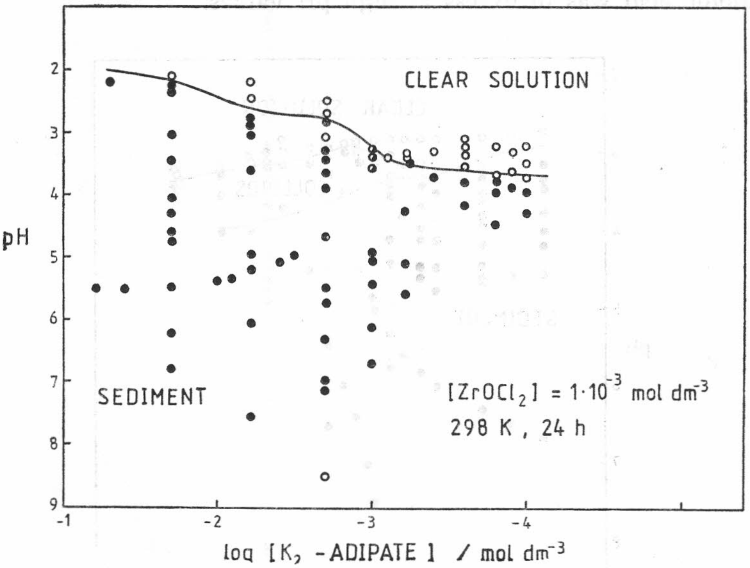

Figure 3. The ground plan of a three dimensional concentration diagram in the system $ZrOCl_2 = 1 \cdot 10^{-3}$ mol dm^{-3}, K_2 — adipate various, pH various (295 K, 24 h aging). Symbols : : circles = clear solution, semi-dots = colloids, dots = precipitate.

Figure 3 represents the ground plan of the precipitation diagram of zirconium salts in the presence of potassium adipate. Turbidity was measured as a function of pH and of potassium adipate, also for $ZrOCl_2$ equal to $1 \cdot 10^{-3}$ mol dm^{-3}, 24 h after mixing the precipitation components. In the acid region, zirconium adipate is more soluble than zirconium malonate and less soluble than zirconium succinate. In this case soluble complexes of zirconium with adipic acid at high pH were also not found. Several typical precipitates were isolated for characterization in the presence of a large excess of adipic acid ($5 \cdot 10^{-2}$ mol dm^{-3}) at pH 2.25, and then in the presence of a small excess of adipate ($2 \cdot 10^{-3}$ mol dm^{-3}) at $2.5 < pH < 8.5$. As was found for malonic and succinic acids, the complex with the analogous chemical composition was isolated with adipic acid at pH 3 (Tables I, II and III). A continuous increase in zirconium percentage in the isolated precipitates was also observed with the pH increase at $pH > 3.5$. Malonic, succinic and adipic acids form white, poorly crystalline complexes with zirconium at $pH < 3$, therefore the obtained X-ray diffraction patterns were not useful for characterizing the compounds. Once isolated, compounds dissolve neither in water nor in common organic solvents. Their physical and spectral properties are very similar to the complexes isolated previously with maleic and phtalic acids.[2]

TABLE I

Analytical Data

Compound	% found			% required		
	C	H	Zr	C	H	Zr
$Zr(OH)_3(OOCCH_2COOH)$	14.72	2.66	37.03	14.69	2.46	37.19
$Zr(OH)_3(OOCCH_2CH_2COOH)$	16.87	3.10	35.75	18.53	3.01	35.18
$Zr(OH)_3(OOCCH_2CH_2CH_2COOH)$	23.97	3.87	32.10	25.08	4.21	31.74

TABLE II

Infrared Spectra (cm^{-1})

$Zr(OH)_3(OOCCH_2COOH)$	$Zr(OH)_3(OOCCH_2CH_2COOH$	$Zr(OH)_3OOC(CH_2)_4COOH$
3500 s,b	3500 s,b	3500 s,b
1710 m	1710 m	1696 s
1570 vs	1550 vs	1550 vs
1420 s	1435 s	1420 s,b
1374 s	1395 s	1388 sh
1263 w	1296 w	1298 w
	1225 sh	1195 vw
1169 w	1170 w	1145 vw
950 w	965 sh	930 w
780 vw	800 vw	
710 sh	715 sh	725 w
650 s	640 m	640 m
465 w	460 w	462 w
	355 vw	370 w

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; vw very weak; b, breit

Infrared data are presented in Table II indicating positons of all absorption bands of the isolated complexes. The IR spectra have been very useful in an analysis of the mode of coordination of carboxylate ligands. The presence of Zr—OH stretchings[12] is indicated by the absorption band in the region 3400—3600 cm^{-1}. The absorption bands of medium intensity present at 1710 cm^{-1} for zirconium complexes with malonic and succinic acids and at 1696 cm^{-1} for the complex with adipic, indicate the presence of an uncoordinated COOH group. Namely, the position of this band is very close to that found in the corresponding free acids. A strong absorption band in the region 1550 cm^{-1} for all complexes indicates that in addition to an uncoordinated group, a coordinated COO^- group is also present in all three complexes. The carboxylato group acting as a bridge between the two metal atoms shows the separation of $\nu_a(COO^-) - \nu_s(COO^-)$, which is close to that existing in the free ligand, while for the carboxylato group as a bidentate ligand[12] toward the same metal atom this separation was found to be less than 100 cm^{-1}.

TABLE III

Characteristic COO⁻ Frequencies (cm⁻¹) and $\Delta = \nu_a - \nu_s$

Compound:	$\nu_a(COO^-)$	$\nu_s(COO^-)$	$\Delta = \nu_a - \nu_s$
$C_3H_4O_4$	1725	1419	306
$Zr(OH)_3(OOCCH_2COOH)$	1570	1420	150
$C_4H_6O_4$	1787	1421	366
$Zr(OH)_3(OOCCH_2CH_2COOH)$	1550	1435	115
$C_6H_{10}O_4$	1700	1428	272
$Zr(OH)_3(OOCCH_2CH_2COOH)$	1550	1420	130

Table III shows characteristic COO^- frequencies with calculated separation, Δ. For the isolated complexes separation, Δ, is considerably smaller than for the free ligand but greater than 100 cm^{-1}, indicating the possibility of bridging COO^- groups between the two zirconium atoms. In Table III only the position of the middle absorption band is presented, since malonic and adipic acids exibit three close absorption bands in the 1400 cm^{-1} region. Recently an example of a quadridentate malonate group has been found, making a bridge between four molybdenum atoms.[13] Unfortunately, the infrared spectra were not discussed.

Infrared spectra in Table II show that there is no absorption band in the region 800—1050 cm^{-1}, indicating that $Zr = O$ is not presented by any of the three complexes. This is a different conclusion from that reached by Aggarwal et al.[1] but experimental conditions were not identical and direct comparison is not possible. Physical and infrared spectral data indicate the polymeric nature of zirconium complexes with malonic, succinic and adipic acids. Similar data were obtained for complexes with maleinic and phtalic acids.[2] Polymerization occurs throug coordinated COO^- groups, or, very probably, through OH and COO^- groups simultaneously.

Konunova et al.[7] concluded that in solution all investigated acids with the exception of malonic acid are coordinated to zirconium through one —COOH group. For malonic acid they assume the formation of six-membered ring, very strong complexes (MA_2) similar to zirconium oxalate.

Our results show a disagreement with the last conclusion of Konunova et al.[7] and absolutely no similarity to the zirconium oxalate[10] system. In the present investigation we did not find water soluble complexes of zirconium at high pH values, which indicates that these three acids obviously do not form rings with zirconium. Continuation of the search for other oxygen donor ligands which form complexes with zirconium is in progress.

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SAŽETAK

Taloženje i stvaranje kompleksa cirkonija(IV) s malonskom, jantarnom i adipinskom kiselinom, kod 298 K

Halka Bilinski i Nevenka Brničević

Upotrebom tindalometrijske tehnike, istraženo je taloženje cirkonija(IV) iz vodene otopine cirkonil-klorida (1 mM), u prisutnosti dikarbonskih kiselina: malonske, jantarne i adipinske, kod pH 2—10 i 298 K. U taložnom dijagramu postoji samo jedno područje kod $pH < 2$, u kojemu je cirkonij s ovim kiselinama topljiv. Polimerni, netopljivi spojevi sastava $Zr(OH)_3HA$ (A = malonat, sukcinat i adipat ligand) izolirani su kod $2 < pH < 3$. Kod $pH > 3$ opažen je u svim uzorcima kontinuiran porast postotka cirkonija u talogu, s povećanjem pH, zbog koprecipitacije cirkonij-hidroksida.