Complex Equilibria in Aqueous Solutions of Ti^{3+}–Glycine and –Malonic Acid

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The hydrolytic processes of Ti^{3+} and the equilibria of the Ti^{3+}–glycine (HL) and –malonic acid (H_2L') systems were studied by pH-metry in aqueous solution (25 °C, I = 1.0 mol dm^{-3} KCl). It was demonstrated that more than one equilibrium model are suitable to interpret the hydrolytic reactions. In the Ti^{3+}–glycine system the formation of complexes $[TiHL]^{3+}$ and $[TiL]^{2+}$ were identified; their stability constants are $\log\beta_{TiHL} = 11.44$ and $\log\beta_{TiL} = 9.30$. For the malonato complexes the following stepwise stability constants were determined: $\log K_1 = 6.83$, $\log K_2 = 4.99$, and $\log K_3 = 2.84$. Some aspects of the equilibrium of Ti^{3+} are discussed.

Although in many redox reactions of Ti^{3+} the inner-sphere mechanism clearly indicates strong metal–ligand interactions,[1–7] there are only limited data available on the stability constants of Ti^{3+} complexes. This probably originates in the curious properties of this metal ion. It hydrolyses at relatively low pH producing hydroxo precipitates and its sensitivity to oxidation increases sharply on increasing the pH. As a result experimental work with this metal ion requires very delicate conditions and equilibrium data mainly refer to complexes formed in acidic solutions or very stable complexes with strongly chelating multidentate ligands.[8–13]

In the present work, the equilibria of the Ti^{3+}–glycine (HL) and –malonic acid (H_2L') systems have been studied by pH-metry. The hydrolytic reactions of Ti^{3+} and their effects on the complex equilibria have also been studied.

Experimental

Preparation of Ti^{3+} *Stock Solution.*—To evaporate off any $TiCl_4$ present (b.p. 136 °C at 10^5 Pa), $TiCl_3$ (Fluka) was heated at 150 °C for 1 h. The $TiCl_3$ powder was then dissolved in cool (0—5 °C) HCl solution (3.0 mol dm^{-3}). The Ti^{3+} concentration was determined by cerimetry using ferroin as an indicator. The Ti^{IV} content of the stock solution was determined by control titration as the difference in the Ti^{3+} concentration before and after reduction by Zn amalgam. It always was less than 0.3% of the total.

The acidity of the solution was determined by passing samples of the stock solution through a Varian KS cation-exchange column (H^+-form). The effluents were titrated with standardized KOH. To avoid any effects of oxidation all manipulations and measurements were performed under an oxygen-free argon atomosphere.

All other chemicals were reagent-grade quality. Malonic acid (Fluka), glycine and KCl (REANAL) were recrystallized twice from methanol–water before use. The ionic strength was maintained at 1.0 mol dm^{-3} by KCl.

Equilibrium measurements were carried out on a Radiometer PHM52 pH-meter equipped with a GK-2301B Radiometer combined electrode at 25.0 ± 0.1 °C. The electrode was calibrated according to Irving *et al.*[14] The measurements were performed as titrations. Aliquots (25 cm^3) of the samples were titrated with standardized KOH. The concentration of the metal ion changed in the range 4.3×10^{-3}—2.6×10^{-2} mol dm^{-3}. The ligand-to-metal concentration ratio was varied from 1.2:1 to 9.5:1 for glycine and from 2.4:1 to 6:1 for malonic acid.

The equilibrium calculations were performed using the program PSEQUAD.[15] Assuming the corresponding equilibrium model the difference in the measured and calculated pH or the volume of the titrating solution were minimized.

Results and Discussion

Due to its large positive charge Ti^{3+} is partly hydrolysed even in acidic medium so the formation of hydroxo complexes may affect the complex equilibria in aqueous solution. Although the problem has been studied by several authors[9,16–19] unambiguous results are not available for the hydroxo species. While literature data undoubtedly confirm the formation of monohydroxo species 'the identification of the species $[Ti_2(OH)_2]^{4+}$ while probably correct, still must be considered tentative. . .'.[20] Therefore the system was reinvestigated to obtain reliable data for the conditions employed here.

In the applied concentration range, precipitation and simultaneous oxidation of Ti^{3+} prevented us from obtaining a higher degree of hydrolysis than 50%. The calculations were carried out assuming different equilibrium models and the results, together with literature data, are given in Table 1.

The reinvestigation of this system provided further evidence for the formation of polynuclear species; however, their fraction was too small to give their exact composition. The dimer and the trimer can substitute for each other in the equilibrium models without changing considerably the stability constants for $[Ti(OH)]^{2+}$ and the precision of the fitting. On the other hand it is apparent from the improvement of the fitting parameter (ΔpH) that the formation of some sort of polynuclear complex has to be considered to obtain reliable description of the system. In further calculations the stability constants of model II have been used. Using model III instead of model II does not alter the stability constants for the glycinato and malonato complexes.

In the Ti^{3+}–glycine (HL) system a precipitation occurred at a considerably higher pH than in the aqueous solution of Ti^{3+} (at pH 4.2 instead of 2.5). This and the colour changes observed during the titration (from pink to blue through yellow and green) clearly shows the importance of complex formation reactions. The formation functions for this system were calculated assuming the formation of parent complexes only. The extreme diversity of these curves indicated that protonation and hydrolytic processes strongly influence the equilibria of this system. For the interpretation of the experimental data more than 30 equilibrium models have been tried. A few representative models are shown in Table 2.

Without doubt the calculations justified the formation of complexes $[TiL]^{2+}$ and $[TiHL]^{3+}$. On increasing the pH one or more new species form in the system. They have a common

Table 1. Stability constants for the hydroxo complexes of Ti^{3+}

	$\log\beta_{Ti_i(OH)_j}$[a]					
Ref.	$[Ti(OH)]^{2+}$	$[Ti_2(OH)_2]^{4+}$	$[Ti_3(OH)_3]^{6+}$	$[TiO]^{+}$[b]	$[Ti_2O(OH)]^{3+}$	ΔpH[c]
Model I	-2.30 ± 0.01					0.017
Model II	-2.59 ± 0.03	-3.03 ± 0.04				0.007
Model III	-2.45 ± 0.01		-3.58 ± 0.04			0.007
9[d]	-2.55	-3.30				
16[e]	-1.77 -2.74				[f]	
17[g]				-4.52		
18	[f]			[f]		
19[h]	-2.77	-3.90				

[a] $\beta_{Ti_i(OH)_j} = [Ti_i(OH)_j^{3i-j}][H^+]^j/[Ti^{3+}]^i$. [b] $[TiO]^+$ or $[Ti(OH)_2]^+$. [c] The average difference in the measured and calculated pH. [d] In 3 mol dm^{-3} KBr at 25 °C. [e] In 0.25—1.50 mol dm^{-3} KBr at 25 °C. [f] Identified. [g] In zero ionic strength. [h] In 3 mol dm^{-3} KCl at 25 °C.

Table 2. Stability constants of the species formed in the Ti^{3+}–glycine (HL) system (25 °C, $I = 1.0$ mol dm^{-3} KCl)

	log β		
Species	Model I	Model II	Model III
HL		9.684 ± 0.002	
H_2L^+		12.111 ± 0.003	
$[Ti(OH)]^{2+}$		-2.59	
$[Ti_2(OH)_2]^{4+}$		-3.03	
$[TiHL]^{3+}$	11.44 ± 0.04	11.44 ± 0.04	11.42 ± 0.03
$[TiL]^{2+}$	9.30 ± 0.01	9.30 ± 0.01	9.30 ± 0.01
$[TiL_2]^+$	15.66 ± 0.08		
$[TiL(OH)]^+$		4.48 ± 0.08	
$[Ti_2L_2(OH)_2]^{2+}$			12.11 ± 0.08
V^*/cm^3	1.7×10^{-2}	1.7×10^{-2}	1.6×10^{-2}

* The average difference in the measured and calculated volume of the titrating 0.501 mol dm^{-3} KOH.

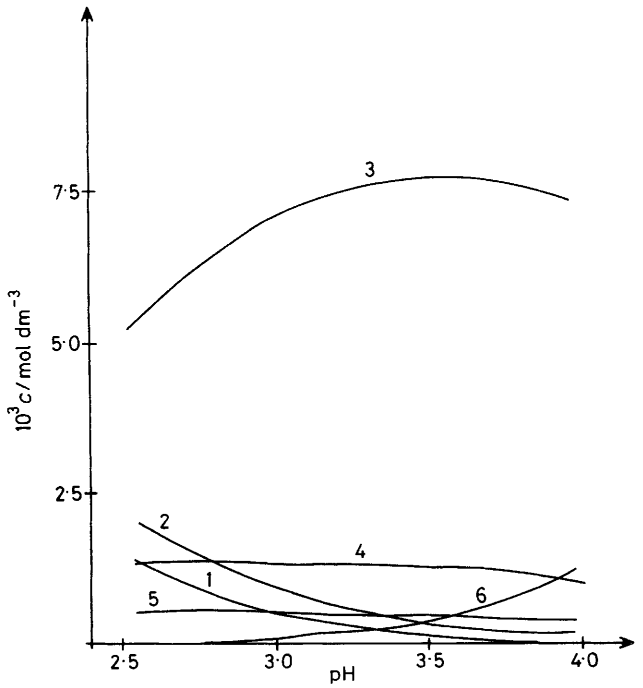

Figure. The concentration–distribution curves for the Ti^{3+}–glycine (HL) system: $c^0_{HL} = 5.06 \times 10^{-2}$ mol dm^{-3}, $c_{Ti} = 1.07 \times 10^{-2}$ mol dm^{-3}. 1, Ti^{3+}; 2, $[TiHL]^{3+}$; 3, $[TiL]^{2+}$; 4, $[Ti(OH)]^{2+}$; 5, $2 \times [Ti_2(OH)_2]^{4+}$; and 6, $[TiL(OH)]^+$

feature of releasing two moles of H^+ per mole of Ti^{3+}; however, their exact composition could not be determined. The concentration–distribution curves for model II are shown in the Figure. The curves have the same feature if $[TiL(OH)]^+$ is replaced by $[TiL_2]^+$ or $[Ti_2L_2(OH)_2]^{2+}$ (models I and III) respectively. Although the three complexes are indistinguishable, the formation of $[TiL_2]^+$ can probably be rejected on the basis of the following consideration. Precipitation occurs when the new species appears in a significant concentration and so this complex can be regarded as the precursor of the hydroxo precipitate. Therefore the formation of a ternary hydroxo complex would be the most plausible explanation for the observed pH effect.

The stability constant obtained for $[TiL]^{2+}$ is considerably higher than that published by Farooq *et al.*[21] (logβ = 8.5). In that paper no experimental details were given and thus it is not clear how the authors could avoid precipitation and simultaneous oxidation of Ti^{3+} at a 2:1 ligand-to-metal concentration ratio in the applied high pH range. The difference between the earlier published and our data is probably caused by some artefact in the previous work.

The stability constant of the mono complex with glycine, $[TiL]^{2+}$, is higher by three orders of magnitude than that with oxalic acid ($\log K_1 = 6.45$).[11] Since both ligands form simple five-membered chelate rings this suggests a higher affinity of Ti^{3+} towards N-donors than O-donors.

The equilibria of the Ti^{3+}–malonic acid (H_2L') system were studied at ligand-to-metal concentration ratios of higher than 2:1. The coincidence of the formation functions at different ligand and metal concentrations demonstrated that neither protonated nor ternary hydroxo complexes form under our conditions and the titration curves could be interpreted by the formation of parent complexes $[TiL']$, $[Ti(L')_2]^-$, and $[Ti(L')_3]^{3-}$ only. The stepwise stability constants are: $\log K_1 = 6.83 \pm 0.04$, $\log K_2 = 4.99 \pm 0.02$, and $\log K_3 = 2.84 \pm 0.03$ respectively (at 15 °C and $I = 0.5$ mol dm^{-3} KCl, $\log K_1 = 6.53$).[22]

Malonic acid forms less stable complexes with Ti^{3+} than does glycine, but hydroxo complexes have a negligible effect on the equilibria of this system for the following reasons: (*i*) due to the relatively low basicity of malonate the free ligand concentration is sufficiently high even in acidic solutions to shift the complexation reactions to the low pH range, suppressing the hydrolytic processes; (*ii*) on co-ordination the negatively charged ligand strongly reduces the affinity of the central ion towards OH^-. The difference in the stepwise stability constants for complexes $[TiL'_i]^{3-2i}$ is larger than expected from statistical considerations. While for oxalato complexes no special effect was observed, $\log(K_1/K_2) = 0.41$,[11] in the case of malonato complexes the difference is considerably larger, $\log(K_1/K_2) = 1.84$, and is attributed to the larger size of the chelate ring in the latter.

Titanium(III) exhibits similar behaviour to Fe^{3+} and is primarily related to the same charge on these ions. It is remarkable, however, that bidentate ligands co-ordinate more strongly to Fe^{3+} than to Ti^{3+}. The stability constants for mono complexes with oxalate, malonate, and glycinate are 7.54, 7.46, and 10.00 for Fe^{3+}[13] and 6.45,[11] 6.83, and 9.30 for Ti^{3+}, respectively. This trend reflects the difference in the size of the two metal ions.

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