

## Complex formation of In(III) with D-gluconate and gluconate in neutral aqueous perchlorate solutions in wide range of pH

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The mechanism of complexation of In(III) with D-gluconate and glycolate was investigated in chemically inert aqueous perchlorate solutions with an overall ionic strength  $\mu = 0.1$  at pH = 7.0(3) and pH = 12.50(2) both by the method of perturbed angular  $\gamma$ - $\gamma$ -correlation measurements using one HPGe detector only (1-PAC) and by an electromigration technique.

Perturbed angular  $\gamma$ - $\gamma$ -correlation (PAC) measurements using one HPGe detector only (1-PAC) and the free-electrolyte continuous electromigration technique for the on-line determination of absolute migration velocities of radio-ions were described in details elsewhere [2,3].

No-carrier-added <sup>111</sup>In ( $T_{1/2} = 2.81$  d) was purchased from Mallinckrodt, in 0.1 M HCl stock solution with a specific activity of 370 MBq/ml. Aqueous solutions of type NaL / NaClO<sub>4</sub> / NaOH were prepared for the investigations, where NaL represents sodium glycolate or D-gluconate. Appropriate amounts of NaOH were added to the solutions to adjust their pH to 7.0(3) and 12.50(3), while maintaining a constant overall ionic strength of  $\mu = 0.1$ . For all measurements carrier amounts of 10<sup>-5</sup> M indium(III) perchlorate were added. 1-PAC measurements were performed using polyethylene vials ("Eppendorf") of 2 ml volume. The activity of the samples was 40-50 kBq. The volume of each sample was 0.5 ml. The measurements were carried out with a coaxial HPGe detector of 250 cm<sup>3</sup> volume, 64.8% relative efficiency (1332 keV) at room temperature.

The overall ion mobilities were measured at  $T = 298.1(1)$  K at an electric field intensity of 10 V/cm. About 1-2  $\mu$ L of the <sup>111</sup>In solutions (~100-200 kBq) were injected into the electromigration tube, which contains the electrolyte.

In the region of pH  $\approx$  6-12.7, In(III) forms an insoluble hydroxide In(OH)<sub>3</sub>(c). The individual  $R_{\gamma_1+\gamma_2}$ -value for this species is  $R_{\gamma_1+\gamma_2} = 0.9636(14)$  and is close to the literature value [2]. In order to investigate the influence of the pH on the mechanism of complexation of D-gluconate and glycolate, the dependencies of  $R_{\gamma_1+\gamma_2}$ -values on the concentration of the ligands were measured at pH = 7.0(3) and pH = 12.50(2) (Fig. 1a). For D-gluconate concentrations of  $< 7 \cdot 10^{-3}$  M, at pH = 7.0(3) the  $R_{\gamma_1+\gamma_2}$ -values correspond to those of In(OH)<sub>3</sub>(c). With increasing ligand concentration the  $R_{\gamma_1+\gamma_2}$ -values decrease, reflecting dissolution of the hydroxide. At pH = 12.50(3), formation of In-D-gluconate complexes was obtained at lesser concentration of the ligand, i.e. already at  $> 10^{-4}$  M (Fig. 1a). For glycolate, the dissolution of the hydroxide occurred at  $[L] > 4 \cdot 10^{-2}$  M independently of the pH of the medium. Glycolate has a lower tendency for complex formation compared with D-gluconate.

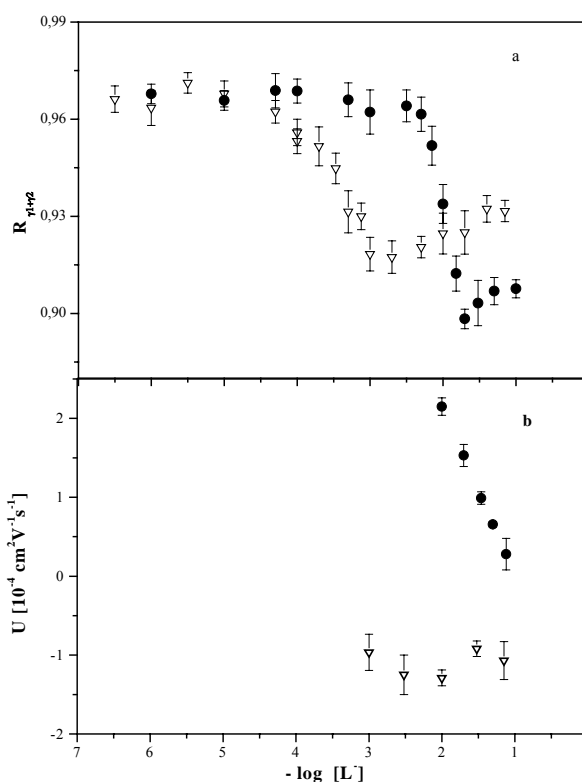


Figure 1.

(a)  $R_{\gamma_1+\gamma_2}$  -value versus D-glyconate concentration. NaL / NaOH / NaClO<sub>4</sub> electrolytes,  $\mu = 0.1$ , room temperature,  $C_{\text{In(III)}} = 10^{-5}$  M, at pH = 7.0(3) (circles); at pH = 12.50(3) (triangles); (b) overall ion mobility of <sup>111</sup>In<sup>3+</sup> species versus D-gluconate ligand concentration. NaL / NaOH / NaClO<sub>4</sub> electrolytes,  $\mu = 0.1$ ,  $T = 298.1(1)$ ,  $C_{\text{In(III)}} = 10^{-5}$  M, at pH = 7.0(3) (circles); at pH = 12.50(3) (triangles).

To determine whether the hydroxylic groups are involved in the complexation, the overall ion mobilities of the In(III)/D-gluconate complexes were measured at pH = 7.0(3) and pH = 12.50(2) in the range of the ligand concentration  $10^{-3} - 10^{-1}$  M (Fig. 1b). At pH = 7.0(3) the In species migrate as cations. The corresponding stoichiometry may be represented by the following equilibrium:  $\text{InL}^{2+} \rightarrow \text{InL}_2^+ \rightarrow \text{InL}_3^0$ . Estimations of the direction and velocity of the migration thus lead to the conclusion, that at pH = 7.0(3) the ligand has a charge of 1- (monodentate coordination), corresponding to the dissociation of carboxylic groups. At pH = 12.50(2) the ligand is 2- charged (bidentate coordination), corresponding to an additional dissociation of one of the hydroxylic groups.

Changes of the mechanism of complexation from mono to bidentate coordination for D-gluconate were found to occur at pH  $> 11$ .

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