

Quantitative determination of indium (^{111}In) hydrolysis by a $\gamma\gamma$ -perturbed angular correlation one detector method (1-PAC)

KP Zhernosekov[‡], NA Korolev^{*}, DV Filosofov^{*}, AF Novgorodov^{*}, F Rösch[‡]

^{*}Joint Institute of Nuclear Research, LNP, 141980 Dubna, Russia; [‡]Institut für Kernchemie, Johannes Gutenberg-Universität Mainz, Germany

To evaluate the potential of the method of perturbed angular γ - γ -correlation measurements using one HPGe detector only (1-PAC) for the measurement of quantitative parameters of the chemical reactions in solutions, the hydrolysis equilibria of In(III) have been investigated.

The underlying physical phenomena of the PAC methods are (i) an angular correlation between two cascade γ -quanta in the decay of the probe-nucleus and (ii) the perturbation of this correlation caused by interaction of the nucleus with its environment (hyper fine interaction). The time-integrated angular correlation of cascade γ -rays is given by:

$$W(\theta, T) = 1 + A_{22}G_2(\infty)Q_2P_2(\cos(\theta)) + \dots$$

where A_{ij} are the angular correlation coefficients, $P_i(\cos\theta)$ are the Legendre polynomials, Q_i corresponds to a geometry coefficient that includes influence of finite sizes of both the detector and the sample and $G_i(\infty)$ are the time-integrated angular correlation perturbation factors. The relative probability to detect the cascade γ -rays γ_n, γ_m ($R_{\gamma_n\gamma_m}$) at an angle θ , at the individual $A_{ij}, G_i(\infty)$ and Q_i values is equal to $W(\theta, \infty)$:

$$R_{\gamma_n\gamma_m} = R_{\gamma_n\gamma_m}^i W_{A_{ij}, G_i, Q_i}(\theta, \infty)$$

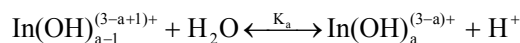
The possibility to use only one detector (1-PAC method) was described in detail elsewhere [1]. The characteristic parameter is the relative probability $R_{\gamma_n\gamma_m}$ at an angle of 0° .

Non-carrier-added ^{111}In ($T_{1/2} = 2.81$ d), was purchased from Mallinckrodt in 0.1 M HCl stock solution. The specific activity of the solution was 370 MBq/ml. The hydrochloric acid was removed by evaporation and the residue was then dissolved in 0.01 M HClO_4 .

The inert background perchlorate solutions with an overall ionic strength $\mu = 1$ of the electrolyte media $\text{Na}^+/\text{H}^+/\text{OH}^-/\text{ClO}_4^-$ were prepared using p.a. chemicals (Merck) and analytical grade water.

1-PAC measurements were performed using polyethylene vials of 2 ml volume. The activity of the samples was 40-50 kBq. Carrier amounts of 10^{-5} M indium (III) perchlorate were added. The volume of each sample was 0.5 ml. After the measurements, the pH of the samples was determined by means of a pre-calibrated glass electrode using standard buffer solutions. The dependence of $R_{\gamma_1\gamma_2}$ on the pH of the media at room temperature is illustrated in Figure 1.

The hydrolysis of In^{3+} can be expressed as (Eq.1):



K_a ($a \geq 1$) - the stepwise stoichiometric constants.

The change of the $R_{\gamma_1\gamma_2}$ -value with increasing pH reflects the transition of the radionuclide form in the order of:

$\text{In}^{3+} \rightleftharpoons \text{InOH}^{2+} \rightleftharpoons \text{In}(\text{OH})_2^+ \rightleftharpoons \text{In}(\text{OH})_3(\text{c}) \rightleftharpoons [\text{In}(\text{OH})_4]^-$. The measured value of $\bar{R}_{\gamma_1\gamma_2}$ reflects the weighted sum of

individual $R_{\gamma_1\gamma_2}^i$ values over all species of indium in the studied system. Using the stepwise stoichiometric hydrolysis

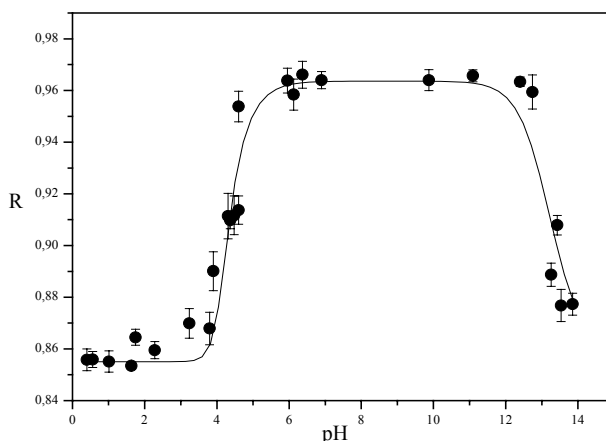


Figure 1. $R_{\gamma_1\gamma_2}$ -value versus pH in NaClO_4 ($\mu = 1$), room temperature.

constants, the $\bar{R}_{\gamma_1\gamma_2}$ value may be expressed as a function of the pH concentration as follows (Eq.2):

$$\bar{R}_{\gamma_1\gamma_2} = \frac{R_{\gamma_1\gamma_2}^{\text{In}^{3+}} + R_{\gamma_1\gamma_2}^{\text{InOH}^{2+}} \frac{K_1}{[\text{H}^+]} + R_{\gamma_1\gamma_2}^{\text{In}(\text{OH})_2^+} \frac{K_1 K_2}{[\text{H}^+]^2} + R_{\gamma_1\gamma_2}^{\text{In}(\text{OH})_3(\text{c})} \frac{C_{\text{In}^{3+}}}{K_s [\text{H}^+]^3} + R_{\gamma_1\gamma_2}^{\text{In}(\text{OH})_4^-} \frac{C_{\text{In}^{3+}} K_4}{K_s [\text{H}^+]^4}}{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1 K_2}{[\text{H}^+]^2} + \frac{C_{\text{In}^{3+}}}{K_s [\text{H}^+]^3} + \frac{C_{\text{In}^{3+}} K_4}{K_s [\text{H}^+]^4}}$$

where $C_{\text{In}^{3+}}$ is the overall concentration of indium and K_s the solubility constant of $\text{In}(\text{OH})_3(\text{c})$ -product. The $R_{\gamma_1\gamma_2}^i$ -values for the individual species may be derived from the experimental data by a simple interpolation.

The K_a -values obtained from the fit of the experimental data $\bar{R}_{\gamma_1\gamma_2} = f(\text{pH})$ with Eq.(2) (solid line in Figure 1) are given in Table 1. In order to reduce the number of variables in Eq.(2) the value of K_1 was fixed as $\log K_1 = -5.02$ [2].

It could be shown that the proposed scheme of the physico-chemical treatment of experimental 1-PAC data is suitable for the quantitative investigation of indium equilibria. However, the values of K_2, K_s and K_4 are affected by relatively high errors. Moreover, K_2 significantly lower compared to [2], while K_s and K_4 are higher.

The 1-PAC method will allow quantitative treatment of chemical equilibria, supposed the number of experimental data points adequate to the number of variables to be calculated.

Table 1. Stepwise complex formation constants ($\log K_a$) for the hydrolysis of indium. $\log \beta_4$ is the overall complex formation constant. Background electrolyte: $\text{NaClO}_4, \mu = 1$, room temperature.

$\log K_1$	$\log K_2$	$\log K_s$	$\log K$	Ref.
fixed	-3.5(7)	7.7(5)	-12.9(9)	This work
-4.00	-3.82	5.07	-9.67	[2] [*]
-5.02	-4.33	6.60	-10.0	[2] ^{**}

* - At infinite dilution ($\mu = 0$), at 25°C

** - by evaluating ($\mu = 1$)

[1] D.V. Filosofov et. al, Appl. Rad. and Isot. **57**, 437 (2002). [2] Baes C.F., Mesmer R. The Hydrolysis of Cations. // Krieger publ., Malabar, Florida (1976).