^{111}Cd Time Differential Perturbed Angular Correlation Studies of High Specific Activity ^{111}In-Aqueous Solutions

Z. Z. Akselrod, D. V. Filossofov[a], J. Buša[a], T. Bušova[b], O. I. Kochetov[a], N. A. Lebedev[a],
A. F. Novgorodov[a], V. N. Pavlov[a], A. V. Salamatin[a], E. N. Shirani[c], and V. V. Timkin[a]
Skobeltsyn Institute of Nuclear Physics, Moscow State University, 119899 Moscow, Russia
[a] Joint Institute for Nuclear Research, LNP, P. O. Box 79, Moscow, Russia
[b] P. J. Šafarik University, Department of Organic Chemistry, 04167 Košice, Slovakia
[c] Vereshchagin Institute of High Pressure Physics, RAS, 142092 Troitsk, Moscow reg., Russia
Reprint requests to Dr. Z. Z. A.; Fax: +7-095-939-08-96; E-mail: akselrod@nusun.jinr.ru

Z. Naturforsch. **55 a,** 151–154 (2000); received August 23, 1999

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions,
Leipzig, Germany, July 25 - 30, 1999.

Time-differential PAC measurements have been made using the high specific activity of ^{111}In, both in aqueous solutions of the ClO^-_4, NO^-_3 and Cl^- at pH values between 1.0 and 9 and temperatures between 186 and 293 K.

Key words: ^{111}In; ^{111}Cd; High Specific Activity; Nuclear Quadrupole Interaction (NQI); Time Differential Perturbed Angular Correlation (TDPAC).

Introduction

^{111}In is an important nuclide for nuclear medicine due to its convenient half-life and emission of γ-ray photons suitable for detection by imaging devices. At the same time ^{111}In (Electron-Capture, $\tau_{1/2}$ = 2.8 d) → ^{111}Cd is one of the most popular probes used in time-differential perturbed $\gamma\gamma$-angular correlation (TDPAC) measurements. The excited state ($7/2^+$, 420 keV) of ^{111}Cd populated via the EC decay of ^{111}In deexcites by the $\gamma\gamma$-cascade of 171 - 245 keV to the ground state ($1/2^+$) through the isomeric intermediate state ($5/2^+$, 245 keV, $\tau_{1/2}$ = 84.5 ns, Q = +0.83 b). The angular correlation of this cascade is largely anisotropic ($A_2^{max}(\%) = -18.0$).

The TDPAC technique lends itself to a study of relaxation phenomena in pure liquids or solutions. In aqueous solutions the quadrupolar relaxation observed might be strongly influenced by complex formation. The formation of hydrolysis products of In^{3+} has been the subject of a number of previous studies using ^{111}In-TDPAC spectroscopy [1 - 3]. In^{3+} is known to exist as a pure aqua-complex $[In(H_2O)_6]^{3+}$ only in fairly acid solutions (pH < 3.0). The fluctuations of the EFG in these monomeric species due to tumbling are likely to be small and fast enough so that for pH 2.0 the angular correlation is found to be perturbed rather weakly. It was found that at intermediate pH values (> 4) the perturbation pattern is consistent with the formation of less symmetrical complexes and larger, more slowly tumbling aggregates.

The chemical form of In with its extremely low concentration at intermediate pH values is very hard to control due to the tendency of indium hydroxides (i) to bind to the walls of the vessel containing the aqueous solution and (ii) to precipitate with the hydroxides of chemically similar metals (Fe^{3+}, etc.) contained in the solution as a result of using various reagents at various stages of separation and cleaning of the initial activity and the preparing of the solution samples.

The present paper is concerned with $\gamma\gamma$-TDPAC of ^{111}Cd in high specific activity ^{111}In-aqueous solutions of the ClO^-_4, NO^-_3 and Cl^-. Emphasis is to put on purity of the chemical form of In in the studied aqueous solutions. The measurements have been made at pH values between 1.0 and 9 and temperatures between 186 and 293 K. Likewise, the effect of the ^{111}In adhesion on the vessel walls was investigated using containers of polyethylen and teflon.

Experimental Methods

^{111}In was produced via the reaction ^{109}Ag(α,2n) ^{111}In by irradiation of a metallic silver target with α-particles with E_α = 30 MeV at the U-200 cyclotron of the JINR. The active layer of the target ($\approx$100 μm) was dissolved in 3 - 5 ml of concentrated HNO_3. Then 3 mg of $La(NO_3)_3$ and NH_4OH were added, bringing this solution up to pH $\geq$ 8. ^{111}In precipitates with $La(OH)_3$, while Ag and ^{109}Cd stay in the solution. The precipitate of $La(OH)_3In^*$ was redissolved in HNO_3 and was precipitated again by adding NH_4OH. This procedure was repeated 5 times, and finally the precipitate was washed with H_2O.

For the cleaning of ^{111}In, the precipitate of $La(OH)_3In^*$ was dissolved in a small volume of HCl bringing up to $[H^+] \approx 0.1$ M. The solution was transferred to a column (ø = 3 mm, h = 100 mm, Dowex 50Wx8, 200 - 400 mesh, in H$^+$-form). The column was washed consecutively with solutions of 0.1 M and 0.25 M HCl (with 5 v_0). ^{111}In eluates by 0.5 M HCl in $\approx$ 0.5 ml. La(III) and the possible contaminants of Fe(III), Al(III) and rare-earth elements stay in the column. The ^{111}In eluate was evaporated to dryness and redissolved in a small volume of 0.1 M HCl. Then the solution was transferred to a quartz column (ø = 1.25 mm, h = 30 mm, Aminex A-6, in H$^+$-form), and the column was washed analogously. ^{111}In eluates by 0.5 M HCl in $\approx$ 50 μl.

The activity of the purified ^{111}In preparation yielded $\approx$ 20 mCi. A salt precipitate had not been seen on the teflon mount on evaporating. The control experiments with $InCl_3$ and $FeCl_3$ yielded that the salt precipitate ammounts to $\approx$ 100 ng. As 20 mCi ^{111}In corresponds to *approx* 2.6×10^{13} atoms, and the weight of an adequate amount of $InCl_3$ equals 10 ng, it is possible to conclude that in the initial ^{111}In preparation there is 1 atom of ^{111}In adequate to $\leq$ 10 atoms of the chemically identical elements.

Samples for the TDPAC measurements were prepared by dissolving of ^{111}In in HCl (pH = 3) bringing the specific activity up to $\approx$ 5 Ci/l. The solution aliquot (30 μCi) on the teflon mount was evaporated to dryness and with added $\approx$ 50 μl H_2O, again evaporated to dryness at the same temperature ($T \approx 80$ °C). ^{111}In was removed from the mount by an adequate volume of the solution of study with estimated pH values and reagent concentrations, and transferred to the operative container. The ^{111}In concentration in the sample was estimated to be $\approx 5\times10^{-10}$ M. The constant ionic strength ($I = 2.0\times10^{-3}$ M) in the samples (pH > 3) was held by the adding $NaCl_4$ ($[NaCl_4] = 10^{-3}$ M). The relative contents of trivalent contaminants in the reagents were $< 10^{-6}$. The pH values in the samples were controlled before and after the TDPAC measurements.

The ^{111}In-release from the irradiated silver as well as the radiochemical purity in all stages of the cleaning was measured by means of a Ge(Li)-detector.

The TDPAC measurements were made using a 4-detector spectrometer with NaJ(Tl) scintillators (40×40 mm) arranged in the plane with intervals of 90 °. Coincidence counts $W(\theta, t)$ within a resolution time of 2.5 ns were accumulated between $\theta = 90°$ and 180° [4].

The temperature experiments (186 to 273 K) were performed with a cryostat. The sample temperature was kept constant (± 0.5 K) by a preheated nitrogen steam.

For the least squares minimization of the angular correlation perturbation of models (i) $A_2G_2(t) = a_0 + a_1e^{-\lambda 2t}$ (dynamic) and (ii) $A_2G_2(t) = a_0 + a_1\cos(\omega_0 t)e^{-\Lambda t}$ (static), adequate programmes in the MATLAB system were used.

Results and Discussion

The time spectra observed at low pH ($\leq$ 3) yielded the typical patterns for the unperturbed function $G_2(t)$ independent of the container material. The $G_2(t)$ curves show a slow decay corresponding to very small values of λ_2. This shape is consistent with the ^{111}In being subject to a rapidly-rotating electric field gradient. It is assumed that in these cases In-hydroxides are monomeric complexes.

In case of the polyethylene container as the pH increases, the $G_2(t)$ curves show the typical pattern of anisotropy which corresponds to a static quadrupole interaction (see Figure 1b)). It was found that after the solution was withdrawn from the container, up to 90% of the ^{111}In became wall-bound.

Fig. 1. TDPAC spectra of the 171-245 keV $\gamma\gamma$-cascade in ^{111}Cd, measured with ^{111}In: a) in H_2O, pH = 7, T = 293 K, TEFLON; b) in H_2O, pH = 7, T = 293 K, POLYETHYLEN; c) in HNO_3, pH = 2, T = 253 K; d) in HNO_3, pH = 2, T = 186 K; e) in HCl, pH = 2, T = 250 K; f) in HCl, pH = 2, T = 186 K. The solid curves through the data were calculated by the least-squares method according to the dynamic (a, c, d, e, f) or static (b) character of hyperfine interaction.

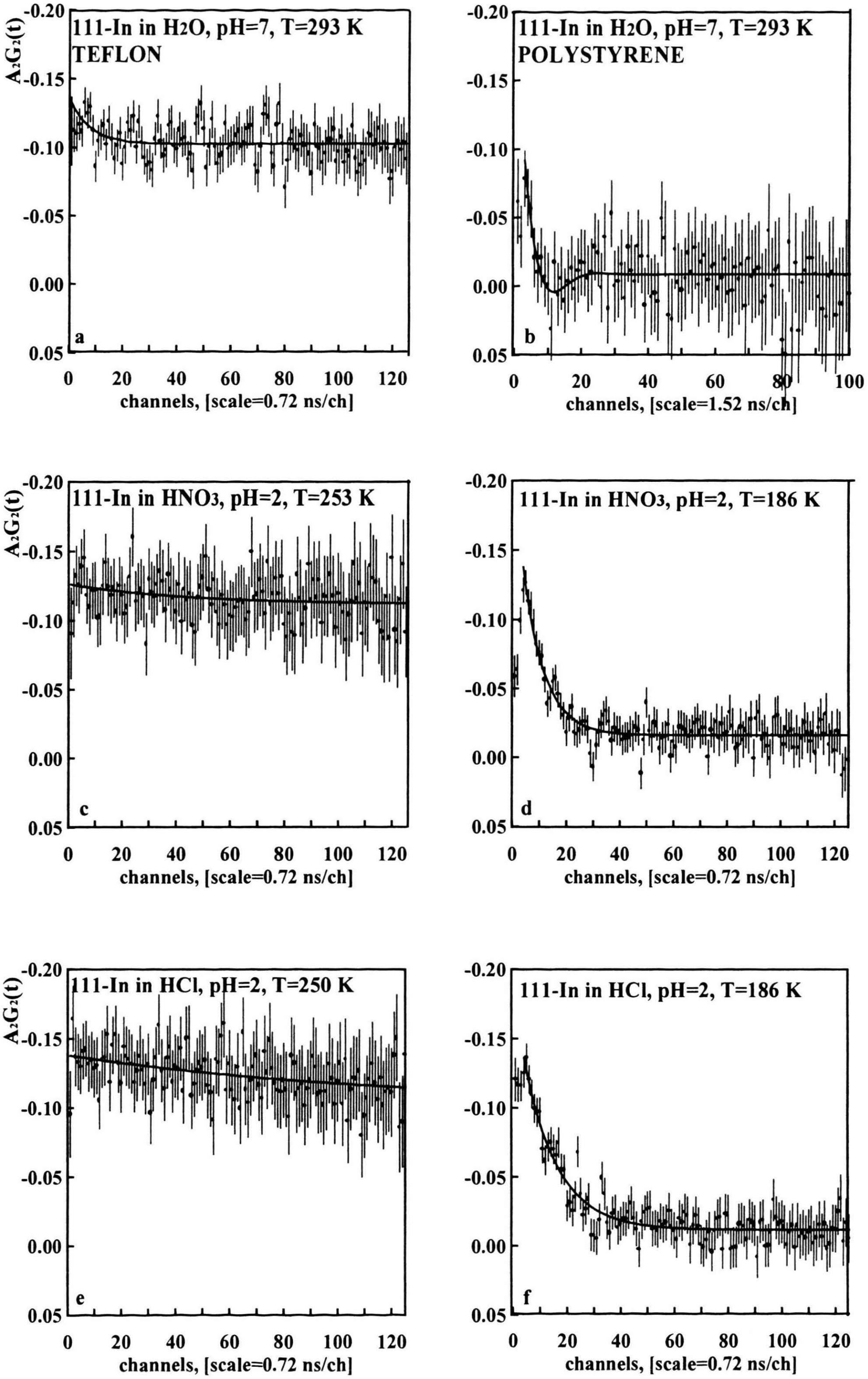
111-In in H2O, pH=7, T=293 K
TEFLON
111-In in H2O, pH=7, T=293 K
POLYSTYRENE
111-In in HNO3, pH=2, T=253 K
111-In in HNO3, pH=2, T=186 K
111-In in HCl, pH=2, T=250 K
111-In in HCl, pH=2, T=186 K
A2G2(t)
-0.20
-0.15
-0.10
-0.05
0.00
0.05
channels, [scale=0.72 ns/ch]
channels, [scale=1.52 ns/ch]
0
20
40
60
80
100
120
a
b
c
d
e
f

Table 1. The temperature dependencies of ^{111}Cd TDPAC spectra measured with ^{111}In in HNO_3 and HCl solutions (pH = 2). The relaxation parameter $\lambda_2(T)$ was computed from the slope the $A_2G_2(t)$ curves by the least-squares method according to the dynamic character of hyperfine interaction: $A_2G_2(t) = a_0 + a_1 e^{-\lambda_2 t}$.

T	λ_2, [$10^9 s^{-1}$]		a_0		a_1	
[K]	HNO_3	HCl	HNO_3	HCl	HNO_3	HCl
253	0.029(1)	0.002(1)	–0.112(1)	–0.00(3)	–0.014(1)	–0.136(3)
231	0.020(1)	0.003(1)	–0.063(2)	–0.00(4)	–0.07(1)	–0.13(4)
222	0.021(1)	0.017(1)	–0.016(5)	–0.066(2)	–0.113(4)	–0.066(2)
201	0.100(2)	0.077(2)	–0.009(1)	–0.032(1)	–0.145(2)	–0.118(1)
193	0.160(2)	0.095(1)	–0.009(1)	–0.011(1)	–0.179(1)	–0.155(1)
186	0.174(2)	0.111(2)	–0.016(1)	–0.012(1)	–0.177(1)	–0.158(1)

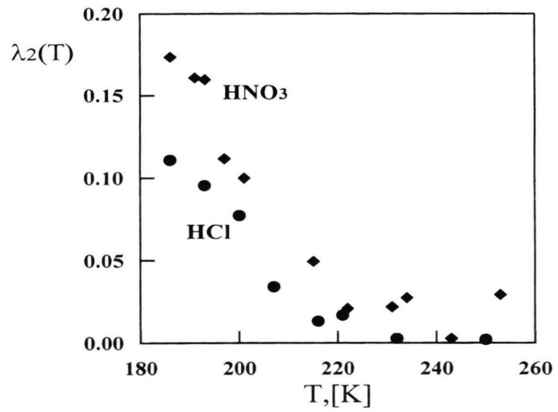

Fig. 2. The relaxation parameter $\lambda_2(T)$ computed from the slope of the $A_2G_2(t)$ curves by the least-squares method according to the dynamic character of the hyperfine interaction vs. temperature for ^{111}In in HNO_3 and HCl solutions.

At the same solutions in the case of the teflon container as the pH increases (up to 9), the angular correlation is unperturbed (see Figure 1a)). Likewise the absence of the sorption has been supported by means measurements with a Ge(Li)-detector.

It should be pointed out that when the time spectra observed in neutral media (pH = 7) in the teflon container yield a static perturbation of the angular correlation, repetitive purification of initial activity is needed. The result of repetitive purification is that the following TDPAC measurements show the unperturbed patterns of $G_2(t)$. In the previous studies these perturbations of the angular correlation observed in the neutral media were attributed to In-aggregates with molecular weights up to 10^8 - 10^9 a.u.m. Such aggregates, however, are unlikely for the extremely low In concentrations. Apparently the static character of these perturbations of the angular correlation is due to the In precipitation with the hydroxides of the contaminants (predominantly Fe^{3+}) contained in the target and reagents [5].

It can be concluded that in the case of the high specific ^{111}In activity the unperturbed angular correlation observed for neutral aqueous solutions may be consistent with the assumption that In stays in a monomeric complex.

The results of the temperature TDPAC studies for the HNO_3 and HCl solutions (pH = 2) are shown in Fig. 1c) - f). The relaxation parameters $\lambda_2(T)$, computed from the slope of the $A_2G_2(t)$ curves, are presented in Table 1 and plotted in Figure 2. The dynamic character of the perturbation of the angular correlation in the frozen solution may be attributed to:

(i) Ice, freezing from the solution and increasing the acid concentration. Then the In might be located in the liquid phase of concentrated acid. However, this is unlikely for the low initial acid concentration (10^{-2} M) as well as ^{111}In concentration in the solution. The conclusion that ^{111}In stays in the solid phase is supported by the absence of peculiarities in the dynamic character of the time spectra (HNO_3) at the junction of the eutectic temperature (230 K).

(ii) The formation of the liquid phase in the ice structure might be due to the after effects of the ^{111}In (EC) ^{111}Cd electron capture decay. This conclusion could be examined by means the TDPAC technique with a source of ^{111m}Cd (IT, $\tau_{1/2}$ = 48.6 min)^{111}Cd.

(iii) Effects due to the ice structure and hydrogen bounding.

[1] G. R. Demille, D. L. Livesey, K. Mailer, and S. P. Turner, Chem. Phys. Lett. **44**, 164 (1976).
[2] A. Shukri, F. A. Smith, and P. J. Marsden, Appl. Radiat. Isot. **39**, 9 (1988).
[3] F. A. Smith and P. J. Marsden, Appl. Radiat. Isot. **39**, 15 (1988).
[4] V. B. Brudanin, O. I. Kochetov, A. V. Salamatin, I. Stekl, V. V. Timkin, A. V. Zernov, L. N. Fomicheva, E. N. Shirani, A. V. Tsvyashchenko, and Z. Z. Akselrod, B. Abstr. XIY Int. Symp. NQI **P14**, 93 (1997).
[5] C.F.Baes, Jr., R.E.Mesmer, Oak Ridge National Laboratory, Oak Ridge, Tennessee, "The Hydrolysis of Cations", printed and published by R. E. Krieger Publishing Company, Inc., Krieger Drive Malavar, Florida 1986.