Positron annihilation studies in binary solid solutions of metal betadiketonates, using lifetime and Doppler broadening spectroscopies
J. Machado, A. Porto, C. Carvalho, W. Magalhaes, A. Marques-Netto

To cite this version:

HAL Id: jpa-00251471
https://hal.archives-ouvertes.fr/jpa-00251471
Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Positron annihilation studies in binary solid solutions of metal beta-diketonates, using lifetime and Doppler broadening spectroscopies

J.C. MACHADO, A.O. PORTO, C.F. CARVALHO, W.F. MAGALHAES and A. MARQUES-NETTO

Departamento de Química, ICEx, UFMG, C.P. 702, 31270 901 Belo Horizonte M.G., Brazil

ABSTRACTS

Positron annihilation lifetime (LS) and Doppler broadening annihilation radiation lineshape (DBARL) spectroscopies measurements were performed in several binary solid solutions of the general formula $M_{(1-x)} G_x L_3$, where $M = Al$(III), $Ga$(III), or $In$(III), as matrix; $G = Cr$(III), $Mn$(III), $Fe$(III), $Co$(III), $Ru$(III), $Rh$(III), and $Ir$(III), as guest molecules, $L =$ acetylacetone (acac) or dipivaloylmethane (dpm), and $X =$ guest molecule mole fraction. The studied systems can be classified in two groups: the first one presenting only inhibition of positronium formation and the second one presenting inhibition and quenching effects. The inhibition and quenching constants were determined.

INTRODUCTION

In previous publications (1,2) we have discussed the positronium (Ps) formation and inhibition effect in binary solid solutions of the general formula $Al_{(1-x)} G_x (acac)_3$, where $G = Cr$(III), $Fe$(III) and $Co$(III), as guest molecules, and $Al$(acac)$_3$ as the matrix, studied by LS technique.

For a better understanding of the positron annihilation behaviour in this type of systems, new measurements were carried out. Owing to the properties of $Cr^{3+}$, $Fe^{3+}$, $Co^{3+}$, $Mn^{3+}$ ions or their complexes as inhibitors and/or quenchers, the host $Al$(III), $Ga$(III), and $In$(III) complexes (in which Ps formation is very efficient) can be regarded as "nonpolar solvents", while the guest $Cr$(III), $Mn$(III), $Fe$(III), $Ru$(III), $Co$(III) and $Rh$(III) complexes, in which any Ps is hardly formed, can be considered as solutes.

EXPERIMENTAL

The metal acetylacetonates and dipivaloylmethanates were synthesized as described in the literature (3-4), with some modifications, when necessary. The purification and characterization of the pure compounds are described elsewhere (1-2).

Solid solution preparation, positron source, the lifetime spectrometer and the lifetime spectra analysis were described in
RESULTS AND DISCUSSION

The LS and DBARL parameters for Al(acac)$_3$, Ga(acac)$_3$, In(acac)$_3$ and Al(dpm)$_3$ are shown in Table 1. The o-Ps intensities ($I^0_3$), for the other pure compounds (guest molecules) are lower than 6% and the o-Ps lifetimes ($\tau_3$) are meaningless, as discussed before (1). The FWHM values for the latter compounds are in the range (2.76-2.90) keV.

Table 1 - LS and DBARL parameters for the matrix compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau_3^0$ (ns)</th>
<th>$I_3^0$ (%)</th>
<th>FWHM (keV)</th>
<th>Compound</th>
<th>$\tau_3^0$ (ns)</th>
<th>$I_3^0$ (%)</th>
<th>FWHM (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(acac)$_3$</td>
<td>1.23</td>
<td>44.0</td>
<td>2.44</td>
<td>Ga(acac)$_3$</td>
<td>1.13</td>
<td>46.4</td>
<td>2.44</td>
</tr>
<tr>
<td>Al(dpm)$_3$</td>
<td>1.62</td>
<td>59.0</td>
<td>2.30</td>
<td>In(acac)$_3$</td>
<td>1.11</td>
<td>46.2</td>
<td>2.50</td>
</tr>
</tbody>
</table>

The twelve studied binary solid solutions are collected in Table 2 with their inhibition ($k$) and quenching ($k'$) constants. The systems are separated in two groups: the first one for which the only observed effect is an inhibition of Ps formation and the second one presenting both the inhibition and quenching effects.

Table 2 - The inhibition and quenching constants for the $M_{(1-x)}G_{x,L_3}$ systems, determined by using equations $I_3 = I_3^0/(1 + kX)$ and $1/\tau_3 = 1/\tau_3^0 + k'X$, respectively, except for No. 7 to 9.

<table>
<thead>
<tr>
<th>No.</th>
<th>Group 1</th>
<th>$k$</th>
<th>Group 2</th>
<th>$k$</th>
<th>$k'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al$_{(1-x)}$Co$_x$(acac)$_3$</td>
<td>256</td>
<td>7</td>
<td>Al$_{(1-x)}$Cr$_x$(acac)$_3$</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Ga$_{(1-x)}$Co$_x$(acac)$_3$</td>
<td>255</td>
<td>8</td>
<td>Al$_{(1-x)}$Mn$_x$(acac)$_3$</td>
<td>138</td>
</tr>
<tr>
<td>3</td>
<td>In$_{(1-x)}$Co$_x$(acac)$_3$</td>
<td>456</td>
<td>9</td>
<td>Al$_{(1-x)}$Cr$_x$(dpm)$_3$</td>
<td>2.9</td>
</tr>
<tr>
<td>4</td>
<td>Al$_{(1-x)}$Ru$_x$(acac)$_3$</td>
<td>260</td>
<td>10</td>
<td>Al$_{(1-x)}$Co$_x$(dpm)$_3$</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>Al$_{(1-x)}$Fe$_x$(acac)$_3$</td>
<td>138</td>
<td>11</td>
<td>Al$_{(1-x)}$Mn$_x$(dpm)$_3$</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>Al$_{(1-x)}$Rh$_x$(acac)$_3$</td>
<td>18</td>
<td>12</td>
<td>Al$_{(1-x)}$Fe$_x$(dpm)$_3$</td>
<td>13</td>
</tr>
</tbody>
</table>

The behaviour of the systems of Group 1 is very similar, as observed before, the system no 1, included here just for comparison (1). For this group the FWHM vs. X curves, as expected, show an increase of the FWHM parameter with the increase of the
guest molecule concentration. For the systems number 10 to 12 of Group 2 the FWHM values increase with $X$, and $1/\tau_3$ values increase linearly with $X$, suggesting a quenching effect by oxidation mechanism. For the systems number 7 to 9, the FWHM values decrease with $X$, suggesting a quenching effect by spin conversion mechanism. The corrected intensities, $I_3^{\text{corr}}$, were determined by using the usual expressions cited in the literature (6).

Finally, to verify the behaviour of solid solutions in which $\text{Ps}$ formation, both in the matrix and in the guest molecules, is efficient, we have studied the system $\text{Al}_{1-x}\text{Ir}_x(\text{acac})_3$. The $\text{o-Ps}$ intensity, $\text{o-Ps lifetime}$, and FWHM for the pure Ir(III) acetylacetonate are: 27.00 %, 1.180 ns and 2.57 keV. For this system $I_3$ decreases linearly with $X$, according to

$$I_3 = [I_3^{0}(\text{Al})\cdot X_{(\text{Al})}] + [I_3^{0}(\text{Ir})\cdot X_{(\text{Ir})}]$$

while $\tau_3$ remains practically constant in the full range of the studied concentration.

For all the studied systems it was observed that for the corresponding mixtures, prepared as blanks, $I_3$ decreases linearly with the concentration and $\tau_3$ remains constant and near the $\text{o-Ps}$ lifetime of the matrix compound, as observed before (1,2).

REFERENCES


[Acknowledgements to FAPEMIG, CAPES and CNPq]