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ABSTRACT

Positron lifetime studies were performed in the amorphous and liquid phases of glycerol-water solutions over a broad temperature range. The effect of various inorganic quenchers and inhibitors of different concentrations was investigated in both phases. The temperature dependence of the quenching supports the assumption that the quenching is diffusion-controlled. Significant changes in the lifetime parameters were found in the vicinity of the phase transformation temperature.

АННОТАЦИЯ

Проводились измерения длительности жизни позитронов в смеси глицерина с водой в широком диапазоне температур в аморфной и жидкой фазах. В обеих фазах изучалось влияние неорганических гасящих и ингибиторных добавок различной концентрации. Измеренная температурная зависимость подтверждает предположение о значительном влиянии диффузии на явление гашения. Измерены существенные изменения параметров длительности жизни вблизи температуры фазовых переходов.

KIVONAT

Pozitron-élettartam méréseket végeztünk glicerin-víz keverékben széles hőmérséklet-tartományban amorf és folyadék-fázisban. Mindkét fázisban tanulmányoztuk különböző koncentrációban bevitt szervesetlen quencher és inhibitor anyagok hatását. A quenches mért hőmérsékletfüggése alátámasztja azt a feltevést, hogy a jelenséget a diffúzió nagyban befolyásolja. Az élettartam-paraméterekben jelentős változást mértünk a fázisátmeneti hőmérséklet közelében.

1. INTRODUCTION

Recently an extremely active interest has been shown in positronium chemistry, especially in questions concerning the inhibition and quenching of positronium and its formation in different substances [1-7]. The kinetics of positronium reactions have been investigated extensively [8-14] and many enlightening conclusions have been drawn mainly on results of positron lifetime measurements carried out using a broad range of chemicals of different concentrations [15-35].

In an "ideal pure" substance where positronium can be formed it is assumed that the positron lifetime spectrum is composed of three components: $\tau_0/\sim 0.1$ ns/ with intensity I_0 representing the annihilation of p-Ps, $\tau_{1f}/\sim 0.2-0.4$ ns/ with I_{1f} intensity originating from the so-called "free annihilation", $\tau_2/\sim 0.7-5$ ns/ with intensity I_2 belonging to the annihilation of o-Ps. If inhibition of positronium formation is caused by certain chemicals the I_2 value will decrease - depending on the concentration of the reagent - leaving the value of τ_2 constant. On the other hand the positronium quenching will result predominantly in a decrease of the lifetime of the o-Ps. If both effects are present at the same time it can be quite hard to determine the correct values of τ_2 , I_2 since the assumption $I_2 = 3 I_0$ no longer holds true thereby increasing the uncertainties of the evaluation. In most cases the evaluation is somewhat uncertain so far as the short lifetime value and its intensity are concerned, with only the $I_1 = I_0 + I_{1f}$, $\tau_1 = f(\tau_0, \tau_{1f})$ and τ_2 , I_2 parameters being calculated from the measured spectra. The investigation of positron annihilation in the liquid and amorphous phases of glycerol-water solutions can be of special importance because the inhibition and quenching effects of solutes could possibly be adequately distinguished when performing the measurements in a broad temperature range.

Our aim has been to study the inhibition and quenching procedures in the presence of various inorganic ions of different concentrations in liquid and solid phases of glycerol-water, studying at the same time the formation and annihilation of Ps and its phase-dependence, to determine whether it could be influenced by inhibitors and quenchers in the solid phase, indicating thus the formation of positronium.

It has been expected at one and the same time that such measurements might well yield useful information about the validity of the spur reaction model [6].

2. EXPERIMENTAL

A glycerol-water /13 % H₂O/ solution was chosen as basic material for the experiments because it has a well-known glassy structure in the solid phase and on the other hand due to its being a suitable solvent for the chemicals used. The selection of chemical reagents based on previous results was intended to include possible pure inhibitor, quencher-inhibitor and "neutral" diamagnetic reagents.

The glycerol and all the other chemicals used were of analytical purity and were produced by REANAL, Budapest. The lifetime measurements were carried out using a fast-slow coincidence apparatus of improved energy selection and self-resolution shape with the use of NE 111 scintillators, XP 1023 photomultipliers and ELSCINT STD N-1 /snap-off/ discriminators. After selecting the proper input signal range by appropriately chosen attenuators [36], a 290 ps FWHM value - as determined by ⁶⁰Co - was achieved and maintained during all the measurements. The measured spectra were recorded on a 512-channel multichannel analyser.

The measurements have been performed using ²²Na of some 20 μCi activity diffused into very thin glass foils by thermic ion exchange [37,38]. All sample preparations were carried out by carefully reproducing the procedure developed and described earlier [38].

The temperature dependence of the annihilation spectra was measured by applying a cold-finger type cryostat - similar to that in ref. [37] - filled with liquid nitrogen.

Computer evaluation of the spectra was done by a least-squares fitting program. The evaluation was performed with the assumption of two and three components with the two-component evaluation yielding better X² values. Consequently, we used the results of the two-component evaluation not forgetting the possible slight changes of τ₂, I₂ caused by this artificial limitation [7]. Special care was taken to avoid fast cooling and freezing as it had been proved earlier [19] to affect strongly the I₂ values measured in the solid phase.

3. RESULTS

The dependence of τ₂ values on temperature for the pure solvent and the solutions are shown in Fig. 1/a, while that of I₂ values for the same set of samples is shown in Fig. 1/b. The results clearly show the inhibition and quenching of Fe/ClO₄/₂ depending on its concentration and, moreover the

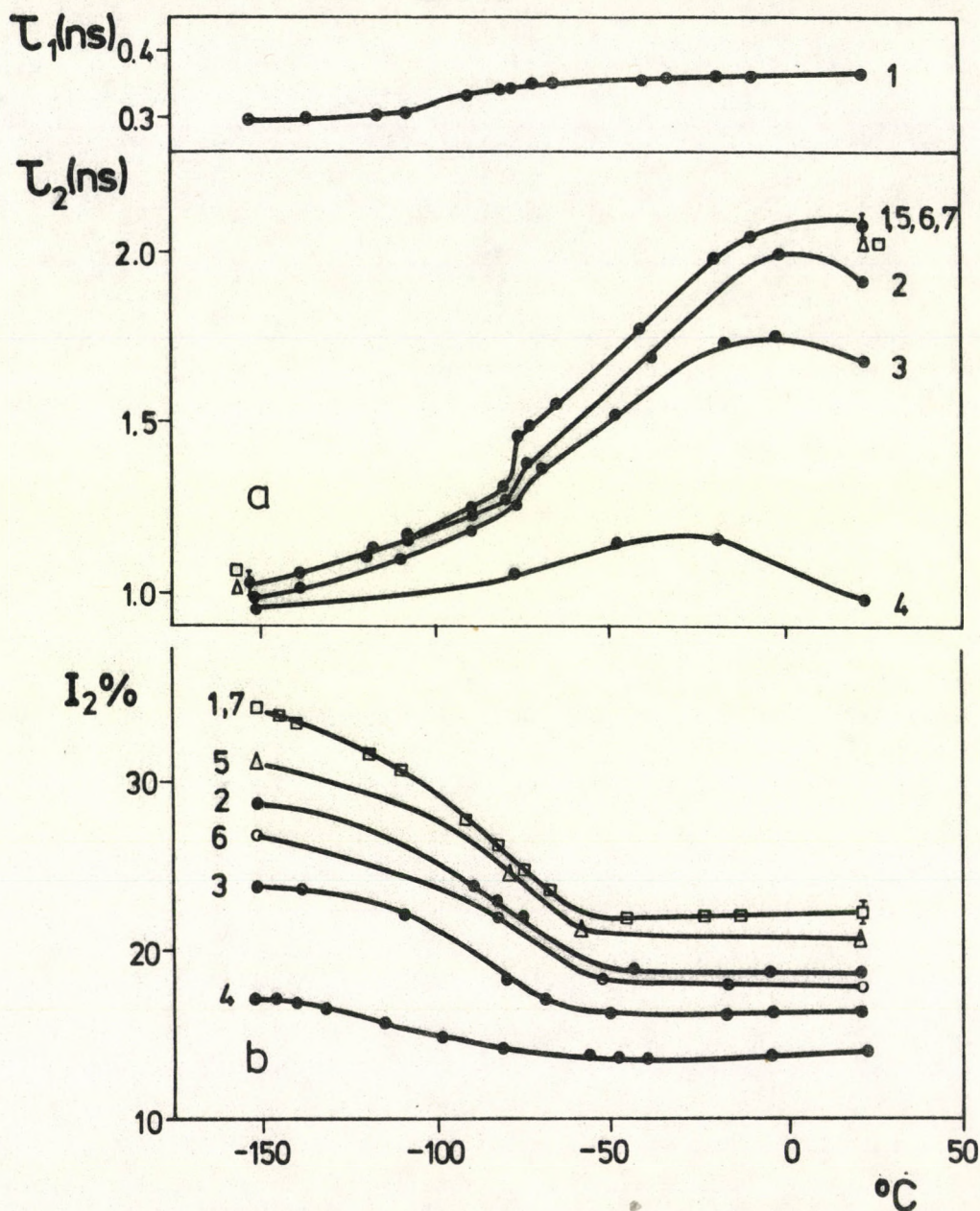


Fig. 1. The temperature dependence of τ_1, τ_2 / /a/ and I_2 / /b/ values measured in pure glycerol-water /13 wt% H_2O / solution and in the presence of various quenchers and inhibitors.
 1., pure glycerol-water; 2., 0,05 M $Fe/ClO_4/2$;
 3., 0,25 M $Fe/ClO_4/2$; 4., 1,25 M $Fe/ClO_4/2$;
 5., Δ 0,05 M $Mg/ClO_4/2$; 6., 0,1 M $HClO_4$; 7., \square 0,05 M $NaClO_4$

"inertness" of $NaClO_4$. The concentrations of $NaClO_4$ and $HClO_4$ solutions were chosen so as to keep these solutions containing ClO_4^- ions the same as in $Fe/ClO_4/2$ solutions. The temperature dependence of $Fe/ClO_4/2$ solutions shows maximum in τ_2 with decreasing temperature. In the range of lower temperatures τ_2 has nearly the same values more or less independently of the amount of

chemicals used.

It is apparent from the figure that the addition of HClO_4 to the glycerol causes an inhibition of Ps formation both in the solid glass and liquid phases. It should be noted that the measure of decrease in I_2 is approximately the same in both phases thereby showing the inhibition of the long-lived formation. With decreasing temperature the I_2 value increases for all the components investigated.

There is a significant change in lifetime parameters in the vicinity of the glass transformation temperature [39].

The inhibition effect caused by $\text{Fe/ClO}_4/2$ is attributable to electron scavenging by Fe^{2+} in the positron spur. Similar explanation can be given for the inhibition by $\text{Mg/ClO}_4/2$ too.

A reasonable interpretation of the inhibition effect of HClO_4 is that it is due to the presence of H^+ ions; the ClO_4^- ion seems not to have an effect because in NaClO_4 solutions the inhibition effect was not observed.

In the solid phase the inhibition, i.e. the decrease in I_2 as compared to the I_2 value of glycerol-water, is remarkable giving evidence that the inhibition is not controlled by the diffusion of electron acceptors. This fact seems to support the spur model since the number of electrons in the spur - possibly moving equally well both in the solid and in the liquid phase - attracted by positive ions resulting thus in a decrease in Ps formation may be similar if these positive ions diffuse in the liquid phase or are strongly localized in the glassy phase. The very few measurements reported in glassy phases when investigating quenching and inhibition [9,40] state the possibility of Ps-formation in amorphous solids, but some of the results obtained from solid molecular substances showed evidence not of positronium but of some other positron bound-system formation, underlining the importance of the basic material used.

The increase of I_2 with decreasing temperature is a noteworthy effect but for its interpretation further studies are required.

The quenching effect of $\text{Fe/ClO}_4/2$ can be attributed to the paramagnetic Fe^{2+} ions. The concentration-dependent maximum in τ_2 values for glycerol containing $\text{Fe/ClO}_4/2$ seems to suggest a diffusion-controlled character for the quenching. The motion of Fe^{2+} ions is slowed down by the strongly increasing viscosity of glycerol as the temperature decreases; the higher the concentration of the paramagnetic Fe^{2+} ions the lower the temperature belonging to the above maximum /i.e. the higher the quenching effect of the Fe^{2+} ions "enclosed" by the viscous liquid which accounts for the remaining quenching in the case of higher Fe^{2+} concentration/. The decrease of τ_2 at lower temperature stems from the decrease in the free volume in the system.

These results show that the glycerol-water system is a useful solvent for the investigation of quenching and inhibition of the ions and enables the separation of the quenching and inhibition effects in different phases.

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