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Inhibition and Quenching of Positronium in Polymeric materials

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Abstract: Positron Annihilation Lifetime Spectroscopy (PALS) is used to study the effect of doping on the microstructure of polymeric materials. In case of halogens and metal salts as dopants, a decrease in ortho-Positronium (o-Ps) life time (τ_3) and intensity (I_3) is observed with increase in concentration of the dopant in the host (polymeric material). The inhibition and quenching of positronium by the dopant has been quantitatively investigated, and the inhibition constant is determined for the case of iodine doped polyvinylalcohol (PVA) to be $\alpha = 0.029$ mol^{-1}. It is $\alpha = 0.022$ mol^{-1} in silver nitrate doped polyacrylamide (PAM) and $\alpha = 0.072$ mol^{-1} in barium chloride doped PVA. The inhibition of positronium formation is found to be more dominant than the quenching process in these samples. The calculations of inhibition constant and quenching rate constant are discussed.
Keywords: Inhibition, Quenching, Positronium, Positron lifetime technique, Doped polymeric materials.

1. Introduction:

Positron Annihilation Lifetime Spectroscopy (PALS) is used to study the changes in free volume size and concentration of free volume holes in polymeric materials which have been subjected to doping with chemical agents [1-5]. The process of doping involves treating the polymeric material with chemical agents like halogens, involves red-ox reactions with polymers, and a concomitant increase in electrical conductivity of the material. In case of polymers, the PALS spectrum is analyzed to extract three lifetime components and their corresponding intensity using a computer program [6]. The longest lifetime component (τ_3) corresponds to ortho-positronium (o-Ps) life time. The corresponding intensity (I_3) is a measure of number density of free volume holes, and is a measure of probability of positronium (Ps) formation in the polymeric material. The process of quenching and inhibition of Ps has been described by Tao [7-8].

2. Results and Discussion:

The research work on doped polymeric systems using PALS in the case of halogen doped polymeric materials reveals that iodine acts as both a chemical quenching agent and an inhibitor of Ps formation [1]. A polymer – iodine complex could be a weak quencher of o-Ps, and a stronger inhibitor of Ps formation, when compared to free polymer molecules. The intensity (I_3) decreases on initial doping of concentration, whereas the decrease in τ_3 is small, indicating the inhibition of Ps is dominant. The estimation of free volume hole size from o-Ps lifetime is complicated in this case, because of the process of quenching of positronium. The interaction of dopant ions with Ps gives rise to an oxidation reaction which leads to reduction in lifetime of Ps in polymer matrix. The positronium reaction behavior can be detected by using an expression of ortho-positronium reaction rate,

$$\lambda_3 = \lambda_3^o + kC \qquad (1)$$

In equation (1), λ_3 and λ_3^o are the o-Ps annihilation rates at concentration '*C*' of the dopant and in pure matrix (*C*=0) respectively, and '*k*' is the reaction rate constant which is obtained from the slope of the plot of o-Ps annihilation rate λ_3 ($= \tau_3^{-1}$) verses dopant concentration (*C*). This linear behavior indicates that quenching of positronium takes place in the system. The decrease in the o-Ps intensity I_3 is due to reduction in the number density of o-Ps annihilation sites. It could also be due to decrease in the probability of o-Ps formation (inhibition of Ps formation). The inhibition constant (α) can be calculated from the intensity of o-Ps component (I_3) at different concentrations of the dopant.

$$\alpha = \frac{1}{C}\left(\frac{I_3(0)}{I_3(C)}\right) - 1 \qquad (2)$$

In equation (2), α is inhibition constant, $I_3(0)$ is o-Ps intensity at zero concentration of dopant (undoped sample) and $I_3(C)$ is o-Ps intensity at the dopant concentration '*C*'. The variation of I_3 versus iodine concentration (*C*) in PVA sample is shown in figure (1), for low concentrations of the dopant. The plot reflects the changes in Ps formation probability in the sample. The inhibition of Ps formation is responsible for the sudden drop in the intensity I_3 at lower concentration of the dopant. In the case of iodine doped PVA [1], inhibition of Ps formation is more dominant than the quenching of Ps. In order to understand the inhibition process, I_3 verses inhibition relation, i.e., ratio of $I_3(0)$ to $I_3(C)$, is plotted for different dopant concentrations (*C*), and from the slope of linear fit, the inhibition constant (α) value is obtained. This linear behavior (see figure 2) confirms the strong inhibition characteristics of sample for the formation of the Ps within the composite film of dopant and polymer. The PALS study of barium chloride ($BaCl_2$) doped PVA [2] shows that both life time of o-Ps τ_3 and corresponding intensity I_3 decrease, as the concentration of the dopant ($BaCl_2$) increases. The inhibition constant (α) for $BaCl_2$ doped PVA is calculated to be 0.072 mol^{-1}.

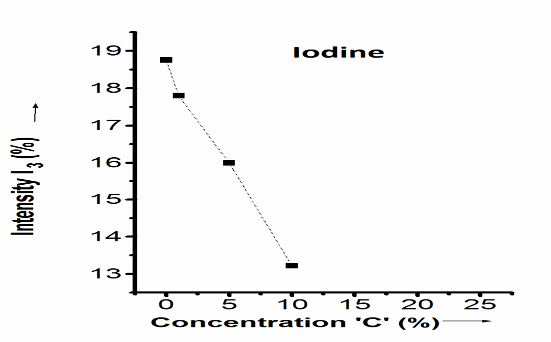

Figure 1. The decrease in I_3 relative to concentration C in case of iodine doped PVA, at lower concentrations of the dopant.

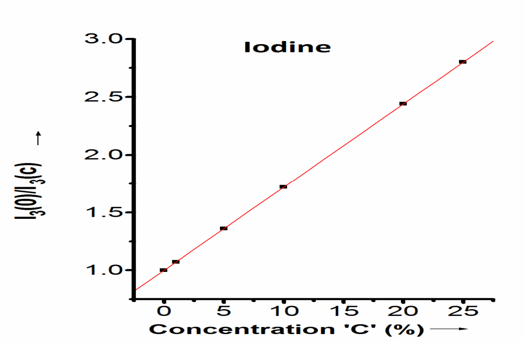

Figure 2. The plot of ratio of $I_3(0)$ to $I_3(C)$ versus Concentration (*C*) of iodine in PVA. The Slope of straight line fit is inhibition constant α = 0.029 mol^{-1} for iodine doped PVA.

Silver nitrate ($AgNO_3$) doped polyacrylamide (PAM) samples were studied by Mukherjee *et al*. [9]. Using the data from this paper, the positron behavior was investigated. It was found that chemical quenching is not the suitable mechanism in $AgNO_3$ doped PAM, but the plot of ratio of $I_3(0)$ to $I_3(C)$ versus Concentration (C) of $AgNO_3$ in PAM gave a very good linear fit, from which the inhibition constant was determined for this sample to be 0.022 mol^{-1}.

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