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Positronium formation in molecular media: The effect of the external electric field

Sergey V. Stepanov,[1] Vsevolod M. Byakov,[1] and Yoshinori Kobayashi[2]
[1]*Institute of Theoretical and Experimental Physics, Moscow 117218, Russia*
[2]*National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan*

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A model is described for positronium (Ps) formation in molecular liquids and polymers. The developed model explicitly takes into account the electrostatic attraction between a deenergized positron and the terminal positron blob. This interaction is caused by the Debye screening of e^+ by intrablob electrons. The positron distribution function is divided into two parts, one describing the positrons e^+_{in} residing within the blob and the other describing the positrons e^+_{out} originally thermalized outside the blob. Because of the energy preference for e^+ to reside within the blob, diffusing e^+_{out} is partially converted to e^+_{in}. An external electric field shifts the e^+_{out} distribution aside from the center of the blob, reduces its diffusion flux into the blob and decreases the Ps yield. The model is compared with experimental data of the electric field effect on Ps formation in neat liquids, amorphous SiO_2, and polymers.

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I. INTRODUCTION

It is well known that positronium (Ps) formation is strongly influenced by external electric fields. First experiments were carried out in low-density simple atomic gases, where Ps is formed predominantly according to the Ore mechanism.[1–3] It implies that a "hot" positron e^{+*} pulls out an electron from a molecule M, forming a Ps atom and leaving behind the radical cation $M^{+\cdot}$: $e^{+*}+M \rightarrow Ps+M^{+\cdot}$. This process is most effective, when the energy W of the positron lies within the interval called the ore gap: $I_G - Ry/2 < W < W_{\text{ex}}$. Here I_G is the first ionization potential of the molecule, W_{ex} is its electronic excitation threshold, and $Ry/2 = 6.8$ eV is the Ps binding energy in vacuum. It is believed that the positron with the energy lower than $I_G - Ry/2$ cannot pick up an electron from a molecule. When $W > W_{\text{ex}}$ electronic excitations and ionizations compete with electron extraction and Ps formation becomes less effective.

Since the mid-1970's Ps formation in the presence of electric fields has been also investigated in liquid and solid paraffins[4,5] as well as in some pure liquids.[6–8] Very high fields ($\gtrsim 1$ MV/cm) overcome the stopping power of the medium related to vibrational excitations (~ 0.01 eV/Å) and accelerate positrons up to the ionization threshold, making them able to ionize molecules, which results in a drastic increase of Ps formation.[9] On the other hand, separation of e^+ from e^- in the presence of moderate electric fields with $D \lesssim 100$ kV/cm causes a reduction of Ps formation in nonpolar liquids and polymers, where e^+ has larger thermalization lengths and mobilities than e^-.[10–13] Nontrivial behavior of the Ps yield vs electric field has been observed in irradiated polymers[14] and in polyethylene (PE) at different temperatures[15] as well as in doped polymers[5] and mixtures.[16,17]

Energetic consideration of the Ps formation shows that the Ore mechanism is inefficient in condensed molecular substances.[18] The Ore gap gets very narrow or even disappears completely. Therefore, the so-called recombination mechanism, according to which Ps is formed via combination of a deenergized positron with one of the electrons in the terminal part of the positron track,[19,20] becomes the main channel of Ps formation. There are two models based on this mechanism, namely, the spur model[21,22] and the blob or the diffusion-recombination model (see Ref. 23, and references therein). In spite of the fact that both of them consider an intratrack electron as a precursor of Ps, they differ in what constitutes the terminal part of the e^+ track.

The quantitative interpretation of the electric field effect on Ps formation within the framework of the spur model relies on the Onsager theory of geminate recombination.[21] At the low-field limit it is reduced to the following formula for Ps formation probability:

$$P_{\text{gr}} = 1 - \left(1 + \frac{eDr_c}{2T}\right)\exp\left(-\frac{r_c}{r_0}\right), \quad r_c = \frac{e^2}{\varepsilon T}. \tag{1}$$

However, some essential problems of this approach were pointed out.[18] Equation (1) has only one fitting parameter r_0, the initial separation of the e^+-e^- pair (r_c is the Onsager radius). Obviously it is not enough to reproduce both the initial Ps yield $P_{\text{Ps}}(D=0)$ and the field dependence of $P_{\text{Ps}}(D)$. This is the reason why experimentalists fit only normalized data of the Ps yield $P_{\text{Ps}}(D)/P_{\text{Ps}}(0)$, paying attention only to the decrement of $P_{\text{Ps}}(D)$ vs D and r_0.

The spur model is based on a two-particle approximation and ignores the fact that Ps formation in condensed medium takes place in the terminal e^+ blob, containing a large number (20–30) of overlapped ion-electron pairs, but not in a spur having a few ion-electron pairs. Meanwhile the blob model is formulated in terms of equations of chemical kinetics and better suited for consideration of intratrack processes involving a large number of the primary particles. The original version of the blob model ("white blob model") neglects any interaction of the positron and its blob. We adopted this assumption because of the presence of two opposite effects. (1) Outdiffusion of intrablob electrons. This makes the outdiffused electrons to reside in an outer region of the blob, which results in the appearance of an excess positive charge in its central region, repelling e^+ from the blob. (2) Rearrangement of intrablob electrons by the presence of e^+ within the blob. This may decrease the total energy of the system because of the Debye screening, resulting in attractive interaction between e^+ and the blob. Recently the blob model was successfully applied to the explanation of the age-momentum correlation data of a polymer[25] and kinetics of accumulation of radiolytic products in aqueous solutions.[26,27]

Here we further develop the blob model for the interpretation of the electric field effect on Ps formation in pure liquids, amorphous SiO_2, and doped polymers. The present formulation takes explicitly into account the electrostatic attraction between a deenergized positron and its terminal blob. We shall call this model the "black blob" model, which indicates that the blob may trap (epi)thermal positrons.[28]

II. QUALITATIVE IDEAS

Just after the last ionization event, spatial distribution of a subionizing positron with some eV of kinetic energy e^{+*} is approximated as a Gaussian function $\exp(-r^2/a_{\text{bl}}^2)$, with dispersion a_{bl}^2 as that of the other intrablob particles. If e^{+*} loses the energy inside the blob, it rearranges the intrablob electron density in such a way that the total energy of the system is minimized because of the Debye screening. The corresponding energy drop is estimated as $W_s \approx e^2/\varepsilon(r_D + a_{\text{bl}}/n_0^{1/3})$, where n_0 is the initial number of ion-electron pairs in the blob and $r_D \approx (4\pi r_c c_{iep})^{-1/2}$ is the Debye radius. If one takes $n_0 \approx 30$ and $a_{\text{bl}} \approx 40$ Å, the initial concentration of ion-electron pairs in the blob, $c_{iep} \approx n_0/\frac{4}{3}\pi a_{\text{bl}}^3 \approx 0.2$ M. So the Debye radius $r_D \approx 4$ Å turns out small in comparison with the average distance $a_{\text{bl}}/n_0^{1/3} \approx 20$ Å between the intrablob electrons. Therefore, W_s becomes of the order of $Tn_0^{1/3} r_c/a_{\text{bl}} = n_0^{1/3} e^2/\varepsilon a_{\text{bl}}$, which is several tenths of eV. This amount of energy is quite sufficient for trapping the thermalized and even some epithermal positrons within the blob.

In contrast to the intrablob electrons, which are tightly kept by electric fields of the positive ions, the subionizing positron easily escapes from the electrically neutral blob. On the other hand, a deenergized intrablob positron cannot escape from the blob as free e^+ because of the Debye screening. Thus it is necessary to distinguish between the inside (e_{in}^+) and outside (e_{out}^+) positrons. When diffusing e_{out}^+ reaches the blob it becomes trapped therein and is converted to e_{in}^+. e_{in}^+, originally thermalized within the blob or entered it later, has a certain probability of forming Ps with one of the intrablob electrons through the reaction $e_{\text{in}}^+ + e^- \rightarrow \text{Ps}$.

Moderate external electric fields ($D < 100$ kV/cm) can neither detrap e_{in}^+ from the blob ($eDa_{\text{bl}}/\varepsilon < W_s$) nor "heat" it ($eD/\varepsilon < |dW_p/dx| \sim 0.01$ eV/Å). They shift the e_{out}^+ distribution, thereby diminishing the diffusion flux of e_{out}^+ into the blob, Fig. 1. This reduces the Ps formation probability P_{Ps}. The above approach naturally explains the electric field effect in PE at low temperatures,[15] where there exists an additional channel of Ps formation, e^+ combination with one of trapped electrons produced as a result of continuous positron irradiation.[29]

The first stage of Ps formation is the encounter of a positron with one of the intrablob electrons, followed by the formation of a weakly bound $e^+ \cdots e^-$ pair. Having about 1 eV of excess energy accumulated in the form of the potential energy of the mutual Coulombic attraction, this pair is transformed to quasifree (QF) Ps in the bottom of the lower-energy band, which is available to an interacting e^+-e^- pair before any rearrangement of the surrounding molecules. Excess energy of the $e^+ \cdots e^-$ pair is lost by vibrational excitations. In this process the total momentum is not conserved, and the pair may gain a certain amount of momentum. Its displacement during the $e^+ \cdots e^- \rightarrow$QF-Ps transition is estimated ~ 50 Å. Thus, whereas a thermalized positron cannot escape from the blob, an electrically neutral e^+-e^- pair can do so.

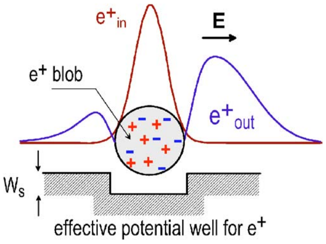

FIG. 1. (Color online) Spatial distribution of the positron density at the Ps formation stage in the presence of an external electric field $\mathbf{E} = \mathbf{D}/\varepsilon$. e_{in}^+ is the density of the positrons bounded within the blob and not perturbed by $\mathbf{E}$. The other part e_{out}^+ is biased by the field.

The last stage of Ps formation is the transformation of QF-Ps to localized Ps. The driving force of this process is the repulsive exchange interaction between the electron constituting the Ps atom and electrons of surrounding molecules. In liquids, the transformation of QF-Ps to localized Ps results in the formation of the Ps bubble.[30]

III. QUANTITATIVE FORMULATION OF THE MODEL

From Fig. 1 it is clear that the assumption of Gaussian distribution functions for all the reactants in the "white" blob model[10,18] is not appropriate, because the e^+ distribution significantly differs from the Gaussian distribution when $W_p < W_s$. So, to evaluate the Ps formation probability we have to calculate the initial e^+ fraction captured inside the blob and then the field-dependent increment of the intrablob positron fraction based on diffusion flux J of e_{out}^+ into the blob. To simulate the attraction between e^+ and its blob we introduce an absorbing or "black" sphere, contrary to the previous white blob model, where any interaction between e^+ and the blob is ignored.

Let a be the radius of the absorbing sphere. Suppose that at $t=0$ positron trapping is just started, i.e., W_p becomes equal to W_s. Just before $t=0$ the e^+ distribution is a Gaussian

$$c_p(\mathbf{r},0) = \frac{1}{\pi^{3/2} a_p^3(0)} \exp\left\{-\frac{[\mathbf{r} - \mathbf{l}_p(0)]^2}{a_p^2(0)}\right\}, \qquad (2)$$

where $l_p(0)$ is the field induced displacement of the e^+ distribution during its thermalization. It is slightly broader than the distribution of the intrablob species, because e^{+*} may escape from the blob during its slowing down from W_0

$\approx 3-5$ eV (on average) down to W_s. Blob expansion during Ps formation is practically negligible; it is governed by the ambipolar diffusion law and proceeds rather slowly owing to the low cation mobility.[18] Thus dispersion $a_p^2(0)$ of c_p is larger than that of the intrablob species $a_{\rm bl}^2$:

$$a_p^2(0) - a_{\rm bl}^2 \approx 4D_p t_{sd} \approx 4D_p \frac{W_0 - W_s}{|dW_p/dt|}. \tag{3}$$

Here t_{sd} is the slowing down time, $D_p = b_p T/e$ is the e^+ diffusion coefficient, and $b_p \sim 10$ (cm^2/V·s is its mobility.[5,12] For a subionizing positron the average energy loss rate $\langle |dW_p/dt| \rangle$ is $\leqslant 0.1$ eV/fs.[32,33] Thus, we obtain $\sqrt{a_p^2(0) - a_{\rm bl}^2} \approx 20-50$ Å. Field-dependent drift of e^{+*} during the slowing down time may be estimated as [see Eq. (3)]

$$\mathbf{l}_p(0) \approx b_p \frac{\mathbf{D}}{\varepsilon} t_{sd} = \frac{e\mathbf{D}}{\varepsilon T} D_p t_{sd} = \frac{e\mathbf{D}[a_p^2(0) - a_{\rm bl}^2]}{4\varepsilon T}. \tag{4}$$

However, this formula overestimates the e^{+*} bias because within the blob the external electric field is efficiently screened by the intrablob charged species.

At $t > 0$ we assume that the positron distribution (2) breaks into two parts. The inner part $c_p(r,t)\theta(a-r)$, describing $e^+_{\rm in}$, rapidly tunes up to the distribution of the intratrack species and becomes proportional to $\exp(-r^2/a_{\rm bl}^2)$. Here we use the following definition of the θ function: if the argument of the θ function is positive, it is equal to unity, in the opposite case it is zero. The outer part $c_p(r,t)\theta(r-a)$ represents the spatial distribution of $e^+_{\rm out}$. Initial positron fractions inside and outside the absorbing sphere at $t=0$ are

$$n_{\rm in}(0) = \int_{r<a} c_p(r,0) d^3 r = \frac{1}{2}\left[\operatorname{erf}(\alpha+\delta) + \frac{\alpha-\delta}{|\alpha-\delta|} \operatorname{erf}|\alpha-\delta| - \frac{e^{-(\alpha-\delta)^2} - e^{-(\alpha+\delta)^2}}{\sqrt{\pi}\delta} \right], \tag{5}$$

$$n_{\rm out}(0) = \int_{r>a} c_p(r,0) d^3 r = 1 - n_{\rm in}(0), \quad \alpha = \frac{a}{a_p(0)}, \quad \delta = \frac{l_p(0)}{a_p(0)}. \tag{6}$$

If there is an additive or scavenger (S), which captures hot positrons, the right-hand side of Eqs. (2), (5), and (6) should be multiplied by $1 - F_+ + F_+ \exp(-c_S/c_{37}^+)$, which represents the probability of e^{+*} escaping the resonance capture by S.[24]

In the absence of external fields ($D=0$) the total diffusion flux $J(t)$ of $e^+_{\rm out}$ into the absorbing sphere is calculated exactly:

$$\begin{aligned} J(t) &= 4\pi a^2 D_p \cdot \nabla\ c_p(r>a,t)|_{r=a} \\ &= \frac{4\pi a}{t} \int_0^\infty r(r+a) G(r,t) c_p(r+a,0) dr \\ &= \frac{4D_p}{\sqrt{\pi} a_p^2(0)} \frac{\alpha}{(1+\vartheta)^{3/2}} \left[e^{-\alpha^2/(1+\vartheta)} \left(1 - \frac{2\alpha^2}{1+\vartheta}\right) \times \operatorname{erfc}\left(\alpha\sqrt{\frac{\vartheta}{1+\vartheta}}\right) + \frac{2\alpha e^{-\alpha^2}}{\sqrt{\pi\vartheta(1+\vartheta)}} \right], \end{aligned}$$

$$c_p(r,0) = \frac{\exp[-r^2/a_p^2(0)]}{\pi^{3/2} a_p^3(0)}, \quad G(r,t) = \frac{\exp(-r^2/4D_p t)}{\sqrt{4\pi D_p t}}, \quad \vartheta = \frac{4D_p t}{a_p^2(0)}. \tag{7}$$

Here we used the standard representation for the solution of a one-dimensional radial diffusion equation through the Green function $G(r,t)$:

$$c_p(r,t) = \frac{1}{r}\int_0^\infty [G(r-a-s,t) - G(r-a+s,t)](s+a) \times c_p(s+a,0) ds. \tag{8}$$

When $D > 0$, there are essential analytical difficulties in the calculation of $J(t)$. So we do the calculation approximately, multiplying $J(t)$ by $\exp[-l_p^2(t)/a_p^2(t)]$, which roughly takes account of the field-dependent bias of $e^+_{\rm out}$. In this exponential

$$l_p(t) = l_p(0) + \frac{eD}{\varepsilon T} D_p t = \frac{eD[a_p^2(t) - a_{\rm bl}^2]}{4\varepsilon T}, \quad a_p^2(t) = a_p^2(0) + 4D_p t. \tag{9}$$

Ps formation probability is obtained as follows:

$$P_{\rm Ps} = k_{ep} \int_0^\infty \frac{n_e n_p^{\rm in}}{V_{\rm bl}} dt. \tag{10}$$

Here $n_p^{\rm in}(t)$ is the in-blob positron fraction, which obeys the equation

$$\dot{n}_p^{\rm in}(t) = J(t) e^{-\lambda_p t} - k_{ep} n_e n_p^{\rm in}/V_{\rm bl} - \lambda_p n_p^{\rm in}, \quad V_{\rm bl} = (2\pi)^{3/2} a_{\rm bl}^3. \tag{11}$$

This equation as well as Eqs. (12) and (13) below is obtained using the prescribed diffusion method.[18,23] Here $\lambda_p = \lambda_2 + k_{pS} c_S$ is the disappearance rate of e^+ due to annihilation ($\lambda_2 = 1/\tau_2$, see Table I) and capture by the solute ($k_{pS} c_S$). It means that the e^+S complex does not contribute to Ps formation. Factor $1/V_{\rm bl}$ on the RHS of Eq. (11) appears because of the assumption that all intrablob species ($e^+_{\rm in}$, e^-, ions) have the same time-independent spatial distribution $\propto \exp(-r^2/a_{\rm bl}^2)$ at all t.

In Eqs. (10) and (11) $n_e(t)$ stands for the number of intrablob electrons. It decreases due to the ion-electron recombination and reaction with the solute

$$\dot{n}_e(t) = -k_{ie} n_i n_e / V_{\rm bl} - k_{eS} c_S n_e, \quad n_e(0) = (1 - F_- + F_- e^{-c_S/c_{37}^-}) n_0, \tag{12}$$

where k_{ie} and k_{eS} are the respective rate constants. The expression for $n_e(0)$ takes account of the possible capture of hot intrablob electrons by the scavenger. A similar equation holds for the number of ions in the blob:

TABLE I. Results of the fit according to the black blob model. $a_{\rm bl}$ was assumed to be equal to 80 Å. For liquids $\tau_{\rm IMR}$ was varied from 10 ps to 1 ns (however, the results are practically undistinguishable.)

Medium	ε	b_p,[a]	b_e	$a_p(0)$ Å	a Å	$k_{ep}\times 10^{-12}$ $M^{-1}\,s^{-1}$	$k_{ie}\times 10^{-12}$ [b] $M^{-1}\,s^{-1}$	$\tau_{\rm IMR}$ ns	τ_2 ns
		cm^2 V^{-1} s^{-1}							
n-C_6H_{14}	1.89	100(9)	0.09	90	64(1)	3.7(1)	60	0.01	0.55
				90	62(1)	21(1)	60	1	
c-C_6H_{12}	2.02	100	0.40	92	52(1)	11(1)	190	0.01	0.50
				92	48(1)	76(4)	190	1	
i-C_8H_{18}	1.94	134(6)	7	95	73(1)	39(1)	2000	0.01	0.53
				95	68(1)	410(10)	2000	1	
C_6H_6	2.28	19(5)	0.13	82	51(1)	13(1)	60[c]	0.01	0.55
				82	49(10)	24(9)	60[c]	1	
amorph-SiO_2	3.9	0(8)		81	97(2)	20(1)	60[c]	∞	0.55
PE Fig. 4(a)	2.3	58(10)	~0.1	87	81(1)	0.8(1)	60[c]	0.01	0.5
PE Fig. 4(b)	2.3[d]	43(10)	~0.1	85	50(1)	1.8(1)	60[c]	0.01	0.5

[a] The data of (Refs. 5 and 12) were multiplied by ε to comply with the definition of b_p here: $\mathbf{v}_p = b_p\mathbf{E}$. For cyclohexane b_p is not available, so we used the value for n-hexane. In the case of experimental $b_p=0$, it was equated to the upper limit given by the reported experimental uncertainty.

[b] Data of k_{ie} were taken from Ref. 35.

[c] For n-C_6H_{14}, c-C_6H_{12}, and i-C_8H_{18} k_{ie} is known. Comparison of the available data with excess electron mobilities b_e showed proportionality $k_{ie}\propto b_e$, which was used to estimate k_{ie} in C_6H_6, SiO_2, and PE.

[d] Numbers of dielectric permittivity of PE/EVA blends with 24, 60, and 100% (weight %) content of EVA are the following: 2.37, 2.70, and 2.88, respectively (Ref. 17).

$$\dot{n}_i(t) = -k_{ie}n_in_e/V_{\rm bl} - n_i/\tau_{\rm IMR}, \quad n_i(0)=n_0, \tag{13}$$

where $\tau_{\rm IMR}^{-1}$ is the ion-molecule reaction rate.

Equations (11)–(13) were solved numerically (Fig. 2) and then using Eq. (10) we calculated the ortho-Ps yield $I_3 = 3P_{\rm Ps}/4\times 100\%$, to compare with the experimental data in Figs. 3 and 4.

IV. STRATEGY OF THE FITTING. RESULTS AND DISCUSSION

Parameters k_{ie}, b_p, and $\tau_{\rm IMR}$ were fixed *a priori* (some k_{ie} and b_p values are available in literature), while k_{ep} and a were obtained by fitting. The ion-molecule reaction time $\tau_{\rm IMR}$ in the investigated media is unknown, but we believe that it lies in the chosen interval 0.01–1 ns (Table I). For SiO_2 $\tau_{\rm IMR}\to\infty$ because ion-molecule reaction does not occur. It is worth mentioning that the data for PE, Fig. 3, were satisfactorily described for $\tau_{\rm IMR}$ not significantly exceeding 0.01 ns.

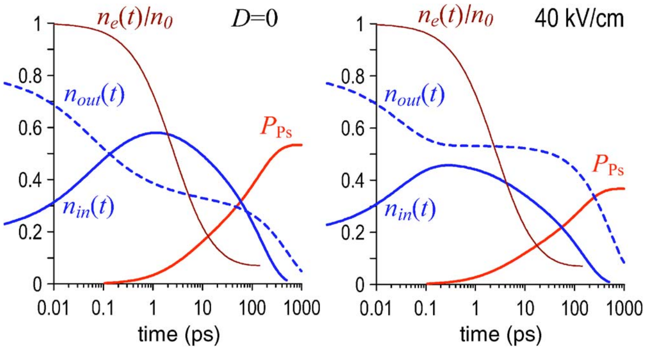

FIG. 2. (Color online) Time evolution of the positron fractions ($e^+_{\rm in}, e^+_{\rm out}$), fractions of the blob electrons and Ps formation probabilities vs t in n-hexane at $D=0$ and $D=40$ kV/cm; $\tau_{\rm IMR}=0.1$ ps.

We equated $a_{\rm bl}$ to 80 Å which was determined by ionization slowing down of the energetic positron during blob formation [in water $a_{\rm bl}$ was estimated 40 Å (Ref. 18)]. $a_p(0)$ and $\mathbf{l}_p(0)$ were calculated based on Eqs. (3) and (4), assuming $\langle W_0\rangle = 3$ eV, $W_s=1$ eV, and $|dW_p/dt| = 10^{14}$ eV/s. Best fit values of a and k_{ep} are given in Table I. $a_p(0)$ is approximately half the values obtained by the white blob model.[10,18] This difference reflects uncertainty in $a_p(0)$ and shows that it is model dependent.

Experimental data in Fig. 3 show that the electric field effect is weakened at high fields. The tendency of the Ps yield leveling off at 50–100 kV/cm is successfully reproduced by the black blob model but not by the white blob model. This is obviously due to the incorporation of a new physical insight in the model, i.e., trapping of the (epi)thermal positron within the blob due to the polarization-electrostatic interaction. Ps formation apparently takes rather long, if there are no competing processes, such as e^+ and e^- scavenging or trapping, Fig. 2.

A. Chlorinated polyethylene

The present model indicates that chlorinated polyethylene (or more specifically the C-Cl bond in it) behaves as a scavenger of hot electrons and inhibits Ps formation in PE, Fig.

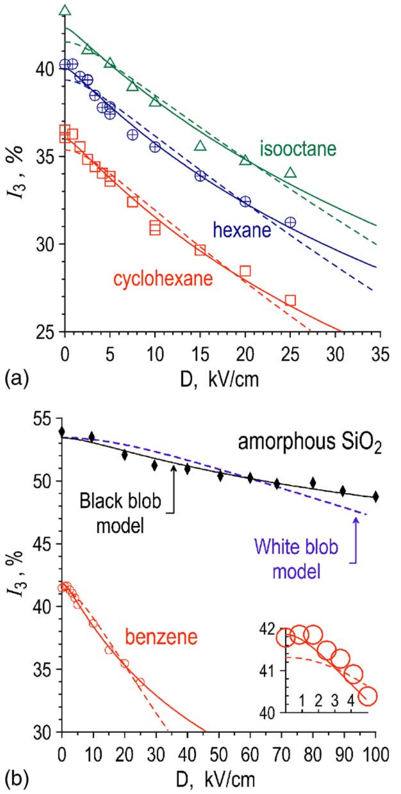

FIG. 3. (Color online) Dependence of o-Ps intensity on external electric field **D** in cyclohexane (□), *n*-hexane (⊕), isooctane (△), amorphous SiO$_2$ (♦), and benzene (○) at room temperature (Refs. 10,31). Solid lines are results obtained with the present model. Results for different τ_{IMR} (see Table I) are essentially identical. Dashed lines represent the fits according to the white blob model (Ref. 18).

4(a). The best fit values of the parameters in Eq. (12) are the following: $F_-=0.6-0.7$, $c_{37}^-=6-8$ M.

An assumption that chlorinated polyethylene (C-Cl) captures thermalized e^- only did not work for whatever value of k_{eS}, which is the only adjustable parameter in the assumption. We also tested a hypothesis of consecutive reactions that Cl firstly captures e^- and then Cl$^-$ traps hot e^{+*}. We found that it was also against the experimental data ($F_+ \to 0$). Finally, another assumption that either chlorinated polyethylene or Cl$^-$ captures a thermalized positron was found to contradict the experiment: $k(e^+ + \mathrm{Cl}) \to 0$ and $k(e^+ + \mathrm{Cl}^-) \to 0$.

B. PE-EVA blends

A more complicated effect is observed in polymer blends of PE and ethylene vinyl acetate copolymer (EVA),[17] Fig. 4(b). In the absence of electric fields the addition of small amounts of EVA to PE decreases the Ps yield. Further addition of EVA results in enhancement of Ps formation and the electric field effect is weakened. The enhancement of the Ps yield was attributed to the decrease in overall crystallinity of the PE/EVA system.[17] However, the disappearance of the enhancement at low temperature observed later[13] may not be fully compatible with this explanation.

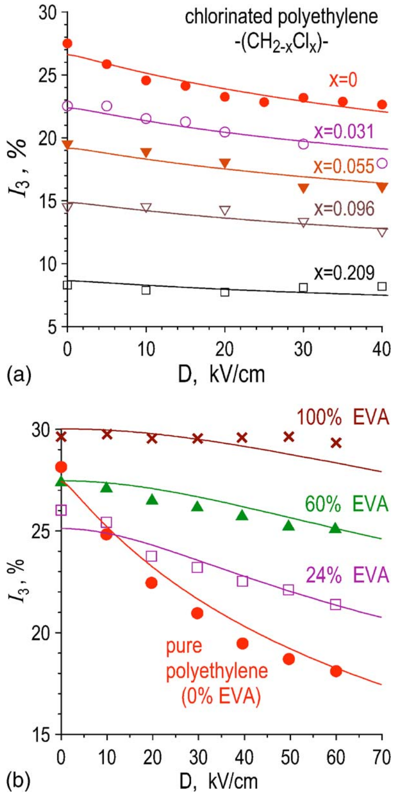

FIG. 4. (Color online) o-Ps intensity vs electric field in chlorinated polyethylene (Ref. 5) and polymer blends between polyethylene (PE) and ethylene vinyl acetate copolymer (EVA) (Ref. 17). Numbers in the figure are EVA contents in weight %. Solid lines represent the fits according to the present model.

One can expect that the high electron density on the C═O bond (carbonyl group) may lead to positron trapping and formation of a bound state,[34] which we denote here as EVAe^+. This process competes with ion-electron recombination and could be responsible for the increase of the Ps yield at high EVA concentrations.

Trapping of e^+_{out} decreases J and, therefore, flattens $P_{\mathrm{Ps}}(D)$. At the same time, one can consider that weakly trapped positrons and electrons, residing within the blob, contribute to Ps formation with roughly the same efficiency as free particles

$$e^+_{\mathrm{in}} + \mathrm{EVA}e^- \to \mathrm{Ps} \quad \text{and} \quad e^- + \mathrm{EVA}e^+ \to \mathrm{Ps}.$$

At high EVA concentrations the following reaction between a trapped electron and a trapped positron may also be possible because of the rather short mutual separations between the two species within the blob: $\mathrm{EVA}e^- + \mathrm{EVA}e^+ \to \mathrm{Ps}$. However, this reaction is supposed to proceed much slowly, so Ps formation in the presence of concentrated vinyl-acetate groups cannot be very high.

All the above processes can be taken into account in the framework of the black blob model. For this we need the following:

(1) Multiply J by $e^{-k_{pS}c_S t}$ (c_S is now the EVA concentration) to account for the trapping of e^+_{out}.

(2) Replace the term $\lambda_p n_p^{\rm in}$ on the RHS of Eq. (11) by $\lambda_2 n_p^{\rm in}$, which implies that the intrablob positron $e_{\rm in}^+$, even trapped by EVA, can participate in Ps formation (with nearly the same rate constant).

(3) Add the following equation for the number of EVAe^-, n_{S^-}:

$$\dot{n}_{S^-}(t) = k_{eS} c_S n_e - k_{pS^-} n_{S^-} n_p^{\rm in}/V_{\rm bl}, \quad n_{S^-}(0) = 0. \qquad (14)$$

(4) Add to the equation of the Ps formation probability a new term

$$P_{\rm Ps} = k_{ep} \int_0^\infty \frac{n_e n_p^{\rm in}}{V_{\rm bl}} dt + k_{pS^-} \int_0^\infty \frac{n_{S^-} n_p^{\rm in}}{V_{\rm bl}} dt, \qquad (15)$$

which accounts for the reaction between an intrablob positron and S^- (EVA$^-$). For simplicity we assume in the following that $k_{pS^-} \approx k_{ep}$.

By comparing the calculated theoretical curves [Eq. (15)] with experimental data Fig. 4(b), we can estimate the rate constants k_{eS} and k_{pS} of the reactions of electrons and positrons with the carbonyl group (C═O bond). In the investigated samples EVA may not be uniformly distributed and form domains in the PE matrix.[17] Here for simplicity we assume that the distribution of EVA is homogenous. In pure EVA with an ethylene content of 86% and a vinyl acetate content of 16% CO concentration is 0.56 M. Assuming that the densities of EVA and PE are approximately the same ($\approx 0.92-0.94$ g/cm^3), we obtain $c_S \equiv c_{\rm CO} \approx 0.57W$, where W is the weight % of EVA in PE-EVA blends shown in Fig. 4(b). This value of c_S gives $k_{pS} = 1.0(1) \times 10^{12}$ M^{-1} s^{-1} and $k_{eS} = 0.8(1) \times 10^{10}$ M^{-1} s^{-1}. It seems that the ratio of these numbers correlates well with the mobilities of e^+ and e^- in PE (Table I). It implies that reactions (trapping) of e^+ and e^- are diffusion controlled.

Note that the present model gives the formation probability $P_{\rm Ps}$ of Ps in the quasi-free state. Its transformation to localized Ps apparently proceeds rather fast in molecular liquids. So it is justified to compare $3P_{\rm Ps}/4$ with experimentally observed o-Ps intensity I_3. In solids QF-Ps → loc-Ps transformation probably needs longer time. This process, which may result in a decrease of the ratio of k_{ep} to k_{ie} (Table I, solid PE), is not explicitly taken into account in the present model.

V. CONCLUSIONS

We have developed a model to account for the electric field effect on Ps formation at room temperature. The model explicitly takes into account the electrostatic attraction between a positron and its terminal blob, a cloud of a large number of ion-electron pairs at the end of the e^+ track. In essence this interaction is the Debye screening of the positron by intrablob charged species, which leads to some energy reduction ($\lesssim 1$ eV) for the positron residing within the blob.

The model successfully explains the experimental data in pure liquids, amorphous SiO$_2$ and polymers. It gives reasonable values for the fitting parameters: a is close to the value of $a_{\rm bl}$, reaction rate constants are close to what may be expected from the radiation chemistry data. Unfortunately, the recombination rate constant k_{ep} is rather uncertain because of its strong correlation with the poorly known rate $1/\tau_{\rm IMR}$ of the ion-molecule reaction.

We showed that chlorinated polyethylene (or the C-Cl bond in it) is a scavenger of epithermal electrons. We also showed that in EVA-PE polymer blends the carbonyl group (C═O bond) serves as a weak scavenger of thermalized electrons and positrons, which could be responsible for the weakening of the electric field effect at high fields and also for the enhancement in Ps formation at high EVA concentrations. It should be emphasized that we succeeded in explaining the weakening of the electric field effect at 50–100 kV/cm. For the better explanation of the data, we need to consider the dependence of the e^+ slowing down rate on EVA concentration.

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