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Effect of water-soluble electron scavengers on positronium formation in AOT/water/isooctane microemulsions

V.S. Subrahmanyam [a], M.F. Ferreira Marques [b], G. Duplâtre [c,*]

[a] *Departamento de Física, Universidade de Coimbra, 3004-516 Coimbra, Portugal*
[b] *Instituto Superior de Engenharia, 3031-601 Coimbra, Portugal*
[c] *Laboratoire de Chimie Nucléaire, IReS, UMR 7500 IN2P3 / CNRS-ULP, B.P. 28, 67037 Strasbourg Cedex 2, France*

Abstract

In a previous work reporting on positron annihilation lifetime spectroscopy (LS) measurements in AOT/water/isooctane microemulsions, a model was established leading to the satisfactory description of both triplet positronium (o-Ps) formation and decay. The model proposes that a large proportion of Ps is formed in the aqueous pseudophase, a fraction of which can diffuse out to the organic phase. It thus predicts that an electron scavenger, soluble in the aqueous pseudophase only, should have an inhibiting action on both those species decaying in the aqueous (o-Ps^{aq}) and organic (o-Ps^{org}) phases. To assess this prediction, measurements are performed with efficient inhibitors of Ps formation, incorporated into the reverse micelles: $Te(OH)_6$, KNO_3, and $HgCl_2$. The last solute is also known as a Ps quencher in water. In all three cases, the lifetime results show that the radii of the water cores remain unaltered by the presence of the additives. As expected, the intensities of both o-Ps^{aq} and o-Ps^{org} decrease with increasing solute concentration. However, the quenching power of $HgCl_2$ is suppressed in the water aggregates; this is probably due to the association of the Hg^{2+} cations with the sulphonate groups of AOT. On this basis, the inhibition of $HgCl_2$ is attributed to positron capture by the Cl^- ions. The inhibition constant of $Te(OH)_6$, KNO_3 and Cl^- are all found to be about 65% of what they are in pure water. Qualitatively, this is ascribable to the existence of mixed water–isooctane positron spurs. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In a recent series of papers [1–3], positron annihilation lifetime spectroscopy (LS) has been applied to the study of reverse micelles in sodium AOT/water/isooctane mixtures. The probe used was the long-lived triplet state of positronium (Ps), the bound state of a positron (e^+) with an electron (e^-), whose lifetime and relative abundance (intensity) both depend on the physico-chemical properties of the medium, allowing one to obtain information on the structure and other characteristics of microheterogeneous systems [1–10]. The LS spectra were found to include four components, assigned to four distinct positron states. In increasing order of lifetime values, these are the short-lived singlet states of positronium (*para*-positronium, p-Ps), free positrons, and the two long-lived triplet states of positronium (*ortho*-positronium, o-Ps) decaying in the aqueous core of the micelles (o-Ps^{aq}) and in the organic solvent (o-Ps^{is}), respectively. By examining the values of the various parameters related to the o-Ps states, viz.

* Corresponding author. Fax: +33-3-88-1064-31

their relative intensities and lifetimes, two main conclusions were drawn [1]:

1. Those positronium atoms which are formed in the aqueous pseudophase can diffuse out to the organic solvent. This was established from the fact that the o-Ps^{aq} lifetime is much shorter than in pure water, although the micelles do not possess any significant chemical property to promote Ps lifetime quenching.

2. A large proportion of Ps is produced in the aqueous cores of the micelles, in spite of their rather low volume fraction. This conclusion was suggested by the fact that, with increasing micellar concentration, the total o-Ps intensity in the system rapidly approaches that of o-Ps in pure water [1], whereas the micelles show little tendency to inhibit Ps formation [10]. As was verified by studying the effect of a water-insoluble electron scavenger, CCl$_4$, in the micellar system, this is to a large extent due to the existence of mixed water/isooctane spurs [2]. The spurs are those regions of the liquid where e$^+$ can form Ps by reacting with one of the electrons it has released by ionising the medium, at the end of its track [11]. A mixed spur thus corresponds to this situation where a e$^+$ (or e$^-$) present in the aqueous pseudophase near the water–isooctane interface can form Ps in water by reacting with a e$^-$ (or e$^+$) initially present in the organic solvent.

On the above grounds, a general quantitative model was proposed [1], leading to the satisfactory description of both Ps formation (intensities) and decay (lifetimes) in the reverse micellar system, as a function of various parameters: AOT concentration (C_{AOT}), water/AOT mole ratio (w_0) and temperature (T). For the lifetimes, a rigorous equation was derived, based on the diffusive motion of the Ps atoms. Apart from the Ps diffusion constant (D_{Ps}), which can be evaluated through the Stokes–Einstein equation [1], this equation involves two fitting parameters: the radius of the spherical aqueous core of the micelles (r_0) and a transmission factor (h), which varies from $h = 0$ for impermeable spheres, to $h = \infty$ for totally permeable spheres. Given the value of the aqueous core radius, known for some specific conditions ($r_0 = 3.6$ nm for $C_{AOT} = 0.1$ M, $w_0 = 20$ and $T = 294$ K [12,13]), it was possible to deduce $h = 0.1205$ nm^{-1} and, thereafter, to derive values for r_0

as a function of C_{AOT}, w_0 and T from the measured o-Ps^{aq} lifetimes. The values of r_0 derived for various AOT micellar systems [1–3] agree well with those obtained from other techniques [12–17].

Concerning the intensities, the model implies a semi-empirical fitting parameter, A_{trap}, which allows one to determine the probability ($A_{trap}C_{AOT}$) that the energetic positrons end up in the aqueous pseudophase before forming Ps. It was found that A_{trap} is a function of the sectional area of the micellar cores (πr_0^2), as expected for energetic particles [1,3].

Following the previous conclusions, the aim of the present paper is to further assess the validity of the model as regards Ps formation. Thus, as a complement to our study on CCl$_4$, a solute which inhibits Ps formation in the organic phase, experiments were carried out with solutes that are known to be Ps inhibitors soluble only in the aqueous pseudophase. If Ps formation predominantly occurs in the water cores of the micelles, the model predicts that the addition of such solutes should have an inhibiting action on both the o-Ps^{aq} and o-Ps^{is} components. The solutes chosen are known to be very efficient electron scavengers and, therefore, very efficient Ps inhibitors: Te(OH)$_6$, KNO$_3$ [11] and HgCl$_2$ [18].

2. Experimental

The sodium AOT (di-2-ethylhexylsulphosuccinate, from Sigma) was purified by dissolving in methanol, then filtering in the presence of alumina before evaporating the solvent [19]. The chemicals, isooctane, Te(OH)$_6$, KNO$_3$ and HgCl$_2$, from Merck, were pure grade and used as supplied. The measurements were carried out at (294 ± 0.5) K. For the sake of comparison, the experiments on Te(OH)$_6$ in the micellar system, with $C_{AOT} = 0.1$ M and $w_0 = 30$, were performed both in Coimbra (concentration range: 0.025–0.15 M) and in Strasbourg (0.05 to 0.12 M). The studies on KNO$_3$ (0.06 to 0.96 M) and HgCl$_2$ (0.05 to 0.24 M) incorporated into the AOT/water/isooctane micellar system with $C_{AOT} = 0.1$ M and $w_0 = 20$, were carried out in Strasbourg.

The positron source consisted of ca. 4.4×10^5 Bq ^{22}Na diffused in a thin sodium glass film, sustained by an all-glass holder, yielding a source correction of

about 10% [20]. The solutions were degassed in Pyrex tubes through the usual freeze–pump–thaw cycles to avoid any interference due to oxygen. The source was subsequently immersed into the solutions.

The LS spectra were recorded using fast–fast systems, based on BaF_2 scintillators or NE111 plastic scintillators, with time resolutions of 175 ps and 292 ps, in Coimbra and Strasbourg, respectively. To avoid any distortion due to the non-Gaussian distribution of the counts in the channels of the LS spectra, the integrated counts were kept at about 10^6.

As mentioned above, the spectra were analyzed in terms of four components with lifetimes τ_i (or decay rate constants $\lambda_i = 1/\tau_i$) and intensities I_i. Subscripts $i = 1, 2, 3$ and 4 correspond to singlet positronium (p-Ps), free positrons and triplet positronium (o-Ps) in water and in isooctane, respectively. The corresponding values for the pure solvents, water and isooctane, will be denoted by superscripts 'aq' and 'is'.

For a better definition of the various LS parameters each sample was measured several times (typically 6).

With all parameters free in four-component analyses of the spectra, the experimental error for the longest-lived o-Ps parameters, τ_4 and I_4, were about 30 ps and 0.3%, respectively. For the second longest-lived component, the errors were larger (30 to 100 ps for τ_3 and 0.2 to 0.6% for I_3). In all cases, the longest lifetime τ_4, appears to be very close to τ_3^{is}: more consistent results were thus obtained when τ_4 was set at the value of τ_3^{is}, with errors dropping to 25–60 ps for τ_3 and 0.1–0.4% for I_3. As I_4 is always higher than I_3, the corresponding errors (0.1–0.2%) are smaller than those associated with the third component.

## 3. Results and discussion

3.1. LS lifetimes

The average free positron lifetime, $\tau_2 = (377 \pm 5)$ ps, is in excellent agreement with the value previously determined [1].

With all parameters free, the lifetime of the long-lived component, τ_4, related to o-Ps decay in the organic phase, appears to be the same, within experimental errors, as that in pure isooctane (τ_3^{is}) over the explored concentration range for any of the solutes. This confirms that Ps does not react significantly with the AOT molecules, neither is it affected, in that phase, by any of the three additives.

For a given w_0 ratio, τ_3 appears to be constant, independently of the solute concentration. The values are (1250 ± 50) ps and (1240 ± 40) ps for the various $Te(OH)_6$ concentrations, from ca. 40 measurements each in the Coimbra and Strasbourg laboratories, respectively. These values agree well with those previously found in the absence of solute [1,3]: 1247 and 1242 ps, respectively. For KNO_3 and $HgCl_2$, the τ_3 values are (1070 ± 35) ps and (1065 ± 40) ps, respectively, as deduced from about 50 measurements for the various concentrations: these also agree well with the value published in the absence of additive, 1067 ps [1,3].

As previously, the lower values of τ_3 as compared to $\tau_3^{aq} = 1810$ ps [21,22] denote the outdiffusion (k_{out}) of o-Ps^{aq} from the micelles, according to the following scheme:

$$2\gamma \overset{\lambda_3^{aq}}{\leftarrow} o - Ps^{aq} \overset{k_{out}}{\rightarrow} o - Ps^{is} \overset{\lambda_3^{is}}{\rightarrow} 2\gamma \qquad (1)$$
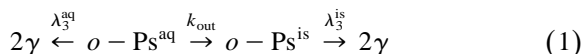
The relevant equations, expressing τ_3 as a function of the radius of a spherical micelle (r_0) and a transmission factor (h) have been published previously [1–3]. Using the value determined for h (0.1205 nm^{-1}) and the corresponding o-Ps lifetime (τ_3), the aqueous core radius (r_0) is deduced. For the AOT(0.1 M)/water($w_0 = 30$)/isooctane + $Te(OH)_6$ system r_0 is found to be 5.37 nm (Coimbra), and 5.31 nm (Strasbourg). For the AOT(0.1 M)/water($w_0 = 20$)/isooctane + KNO_3 or $HgCl_2$, r_0 is found to be 3.63 nm and 3.59 nm, respectively. The above values are in excellent agreement with those found in the absence of the additives, 5.30 nm [1] and 5.37 nm [3] for $w_0 = 30$, and 3.60 nm ($w_0 = 20$) [1,3], respectively.

Neither $Te(OH)_6$ nor KNO_3 should quench the o-Ps lifetime in water [11]: the fact that τ_3 remains constant thus merely reflects the absence of any effect of these solutes on the size of the aggregates, in the concentration range studied.

Such a behaviour is expected for $Te(OH)_6$, as a neutral molecule. For the nitrate ion, some increase

in the aggregate radius might have appeared, as is the case for direct micelles in aqueous solutions in the presence of added ions [23], due to some increased ion association at the interface between the micelle anionic heads and the K^+ cations. As it seems, the concentrations used are too low for such a phenomenon to be effective. However, as noted later on, the microemulsions become unstable for KNO_3 concentrations above 0.24 M.

On the contrary, $HgCl_2$ in water should quench o-Ps rather effectively, with a reaction rate constant $k' = 6.4 M^{-1} ns^{-1}$ [18]. Fig. 1 compares the experimental variation of τ_3 with $HgCl_2$ concentration to what would be expected on the basis of the above k' value. Therefore, some specific process must exist that hinders the quenching action of $HgCl_2$. This is discussed further on, after examination of the intensity variations.

3.2. LS intensities

Fig. 2 shows the variation of I_3, I_4 and the total o-Ps intensity, $I_{tot} = I_3 + I_4$, with $Te(OH)_6$ concentration: although not soluble in the organic phase, this solute appears to inhibit both the o-Ps^{aq} and o-Ps^{org} populations. Quantitatively, semi-empirical equations have been established previously that express I_3 and I_4 as a function of solute concentration (C) [1,2]. The fitting parameters are: A_{trap}, which gives the probability ($A_{trap}C_{AOT}$) for a positron to end up in the aqueous pseudophase; k_{AOT} and k,
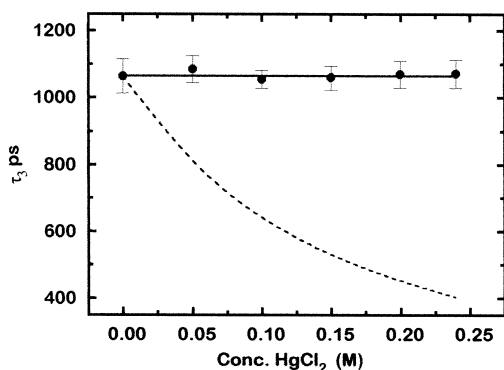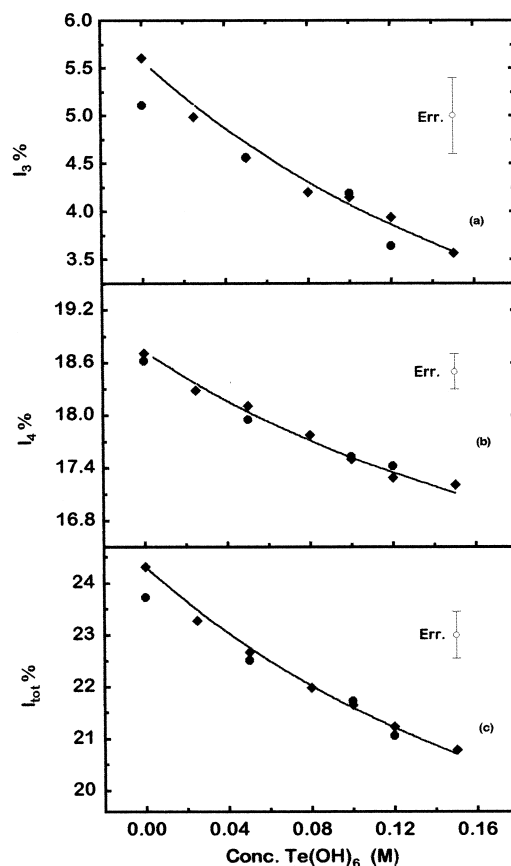

Fig. 2. Variations of (a) I_3 (%), (b) I_4 (%) and (c) I_{tot} (%), from the analysis of the LS spectra, with $Te(OH)_6$ concentration in AOT(0.1 M)/water($w_0 = 30$)/isooctane microemulsions. Data from Strasbourg (●) and from Coimbra (♦). For the solid line, see text.

Fig. 1. Variation of τ_3 with $HgCl_2$ concentration in AOT(0.1 M)/water($w_0 = 20$)/isooctane microemulsions. The solid line indicates the experimentally observed variation and the dashed line represents the expected variation for $k' = 6.4 M^{-1} ns^{-1}$.

which are the inhibition constants of the AOT sulphosuccinate polar heads and of the solute in the water aggregates, respectively. Other parameters, known from our previous study in the absence of solute, are: $\tau_3^{aq} = 1.81$ ns and $I_3^{aq}(0) = 27.1\%$, $\tau_4 = \tau_3^{is} = 4.09$ ns and $\tau_3^{is}(0) = 46.8\%$, together with $h = 0.1205$ nm^{-1}. Setting all parameters, including A_{trap} and k_{AOT}, to the previously determined values [1] leads to a very good agreement with the experimental plots, as shown by the solid lines in Fig. 2, with $k = 6.95$ and $k = 6.40 M^{-1}$ for $Te(OH)_6$ from the Coimbra and Strasbourg data, respectively. Both values are lower than $k = 10.5 M^{-1}$ as measured in pure water [11].

For KNO_3, I_3, I_4 and I_{tot} also decrease with increasing concentration C, up to 0.24 M. Above the latter concentration however, I_4 and I_{tot} increase again (Fig. 3): this is likely to be due to some separation of the two phases, as could be visually observed. In the range where inhibition is effective, similar agreements as for $Te(OH)_6$ are found (solid lines in Fig. 3), with an inhibition constant at $k = 2.5$ M^{-1}. This too is lower than $k = 3.9$ M^{-1} determined in pure water [11].

An additive that is a Ps inhibitor, soluble in the aqueous pseudophase only, should decrease I_3 as is experimentally observed for both solutes. However, the decrease in I_4, which includes some of the o-Ps fraction initially formed in water having diffused out
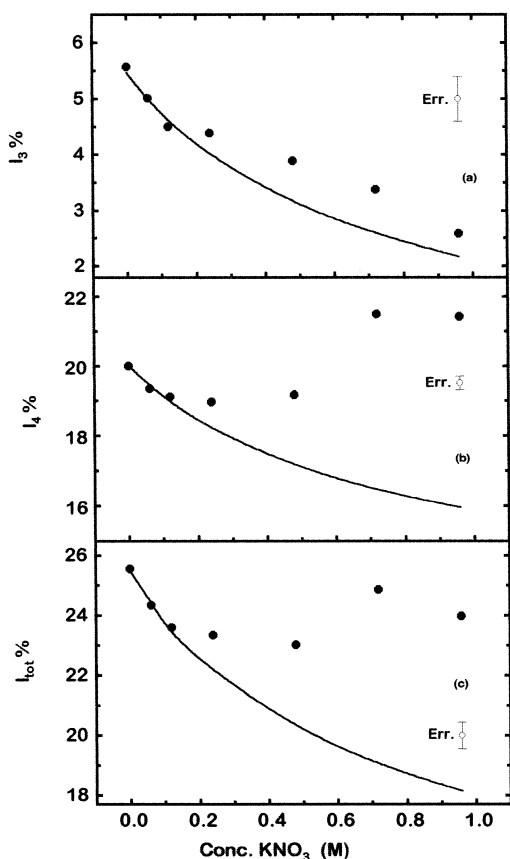
to the organic solvent, together with the fact that I_{tot} is close to I_3^{aq}, strongly suggest that Ps formation occurs to a large extent in the water aggregates, as concluded in our previous work [1,3].

Quantitatively, the inhibiting effects of the solutes are lower by about 36% for both $Te(OH)_6$ and KNO_3 as compared to pure water. Such a similar decrease points to a common origin and should find an explanation in terms of mixed water–isooctane positron spurs.

In the previous work, CCl_4, a strong water-insoluble electron scavenger, was found to inhibit Ps formation in the organic solvent with the same inhibition constant as in pure isooctane, $k = 36.6$ M^{-1} [2]. However, this solute also promotes some inhibition ($k = 5.1$ M^{-1}) of those Ps being formed in the water aggregates, and this was attributed to the existence of mixed spurs: although not present in water, CCl_4 can capture some of those electrons, initially located in isooctane, that would have otherwise been attracted into the water aggregates and react therein with a positron.

A very simple geometric approach led to a satisfactory prediction of the CCl_4 inhibition constant in the aggregates, by considering the Onsager radius (R_{Ons}), the distance at which the attractive potential between e^+ and e^- is overcome by the thermal energy, as the limiting distance for the e^+/e^- reaction. On this basis, mixed spurs can exist within a spherical crown having the edge of the water aggregates as outer limit and R_{Ons} as thickness. Their proportion (p) is given by the ratio of the volume of that spherical crown to the total volume of the aggregates, as:

$$p = \left[r_0^3 - (r_0 - R_{Ons})^3 \right] / r_0^3 \qquad (2)$$

A positron or an electron initially present at a distance greater than or equal to R_{Ons} from the interface will form Ps within a purely aqueous spur; otherwise, within the outer spherical crown, they belong to a mixed spur. In the crown, CCl_4 should little interfere with electrons whose fate is to form Ps at a distance R_{Ons} from the interface; whereas this solute should be efficient to scavenge about half of those electrons that would have formed Ps exactly at the interface. In average, CCl_4 should thus have its

Fig. 3. Variations of (a) I_3 (%), (b) I_4 (%) and (c) I_{tot} (%), from the analysis of the LS spectra, with KNO_3 concentration in AOT(0.1 M)/water($w_0 = 20$)/isooctane microemulsions. For the solid line, see text.

inhibiting capability reduced to $1/4$, this applying only to fraction p of the Ps formed in the water aggregates. For $w_0 = 10$, one has $r_0 = 2.23$ nm [1,2] and using the value of R_{Ons} for bulk water, which is about 0.7 nm [24] (for $w_0 > 8$, the properties of the water in the microemulsions are not expected to be very different from those of bulk water, see for example [25]), in Eq. (2), we get, $p = 68\%$ for the proportion of mixed spurs. The inhibiting efficiency of CCl_4 is thus expected to be about $1/4$ of p what it is in pure isooctane. This corresponds to an inhibition constant of 6.2 M^{-1}, instead of 36.6 M^{-1} in pure isooctane [2], which compares well with 5.1 M^{-1} as experimentally found.

In the present case, the water-soluble solutes should be efficient in scavenging all of the electrons able to form Ps at a distance greater than or equal to R_{Ons} from the interface, and about half of those that would form Ps exactly at the interface. Thus, the ratio of the expected inhibition constant in the micelles to that known in pure water should be given by:

$$k(\text{mic})/k(H_2O) = (1-p) + 3/4p \qquad (3)$$

For $w_0 = 30$, one has $r_0 = 5.3$ nm [1], giving $p = 35\%$, while for $w_0 = 20$, the values are $r_0 = 3.6$ nm and $p = 48\%$. Thus, from Eq. (3), the global average ratio of the inhibition constants should be about 90% in the case of $Te(OH)_6$ and 88% for KNO_3. Both values are higher than some 65% experimentally found.

The concept of mixed spurs thus appears to predict correctly both some inhibiting action of water-insoluble solutes and a decrease in the inhibiting efficiency of purely water-soluble solutes towards those Ps atoms formed in the water aggregates. Quantitatively however, the simple geometrical approach used is clearly insufficient. This may be due in part to the choice of the Onsager radius as the limiting distance for the e^+/e^- reaction, and other possibilities, such as the thermalization distance, which is larger than R_{Ons}, could lead to a better agreement. Nevertheless, on the very short time scale where Ps is formed, before the reacting particles become solvated [11], even complete deterministic equations are not likely to be useful: complex stochastic calculations focusing on the positron end-

of-track appear promising [26], but these are out of scope of this paper.

In the case of $HgCl_2$, setting all other parameters to the previous values [1] leads to a ratio of the inhibition constants in the micelles ($k = 2.7$ M^{-1}, see solid line in Fig. 4) and in water ($k = 15$ M^{-1}) [18] of 18% only, which is significantly lower than for the other two solutes. Together with the complete loss of quenching ability (see Fig. 1) for this solute, this very low inhibiting power strongly suggests that $HgCl_2$ does not exist as such in the water aggregates. The association constant for this solute is very high, so that at the concentrations used it should be present in the form of a neutral molecule [27]. However, as is the case for many metal ions with sulphonates, a
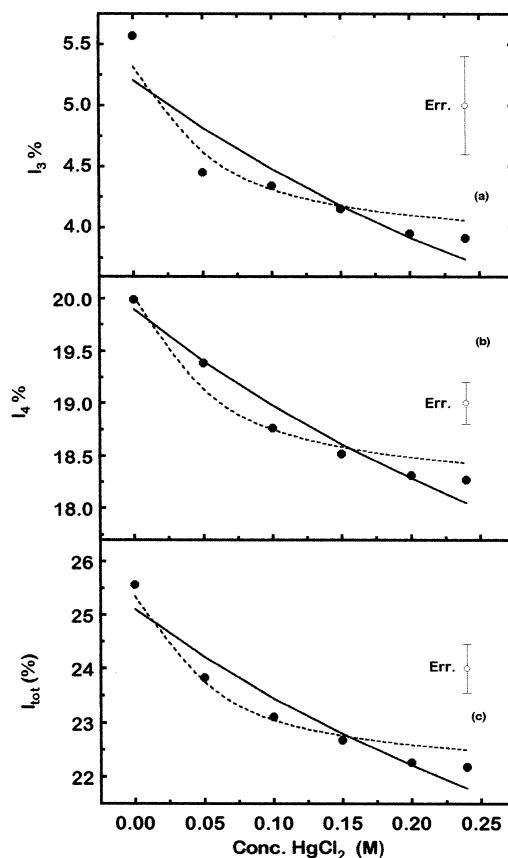

Fig. 4. Variations of (a) I_3 (%), (b) I_4 (%) and (c) I_{tot} (%), from the analysis of the LS spectra, with $HgCl_2$ concentration in AOT(0.1 M)/water($w_0 = 20$)/isooctane microemulsions. The solid and dashed lines are fitted on the hypothesis of total inhibition by $HgCl_2$ or limited inhibition by Cl^-, respectively (see text).

stronger association of Hg^{2+} may occur with the sulphosuccinate moieties of the micelles [27]. On this hypothesis, most of the quenching and inhibiting properties of Hg^{2+} would be hindered. Taking a polar head diameter of about 0.5 nm, these ions would be confined to a very small region of the aqueous system, somewhat outside of it at the interface, representing some 4% only of the water pools. In this case, it is expected that most of the inhibition observed would not arise from electron capture by the Hg^{2+} ions, but rather from positron scavenging by the Cl^- ions that would remain dispersed in the water aggregates. To assess this possibility, the data were therefore fitted by using the limited inhibition expression relevant to the case of inhibition by Cl^- [11]. Fixing the fraction of Ps liable to limited inhibition in water to 0.28 [11], the ratio of the Cl^- partial inhibition constant in the micelles (22.8 M^{-1}, see dashed line in Fig. 4) and in water (32 M^{-1}) [11] is found to be 71%. This value, probably slightly overestimated due to the small inhibition expected from the Hg^{2+} ions which is not taken into account, is quite consistent with some 65% found for the other solutes.

4. Conclusion

The influence of three water-soluble inhibitors of Ps formation in AOT/water/isooctane microemulsions has been examined: $Te(OH)_6$, KNO_3 and $HgCl_2$, the last solute being also a Ps quencher. The results strongly support the idea that a large proportion of Ps is formed in the water cores of the microemulsion, part of which diffuses out to the organic phase. The lifetime data indicate that in the concentration range studied, the additives do not modify significantly the radius of the aqueous cores, although the micellar systems become unstable with KNO_3 above 0.24 M. In all cases, the inhibition of Ps formation by the additives in the water aggregates is found to be smaller than what it is in pure water. The loss in the inhibiting efficiency is about the same for $Te(OH)_6$ and KNO_3, and is qualitatively predicted when considering the presence of mixed water–isooctane positron spurs. There is no a priori reason that would hinder a positron in a water aggre-

gate to react with an electron from outside the aggregate and vice-versa. In this framework, as is experimentally confirmed, a water-insoluble compound can interfere to some extent on the Ps formation process by scavenging some of the particles on their way to the aggregates. Conversely, a water-soluble solute should lose part of its inhibiting efficiency, as it cannot react with the incoming particle as long as it is in the organic solvent.

In the case of $HgCl_2$, the lifetime data show no quenching action by this solute, whose inhibiting power is considerably more reduced as compared to the other two solutes. The association of the Hg^{2+} ions with the sulphosuccinate groups of AOT is a likely explanation to this behaviour. On this hypothesis, the inhibition observed should be due essentially to the Cl^- ions, which are known to promote limited inhibition of Ps formation in water. On these grounds, the decrease in the inhibition of these ions in the micelles as compared to pure water is found to be in reasonable agreement with what is found for $Te(OH)_6$ and KNO_3.

The present experiments show that examining the effect of solutes on Ps formation can yield valuable information on very fast radiolytic processes occurring in microheterogeneous systems. Furthermore, both the inhibiting and quenching power of the solutes are indicative of the location of the solutes.

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