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IN AQUEOUS SDS SOLUTIONS

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## MICELLAR EFFECTS ON POSITRONIUM LIFETIME IN AQUEOUS SDS SOLUTIONS

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## SUMMARY

Positron lifetime measurements have been performed in aqueous SDS /Sodium Dodecyl Sulphate/ solutions. The lifetime distributions measured by fast-slow coincidence technique have been found to be influenced by surfactant concentration, which varied in the range of  $1.25 \cdot 10^{-3}$ – $3.2 \cdot 10^{-1}$  mol/dm<sup>3</sup> /i.e.  $2.27 \cdot 10^{-5}$ – $5.82 \cdot 10^{-3}$  mole fractions/.

The lifetime of the long living component connected to positronium formation and decay increases with increasing surfactant concentration. Lifetime data suggest that a direct positronium-micelle electron-exchange reaction leading to pick-off annihilation is contraindicated.

## АННОТАЦИЯ

Проводилось изучение времен жизни позитрона в водных растворах NaLS /лаурилсульфат натрия/. Концентрация поверхностноактивного вещества /ПАВ/, изменявшаяся в области концентраций  $1.25 \cdot 10^{-3}$ – $3.2 \cdot 10^{-1}$  мол/дм<sup>3</sup> /что в мольных долях составляет  $2.27 \cdot 10^{-5}$ – $5.82 \cdot 10^{-3}$ /, влияла на распределение времен жизни, снятое с помощью техники быстрого-медленного совпадения.

Повышение концентрации ПАВ приводит к увеличению времени жизни долгоживущего компонента, происходящего от атомов позитрония. Полученные данные по временам жизни ставят под сомнение возможность протекания непосредственной электронообменной реакции между атомами позитрония и мицеллами, приводящей к "pick-off" аннигиляции.

## ÖSSZEFOGLALÁS

Pozitron-élettartam vizsgálatokat végeztünk NaLS /nátrium lauril-szulfát/ vizes oldataiban. A felületaktív anyag koncentrációja, amely az  $1.25 \cdot 10^{-3}$ – $3.2 \cdot 10^{-1}$  mol/dm<sup>3</sup> /azaz moltörtekben kifejezve a  $2.27 \cdot 10^{-5}$ – $5.82 \cdot 10^{-3}$ / tartományban változott, befolyásolta a gyors-lassu koincidencia technikával felvett élettartam-eloszlásokat.

A felületaktív anyag koncentrációjának növelése a pozitronium atomtól származó hosszú élettartamu komponens élettartamának növelését eredményezte. Az élettartam-adatok valószínűtlenné teszik, hogy a pozitronium atomok és a micellák között egy közvetlen, pick-off annihilációra vezető elektron-kicserélődési reakció játszódjék le.



## 1. INTRODUCTION

As a result of intricate processes, positrons injected into condensed media annihilate. For most of these processes the annihilation of positrons takes place 0.1-0.5 nsec after having entered the condensed phase. In the case of positronium formation however, lifetimes can reach about 1-10 nsec.

Judging by the longer lifetimes, the experimental investigation of positronium formation and annihilation is a relatively simple task and, as reported in many papers, this process is sensitive to the changes in the electron density [1,2].

Electron density in micellar solutions shows an abrupt change in the vicinity of micelles. Several works are devoted to study the effect of micellization on positron annihilation parameters [2-8], and connections were found between surfactant concentration and

- a./ relative intensity [3-7] and lifetime [3] of the long lived spectral component, and
- b./ line-shape parameters in angular correlation measurements [8].

For aqueous SDS /Sodium Dodecyl Sulphate/ micellar solutions relative intensity [4] and line-shape [8] data are available; the aim of this paper is to present our experimental results concerning the complementary spectral quantity, the positron lifetime.



## 2. MATERIALS

Laboratory purity SDS (MERCK) was carefully purified by fractional recrystallization from saturated solutions of SDS in a 1:1 mixture of ethanol and benzene.

The purified materials was tested partly by surface tension measurements [9], partly by mass spectroscopic analysis of the equilibrium vapour field of the heated solid SDS sample. The analysis carried out on an MM12 FIA type mass spectrometer led only to 1-dodecene; the semiquantitative results showed that the purification procedure reduced it by about two orders of magnitude compared with that measured in the original material [10].

## 3. EXPERIMENTAL

Positron lifetime measurements were carried out on a fast-slow coincidence apparatus composed of XP1023 photomultipliers and NE111 plastic scintillators. The fast timing is obtained from ELSCINT STD N-1 (snap-off) discriminators and the energy selection is improved by a purpose-designed fast differential discriminator. The proper input signal range to the timing units is selected by use of attenuators [11,12] thus a self resolution of about 300 psec FWHM could be obtained for  $^{60}\text{Co}$  with energy windows of about 40%.

Positrons are emitted from  $^{22}\text{Na}$  atoms diffused by thermic ion exchange into a very thin ( $1.2 - 2 \text{ mg/cm}^2$ ) sodium glass foil [13]. The foil-source of about  $7 \cdot 10^5 \text{ Bq}$  activity was introduced into the solution to be studied.

The sample holder was a double walled Pyrex ampoule by means of which the temperature could be stabilized to  $\pm 0.5^\circ\text{C}$ . All samples were prepared by the freeze-thaw technique [13].

A stock solution was prepared by dissolving  $0.32 \text{ mol/dm}^3$  SDS in double-distilled water containing  $0.15 \text{ mol/dm}^3 \text{ NaCl}$ . Solutions of different SDS concentrations in the range of  $0.00125 - 0.32 \text{ mol/dm}^3$ , that is,  $2.27 \cdot 10^{-5} - 5.82 \cdot 10^{-3}$  mole fractions, were prepared by consecutive dilutions of the stock solution with double-distilled water containing  $0.15 \text{ mol/dm}^3 \text{ NaCl}$ .



#### 4. RESULTS AND DISCUSSION

Positron lifetime spectra were computer evaluated using the POSITRONFIT EXTENDED program [14] adjusted to IBM data base under IBM OS operating system [15]. Evaluation procedures were carried out assuming three characteristic spectral lines and they resulted in lifetimes of about 0.2, 0.5 and 1.9 nsec. The medium lifetime is attributed to the so-called free annihilation (without bounded positron formations) and it is supposed to be a bulk-effect. The first and last values are assumed to arise from the bounded electron-positron systems of spin  $S=0$  and  $S=1$  (para- and orthopositronium), respectively and are assumed to be influenced by the presence of micelles. Lifetimes are drawn in Fig. 1 and relative intensities in Fig. 2.

The reliability of our data is judged from three points of view. First, it is characterized with the standard deviations of results obtained from repeated measurements in double distilled water containing  $0.15 \text{ mol/dm}^3 \text{ NaCl}$ . Results of six independent measurements separated by at least one week are summarized in Table 1:

		$\tau_1$ (nsec)	$I_1$ (%)	$\tau_2$ (nsec)	$I_2$ (%)	$\tau_3$ (nsec)	$I_3$ (%)
mean values	m	0.160	44.50	0.481	39.28	1.788	16.22
standard deviations	s	0.029	8.91	0.037	7.78	0.070	1.35
relative st. deviations	s/m	0.183	0.002	0.078	0.198	0.039	0.084
relative RMS errors	$s/\sqrt{6}$ m	0.075	0.082	0.032	0.081	0.016	0.034

Table 1

*Mean values and standard deviations of independent positron lifetime measurements in double distilled water containing  $0.15 \text{ mol/dm}^3 \text{ NaCl}$ .*

Second, to all data fitted by the computer program a chi-square value is assigned. In our case the chi-square distribution function can be approximated with a Gaussian of mean value 1 and of standard deviation 0.05-0.1. For all data published the



chi-square values are less than 1.5 and characteristically fall into the range 0.9-1.2. (It should be noted that lifetime data vary very slightly in a wide range of the other parameters being fitted.)

The third test for our data is the tendency of medium positron lifetimes and relative intensities, see *Figs. 1* and *2*; the explanation follows later.

Unfortunately, a detailed, quantitative theory describing positron interactions in the condensed phase is not yet available and thus our statements concerning any connection between the components of positron lifetime spectra and the microstructure of micellar solutions must remain qualitative.

The results listed in *Table 1* and drawn in the figures show that in our experimental conditions lifetime data have much better reproducibility than relative intensities and for this reason relative intensities are preferably not used in making conclusions. If at least two independent results are available, data points and their RMS errors (otherwise their standard deviations estimated on the basis of results listed in *Table 1*) are drawn.

Spectral components  $\tau_2$  and  $I_2$  marked by (•) in *Fig. 1* and *2* in the given concentration range have a slight dependence on the surfactant concentration; lifetime data are constant within the experimental error in accordance with the expectation that the medium spectral component arises from a bulk effect [16].

On the basis of data reported by Ache [4] a definite decrease in the relative intensity of the long lived spectral component vs. surfactant concentration due to the inhibition of positronium formation is expected. Our  $I_3$  data presented above show only a slight - if any - inhibition. This deviation from the expectation is probably due to the differences in the systems investigated and in the evaluation conditions. Data presented in Ref. [4] correspond to pure micellar solutions without NaCl present and in the evaluation procedures two spectral components have been assumed. In a preliminary report [17] we found a systematic decrease of the inhibition effect whence a three-component parametrization of the evaluation procedures instead of two-component one has been applied.



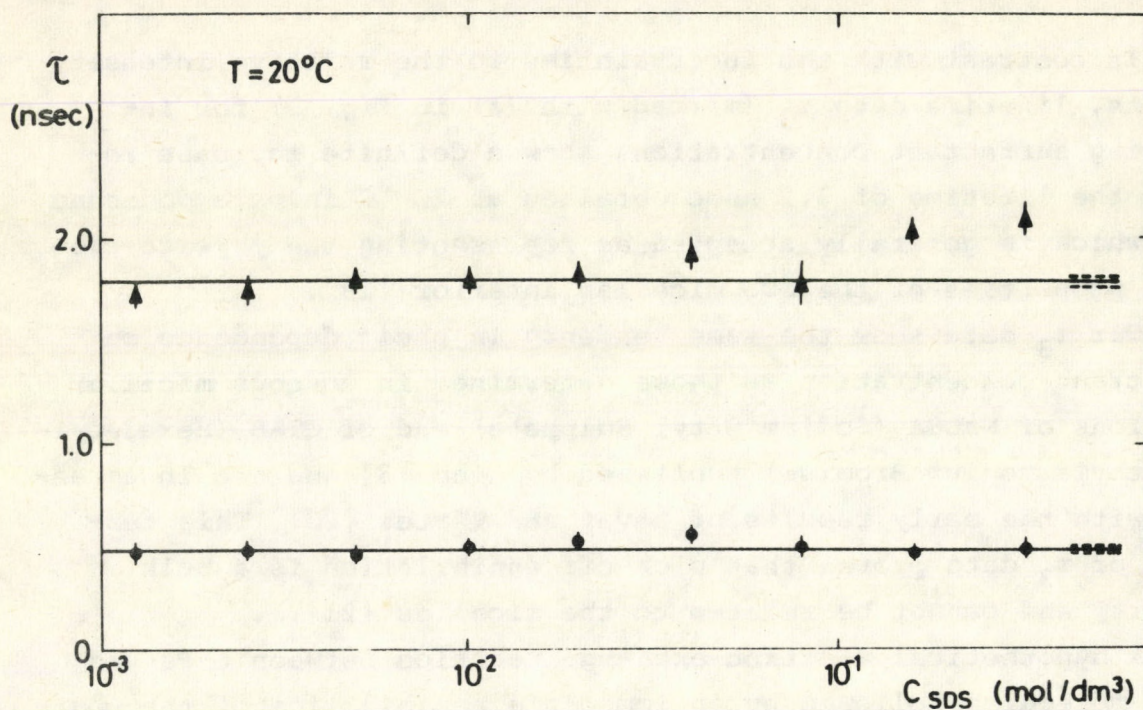


Fig. 1

Lifetime values ( $\tau_2$ -•,  $\tau_3$ -▲) vs. SDS surfactant concentration.

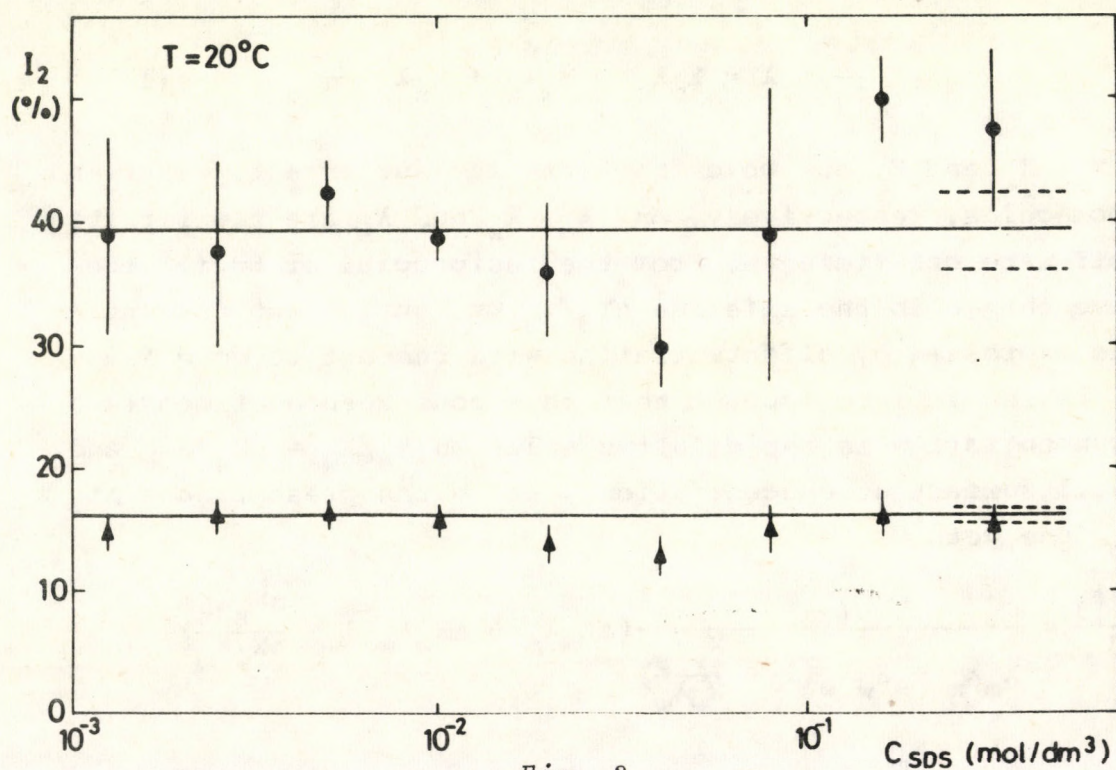


Fig. 2

Relative intensity values ( $I_2$ -•,  $I_3$ -▲) vs. SDS surfactant concentration.



In contrast with the incertainties in the relative intensity results, lifetime data  $\tau_3$  (marked with (▲) in *Fig. 1*) for increasing surfactant concentrations show a definite increase towards the lifetime of 3.2 nsec obtained at 20 °C in pure dodecane [18] which is generally accepted as representing the physico-chemical properties of the SDS micellar interior [19].

Our  $\tau_3$  data show the same tendency in their dependence on surfactant concentration as those determined in aqueous micellar solutions of NaOSA (Sodium Octyl Sulphate) and of CTAB (Hexadecyltrimethylammonium Bromide) published by Ache [3] and are in agreement with the early results of Lévay and Vêrtes [20]. This tendency of  $\tau_3$  data proves that pick-off annihilation is a bulk property and cannot be related to the micelles [21].

A hypothetical electron-exchange reaction between o-Ps and other molecules followed by an immediate annihilation of the positron could be described as a bimolecular process having a rate coefficient  $\lambda$  given as a linear combination of the mole fractions of the different type of molecules present:

$$\frac{1}{\tau_3} \sim \lambda = X_m \lambda_m + X_w \lambda_w + X_s \lambda_s, \quad (1)$$

where  $X_m$ ,  $X_w$  and  $X_s$  are mole fractions for surfactant, water and NaCl molecules, respectively, and  $\lambda_m$ ,  $\lambda_w$  and  $\lambda_s$  are their partial pick-off rate coefficients. From the reciprocal of Eq.(1) the relative change in the lifetime  $\Delta\tau_3/\tau_3$  vs. surfactant concentration is expressed by differentiating with respect to mole fractions; taking it into account that as a consequence of constant NaCl concentration in the diluting solution  $X_s/X_w = \Delta X_s/\Delta X_w$  and, for small surfactant concentrations, as in the present case  $\Delta X_w = -\Delta X_m$ , one gets

$$\begin{aligned} \frac{\Delta\tau_3}{\tau_3} = & \frac{(-1)}{X_m \lambda_m + X_w \lambda_w (1 + \frac{X_s \lambda_s}{X_w \lambda_w})} (\Delta X_m \lambda_m + \Delta X_w \lambda_w (1 + \frac{\Delta X_s \lambda_s}{\Delta X_w \lambda_w})) = \\ & - \frac{\Delta X_m}{X_m + X_w \cdot k \frac{\lambda_w}{\lambda_m}} (1 - k \frac{\lambda_w}{\lambda_m}), \end{aligned} \quad (2)$$



where  $k$  stands for both expressions  $1 + \frac{X_s \lambda_s}{X_w \lambda_w}$  and  $1 + \frac{\Delta X_s \lambda_s}{\Delta X_w \lambda_w}$ .

On the basis of data obtained for pure dodecane [18]  $\lambda_m \sim (3.2 \text{ nsec})^{-1}$ , for NaCl solutions from Table 1  $k \lambda_w \sim (1.79 \text{ nsec})^{-1}$ , the ratio  $k \lambda_w / \lambda_m = 1.79$  and thus the relative change in  $\tau_3$  at  $c_{\text{SDS}} = 0.32 \text{ mol/dm}^3$ , that is at  $X_m=0$ ,  $X_w=1$  and  $\Delta X_m = 5.82 \cdot 10^{-3}$  is given as

$$\left. \frac{\Delta \tau_3}{\tau_3} \right|_{X_m=0} = - \frac{\Delta X_m}{X_w k \frac{\lambda_w}{\lambda_m}} \left( 1 - k \frac{\lambda_w}{\lambda_m} \right) = \frac{5.82 \cdot 10^{-3} \cdot 0.79}{1.79} \sim 2.5 \cdot 10^{-3} \quad (3)$$

On the other hand, the measured  $\tau_3$  data in Fig. 1 define a relative change

$$\left. \frac{\Delta \tau_3}{\tau_3} \right|_{X_m=0} = \frac{\tau_3(0.32 \text{ mol/dm}^3) - \tau_3(0)}{\tau_3(0)} = \frac{2.1 - 1.79}{1.79} \sim 0.17 \quad (4)$$

which deviates from the result of Eq.(3) by about two orders of magnitude, contradicting the assumption of pick-off annihilation mechanism.

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