Positron studies on reverse micellar systems of AOT/isooctane/water

M.F. FERREIRA MARQUES, C. LOPES GIL*, A.P. DE LIMA*, H.D. BURROWS** and M. DA GRAÇA MIGUEL**

Instituto Superior de Engenharia, 3000 Coimbra, Portugal

** Departamento de Física da Universidade, 3000 Coimbra, Portugal*

*** Departamento de Química da Universidade, 3000 Coimbra, Portugal*

ABSTRACT

AOT/Isooctane and water/AOT/Isooctane systems have been studied by positron annihilation techniques. Studies of the binary system show that AOT is a strong positron scavenger and support the idea of polydisperse aggregates. Results, for the ternary system, indicate the presence of monomers, even when aggregates are present, and show that Ps is in a water-free region. The effects of the addition of nitrobenzene, sodium nitrobenzoate and 4-phenylbutyric acid to the ternary system are studied. Ps reveals high reactivity towards nitrobenzene which is shown to be present both in isooctane and inside the aggregates.

INTRODUCTION

Positron annihilation techniques (PAT) provide a powerful method to study structures and changes in a variety of systems, including amphiphile solutions. Reports have been given of amphiphile aggregation in aqueous and non-aqueous solutions studied by PAT [1]. We concentrate here on two and three component systems involving AOT (sodium di-2-ethylhexylsulfosuccinate) in non-polar organic solvents. Although the type of aggregation is still not well defined, it is generally agreed that reversed micelles or microemulsions are formed [2].

If positrons (e^+) are introduced into matter, they may combine with an electron to form a positronium atom, Ps. Ps can exist in two states, p-Ps, with 125 ps lifetime, and o-Ps, whose lifetime (ns time scale) is determined by pick-off reaction in the solvent. Studies of formation and decay of o-Ps can be particularly valuable in giving structural information on multiphase systems [3].

EXPERIMENTAL

AOT was dissolved in methanol, filtered with alumina and the solvent evaporated. Other reagents were of the purest grade available. Solutions were degassed using freeze-pump-thaw cycles. A 12 μ Ci ^{22}Na positron source was introduced inside the reaction cell. The source was prepared by evaporation of carrier free $^{22}\text{NaCl}$ aqueous solution on a thin glass blade and further diffusion of the ^{22}Na into the glass. Positron lifetimes and Doppler lineshape parameter, I_v (integrated over ± 2.0 mrad around the peak) were measured. Time spectra were analysed assuming triexponential decay using the program POSITRONFIT [4], with the constraints $\tau_1(\text{p-Ps}) = 125$ ps, and $I_1 = I_3 / 3$.

RESULTS AND DISCUSSION

With the triexponential analysis, three lifetimes ($\tau_{1,2,3}$) and intensities ($I_{1,2,3}$) were obtained. The most valuable information comes from the decay of quasi-free e^+ (τ_2) and of o-Ps (τ_3) and from the formation of o-Ps (I_3). In binary AOT/isooctane solutions, a pronounced decrease in I_3 was observed for low

concentrations, after which the decrease became less marked (Fig. 1). Similar behaviour was observed with I_V , which suggests that AOT is an efficient scavenger of e^+ . However, the values of τ_3 are not so strongly affected by the AOT (3.92 - 3.72 ns) showing that the surfactant does not greatly affect the pick-off. Concerning the annihilation of quasi-free e^+ , values of $\tau_2=415$ ps for pure isooctane and $\tau_2=385$ ps for 2.5 mM AOT were observed supporting the interpretation, from I_3 and I_V measurements, that AOT is a good positron scavenger. τ_2 also does not change significantly above *ca* 2.5 mM AOT. In contrast to a previous view [5], this suggests that, in this binary system, aggregates are not strong scavengers of e^+ or o-Ps and that monomers are still present even at high AOT concentration. These results are consistent with multiple equilibrium surfactant aggregation and with the presence of polydisperse aggregates.

Fig. 1 - I_3 as a function of AOT concentration

surfactant concentration, the values for 100 mM AOT in isooctane with and without water (3.68, 3.72 ns) are virtually identical and are much longer than in pure water (1.8 ns), showing that Ps annihilates in a water free region.

The ternary water/AOT/isooctane system was also studied at constant AOT concentration (100 mM), varying w_0 values from 2 to 10 (Fig. 2). Although there is disagreement on the amount of water necessary for formation of well-defined aggregates, it is generally accepted that, at high w_0 values, such aggregates exist and their volume is linearly related to w_0 [6]. Figure 2 shows an initial decrease in I_3 with increasing w_0 . This can be attributed to the increasing volume fraction of inverse micelles. The levelling off of I_3 at high w_0 is consistent with the idea that well defined aggregates only appear above $w_0 \approx 5$. At constant AOT concentration, the increase in size with w_0 is counterbalanced by the decrease in aggregate concentration. I_V measurements support the picture presented by the I_3 data. Over the range studied, τ_3 is independent of w_0 , showing that pick-off does not appear to be dependent on the size of aggregates. This again supports the idea that o-Ps is not in a region where there is considerable contact with water. For $w_0 \geq 5$, a value of $\tau_2=396$ ps is observed, which seems to be the lifetime of e^+ trapped in micelles.

Additives which strongly inhibit Ps formation were studied (Fig. 2). For a fixed nitrobenzene concentration (10 mM), the clear decrease in I_3 shows that this additive inhibits Ps formation, although the effect becomes less marked at higher w_0 values. The same behaviour is observed with I_V . τ_2 is not changed with the additive but τ_3 , although reduced, remains independent of w_0 . This can be explained by the high reactivity of Ps towards nitrobenzene.

For 4-phenylbutyric acid, although τ_2 and τ_3 did not change significantly, I_3 showed a small decrease, suggesting that, although this species can scavenge e^+ , in the reversed micellar medium it is not reactive towards Ps.

Ternary systems water/AOT/isooctane were studied (Fig. 1). At constant water/AOT mole ratio (w_0) size of microemulsions aggregates is thought to be constant, but their number increases with concentration. With 2.5 mM AOT, very similar behaviour was observed as with binary systems. With increasing AOT concentration only a relatively small decrease in I_3 was observed. However, the decrease in I_3 is greater than in the binary system, suggesting that the aggregates are also e^+ scavengers, and thus involved in the decrease of the Ps yield. Again, comparison of I_3 values at 2.5 mM AOT in the presence and absence of water indicates that monomers are strong inhibitors of Ps formation. Further, although τ_3 decreases in AOT/isooctane with increasing

Fig. 2 Effect of increasing water/AOT mole ratio on I_3 for the ternary mixture in the presence of additives.

The effect of nitrobenzene or sodium nitrobenzoate concentration on the ternary system was also studied (Fig. 3 and Table I). A progressive decrease in I_3 and τ_3 was observed with increasing nitrobenzene concentration. Identical behaviour was observed with I_v . This confirms the high reactivity of Ps towards

Fig. 3 - Intensities and lifetimes for different additive concentrations. The squares indicate values observed without additives.

nitrobenzene. Comparison with data of nitrobenzene in isooctane suggests that the inversed micelle aggregates may favour the pick-off. τ_2 values show no significant change. As with τ_3 , I_3 is more strongly affected by nitrobenzene in the ternary system than in pure isooctane. These results indicate that, apart from nitrobenzene being a strong inhibitor of Ps formation, it cannot just be in the isooctane, but must also be present in the aggregates. Since it affects Ps decay, and Ps is not affected by the water in the microemulsions, this means that nitrobenzene is at some point within the AOT layer or at the micellar interface.

Addition of sodium nitrobenzoate (which is water soluble, but insoluble in isooctane), led to a decrease in I_3 . The effect was more marked than that with nitrobenzene. Similar results were obtained with I_v measurements, and suggest that sodium nitrobenzoate, which must be either in water pool or in the micellar interface, is more efficient in trapping e^+ than nitrobenzene.

However, although e^+ appears to penetrate into the micellar interior, as shown by the decreases in I_3 and I_v , the τ_2 values does not change significantly. At present, the reason is not clear. Also the τ_3 value does not change, even though in

aqueous solutions sodium nitrobenzoate has been shown to accelerate Ps pick-off. This lack of effect on τ_3 reinforces the view that Ps does not see the water present in the micelle.

Table I - Data from Water($w_0=10$)/AOT(100mM)/ Isooctane with additive concentration

Conc. mM	+ Nitrobenzene					+ Sodium Nitrobenzoate				
	I_v [± 2.0 mrad]	I_3 [%]	τ_3 [ns]	τ_2 [ps]	$\bar{\tau}$ [ns]	I_v [± 2.0 mrad]	I_3 [%]	τ_3 [ns]	τ_2 [ps]	$\bar{\tau}$ [ns]
0	0.3493	21.6	3.68	396	1.09	0.3493	21.6	3.68	396	1.09
2	0.3489	21.0	3.59	396	1.05	0.3479	20.4	3.55	395	1.02
4	0.3478	20.4	3.54	397	1.02	0.3469	19.7	3.57	396	1.00
6	0.3469	19.8	3.48	396	0.99	0.3459	19.1	3.57	396	0.98
8	0.3462	19.4	3.39	396	0.96	0.3450	18.8	3.60	395	0.98
10	0.3459	19.5	3.34	395	0.95	0.3445	18.4	3.60	395	0.97

REFERENCES

- /1/ VASS,S, Struct. Chem. vol.2 (1991) (167)375, and references therein.
- /2/ ISRAELACHVILI,J.N, "Intermolecular and Surface Forces", Academic Press London 1989.
- /3/ ACHE,H.J, in "Positron and Positronium Chemistry", ed. D.M.Schrader and Y.C.Jean, Studies in Physical and Theoretical Chemistry, 57, pp. 318, Elsevier, NY, 1988.
- /4/ KIRKEGAARD,P, ELDRUP,M, MOGENSEN,O.E and PEDERSON,N.J, Comp. Phys. Comm, 21 (1981) 307.
- /5/ ALFASSI,Z.B and ACHE H.J, J.Phys. Chem. 88 (1984) 4347.
- /6/ IZQUIERDO,C, MOYA,M.L, USERO,J.L, CASADO,J, Mon. fur Chem. 123 (1992) 383.