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Positronium reactions in AOT/n-heptane/water reversed micellar system incorporating metal ions

B. NANDI GANGULY and V.S. SUBRAHMANYAM

Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Calcutta 700064, India

ABSTRACT

The positron annihilation lifetime spectroscopy as a chemical probe has been used to study AOT/n-heptane/water reversed micellar system. The steady increase of the annihilation lifetime τ_3 with the increase in W_0 , the mole ratio of water to surfactant system suggests a gradual swelling of the aggregated structure. The incorporation of metal ions like, Cu^{+2} and Co^{+2} in the microwater pools at varying W_0 values ($W_0 = 5$ to 25) sets in an ordered molecular arrangement of polar and nonpolar zone which can be sensed by the positron lifetime parameters. The discernable feature of the observation is the appearance of a highly quenched additional lifetime component with $\sim 2\%$ intensity at $W_0 = 25$, with the encapsulation of metal ions.

1. INTRODUCTION

Sodium di(2-ethyl hexyl) sulphosuccinate, Aerosol OT (AOT) is a widely used anionic surfactant of biological and technical importance and is known to form inverted micelles in apolar media. Very recently such aggregated systems are progressively studied [1] after the pioneering work of Ache et al., on micelles [2], using positron annihilation lifetime spectroscopy.

In this paper an attempt has been made to study the microphase changes with increase in W_0 , the mole ratio of water to surfactant in the system. Also, the solubilization of metal ions in the reversed micellar system at varying W_0 values excites certain interesting features which have been brought out in this paper.

2. EXPERIMENTAL

AOT was a product of Sigma, n-heptane was procured from E-Merck, Germany and the salts of CuCl_2 and CoCl_2 were procured from E-Merck, India. Triple distilled water was used for the preparation of micelles. The solutions were contained in special reaction vials and flushed thoroughly with pure argon gas.

The source of positrons was ^{22}Na ($\sim 4 \mu\text{Ci}$), deposited on a thin layer mylar film and sealing was done by using another identical mylar film on top of it. This source was put in the specimen container and placed between the two plastic scintillator detectors in a slow-fast coincidence circuit. The positron lifetime spectrometer had a prompt time resolution (FWHM) of 260 ps for the prompt ^{60}Co γ -rays. The long lived pick-off component τ_3 (decay constant, $\lambda_3 = 1/\tau_3$) and its intensity, I_3 were extracted from the lifetime distribution data using the programmes, POSITRONFIT and RESOLUTION [3].

3. RESULTS AND DISCUSSION

The reversed micellar system chosen here is Areosol OT/ n-heptane incorporating minute quantities of water. As the operational CMC of AOT occurs around 2mM concentration [4] in the various nonpolar systems studied, the concentration of AOT in n-heptane was maintained at 5mM and above. The mole ratio of [water]/[surfactant] = W_o were varied from 0 - 25. The results (fig. 1) show a very gradual change up to $W_o = 10$. Above $W_o = 10$, there is a clear change in the trend, showing a regular increase in τ_3 . The corresponding I_3 values remain almost to near constancy.

The results shown here however, show a different trend than those of reference [4], as the micelles formed with 100mM concentration of AOT in isooctane (as described in reference [4]) are much larger in size and thus might exhibit a different property.

Presently in the system studied, as the magnitude of I_3 remains more or less constant, it can be inferred that there is no change in inhibition process taking place and the origin of this long lived component remains the same. The rising trend of the τ_3 values would suggest that Ps reactivity is affected by the form and size of the reversed micelle. A step wise change of τ_3 with $W_o > 10$, would actually mean an onset of larger micelles with solubilized water, or larger swelling of the aggregated structure [5]. This observation could be corroborated with the observations of Eicke et al., [6], where in the apparent average molecular weight showed a steep rise above $W_o=10$, indicating the coalescence of reverse micelles with solubilized water.

The sensitivity of the annihilation process of the long lived pick-off component has been recognised in the experiments with liquid crystals [7], and in micelles earlier [2]. This phenomenon has been repeatedly observed by us in the reversed micelles and microemulsions under investigation [5]. Thus it can be inferred that the nature of the structural changes in the surfactant aggregation has profound influence on the lifetime of the long lived positronium component.

The incorporation of the metal ions in the reversed micelles and its solubilization certainly involves the binding of the polar head groups. One of the discernable features of the present observations is the detection of an additional long lived component in the reversed micellar phase with $W_o = 25$, upon incorporation of either Co^{2+} or Cu^{2+} ions (table 1). The longlived pick-off component a) 2.7 ns could be assigned to the nonpolar phase which showed a gradual increase with W_o (fig. 1) and is attributed to the structural order of the reversed micellar phase. This was accompanied with another extra component b) ≈ 0.61 ns with 2% intensity which was actually resolvable from the rest of the other components, using a 4 component fit. This means, a part of the long lived pick-off component is affected by the restricted polar zone [5], (fig. 2).

Fig. 1. Variation of the long lifetime component τ_3 and its intensity I_3 in AOT/n-heptane/water system.

TABLE I

Reversed Micellar Phase	Long-lived components τ_3 (ns)	Intensities I_3 (%)	variance of fit
$\text{Co}^{+2} + \text{W}_o = 10$	2.75 ± 0.016	27.1 ± 0.12	1.0
$\text{Co}^{+2} + \text{W}_o = 15$	2.70 ± 0.013	27.2 ± 0.17	1.09
$\text{Co}^{+2} + \text{W}_o = 20$	2.71 ± 0.01	27.6 ± 0.16	1.0
$\text{Co}^{+2} + \text{W}_o = 25$	a) 2.84 ± 0.01 b) 0.59 ± 0.02	27.0 ± 0.12 2.0 ± 0.2	0.95
$\text{Cu}^{+2} + \text{W}_o = 10$	2.65 ± 0.01	27.4 ± 0.23	1.0
$\text{Cu}^{+2} + \text{W}_o = 15$	2.61 ± 0.01	27.9 ± 0.22	0.99
$\text{Cu}^{+2} + \text{W}_o = 20$	2.63 ± 0.01	28.5 ± 0.27	0.9
$\text{Cu}^{+2} + \text{W}_o = 25$	a) 2.53 ± 0.01 b) 0.68 ± 0.01	27.5 ± 0.20 2.2 ± 0.10	1.1

When the molecules are in a better order with marked polar and nonpolar zone, it increases the polarization power with increased electric field strength. The influence of this electric field on τ_3 can be considerable to detect and resolve another shorter extra component [5,7]. However it is usually not possible to resolve this extra component directly. In most of the this is very close to $\lambda\tau$, the annihilation lifetime of free positrons and appear together with the latter as the short lived component in the life time spectra.

4 CONCLUSION

- (i) The steady increase of annihilation lifetime of the pick-off component with $\text{W}_o > 10$ indicates a large swelling effect of the micelles.
- (ii) One of the significant observations is the appearance of a highly quenched additional lifetime component of 0.61 ns with 2% intensity at $\text{W}_o = 25$, with the incorporation of metal ions.

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Fig. 2. A schematic representation of the reversed micelle of Aerosol-OT (AOT) showing the different regions of the micellar interior, with the metal ions.