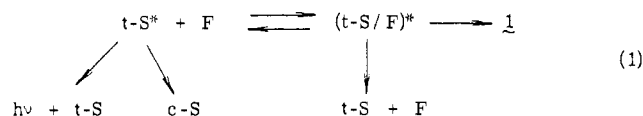
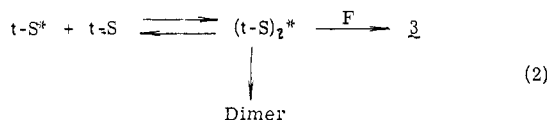


tane or oxetane formation establishes that singlet stilbene is a precursor of both cycloadducts, as is the case for stilbene additions to electron-rich alkenes.<sup>11</sup> At low stilbene concentration (0.01 M) cyclobutane **1** is the major product and a plot of  $\Phi_1^{-1}$  vs. [fumarate]<sup>-1</sup> is linear, as expected for a singlet cycloaddition process. The observation of weak exciplex fluorescence and the stereospecific formation of the dimethyl truxinate with maximum  $\pi$ -orbital overlap<sup>7</sup> are both consistent with an exciplex intermediate (eq 1). The low limiting quantum



yield for cyclobutane formation (0.04) indicates the presence of other efficient exciplex decay channels, as is the case for the phenanthrene-dimethyl fumarate exciplex.<sup>12</sup> Interestingly, the limiting quantum yield is similar to the quantum yield for formation of **1** upon excitation of the stilbene-dimethyl fumarate ground-state complex (Table II).<sup>13</sup>

Quantum yields for oxetane formation ( $\Phi_3$ ) increase with increasing stilbene concentration, but are relatively insensitive to dimethyl fumarate concentration (Table I). Oxetane formation via interception of stilbene excimer by ground-state dimethyl fumarate (eq 2) provides the only satisfactory ex-



planation of the stilbene dependence of  $\Phi_3$ .<sup>14</sup> Self-quenching of stilbene fluorescence and isomerization become significant for stilbene concentrations above  $10^{-2}$  M.<sup>15</sup> Stilbene excimer fluorescence has been observed following  $\gamma$  irradiation of stilbene in a squalene glass at 77 K,<sup>16</sup> but cannot be detected at room temperature in solution, presumably owing to the efficient formation of stilbene dimer.<sup>15</sup> Increasing dimethyl fumarate concentration would be expected to increase  $\Phi_3$  according to eq 2; however, quenching of stilbene singlet by dimethyl fumarate (eq 1) inhibits stilbene excimer formation. The concurrent operation of eq 1 and 2 leads to complex kinetics which will be discussed in a full paper.

In conclusion, quenching of singlet *trans*-stilbene by dimethyl fumarate results in formation of cyclobutane **1**, whereas quenching of stilbene excimer results in formation of oxetane **3**. We are currently investigating other cases in which the bimolecular chemistry of the singlet state differs from that of the excimer or exciplex.<sup>17</sup>

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- The structures of **1** and **2** were confirmed by comparison with authentic samples.<sup>9</sup> The major oxetane (**3**) was recrystallized from methanol to yield white needles (mp 71–72 °C): NMR (CDCl<sub>3</sub>)  $\delta$  3.75 (s, 3 H), 3.78 (s, 3 H), ~3.75 (1 H), 6.17 (1 H), 6.39 (d,  $J$  = 15.7 Hz, 1 H), 7.30 (s, 10 H), and 7.54 (d,  $J$  = 15.7 Hz, 1 H); IR (KBr) 5.84, 6.12, 9.43, and 14.22  $\mu$ ; mass spectrum (10 eV)  $m/e$  218 (loss of benzaldehyde), 171, 159, 144 (loss of stilbene),

115. The minor oxetane **4** could not be isolated in pure form; however its NMR spectrum was similar to that of **3**.

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- The formation of small amounts of *cis*-stilbene and **3** upon 365-nm irradiation probably results from some direct excitation of uncomplexed stilbene.
- Oxetane formation via interception of the stilbene-dimethyl fumarate exciplex by ground-state stilbene can be excluded on the basis that the quantum yield for oxetane formation does not increase with increasing dimethyl fumarate concentration.
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## Determination of Critical Micelle Concentrations in Micellar and Reversed Micellar Systems by Positron Annihilation Techniques<sup>1</sup>

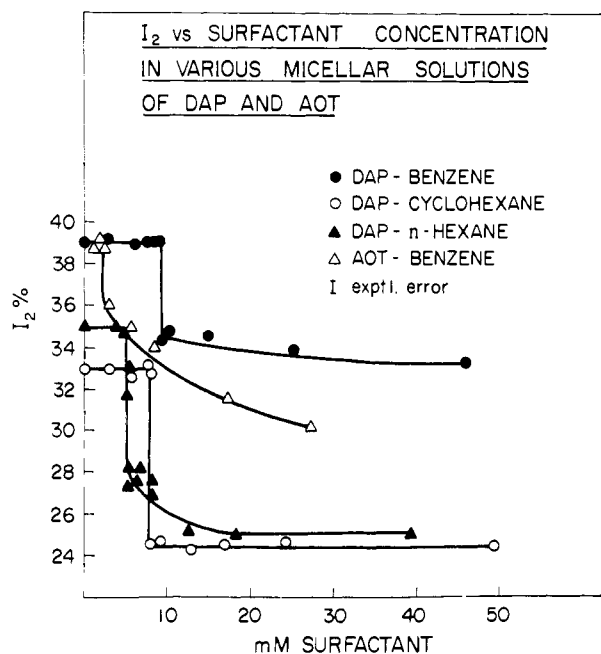
Sir:

An important parameter in the study of micellar systems,<sup>2</sup> whose relevance in energy conversion and storage as well as in tertiary oil recovery is well recognized, is the so-called critical micelle concentration (cmc). The critical micelle concentration is defined as the narrow range of surfactant concentration at which the micelles first become detectable, usually by some change in the physical properties, such as interfacial tension, electric conductivity, emf, pH, specific heat, viscosity and the optical and spectroscopic properties of the solution. These methods generally provide clear evidence for the formation of micelles; however, since the observed variation of the above physical properties at the cmc is not abrupt but occurs more or less gradually, extrapolations are required which in turn introduce an uncertainty in the determination of the cmc.

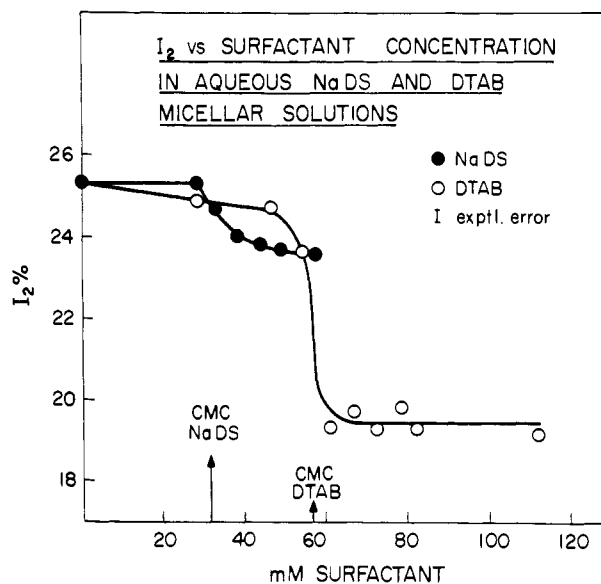
In the following we would like to discuss the applicability of the positron annihilation technique<sup>3</sup> as a simple method for the accurate determination of cmc. This method takes advantage of the fact that the lifetime and the annihilation characteristics of a positron and the formation of the positronium atom (Ps), which is the bound state of a positron and an electron, are determined by their microscopic chemical and physical environment.<sup>3</sup>

The sensitivity of, e.g., the positronium formation process toward structural changes has already been previously recognized in experiments with liquid crystals,<sup>4-7</sup> where the variations in the mesomorphic phases were clearly reflected in the positron lifetime characteristics. Thus one could expect that the formation of micelles leading to structural changes in the solution should also result in distinct variations of the positron lifetime parameters.

In the following, we should like to report the results of a preliminary study of positron interactions in solutions with various amounts of surfactants present. Six different micellar systems were studied. Dodecylammonium propionate (DAP) in benzene, cyclohexane, and *n*-hexane; sodium di(2-ethylhexyl)sulfosuccinate (Aerosol OT or AOT) in benzene; sodium decylsulfate (NaDS) and decyltrimethylammonium bromide (DTAB) in water.



**Figure 1.**  $I_2$  (%) vs. surfactant concentration in solutions of DAP in benzene, cyclohexane, and *n*-hexane and AOT in benzene (at room temperature).



**Figure 2.**  $I_2$  (%) vs. surfactant concentration in aqueous solutions of NaDS and DTAB in water (at room temperature).

The solutions were prepared following the previously reported procedures.<sup>2b</sup>

Positronium lifetime distributions were obtained by standard techniques.<sup>8</sup> The lifetime spectra were separated as previously discussed into two components, a short-lived component, which is the result of *p*-Ps, free positron annihilation, and epithermal Ps interactions, and the long-lived component, with a decay constant  $\lambda_2$  and an associated intensity,  $I_2$ , which originates from the reactions and subsequent annihilation of thermalized or nearly thermalized *o*-Ps atoms. While, the  $\lambda_2$  values seem to be only slightly affected by micelle formation in these solutions, a drastic change in the intensities  $I_2$  can be observed at the previously reported cmc as shown in Figures 1 and 2. In contrast to the results obtained by optical and spectroscopic techniques, where the cmc is characterized by a more gradual change,<sup>2b-e,9</sup> in the present investigation the  $I_2$  values show a very abrupt discontinuity at the cmc and thus allow a more accurate determination.

**Table I.** Cmc Values Obtained in This Study by Positron Annihilation Techniques and Previously Reported Literature Values<sup>a</sup>

Surfactant	Solvent	cmc, mM	
		This study	Lit.
DAP	Benzene	8.75 ± 0.25	3-7
	Cyclohexane	8.26 ± 0.25	8 <sup>b</sup>
	<i>n</i> -Hexane	6.15 ± 0.45	6 <sup>c</sup>
AOT	Benzene	2.20 ± 0.10	2.0-2.7
NaDS	Water	32 ± 1	33
DTAB	Water	57 ± 1	65

<sup>a</sup> Reference 2b. <sup>b</sup> Dodecylammonium butanoate. <sup>c</sup> In octane.

Although the parameters which control the positronium formation process, and consequently  $I_2$ , are not unambiguously known,<sup>3</sup> the results of this study clearly show that this simple technique can be easily used for the determination of cmc's, not only in aqueous solutions, but that it is also very effective in nonaqueous solutions and therefore provides a generally applicable method for the study of properties of micelles and inverted micelles.

The cmc's obtained in this study are listed in Table I where for comparison previously reported literature value<sup>2b</sup> can also be found.

## References and Notes

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## A Cyclic Disulfurane with S-O, S-C, and/or S-N Bonds. 3. Some New Cyclic S,S-Bis(trifluoromethyl)catecholatosulfur(IV) Compounds<sup>1</sup>

Sir:

Tetracoordinate sulfur(IV) compounds have been studied<sup>2</sup> over the years and several routes have been developed for their synthesis.<sup>3-17</sup> In our continuing design of routes to sulfuranes, we now wish to report two new syntheses of sulfuranes. It has been possible to synthesize sulfuranes I and II, the first stable members of a new family with two tetracoordinate sulfur(IV) atoms bonded to carbon, oxygen, and/or nitrogen per molecule,