

## INVERTED MICELLES OF AOT AS ELECTRON SCAVENGERS IN 3-MP AT 77 K IN THE ABSENCE AND PRESENCE OF WATER

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**Abstract**—Pulse radiolysis of bis (2-ethylhexyl)sulfosuccinate (AOT) solutions in 3 methylpentane (3 MP) at 77 K leads to the formation of a species absorbing at around 450 nm. This absorption is believed to result from the scavenging of electrons by AOT inverted micelles. The electron scavenging capacities of an AOT solution depend on the aggregation number of the micelles. The addition of water leads to less efficient electron capture which is explained by an increase of the aggregation number. This increase is of the same order of magnitude as measured by other techniques at room temperature.

### INTRODUCTION

IN THE past few years there has been a growing interest in the use of micellar systems as reaction media, for example for investigations of the role of molecular organization in biochemical processes. Enzymes entrapped in inverted micelles of surfactant have been investigated as models of biological membrane structures.<sup>(1)</sup> Inverted micelles formed by sodium bis (2-ethylhexyl) sulfosuccinate (AOT) dissolved in nonpolar solvents have been used to entrap cytochrome *c* in a water pool.<sup>(2,3)</sup> Photochemically or radiolytically generated electrons were used to study electron transfer through the interface formed by the polar headgroups of the surfactant around the protein.<sup>(3)</sup> Scavenging of electrons by the polar headgroups was proposed as a possible mechanism for the rapid decay of the solvated electrons in those systems.

We have studied the radiation chemistry of the AOT/3 methylpentane (3 MP)/water system at 77 K. At this temperature the system is in the glassy state and diffusion is slowed down. Solubilization of acceptors in the water core at low temperature makes it possible to study the influence of the interface on electron transfer processes without contributions from diffusion or exchange of surfactant or acceptor molecules between micelles.

We have found that AOT micelles have electron-scavenging properties at 77 K. A characteristic absorption spectrum was observed. This absorption is ascribed to an electron-attachment product of AOT. Following the approach of Dainton, Rice and Pilling<sup>(4,5)</sup> the time dependent electron scavenging of

trapped electrons is analyzed. The aggregation of AOT into micelles is taken into account by using the scavenging volume overlap parameter  $\phi(t)$  as introduced by Huddleston and Miller.<sup>(6)</sup>

### EXPERIMENTAL

The AOT used was from Fluka "purum". The impurities, 0.3% Na<sub>2</sub>SO<sub>4</sub>, 0.01% Na<sub>2</sub>SO<sub>3</sub> and minor quantities of semister, alcohol, carboxylate<sup>(7)</sup> are believed to be of negligible influence on our pulse radiolysis experiments at low temperature. AOT samples recrystallized from methanol gave the same results as untreated samples. 3 MP and methylcyclohexane were from J. T. Baker (A.R.). Water was deionized and triply distilled. Samples were prepared by dissolving AOT in 3 MP and the concentrations were determined at room temperature. In some cases a small amount of water was added and dissolved by shaking or by short treatment in a bath-type sonicator. Argon was bubbled through the solutions prior to use. No detectable loss of 3 MP by evaporation occurred when the bottle containing the solution was cooled with ice. Deoxygenated solutions were quickly injected into a polystyrene cell (optical path length 1 cm) immersed in liquid nitrogen. Frozen samples were transferred to an optical cryostat (Cryocon XL500), which was precooled to 77 K. Helium was used as an exchange gas.

The electron pulses (0.55  $\mu$ s duration) were produced by a 2 MV Van de Graaff accelerator. The pulse dose was about 20 Gy (2 krad) and was measured at room temperature with a thiocyanate solution. The absorbed dose measured in the aqueous system was not corrected for differences in electron densities between the solution under investigation and the dosimetry solution.

The optical detection system for the visible region (350–700 nm) consisted of a 450 W Xe lamp, two Bausch and Lomb grating monochromators (one on each side of the cryostat) and an RCA R928 photomultiplier. The

bandwidth was smaller than 5 nm and filters were used to suppress second order light and Cerenkov light. Bleaching was prevented by using low light intensities. The IR part of the spectrum was recorded with a Ge 7460 photodiode (Rofin). In this case the monochromator behind the cryostat was replaced by an IR transmission filter. Owing to the low radiance of the Xe lamp in this wavelength region only the emission lines of the lamp were used. The bandwidth (determined by the first monochromator) was between 18 and 25 nm.

The signals were registered by a Tektronix R7612D digitizer, processed by a PDP 11/23 computer and stored on a floppy disk unit.

The absorption signal at short times was corrected for the luminescence of the cryostat windows.

## RESULTS

### 1 The spectrum extrapolated to the end of the pulse

Figure 1 gives the absorption spectra of AOT/3MP mixtures immediately after the pulse. The IR absorption, ascribed to the trapped electron,<sup>(8)</sup> decreases upon increasing AOT concentration whereas a new absorption band at 450 nm increases. The spectra in Fig. 1 have not been corrected for the absorption of the polystyrene cell (included in Fig. 1).

The unit for absorption OD/krad is expressed in

$$\epsilon G \left( \frac{1}{100 \text{ eV}} \text{ M}^{-1} \text{ cm}^{-1} \right)$$

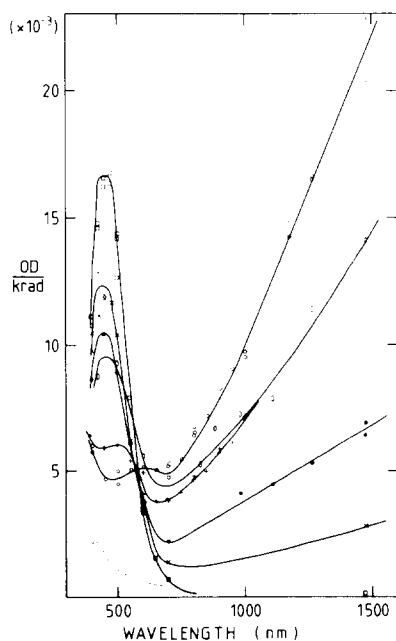


FIG. 1. Absorption spectra immediately after the electron pulse in 3 MP/AOT mixtures. ○: [AOT] = 0; +: [AOT] = 45 mM; □: [AOT] = 65 mM; ●: [AOT] = 173 mM; ×: [AOT] = 285 mM; □: [AOT] = 470 mM. The dotted line is the absorption spectrum of the cell.

by the relation

$$\epsilon G = \frac{9.65 \times 10^5}{d \rho} \cdot \frac{\text{OD}}{\text{krad}}$$

where  $d$  is lightpath (cm) and  $\rho$  is density (g/ml).

The polystyrene cell contributes an absorption band with a maximum at 410 nm at room temperature.<sup>(9)</sup> The spectrum observed at 77 K with  $\epsilon G = 0.91 \times 10^4$  was similar to that of Ref. 8 ( $0.83 \times 10^4$  at room temperature at 60 ns).

The spectrum measured at zero AOT concentration is in agreement with the spectrum found by Klassen<sup>(10)</sup> and Buxton<sup>(11)</sup> in 3 MP. In Fig. 2 the yield at 1475 nm, 1  $\mu$ s after the pulse is plotted as a function of AOT concentration. The log (yield) is a linear function of AOT concentration.

### 2 The time dependence of the absorption at 1475 nm

The decay of the trapped electron was measured from 50  $\mu$ s to 100 ms. The decay at zero AOT concentration as measured both at 800 nm and at 1475 nm is in good agreement with the results of Klassen.<sup>(12)</sup> The decay curves in the presence of AOT were corrected for the decay in the pure matrix. The corrected absorption decays almost linearly with log (time) (Fig. 3). Since the absorbance of the trapped electrons decays almost logarithmically over several orders of time at all AOT concentrations measured, we believe that this decay occurs by tunnelling of the electrons from their trapping sites to AOT molecules. As indicated by Dainton, Rice and Pilling<sup>(4,5)</sup> a good approximation to describe electron tunnelling for  $t > 10^{-12}$  s is given by equation (1)

$$(1) \quad \frac{A(t)}{A_0} = f(S) \exp \frac{-2.52S}{\beta^3} \left( \ln \frac{t}{t_1} \right)^3$$

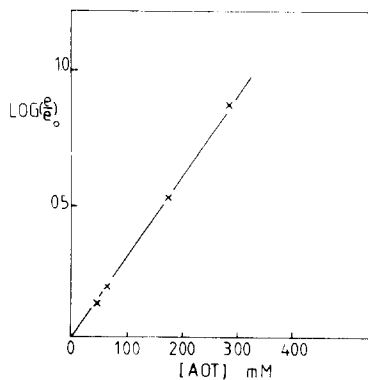


FIG. 2. Yield of the trapped electrons as measured at 1475 nm as a function of AOT concentration ( $\epsilon$ ) relative to the yield measured at zero AOT concentration ( $\epsilon_0$ ).

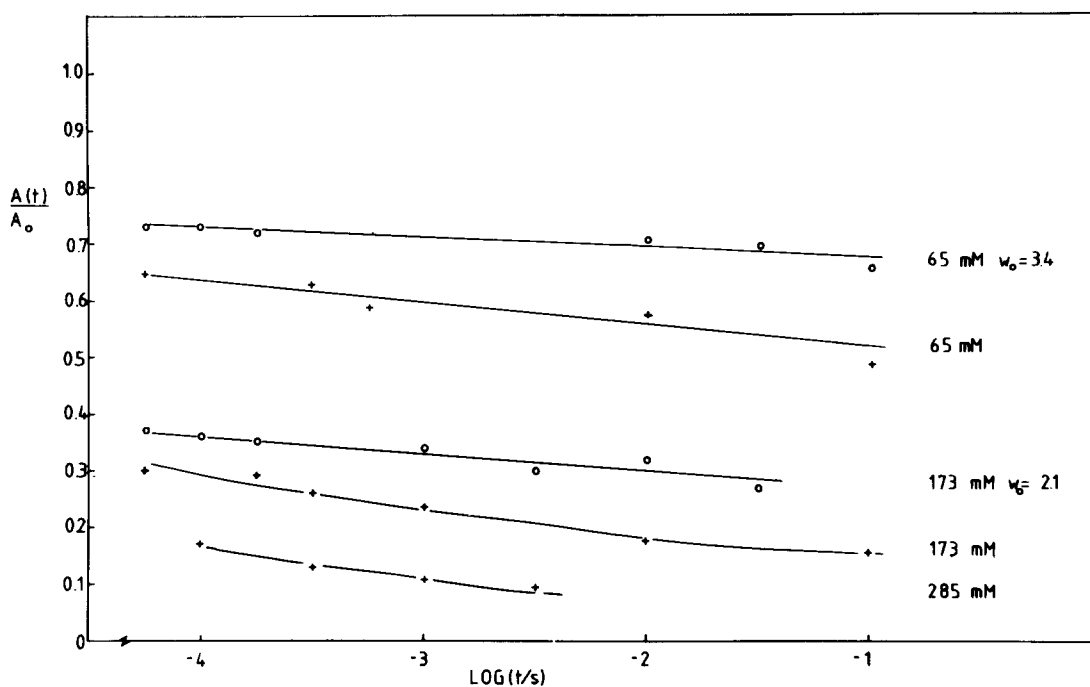


FIG. 3. Decay of the trapped electrons. The absorbance  $A(t)$  at each time is divided by the absorbance  $A_0$  in the pure matrix at the same time  $t$ . Measurements are at 1475 nm.

where  $A(t)$  is the absorbance at time  $t$ ,  $A_0$  the absorbance at time  $t$  in the absence of scavengers,  $S$  the molar concentration of the scavenger,  $\beta = 2(2m\Delta V)^{1/2}/\hbar$  (expressed in  $\text{nm}^{-1}$ ) if the barrier is rectangular with a height  $\Delta V$  and  $t_1$  is a reciprocal frequency factor. The factor  $f(S)$  was added to correct for dry electron scavenging and/or the formation of trapped electrons within the encounter radius of the scavenger. We fitted the decay curves of the electron at 1475 nm by plotting  $\log A(t)/A_0$  vs  $\log(10^{14} t)^3$ . The results are shown in Fig. 4. From the slope of these plots  $\gamma$  which is given by equation (2)

$$(2) \quad \gamma = \frac{13.37S}{\beta^3}$$

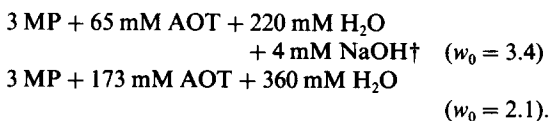
with  $S$  expressed as usually in mol/l,  $\beta$  in  $\text{nm}^{-1}$  was calculated.

From the ordinate intercept  $f(S)$  was found. Results are given in Table 1. The value of  $\beta$  thus estimated is relatively insensitive to the choice of  $t_1$ . Variation of  $10^{-16} < t_1 < 10^{-12}$  s gives variations in  $\beta$  of  $\pm 15\%$ . Variations in  $f(S)$  are larger. We expect

from equation (2) a linear dependence of  $\gamma$  on  $S$ , so the value found for  $\beta$  for all concentrations should be the same. The values for  $\beta$  were calculated assuming that the scavenger concentration in the sample at 77 K is 1.33 times the concentration at room temperature, due to volume contraction of the 3 MP glass.<sup>(13)</sup> For the three different concentrations these values are in good agreement.

### 3 Addition of water to the AOT/3 MP mixtures

At room temperature large quantities of  $\text{H}_2\text{O}$  can be added to AOT/3 MP mixtures. A value for  $w_0$  ( $=[\text{H}_2\text{O}]/[\text{AOT}]$ ) of 20 can be easily obtained. On rapid cooling to 77 K it was only possible to obtain clear samples when  $w_0$  was smaller than 4. Two water concentrations were studied (various samples)



The effects of the presence of water on the spectra immediately after the pulse are an increase of the trapped electron yield but a decrease of the 450 nm species.

<sup>†</sup>The NaOH was added to prevent the crystallization of the water.

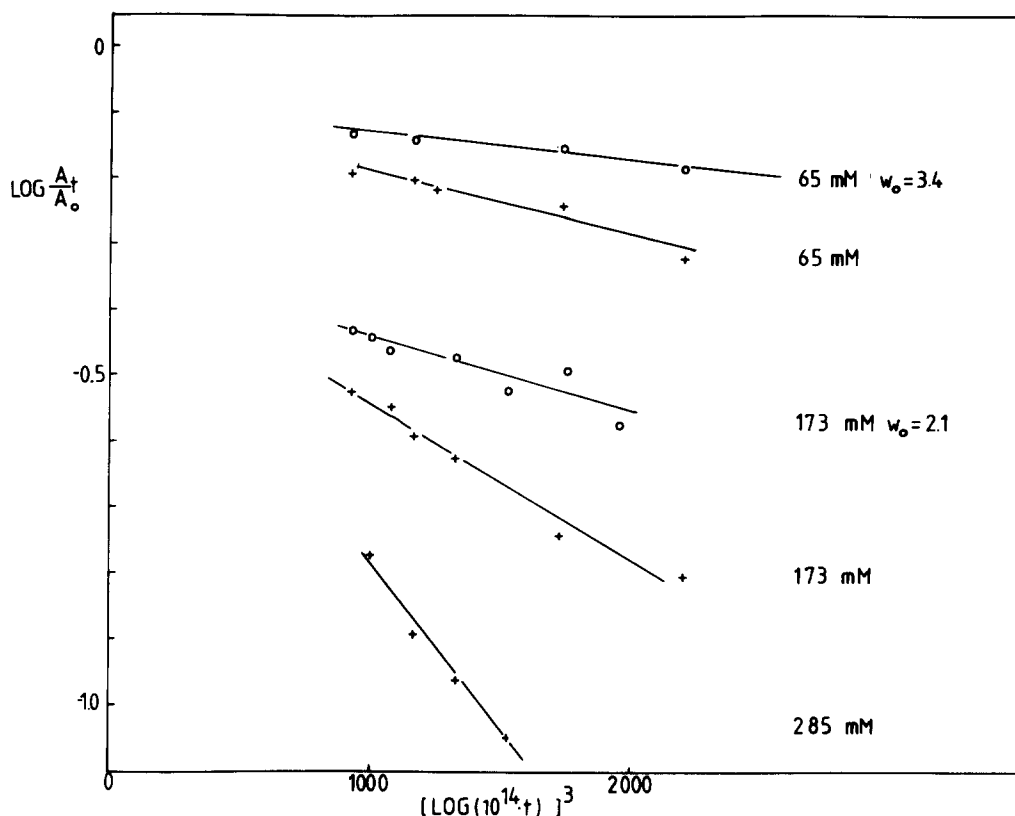


FIG. 4. A plot of  $\log[A(t)/A_0]$  vs  $[\log(10^{14}t)]^3$ . A linear behaviour is observed in accordance with equation (1).

An additional absorption possibly due to electrons solvated in a water environment<sup>(14)</sup> was not found. After correction for the cell and the absorption of the trapped electron at this wavelength, the yield of the species absorbing at 450 nm was about 70% in the  $w_0 = 3.4$  and  $w_0 = 2.1$  samples as compared to the dry

samples. The trapped electron yields were about 14% higher in both samples.

The decay of the trapped electrons as plotted in Fig. 3 changes drastically with the water content. Again  $\log A(t)/A_0$  is plotted as a function of  $(\log(10^{14}t))^3$  (Fig. 4). The  $\beta$  values calculated from the

TABLE I. RESULTS OF THE FIT OF OUR DATA TO EQUATION (1) ( $t_1 = 10^{-14}$  s)

scavenger	S (mM) <sup>(1)</sup>	$w_0$	$\gamma \times 10^5$	$\beta$ (nm <sup>-1</sup> ) <sup>(2)</sup>	f (S)
AOT	65	0	9.9±1.6	22.7±1.2	0.81±0.03
	173	0	23.5±2	23.6±0.7	0.50±0.04
	285	0	44 ±8	22.6±1.4	0.45±0.15
AOT/H <sub>2</sub> O	173	2.1	12.5±1.0	29.1±.8	0.48±0.02
	65	3.4	3.5±0.7	32 ±2	0.80±0.03
Biphenyl	4		7.9±0.8	9.4±0.3	0.95±0.03

(1) S(mM) concentration at room temperature.

(2) Errors are 1 x standard deviation from fit.

TABLE 2. ASSOCIATION NUMBERS OF AOT

$w_0$	Keh et al.	Tavenier et al.	This work
0	—	18	15
1	32	19	—
2.1	40	22	29
3.4	51	30	39

slopes are larger than in the dry samples, and the effect is strongest in the sample with the higher  $w_0$ . The  $f(S)$  factors are about the same.

#### 4 Biphenyl as a scavenger

4 mM Biphenyl was dissolved in 3 MP. The decay curve of the trapped electrons was analyzed by means of equation (1). The results are included in Table 1. The value found for  $\beta$  is much smaller than for AOT. In 3 MP biphenyl is as effective as  $\text{CCl}_4$  in reducing the trapped electron yield at 77 K, even when  $\text{CCl}_4$  is clearly the stronger scavenger when the two scavengers compete with each other for electrons.<sup>(15)</sup>

#### 5 AOT in methylcyclohexane

The absorption spectrum resulting from the irradiation on 250 mM AOT in methylcyclohexane at 77 K is similar to the absorption in 3 MP as a solvent. Both in 3 MP and in methylcyclohexane the spectrum decays slowly and the maximum is slightly redshifted at longer times (more than 1 min).

### DISCUSSION

#### 1 The 450 nm absorption

We ascribe the absorption found in 3 MP/AOT and McH/AOT mixtures to an electron attachment product of AOT. This is based on the following considerations.

(a) The absorption increases with increasing AOT concentration while the trapped electron yield decreases. The electron yield immediately after the pulse shows a logarithmic dependence on AOT concentration (Fig. 2).

(b) The same absorption was found in different solvents.

(c) AOT has two ester groups. Esters show an absorption band around 450 nm after irradiation at 77 K.<sup>(16)</sup>

No growth of the absorption after the electron pulse was observed directly. Still we believe that the decay of the IR absorption after the pulse in the 3 MP/AOT system, corrected for the decay in the pure 3 MP matrix, must be attributed to tunnelling of the electron from its trap to the AOT scavenger. A

rough estimate of the ratio of the extinction coefficients of  $\text{AOT}^-$  at 450 nm and  $e_2^-$  at 1500 nm, derived from the data of Figs. 1 and 4, (corrected for the absorption of the polystyrene cell and the electron) gave a value of 0.1 based on the assumption that in a pure 3 MP matrix at 77 K about 20% of the dry electrons is trapped. The extinction coefficients of  $\text{AOT}^-$  and  $e_2^-$  at 450 nm appear to be almost the same. This means that the increase of  $\text{AOT}^-$  and the concomitant decay of  $e_2^-$  leaves the absorbance at 450 nm unchanged.

#### 2 Electron scavenging by AOT

From Table 1 it can be seen that AOT seems to be a less effective electron scavenger than biphenyl, as judged by the higher value for  $\beta$  found for AOT. At room temperature, however, AOT aggregates to inverted micelles in nonpolar media. Therefore the AOT micelles may be considered poly-functional units with respect to the scavenging of electrons. Huddleston and Miller<sup>(6)</sup> have shown that a difunctional molecule may be a considerably less effective acceptor than two independent monofunctional molecules, when the separation distance between the two reactive groups is a substantial fraction of the tunnelling distance. A factor

$$\phi(t) = \frac{V_n(t)}{V_1(t) + V_2(t)}$$

was defined so that the trapped electron survival probability at time  $t$  can be expressed as

$$P_n(t) = \{P_1(t)P_2(t)\}^{\phi(t)}$$

and

$$P_i(t) = \exp(-S_i V_i(t)),$$

where  $V_i$  is the capture volume associated with acceptor  $i$ .  $S_i$  is the concentration of the acceptor.

This means that in equation (1) we should write  $S\phi$  instead of  $S$ . If we consider that  $n$  AOT molecules aggregate and that at longer times the capture volumes overlap completely we find  $\phi = 1/n$ . Because of the aggregation of AOT, we do not believe that the high value for  $\beta$  found from equation (2) is due to AOT being less effective because of Franck–Condon factors for the electron transfer process. As has been demonstrated recently<sup>(17)</sup>  $\beta$  may be thought to be the sum of a  $\beta_0$  which is scavenger independent and a term  $\lambda$  in which Franck–Condon factors are incorporated. The value found for biphenyl in 3 MP may be close to  $\beta_0$ , since biphenyl and  $\text{CCl}_4$  are the most efficient scavengers in 3 MP.<sup>(15)</sup>

If we now assume that an AOT molecule is as effective as a biphenyl molecule in 3 MP, we can determine  $n$  from  $\gamma = (13.37S/n)/\beta_b^3$  as 15.  $\beta_b$  is the value found for biphenyl.

The strong increase in  $\beta$  caused by the addition of water can now be explained by a change in the aggregation number  $n$  caused by the addition of water. Thus we find for  $w_0 = 2.1$ :  $n = 29$ , and for  $w_0 = 3.4$ :  $n = 39$ . The association numbers found at 77 K are lower limits, since the capture volumes of the  $n$  molecules were assumed to overlap completely. If the overlap is not complete  $\phi$  will be larger than  $1/n$ . As an approximation we take  $n$  molecules distributed uniformly over the surface of a sphere with radius  $r_c < r_t$  (tunnelling distance). Provided  $n$  is large enough, we find that

$$\phi(t) = \frac{1}{n} \left\{ 1 + \frac{r_c}{r_t} \right\}^3.$$

In this case  $\phi$  will be time-dependent. Experiments over more decades of time could test the time-dependence of  $\phi$ . The  $r_c$  may vary with water content, so the increase in  $n$  may be even larger than calculated above.

### 3 Comparison with room temperature data on AOT

At room temperature the association number as a function of water content (in the region  $w_0 < 6$ ) has been investigated by small angle X-ray diffraction<sup>(7)</sup> and fluorescence polarization.<sup>(18)</sup> The aggregation number was found to be independent of concentration for  $[AOT] < 0.3M$ .<sup>(18)</sup> The aggregation number increases with increasing water content. From the results of Keh and Valeur<sup>(18)</sup> on AOT/heptane mixtures  $n$  can be calculated (assuming spherical micelles and by taking the molecular volume of AOT to be  $825 \text{ \AA}^3$  (Ref. 19)). Bearing in mind that aggregation numbers of AOT depend on the solvent and that the values calculated are lower limits, the values found for  $n$  as a function of  $w_0$  from electron scavenging data are consistent with values obtained for these systems at room temperature.

This indicates that upon rapid cooling to 77 K micelles with a small water core exist indeed at this temperature.

### 4 The factor $f(S)$

The increase of water content does not change  $f(S)$  very much. The factor  $f(S)$  can be expressed as<sup>(20)</sup>

$$f(S) = \exp(-S/S_{37}).$$

At short times ( $10^{-14}$  s)  $\phi(t)$  will approach unity (no overlap) so we may calculate  $S_{37}$  by taking  $S$  as if no

aggregation has occurred. The assumption that overlap does not exist at short times can explain why the change in water content does not influence  $f(S)$ . The value for  $S_{37}$  found is  $370 \pm 140$  mM. This value is high when compared to the value found for  $\text{CrO}_2^+$  in an 8M NaOH glass<sup>(21)</sup>:  $45 \pm 15$  mM. The large errors in  $f(S)$  do not permit further conclusions.

## CONCLUSION

Upon rapid cooling AOT exists in 3 MP at 77 K in micellar form as at room temperature. AOT has electron scavenging properties. The scavenging of trapped electrons by AOT micelles is influenced by the water content, because the aggregation number and hence the effective scavenger concentration depend on water content. A characteristic absorption at 450 nm was found and ascribed to an electron attachment product of AOT.

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