

- (13) R. Scheerer, Ph.D. Thesis, TU Berlin, 1977.  
 (14) A. Kira, M. Imamura, and T. Shida, *J. Phys. Chem.*, **80**, 1445 (1976).  
 (15) P. P. Infelta and M. Grätzel, *J. Chem. Phys.*, submitted.  
 (16) M. Maestri, P. P. Infelta, and M. Grätzel, to be published.  
 (17) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2364 (1966).  
 (18) (a) J. J. Katz and J. R. Norris in "Current Topics in Bioenergetics", Vol. 5, Academic Press, New York, N.Y., 1973, pp 41-75. (b) K. Sauer in "Bioenergetics of Photosynthesis", Academic Press, New York, N.Y., 1975, pp 115-181.  
 (19) K. B. Patel and R. L. Wilson, *J. Chem. Soc., Faraday Trans. 1*, 814 (1973).  
 (20) C. Wolff and M. Grätzel, *Chem. Phys. Lett.*, **52**, 542 (1977).

## Study of the Micelle Formation and the Effect of Additives on This Process in Reversed Micellar Systems by Positron Annihilation Techniques<sup>1</sup>

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**Abstract:** The positron annihilation technique was applied to the study of the micelle formation process in reversed micellar systems, Aerosol OT and dodecylammonium propionate in apolar solvents, such as benzene, isooctane, and cyclohexane. The results indicate that the positronium formation probability responds very sensitively to microphase changes in reversed micellar solutions. The abrupt changes in positronium formation probability observed at certain surfactant concentrations appear to coincide with variations in the aggregation state of the surfactant molecules in solutions, as postulated by the modified pseudophase model which considers the possibility of conformational changes between premicellar aggregates, and the surfactant concentrations at which they occur may be interpreted as operational critical micelle concentrations. Additives or probe molecules can affect these changes and shift them to lower surfactant concentrations. The additions of H<sub>2</sub>O and its solubilization in form of clusters inside the reverse micelle leads to microphase changes also detectable by the positron annihilation technique. From a comparison of the rate constants between positronium and probe molecules observed in the neat solvents and in the corresponding micellar solutions it was concluded that the probe molecules are attracted to various degrees by the reverse micelles, the nature of the surfactant and solvent determining the relative distribution of the probe molecule in the outer hydrocarbon layer and in the bulk apolar solvent of the reversed micelles.

### Introduction

The importance of reversed micellar systems formed by the aggregation of surfactant molecules in nonpolar solvents in today's industrial applications, energy storage and conservation, tertiary oil recovery, and dry cleaning processes as well as catalysts in chemical and biological reactions, and biomembrane transport phenomena has recently been more and more recognized.<sup>2,3</sup>

Reversed or inverted micelles can be characterized as aggregates of surfactant molecules with their polar groups concentrated in the interior of the aggregate while their hydrophobic moieties extend into, and are surrounded by, the bulk apolar solvent.

While there is a relatively large body of experimental details available about aqueous micellar systems,<sup>2</sup> information on the physical chemical properties of reversed micelles is still scarce.<sup>3</sup> This is mainly due to the fact that experimental techniques, such as specific conductance, interfacial tension, light scattering, NMR, and other spectroscopic measurements traditionally used for the study of aqueous micelles, are much more difficult to perform in the reversed micellar systems because of the relatively small aggregation number of surfactant molecules in the latter systems as compared to aqueous micellar solutions.

In a previous paper we have reported on the application of the positron annihilation technique as a new, sensitive tool for the study of phenomena involved in the micelle formation and solubilization processes in aqueous media.<sup>4,5</sup> This new method is based on the fact that the reactions as well as the formation of the positronium atom, which is the bound state of an electron and a positron, are greatly dependent on the environment in which these interactions occur.<sup>6</sup> Thus by applying this tech-

nique we were able to study the location of solubilisates, such as nitrobenzene, benzyl alcohol, benzene, hexane, and hexanol, in a variety of aqueous micellar solutions.<sup>4,5</sup> We have also demonstrated<sup>4,5</sup> that the positron annihilation method can serve as a superior analytical probe for the accurate determinations of an important physical chemical property in aqueous micellar systems, namely, the critical micelle concentration (cmc), which is defined as the surfactant concentration at which micelles become first detectable. We were able to show that at the cmc the positronium formation undergoes an abrupt and drastic change, which allows a precise determination of the cmc.

In reversed micellar systems where the number of monomers involved in the formation of the aggregates is rather small, the question exists whether the aggregation can be characterized by a monomer  $\rightleftharpoons$  *n*-mer type association as postulated in aqueous micelles or whether a multiple equilibrium model applies, which assumes stepwise formation of aggregation in an indefinite association process monomer  $\rightleftharpoons$  dimer  $\rightleftharpoons$  trimer  $\rightleftharpoons$  . . . *n*-mer.<sup>3,8</sup>

While the indefinite self-association model would predict that changes in physical properties of reversed micellar solutions with increasing surfactant concentrations are expected to be gradual, <sup>1</sup>H NMR plots, e.g., were found to show obvious breaks at certain surfactant concentrations, which were defined as operational cmc's.<sup>9-12</sup> Even more pronounced and abrupt changes at these cmc's were observed in our laboratory when the positronium formation probability was determined as a function of surfactant concentration.<sup>7</sup>

We therefore have systematically investigated the formation of reversed micelles in a series of apolar solvents by using the positron annihilation technique and included an assessment of the effects of the presence of a third component, an added

solubilise or probe molecule, on the aggregation properties of surfactants in nonpolar solvents, in order to provide more insight into the details of the aggregation processes in reversed micellar systems.

## Experimental Section

**A. Purity of Materials.** Aerosol OT (AOT = sodium di-2-ethylhexylsulfosuccinate) was obtained from American Cyanamid Co. with a stated purity of 100%. It was recrystallized and dried in accordance with the procedures in ref 13.

Dodecylammonium propionate (DAP) was prepared by neutralization of dodecylamine (from Aldrich Co.) with propionic acid (Fisher Scientific Co.) in *n*-hexane.<sup>14</sup> Repeated recrystallization from *n*-hexane resulted in a product with a melting point of 55.0 °C.

Solvents such as *n*-hexane, benzene, and cyclohexane were glass-distilled spectroscopic grades from Burdick and Jackson Laboratories. Isooctane was obtained from Aldrich Co., with the highest purity available. These solvents were further dehydrated by distillation over metallic sodium. The redistilled solvents were stored in desiccators to avoid any further contamination with water.

Nitrobenzene, *p*-nitrophenol, 1-pentanol, and benzyl alcohol were obtained from Fisher Scientific Co. and further purified by conventional methods. Tetracyanoethylene (TCNE) was purchased from Aldrich Co. It was of the highest purity commercially available and used without further purification.

**B. Positron Lifetime Measurements and Preparation of the Samples.** Positron lifetime measurements were carried out by the usual delayed coincidence method as previously described.<sup>15</sup> The resolution of the system, as measured by the fwhm of the prompt coincidence spectrum of a <sup>60</sup>Co source without changing the 1.27- and 0.511-MeV bias, was found to be less than 0.36 ns fwhm. Specially designed cylindrical sample vials (Pyrex glass 100 mm long and 10 mm i.d.) were filled with about 2 mL of the appropriate solution. The positron sources consisted of 3–5 mCi <sup>22</sup>Na diffused into a thin foil of soda lime glass.

The relative amount of positron annihilation occurring in the glass was found to be less than 2%, for which corrections were made. The radioactive glass sources were suspended in the center of the ampule and all solutions were carefully degassed by freeze-thaw techniques to remove oxygen. The vials were subsequently sealed off and the measurements carried out at 22 °C.

**C. General Method of Data Analysis.** The general method of the assessment of data obtained from the determination of the time-dependent two-photon annihilation rate via positron lifetime measurements was discussed in detail in a previous paper.<sup>16</sup> In subsequent papers<sup>4,5,7</sup> it was demonstrated that  $I_2$ , the intensity of the long-lived component in the positron lifetime spectra, which is related to the formation of thermalized ortho-Ps atoms, and  $\lambda_2$ , the slope associated with this component, are highly sensitive to the formation of micelles or micellar structure changes.

In analogy to the data analysis described in detail in ref 5 for the reactions of Ps with probe molecules in aqueous micellar systems, it can be shown that  $\lambda_2$  in a reversed micellar system consisting of a surfactant (concentration  $[S_m]$ ), an apolar solvent, and a probe molecules (concentration  $[M]$ ) is given by the following equation:

$$\lambda_2 = \lambda_s + k^S_{mic}[S_m] + K^P_{obsd}[M_p] + K^A_{obsd}[M_A] \quad (1)$$

$\lambda_s$  is the slope  $\lambda_2$  of the long-lived component found in the pure apolar solvent.  $[M_p]$  and  $[M_A]$  are the probe molecule concentrations in the polar and in the apolar region, respectively.  $K^S_{mic}$  is the observed rate constant for Ps reactions with the reversed micelles, which is usually very small as compared to observed rate constants of probe molecules in either the polar ( $K^P_{obsd}$ ) or apolar environment ( $K^A_{obsd}$ ).

$\lambda_s + K^A_{mic}[S_m]$  is usually combined to  $\lambda_p$ , which is obtained by measuring the slope  $\lambda_2$  in the presence of the surfactant in the apolar medium but without probe molecules present. By appropriate choices of the probe molecules, either soluble in the polar medium but insoluble in apolar medium (i.e.,  $[M_A] = 0$ ) or vice versa ( $[M_p] = 0$ ), eq 1 can be simplified and the rate constants,  $K^P_{obsd}$  or  $K^A_{obsd}$  in the reversed micellar systems can be obtained from

$$K^P_{obsd} \text{ or } K^A_{obsd} = \frac{\lambda_2 - \lambda_p}{[M]} \quad (2)$$

where  $\lambda_2$  and  $\lambda_p$  are the slopes of the second component in the lifetime spectra with and without the probe molecule  $[M]$  present.

In the case of a probe molecule which is partially soluble in two

distinct environments 1 and 2 eq 1 can be approximated as

$$\lambda_2 = \lambda_p + K^1_{obsd}[M_1] + K^2_{obsd}[M_2] \quad (3)$$

where  $K^1_{obsd}$  and  $K^2_{obsd}$  are the observed rate constants for the reaction with the probe molecule in the two environments 1 and 2, and  $[M_1]$  and  $[M_2]$  are the corresponding concentrations of the probe molecules.  $[M_1] + [M_2] = [M]$ .

The intensity  $I_2$  of the long-lived component is directly extracted from the positron lifetime spectra.<sup>15</sup>

As mentioned above  $I_2$  is correlated to the number of ortho Ps atoms reaching thermal energies. The mechanism of the Ps formation in condensed matter is still the subject of some discussion and several different models have been developed to describe the process. The general consensus, however, is that regardless of which model one prefers, the number of Ps formed as well as the number of those Ps atoms which reach thermal energies depends on not only the nature of the environment which determines the number of Ps atoms generated but also on rather subtle chemical reactions with a variety of radiation-induced species generated together with the Ps.<sup>17</sup>

Thus the nature, structure, and other physicochemical properties determine in a rather complex way the magnitude of  $I_2$ , which in turn make this parameter very sensitive to slight changes in the environment and thus useful as a chemical probe.

## Results and Discussion

Several series of experiments were performed with DAP and AOT surfactants in apolar solvents, such as benzene, cyclohexane, and isooctane with or without additives such as H<sub>2</sub>O, 1-pentanol, benzyl alcohol, or probe molecules such as nitrobenzene, *p*-nitrophenol, or tetracyanoethylene present.

In all cases more or less abrupt changes in the positron annihilation parameters  $I_2$  or  $\lambda_2$  were observed in the regions of previously reported cmc's. While both  $I_2$  and  $\lambda_2$  were found to be sensitive to the changes accompanying micelle formation or microphase transitions in these solutions, the method of detecting these changes via the observation of  $\lambda_2$  (or  $K_{obsd}$  for the reaction between Ps and probe molecules present in the micelles solutions) is usually limited to solutions of surfactants with higher cmc's, of the order of about 10 mM, and to ionic micelles.

Thus in the following investigation the experiments were carried out by observing the changes of  $I_2$  (%) as a function of surfactant concentration. This technique<sup>7</sup> is simpler to perform, has less restrictions, and can give accurate breaks in the  $I_2$ -surfactant concentration plots with an experimental error of a few tenths of a millimole/liter.

**AOT and DAP Micellar Systems.** In the first series of experiments positron annihilation measurements were performed in AOT-benzene and AOT-isooctane solutions (Figures 1 and 2). As previously reported the  $I_2$  values exhibit an abrupt change at surfactant concentrations of 2.0–2.2 mM in benzene<sup>7</sup> and 0.6–0.9 mM in isooctane.

These data are in good agreement with the cmc's obtained by Kon-no and Kitahara<sup>18</sup> via light scattering (2.8 mM) and depression of vapor pressure (2.3 mM), and by Muto and Meguro<sup>19</sup> via the dye absorption (TCNQ) technique (2.0 mM), while specific conductivity measurements by Eicke et al.<sup>20</sup> would indicate a lower cmc of about 0.5 mM in benzene (see also Table I).

The present results observed in the less polar isooctane where the change occurs between 0.6 and 0.9 mM seem to confirm the expected trend that the cmc values decrease with the polarity of the solvent. They coincide very closely with the cmc's found by Fendler et al.<sup>2b</sup> in another solvent of similar polarity, cyclohexane, where the corresponding value was 0.95–1.2 mM.

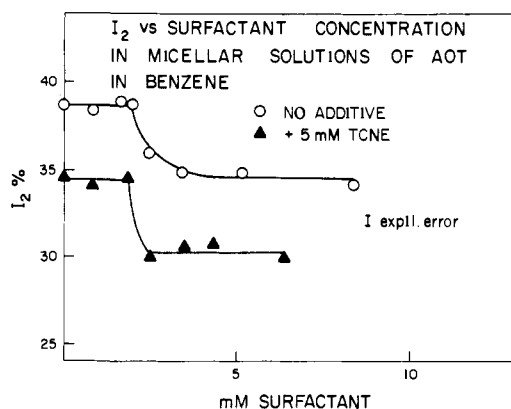
Figures 3 and 4 where  $I_2$  is plotted as a function of surfactant concentration show the results observed in DAP solutions in benzene and cyclohexane.

As summarized in Table I the  $I_2$  values exhibit again an abrupt change at surfactant concentrations which closely

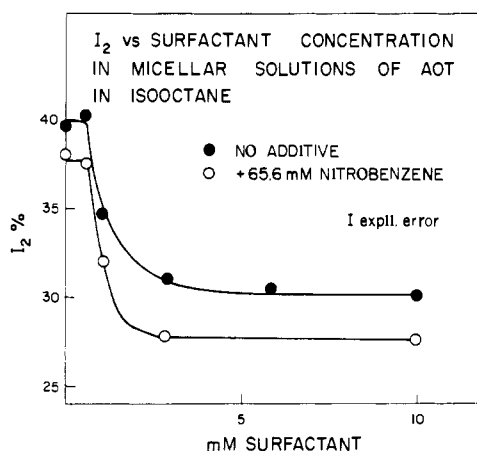
**Table I.** Surfactant Concentrations at Which  $I_2$ -Surfactant Plots Show Pronounced Changes and Previously Reported cmc's

surfactant	solvent	additive	surfactant concn, mM/L		previously reported cmc's					
			onset of drop <sup>a</sup>	midpoint	mM/L	method	ref			
AOT	benzene	none	2.0	2.2	0.95-1.1	2.0	TCNQ solubility	19		
	benzene	5 mM TCNE				1.9	2.1	0.9	iodine solubility	19
		isooctane				none	0.6	0.9	2.3	vap press depress
isooctane	65.6 mM nitrobenzene	none	0.6	1.0		2.8	light scatt	18		
						0.5	spec conduct	20		
DAP	benzene	none	8.7	8.7	3-7	<sup>1</sup> H NMR	9, 10			
	benzene	10 mM nitrobenzene		3.5						
	benzene	10 mM tetracyanoethylene		4.5						
	benzene	0.1 vol % H <sub>2</sub> O		8.6						
	benzene	5 vol % 1-pentanol		6.5						
	benzene	5 vol % benzyl alcohol		5.0						
	cyclohexane	none	8.3	8.3				0.79	TCNQ solubility	21
	cyclohexane	24.7 nM nitrobenzene		4.5						

<sup>a</sup> If it can be clearly recognized.



**Figure 1.**  $I_2$  vs. surfactant concentrations in micellar solutions of AOT in benzene.



**Figure 2.**  $K_2$  vs. surfactant concentrations in micellar solutions of AOT in isooctane.

coincide with the operational cmc's postulated by Fendler et al.<sup>9-10</sup> on the basis of results obtained by using <sup>1</sup>H NMR spectroscopic techniques which range from 3 to 7 mM/L. At variance with Fendler's NMR data<sup>9,10</sup> and our results are data reported by Muto et al.<sup>21</sup> using UV spectrometry in the presence of TCNQ. They quote a cmc of 0.74-0.79 mM in cyclohexane. An explanation for this apparent inconsistency is given in the following paragraph in which the effect of the presence of additives on the cmc is discussed.

While as discussed in a previous communication<sup>7</sup> the abrupt change in  $I_2$  can be interpreted in aqueous micellar systems in terms of the critical micelle concentration (cmc), in reversed micellar system the concept of cmc has been the subject of considerable discussion.<sup>22</sup>

Kertes<sup>23</sup> suggested that in contrast to aqueous micellar systems, where a monomer  $\rightleftharpoons$  micelle equilibrium exists, in nonpolar solvents a multiple equilibrium model applies, which leads to the formation of oligomers (dimers, trimers, tetramers, etc.) all in dynamic equilibrium. This author argues that if a monomer  $\rightleftharpoons$  micelle equilibrium ceases to be operative and is

replaced by a stepwise aggregation equilibrium, the concept of cmc is rendered inapplicable. As a consequence of such an equilibrium conventional physical properties measured in these systems should show a smooth continuity as a function of surfactant concentration and no apparent discontinuities. In this context, the reliability of some of the earlier results observed by several authors<sup>9,24-25</sup> which showed indeed discontinuities, e.g., in the <sup>1</sup>H NMR spectroscopic investigations,<sup>9,10</sup> were questioned by Kertes.<sup>23</sup>

This would be in line with the calculations of Muller<sup>8</sup> which demonstrated that the observed concentration dependence of the <sup>1</sup>H NMR chemical shifts for alkylammonium carboxylates in benzene fits either a single or a multiple equilibrium model equally well. Further support for the multiequilibrium model was obtained by Lo et al.,<sup>36</sup> who carried out vapor pressure osmometry experiments at different temperatures on solutions of DAP in benzene and cyclohexane. These authors claim that their results can best be explained in terms of a multiequilibrium or indefinite self-association model in which the presence

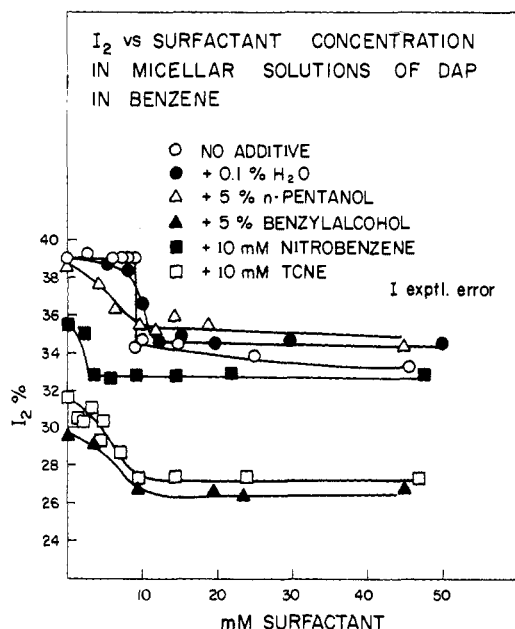


Figure 3.  $I_2$  vs. surfactant concentrations in micellar solutions of DAP in benzene.

of all associating species and the equality of all equilibrium constants are assumed.

However, on the basis of the positron annihilation data, which unambiguously show discontinuities in a physical property ( $I_2$ ) as a function of surfactant concentration, at concentrations which incidentally coincide with the well-defined "operational cmc's" observed by Fendler et al.<sup>9,10</sup> in his  $^1\text{H}$  NMR study as well as in connection with the fact that Fendler's operational critical micelle concentrations correlate so well with the chain length of alkylammonium carboxylates, with the solvent polarities, with the drastic rate enhancements occurring at well-defined surfactant concentration<sup>37</sup> and recent investigations by Eicke et al.,<sup>13,20,38-43</sup> who also observed abrupt changes in physical properties of reversed micellar solutions, e.g., by electric field effect measurements, a reevaluation of the existing hypotheses seems to be in order.

While it is obviously rather difficult to reconcile the latter results with a multiple equilibrium model, they appear to be consistent with the idea of conformational changes taking place during micelle formation as recently proposed by Eicke et al.,<sup>13,38</sup> and explained within the framework of the "pseudophase model".

Eicke and co-workers have investigated the micellization process in AOT dissolved in apolar solvent by vapor pressure osmometry and dipole and dielectric dispersion measurements. Based on these investigations they proposed to interpret the micellization process as a phase change. These authors postulate the existence of pre-micellar aggregates having an initially linear arrangement which can undergo at certain surfactant concentrations a transition to closed aggregates.

The sensitivity of the positron annihilation process toward structural changes has been recognized in experiments with liquid crystals,<sup>44-46</sup> where the variations in the mesomorphic phases were clearly reflected in the positron lifetime characteristics. It seems, therefore, tempting to assume that the observed breaks in the  $I_2$ -surfactant concentration curves also signal phase transitions which the surfactant molecules undergo in the reversed micellar solutions, as postulated by Eicke's pseudophase model. The observed drop in  $I_2$  may therefore be caused by the postulated formation of the closed aggregates. The question whether this process can be considered as the formation of the reversed micelles and whether the

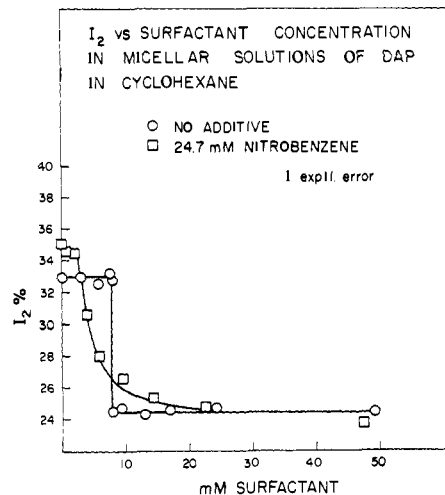


Figure 4.  $I_2$  vs. surfactant concentrations in micellar solutions of DAP in cyclohexane.

surfactant concentration at which this occurs can be called the cmc in these systems will have to remain open for the time being.

It seems important to point out that the changes of  $I_2$  in the pure surfactant-solvent system observed in the present investigation occur within a small surfactant concentration range of about 0.2–0.3 mM/L, which would imply that the change in the microstructure of the solution should also show such a distinct concentration dependence.

A more detailed discussion of the exact nature of the structure variations occurring in the solution which are being probed by this technique will have to be postponed until the mechanism of the positronium formation process is better understood.

**AOT and DAP Micellar Systems in the Presence of Additives.** Additives have been found to show a distinct effect on the surfactant concentrations at which abrupt changes in certain physicochemical properties of the reverse micellar solutions have been observed.<sup>10,19,41</sup>

In order to study the effect of additives on the micelle formation process in the DAP systems small amounts of water, 1-pentanol, benzyl alcohol, or probe molecules such as nitrobenzene were added to the solution. In contrast to the abrupt drop of  $I_2$  in the pure DAP-benzene solution, in the presence of 0.1% water, 5% 1-pentanol, or benzyl alcohol the change in  $I_2$  occurs more gradually and over a considerably wider concentration range of approximately 6–10 mM/L (Figure 3); furthermore, the onset of this change in  $I_2$  is shifted to definitely lower values of surfactant concentration (Table I). An equally dramatic shift in the  $I_2$ -surfactant curves can be observed (Figures 3 and 4) if small amounts of nitrobenzene (10 or 24.7 mM/L) are added to DAP-benzene or DAP-cyclohexane solutions, respectively.

The drop of the  $I_2$  values proceeds definitely more gradually than in the neat system and the onset of this drop is again shifted to drastically smaller concentrations, e.g., in DAP-benzene solution from 8.7 mM/L in the neat system to less than 3.0 mM/L in the presence of 10 mM/L nitrobenzene, and in DAP-cyclohexane from 8.3 mM/L (neat) to less than 2.5 mM/L with 24.7 mM/L present.

On the other hand, in the AOT micellar systems the plots of  $I_2$  vs. surfactant concentration in the presence of 5 mM tetracyanoethylene (in benzene) and 65.6 mM nitrobenzene (in isooctane) provide very little evidence for any change of  $I_2$  as a result of these additions (Figures 1 and 2).

Generally speaking, the effect of additives on the trends observed in the  $I_2$  plots depends, as the results in this study

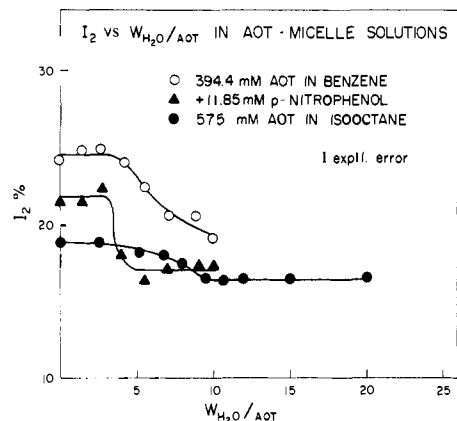


Figure 5.  $I_2$  vs.  $W_{H_2O}/AOT$  in AOT micelle solutions.

indicate, on the nature of surfactant, solvent, and additive (solubilize) and may therefore, in terms of the postulated conformational phase changes, be interpreted as an interference with these phase transitions which could take place in various ways, e.g., depending on the ability of the solubilize to orient itself in the aggregate, strength of its bonding to the head groups, etc.

Of special interest is in this context the effect of solubilized water on reversed micelles. The state of solubilized water has been reported as clusters or pools inside the reversed micelles with fluorescence probes and NMR spectroscopy by Thomas et al.<sup>47,48</sup> More recently Fendler et al.<sup>49</sup> and Eicke et al.<sup>20,40,41</sup> applied vapor pressure osmometry, dielectric dispersion, and ultracentrifuge measurements as well as thermodynamic and statistical calculation to this problem.

Their findings seem to indicate that the solubilization of water into AOT micelles in isoctane expands the size of the reversed micelles. At higher concentrations of water, i.e.,  $W_{H_2O}/AOT > 9$ , which is the ratio of water to AOT molecules, a large aggregated micelle with a water pool inside is supposedly formed which has been defined as a microemulsion.

In the present investigation it was observed that the positron annihilation technique is also able to detect such changes in the microphase. As shown in Figure 5 a more pronounced change of  $I_2$  can be recognized in the  $W_{H_2O}/AOT$  region where supposedly the microemulsion is formed. The observed value of  $W_{H_2O}/AOT$  of  $8.0 \pm 2.0$  at this point agrees very well with Eicke's<sup>40</sup> ultracentrifugal measurements where the plot of the apparent average molecular weight vs.  $H_2O/AOT$  shows a break in the same region. In the case of benzene as solvent our results would predict that the microemulsion is formed at a slightly lower ratio of  $H_2O/AOT$  of about  $5.0 \pm 1.0$ , which demonstrates the effect of various solvents on the phase change. *p*-Nitrophenol additives which most likely will become associated with the aqueous phase inside the microemulsion seem to have little effect on the ratio  $H_2O/AOT$  at which  $I_2$  starts to drop; however, they appear to be able to narrow the  $H_2O/AOT$  region during which microemulsion formation takes place.

**Interaction of Additives with Surfactant Molecules and Their Location in the Micelle.** Information about the reactions of the additive molecules as well as about the degree of interaction with the surfactant or a surfactant aggregate can also be obtained from positron annihilation data.

As stated above, changes in  $\lambda_2$ , or  $K_{obsd}$  if probe molecules are present, are usually small in surfactant solutions with small cmc's and not easily recognizable at low surfactant concentrations. However, the determination of the rate constants for the reaction between Ps and probe molecules can be successfully applied to an evaluation of the location of the probe

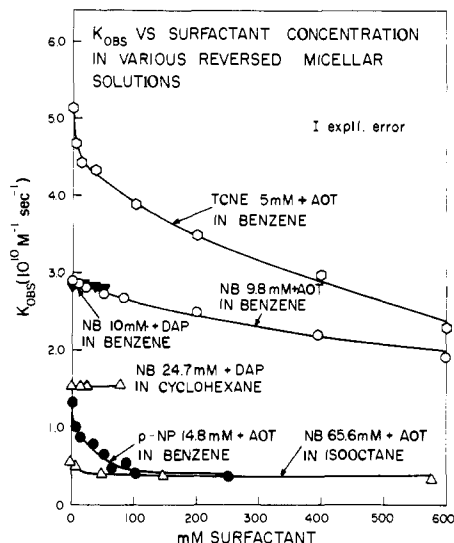


Figure 6.  $K_{obsd}$  vs. surfactant concentrations in various reversed micellar solutions.

molecule in micellar solutions containing larger amounts of surfactants.

The basis for this method is that positronium undergoes reversible molecular complex formation in solutions with compounds, such as nitrobenzene and other strong electron acceptors.<sup>16</sup> These Ps-molecule complexes are stabilized to various degrees in different solvents, which determines the overall reaction rate constants between Ps and the probe molecule. Thus the comparison of the rate constants obtained for Ps interaction with probe molecules in micellar systems with those obtained in other environments (water, hydrocarbon, etc.) provides the desired information about the location of the probe molecule or solubilize in the micellar system.<sup>4</sup> Since Ps reactions are fast in relation to the time to transfer the probe molecule from a micellar to an aqueous environment, and positronium is a neutral species which is not repelled by the charges on the micelle surface and effectively penetrates into the micelle, this method is not affected by the restrictions which a bigger probe molecule usually encounters.

In the present study we have adopted this method to assess the localization of similar probe molecules in reversed micellar systems.

In Figure 6 the observed rate constants,  $K_{obsd}$ , for the reaction of Ps with nitrobenzene, tetracyanoethylene, and nitrophenol in benzene, cyclohexane, or isoctane solutions containing AOT or DAP surfactants, are plotted as a function of the surfactant concentration.

As shown in Figure 6, in the nitrobenzene-DAP system in cyclohexane  $K_{obsd}$  for the reaction of Ps with nitrobenzene shows no significant change with increasing surfactant concentration. This is to be expected since regardless of whether the nitrobenzene residues in the bulk apolar solvent (cyclohexane) or in the region of the micellar hydrocarbon chains (dodecane)  $K_{obsd}$  would remain very similar,  $1.55 \times 10^{10} M^{-1} s^{-1}$  for the former environment vs.  $1.28 \times 10^{10} M^{-1} s^{-1}$  in the latter (Table II).

In benzene solution, however, where  $K_{obsd}$  clearly differs in the two environments, the corresponding value for benzene is  $2.8 \times 10^{10} M^{-1} s^{-1}$  (Table II); again no significant change of the observed  $K_{obsd}$  can be found. This seems to indicate that the major portion of nitrobenzene is located in the bulk apolar solvent.

This effect can be even better studied in AOT solutions where  $K_{obsd}$  in 3-methylheptane, which is identical with the structure of the hydrocarbon chain in AOT, is  $0.59 \times 10^{10} M^{-1} s^{-1}$ , which is considerably different from the  $K_{obsd}$  found for

**Table II.** Rate Constants for Reactions between Ps and Probe Molecules in Various Solvents

probe	solvent	$K_{\text{obsd}}, 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
nitrobenzene	benzene	2.80
	H <sub>2</sub> O	1.05
	isoheptane	0.34
	isooctane	0.69
	2-methylheptane	0.54
	3-methylheptane	0.54
	cyclohexane	1.55
	dodecane	1.28
tetracyanoethylene	benzene	5.15
	3-methylheptane	.99
<i>p</i> -nitrophenol	benzene	1.30
	3-methylheptane	.25

Ps reaction with nitrobenzene (or tetracyanoethylene) in the pure solvents. In this case the  $K_{\text{obsd}}$  values clearly decrease with surfactant concentration.

They approach in the nitrobenzene-AOT-isooctane and *p*-nitrophenol-AOT-benzene systems limiting  $K_{\text{obsd}}$  values at higher surfactant concentrations of  $0.38 \times 10^{10}$  and  $0.40 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively, which closely coincide with those observed for nitrobenzene and *p*-nitrophenol in 3-methylheptane,  $0.56 \times 10^{10}$  and  $0.25 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

Since 3-methylheptane is the hydrocarbon whose structure is identical with the hydrocarbon chain in AOT, these results would suggest that the major portion of the nitrobenzene and *p*-nitrophenol molecules in AOT-isooctane and AOT-benzene solutions, respectively, can be found in the outer hydrocarbon layer of the reverse micelles. In the other solutions such as tetracyanoethylene-AOT and nitrobenzene-AOT in benzene the probe molecules seemed to be somewhat less attracted by the reversed micelle, which may reflect the strong solubility of these compounds in benzene. An estimate of what fraction resides in the region formed by the extended surfactant hydrocarbon chains and in the bulk apolar solvent can be derived from eq 4. In this equation it is assumed that the observed rate constant  $K_{\text{obsd}}$  for the reactions between Ps and reactant is determined by the sum of the weighted averages of the two  $K_{\text{obsd}}$ 's observed in the two different environments or solvents (see also eq 3), i.e.

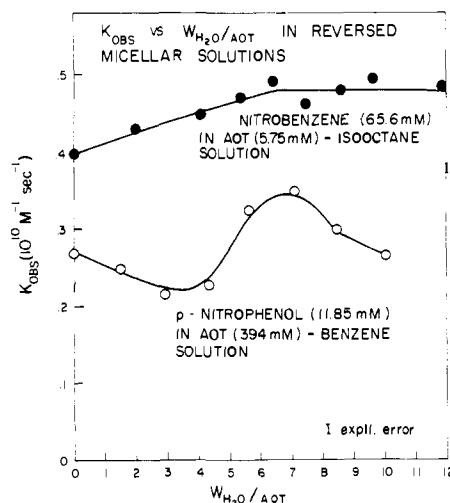
$$K_{\text{obsd}} = K^1_{\text{obsd}} \frac{[M_1]}{[M]} + K^2_{\text{obsd}} \frac{[1 - M_1]}{[M]} \quad (4)$$

or

$$\frac{[M_1]}{[M]} = \frac{K_{\text{obsd}} - K^2_{\text{obsd}}}{K^1_{\text{obsd}} - K^2_{\text{obsd}}} \quad (5)$$

where  $[M_1]/[M]$  is the fraction of the probe molecule M in environment 1, and  $[1 - M_1]/[M]$  in environment 2, and  $K^1, 2_{\text{obsd}}$  are the rate constants measured for Ps reaction with the probe molecules in environments 1 and 2, respectively.  $K_{\text{obsd}}$  are the measured rate constants at various surfactant concentrations, and  $K^1_{\text{obsd}}$  is the rate constant measured in 3-methylheptane if AOT is the surfactant, and in dodecane if DAP is the surfactant.  $K^2_{\text{obsd}}$  is the rate constant observed in the bulk solvent (cyclohexane, benzene) used in the particular experiment. From the values listed in Table II and the actually measured  $K_{\text{obsd}}$  in the various solutions,  $M_1$  can be estimated. Such an approximation suggests that at a surfactant concentration of about 600 mM/L 63.7% of TCNE is located in the outer hydrocarbon layer of the micelle, while the corresponding numbers in the nitrobenzene-AOT-benzene and *p*-nitrophenol-AOT-benzene system are 35.4 and 85.7%, respectively.

These results agree qualitatively with those which one might expect from the solubilities of the probe molecules involved.

**Figure 7.**  $K_{\text{obsd}}$  vs.  $W_{\text{H}_2\text{O}/\text{AOT}}$  in reversed micellar solutions.

*p*-Nitrophenol, e.g., is more polar than the other two and would therefore have a greater tendency to assume a position close to the polar reversed micelles than the other two less polar probe molecules.

The effect of the solubilization of water on the location of probe molecules was investigated in the nitrobenzene-AOT-isooctane and *p*-nitrophenol-AOT-benzene systems. As can be seen from Figure 7 where  $K_{\text{obsd}}$  is plotted as a function of the ratio of  $W_{\text{H}_2\text{O}/\text{AOT}}$  in the nitrobenzene-AOT-isooctane solutions,  $K_{\text{obsd}}$  increases slightly with increasing amounts of H<sub>2</sub>O present. This effect could be explained in terms of a variation in micellar surface charge due to the expansion of the reversed micelle, reducing the attraction between reverse micelle and the probe molecule.

In the case of *p*-nitrophenol-AOT-benzene solution H<sub>2</sub>O additives introduce more drastic changes of  $K_{\text{obsd}}$  (Figure 7). It should be pointed out that this effect is not caused by a change of pH which might occur during the addition of water to the solution. In separate experiments we were able to show that  $K_{\text{obsd}}$  (and  $I_2$ ) observed in these solutions are not affected by a variation of pH ranging from 1.6 to 12.9. While it is difficult at the present time to provide a complete explanation for the observed increase of  $K_{\text{obsd}}$  with  $W_{\text{H}_2\text{O}/\text{AOT}} = 7-8$ , this coincides with the formation of the microemulsion. A systematic study of microemulsions via the positron annihilation techniques is presently in progress in this laboratory.

**Positron Annihilation and UV Spectrometry in TCNE-DAP Solutions in Benzene.** In view of the results obtained in the present investigations which emphasize the effect of additives on the breaks observed in the  $I_2$ -surfactant concentration plots it appeared of interest to evaluate the reliability of some other methods by which cmc's were previously determined in similar reversed micellar systems and which involve the use of additives such as the TCNQ solubilization method.

Muto et al.<sup>19,21</sup> have suggested the use of characteristic spectral changes which occur when tetracyanoquinone (TCNQ), a well-known electron acceptor, was solubilized into surfactant organic solutions above the cmc. These authors assume that this characteristic absorption is caused by the formation of a charge transfer complex between surfactant, e.g., AOT and TCNQ. By measuring the changes in the absorbance as a function of surfactant concentration they claim to have observed breaks in the resulting curves, at certain surfactant concentrations, which they interpret as cmc's. By using this method they found a cmc of 0.74-0.79 mM/L in the DAP-cyclohexane system, as compared with 8.26 mM/L derived from the positron annihilation technique.

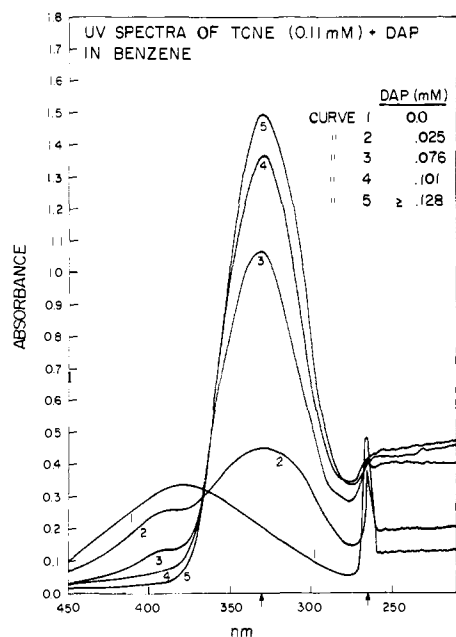


Figure 8. UV spectra of TCNE (0.11 mM) in benzene as a function of DAP concentration.

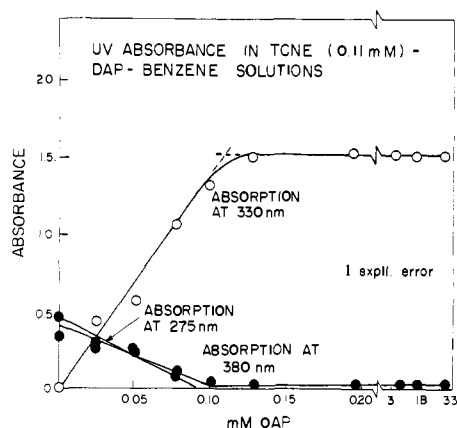


Figure 9. UV absorbance in TCNE (0.11 mM)-DAP-benzene solutions.

Assuming that this shift of the cmc to lower values is the result of the added TCNQ we have carried out a series of similar experiments in DAP-benzene solutions with another strong electron acceptor, tetracyanoethylene (TCNE), utilizing the positron annihilation technique.

The UV spectra in various DAP-benzene solutions containing 0.11 mM/L TCNE are shown in Figure 8. In the absence of DAP, two major absorption bands are observed at 380 and 275 nm. Upon addition of DAP the absorption in these regions decreases, while a new band at 330 nm appears whose absorbance increases until the total DAP concentration becomes equal to the amount of TCNE present, at which point no further variation in the absorbance at 330 nm can be observed (Figure 9). We interpret the 330-nm band as the absorption of a 1:1 molecule complex formed between TCNE and DAP, in analogy to that postulated for TCNQ-DAP.<sup>19,21</sup> It seems important to emphasize that the absorption at 330 nm occurs well below the cmc quoted by Muto et al. (0.79 mM) and that no additional absorption band appears above this concentration which could be attributed to TCNE-DAP (micelle) species. These results may therefore indicate that regardless of the aggregation state of the DAP the same 1:1

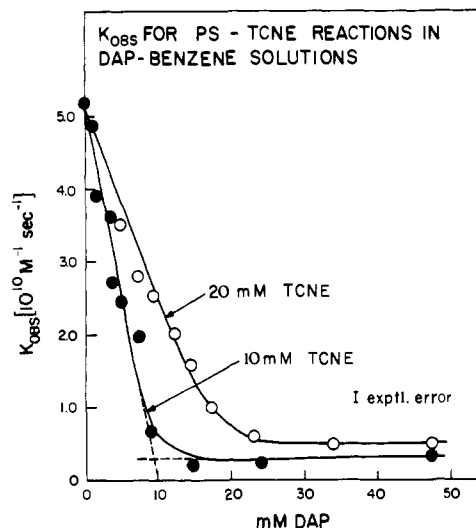


Figure 10.  $K_{\text{obsd}}$  for Ps-TCNE reactions in DAP-benzene solutions.

molecule complex with TCNE is formed, which, however, might participate as such in the association process or that even at surfactant concentrations of less than 0.025 mM micelles or pre-micellar aggregates have been formed to which the DAP-TCNE complex becomes attached.

This latter behavior would resemble very much that observed by Fendler et al.<sup>37</sup> when they studied the DAP-reversed micelle catalyzed mutarotation of 2,3,4,6-tetramethyl- $\alpha$ -D-glucose in benzene or cyclohexane and observed that catalysis occurs even at DAP concentrations well below the apparent cmc, which might be explained in terms of an interaction between small surfactant aggregates and the reagent.

For comparison the positron annihilation data obtained in the TCNE-DAP-benzene system are shown in Figure 3 from where it can be seen that the  $I_2$  values undergo a continuous drop without the abrupt change observed in the neat surfactant system. This may again be interpreted by a more gradual change of certain physical properties or the structure of the solution (vide supra).

The complex formation process can also be followed by the positron annihilation technique. As can be seen in Figure 10 the  $K_{\text{obsd}}$  values decrease linearly with the DAP concentration until TCNE and DAP are present at equimolar concentrations, at which point  $K_{\text{obsd}}$  levels off. In a previous investigation<sup>50</sup> we were able to show that the reactivity of a strong electron acceptor, such as TCNE, towards Ps is greatly reduced if the electron acceptor is bound in the form of a molecule complex with a conventional electron donor. The observed reduction in  $K_{\text{obsd}}$  with DAP concentration therefore further confirms the formation of a 1:1 TCNE-DAP complex; it does, however, not allow any conclusions as to whether or not this complex is solubilized in the micelle.

The results of the present investigation seem to indicate that micelle formation is not a necessary condition for the formation of surfactant-electron donor complexes, but that these molecule complexes are also found with monomeric surfactant molecules, or smaller surfactant aggregates, which renders this kind of cmc determination via solubilization not generally applicable for the investigation of the micelle formation process in reversed micellar systems.<sup>51</sup>

It seems interesting to print out that in contrast to the TCNE-DAP system, the positron data in TCNE-AOT-benzene solution show very little coincidence for the formation of a TCNE-AOT complex as demonstrated by the much less pronounced decrease of  $K_{\text{obsd}}$  with surfactant concentration as shown in Figure 6. The lack of complex formation in the

latter case as compared with the strong complex formation in TCNE-DAP solutions may account for the different behavior observed in the  $I_2$ -surfactant concentration plots of these two surfactant (Figures 1-4). The strong interaction between TCNE and DAP leads to the observed more gradual change in the corresponding curves starting at lower surfactant concentrations whereas the non- or weakly interacting AOT causes no significant variation as compared with the neat results observed in the AOT-solvent systems.

## References and Notes

- (1) Work supported by the U.S. Energy Research and Development Administration. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.
- (2) For recent reviews on micellar systems see, e.g., (a) J. K. Thomas, *Acc. Chem. Res.*, **10**, 133 (1977); (b) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, N.Y., 1975; (c) E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, **6**, 1472 (1970); (d) P. H. Elworthy, A. T. Florence, and C. B. MacFarlane, "Solubilization by Surface Active Agents", Chapman and Hall, London, 1968; (e) C. Tanford, "The Hydrophobic Effect", Wiley-Interscience, New York, N.Y., 1973.
- (3) J. H. Fendler, *Acc. Chem. Res.*, **8**, 153 (1976).
- (4) Y.-c. Jean and H. J. Ache, *J. Am. Chem. Soc.*, **99**, 7504 (1977).
- (5) Y.-c. Jean and H. J. Ache, *J. Phys. Chem.*, **82**, 811 (1978).
- (6) For general references on positron annihilation, see (a) J. Green and J. Lee, "Positronium Chemistry", Academic Press, New York, N.Y., 1964; (b) V. I. Goldanskii, *At. Energy Rev.*, **6**, 3 (1968); (c) J. D. McGervey in "Positron Annihilation", A. T. Stewart and L. O. Roellig, Ed., Academic Press, New York, N.Y., 1967, p 143; (d) J. A. Merrigan, S. J. Tao, and J. H. Green, "Physical Methods of Chemistry", Vol. 1, Part III, D. A. Weissberger and B. W. Rossiter, Ed., Wiley, New York, N.Y., 1972; (e) H. J. Ache, *Angew. Chem., Int. Ed. Engl.*, **11**, 179 (1972); (f) J. H. Green, *MTP Int. Rev. Sci.*, **8**, 251 (1972); (g) V. I. Goldanskii and V. G. Virsov, *Annu. Rev. Phys. Chem.*, **22**, 209 (1971).
- (7) Y.-c. Jean and H. J. Ache, *J. Am. Chem. Soc.*, **100**, 984 (1978).
- (8) N. Muller, *J. Phys. Chem.*, **79**, 287 (1975).
- (9) J. H. Fendler, E. J. Fendler, R. T. Medary, and O. A. El Seoud, *J. Chem. Soc., Faraday Trans. 2*, **69**, 280 (1973).
- (10) E. J. Fendler, J. H. Fendler, R. T. Medary, and O. A. El Seoud, *J. Phys. Chem.*, **77**, 1432 (1973).
- (11) O. A. El Seoud, E. J. Fendler, J. H. Fendler, and R. T. Medary, *J. Phys. Chem.*, **77**, 1876 (1973).
- (12) E. J. Fendler, V. G. Constien, and J. H. Fendler, *J. Phys. Chem.*, **79**, 917 (1975).
- (13) H. F. Eicke and H. Christen, *J. Colloid Interface Sci.*, **48**, 281 (1974).
- (14) A. Kitahara, *Bull. Chem. Soc. Jpn.*, **28**, 234 (1955).
- (15) T. L. Williams and H. J. Ache, *J. Chem. Phys.*, **50**, 4493 (1969).
- (16) W. J. Madia, A. L. Nichols, and H. J. Ache, *J. Am. Chem. Soc.*, **97**, 5041 (1975).
- (17) For a recent discussion of these models see, e.g., (a) R. E. Wild and H. J. Ache, *J. Chem. Phys.*, **65**, 247 (1976); (b) O. E. Mogensen, *ibid.*, **60**, 998 (1974); (c) S. J. Tao, *Appl. Phys.*, **10**, 67 (1976).
- (18) K. Kon-no and A. Kitahara, *Kogyo Kagaku Zasshi*, **68**, 2058 (1965).
- (19) S. Muto and K. Meguro, *Bull. Chem. Soc. Jpn.*, **46**, 1316 (1973).
- (20) H. F. Eicke and V. Arnold, *J. Colloid Interface Sci.*, **46**, 101 (1974).
- (21) S. Muto, Y. Shimazaki, and K. Meguro, *J. Colloid Interface Sci.*, **49**, 173 (1976).
- (22) For a recent review see, e.g., K. L. Mittal, Ed., "Micellization, Solubilization and Microemulsions", Vol. I and II, Plenum Press, New York, N.Y., 1977.
- (23) See, e.g., A. S. Kertes in ref 17, Vol. I, p 445 ff, where earlier references can be found; A. S. Kertes and H. Gutman in "Surface and Colloid Science", Vol. 8, E. Matijevic, Ed., Wiley, New York, N.Y., 1976, pp 193-295.
- (24) P. Debye and W. Prins, *J. Colloid Sci.*, **13**, 86 (1958).
- (25) A. Ray, *J. Am. Chem. Soc.*, **91**, 6511 (1969).
- (26) K. Shinoda and H. Arai, *J. Colloid Sci.*, **20**, 93 (1965).
- (27) C. W. Brown, D. Copper, and J. C. S. Moore, *J. Colloid Interface Sci.*, **32**, 584 (1970).
- (28) S. Kaufman and C. R. Singletery, *J. Colloid Sci.*, **7**, 453 (1952).
- (29) A. Kitahara in "Cationic Surfactants", E. Jungerman, Ed., Marcel Dekker, New York, N.Y., 1970, Chapter I.
- (30) A. Kitahara, *Bull. Chem. Soc., Jpn.*, **28**, 234 (1955); **29**, 15 (1956); **30**, 586 (1957); **31**, 288 (1958).
- (31) A. Kitahara, *J. Colloid Sci.*, **12**, 342 (1957).
- (32) A. F. Sirianni and B. A. Gingras, *Can. J. Chem.*, **39**, 331 (1961).
- (33) J. F. Yan and M. B. Palmer, *J. Colloid Interface Sci.*, **30**, 177 (1969).
- (34) N. Sata and H. Sasaki, *Kolloid-Z.*, **152**, 76 (1957).
- (35) P. Becher, *J. Phys. Chem.*, **64**, 1221 (1960); S. Ross and J. P. Olivier, *ibid.*, **63**, 1671 (1959).
- (36) F. Y.-F. Lo, B. M. Escott, E. J. Fendler, E. T. Adams, R. D. Larsen, and P. W. Smith, *J. Phys. Chem.*, **79**, 2609 (1975).
- (37) J. H. Fendler, E. J. Fendler, R. T. Medary, and V. A. Woods, *J. Am. Chem. Soc.*, **94**, 7288 (1972).
- (38) H. F. Eicke in ref 17, Vol. I, p 429.
- (39) H. F. Eicke, R. Hopmann, and H. Christen, *Ber. Bunsenges. Phys. Chem.*, **79**, 667 (1975).
- (40) H. F. Eicke and J. Rehake, *Helv. Chim. Acta*, **59**, 2883 (1976).
- (41) H. F. Eicke, *J. Colloid Interface Sci.*, **52**, 65 (1975).
- (42) H. Christen, H. F. Eicke, H. Hammerich, and U. Strahm, *Helv. Chim. Acta*, **59**, 1297 (1976).
- (43) H. F. Eicke, J. C. W. Shepherd, and A. Steinemann, *J. Colloid Interface Sci.*, **56**, 168 (1976).
- (44) J. B. Nicholas and H. J. Ache, *J. Chem. Phys.*, **57**, 1599 (1972).
- (45) G. D. Cole and W. W. Walker, *J. Chem. Phys.*, **39**, 850 (1963).
- (46) G. D. Cole and W. W. Walker, *J. Chem. Phys.*, **42**, 1692 (1965).
- (47) M. Wong, J. K. Thomas, and M. Grätzel, *J. Am. Chem. Soc.*, **98**, 2391 (1976).
- (48) M. Wong, J. K. Thomas, and T. Nowak, *J. Am. Chem. Soc.*, **99**, 4730 (1977).
- (49) G. D. Correll, R. N. Cheser, F. Nome, and J. H. Fendler, *J. Am. Chem. Soc.*, **100**, 1254 (1978).
- (50) Y.-c. Jean and H. J. Ache, *J. Phys. Chem.*, **80**, 1693 (1976).
- (51) O. A. El Seoud, M. J. Da Silva, and M. I. El Seoud, *J. Colloid Interface Sci.*, **62**, 119 (1977).

## Permutational Isomerization of Spirosulfuranes Derived from Catechols

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**Abstract:** The variable temperature <sup>13</sup>C NMR spectra of the sulfuranes **3**, **4a,b**, and **5** have been recorded as has the 220-MHz <sup>1</sup>H NMR of **4a,b** and **5**. The spectral data indicate that there is intramolecular ligand reorganization occurring in **3**, **4a,b**, and **5**. The data also show that **4a,b** and **5** do not interconvert at ambient temperature. It is concluded that these spirosulfuranes prefer structures that are trigonal bipyramidal or nearly so.

There has been considerable progress in recent years in the preparation and studies of the chemistry of sulfuranes and persulfuranes.<sup>2</sup> Even more progress has occurred in the related field of phosphorane chemistry.<sup>3</sup> Less progress has been made in studies of hexacoordinated phosphorus compounds which are analogues of the persulfuranes. Although it has been

generally recognized that phosphoranes can exist as trigonal bipyramids, TBP, or square pyramids, SP, it has only recently been shown that in the crystalline state there can be a gradual change in structure from TBP to SP within a series of compounds.<sup>4</sup> The series which has shown this change has the general structure **1**, where the X's are various heteroatoms. A