

# The Phosphorescent State as an ODMR Probe of the Solubilization Site of Naphthalene in Frozen Micelles

Sanjib Ghosh, Michael Petrin, and August H. Maki

Department of Chemistry, University of California, Davis, California 95616

## Introduction

To obtain a better understanding of the structural features characteristic of the equilibrated micelle a solubilized molecule acting as probe may be employed. A good probe is one whose selected physical properties are sensitive to the nature of the microenvironment it experiences and which are readily measured by experiment. The nature of the microenvironment includes the microviscosity, polarity, polarizability and the extent of water penetration in the surfactant aggregates [1].

The solubilization sites of arenes within micelles have been examined by a variety of methods [2]. Pyrene has been used as a probe most extensively [2(b, c), 3]. The study of the systematic variation of selected physical properties of the probe as a function of surfactant chain length can provide information concerning the nature of the solubilization site within a micelle [4].

In a recent investigation [5] of triplet-triplet energy transfer between benzophenone and naphthalene solubilized in frozen sodium dodecyl sulfate micelles, it was shown that optical detection of magnetic resonance (ODMR) of the triplet excited state is capable of distinguishing differences in the microenvironments experienced by a benzophenone donor and the naphthalene acceptor. This study also indicated that micelles retain their structural integrity when frozen to very low temperatures, a conclusion supported by the results of other researchers [6]. Naphthalene (N) was chosen as the probe in these studies rather than pyrene since it should cause less perturbation of the micelle architecture due to its smaller molecular dimensions. In addition, the sublevel kinetics of the N triplet state are well characterized [7].

In this article low temperature phosphorescence, decay and ODMR results in zero applied magnetic field for naphthalene solubilized in a series of anionic sodium (n)-alkyl sulfate ( $\text{NaC}_n\text{S}$ ,  $n = 10, 12, 14$ ) micelles and in cationic (n)-alkyl trimethyl ammonium bromide micelles ( $\text{C}_n\text{TABr}$ ,  $n = 10, 12, 14, 16$ ) are presented as a function of chain length,  $n$ . The results are compared with those observed for N in 20% aqueous glycerol and in n-decane solvents under similar conditions.

Results presented here demonstrate that low temperature phosphorescence and ODMR can be exploited to study differences in the microenvironment experienced by N in cationic  $\text{C}_n\text{TABr}$  and in anionic  $\text{NaC}_n\text{S}$  micelles of varying alkyl chain length. This study also provides further evidence for the presence of weak specific interactions [8, 9] of the trimethyl ammonium head groups with the solubilized arene probe N in the cationic micelles.

## Experimental

$\text{NaC}_{12}\text{S}$  (Bethesda Research Lab),  $\text{NaC}_{10}\text{S}$  and  $\text{NaC}_{14}\text{S}$  (Eastman Kodak) were used as supplied.  $\text{C}_{14}\text{TABr}$  (Aldrich),  $\text{C}_{10}\text{TABr}$ ,  $\text{C}_{12}\text{TABr}$ ,  $\text{C}_{16}\text{TABr}$  and  $\text{C}_{12}\text{TACL}$  (Eastman Kodak) were purified by recrystallization from methanol. Naphthalene was vacuum sublimed several times, and glycerol and n-decane were of spectral grade (Aldrich). Solutions of N and surfactant were prepared using triply distilled, deionized water as solvent as mentioned in our earlier work [5]. The concentration of the amphiphile in each solution was chosen to be 10 times its critical micelle concentration (CMC) at room temperature. The concentration of N in all surfactant solutions was adjusted with respect to the aggregation number at room temperature of each surfactant so as to provide on the average a single probe molecule per micelle.

The emission, decay and zero field ODMR apparatus used has been described elsewhere [5, 10]. Sweep times and

microwave power levels were maintained the same for all slow passage experiments. Fast passage transient ODMR experiments were performed as described elsewhere [11].

## Results

### Phosphorescence spectra of N in micelles

The phosphorescence spectra of N in anionic  $\text{NaC}_n\text{S}$  micelles of differing chain length at 4.2 K are shown in Fig. 1. This figure also presents the phosphorescence spectra of N in 20% aqueous glycerol solution and in n-decane at 4.2 K. The results show that the (0,0)-band of N gradually shifts to the red as the chain length of the micelle increases (Table I). The (0,0)-band energies of N in the micelles studied fall within a range bracketed by that observed for N in 20% glycerol and that obtained in n-decane, where the (0,0)-band is the most red shifted. The phosphorescence emission spectrum of N becomes progressively more resolved and structured as N moves in order from an aqueous 20% glycerol medium, through the  $\text{NaC}_{10}\text{S}$ ,  $\text{Na}_{12}\text{S}$  and  $\text{NaC}_{14}\text{S}$  micelles, and finally to a n-decane medium.

The phosphorescence spectra of N in  $\text{C}_n\text{TABr}$  ( $n = 10, 12, 14, 16$ ) micelles at 4.2 K are presented in Fig. 2. The (0,0)-band is red shifted with an increase in the chain length of the surfactant, and the phosphorescence of N becomes progressively more resolved and structured. The phosphorescence spectrum of N in  $\text{C}_{12}\text{TACL}$  at 4.2 K is essentially the same as that observed in  $\text{C}_{12}\text{TABr}$  and in both cases the (0,0)-band is blue shifted compared with that observed in  $\text{NaC}_{12}\text{S}$ .

The consistent variation of the (0,0)-band of the emission and the degree of resolution of the phosphorescence as a function of surfactant chain length clearly demonstrates that the observed phosphorescence is from N incorporated within the micelles and that the micellar structure is retained at 4.2 K under the experimental conditions used. Micellar structure present at room temperature has been found recently to be retained upon freezing to 4.2 K [6f].

### Lifetime of N in cationic micelles

The decay of the triplet state of N as measured in  $\text{NaC}_n\text{S}$  with varying  $n$ , in  $\text{C}_{12}\text{TACL}$  micelles, in 20% aqueous glycerol, and in n-decane at 4.2 K, was found to be a single exponential with a lifetime of ca. 2.35 sec. The more rapid decays observed for the cationic series micelles, however, are multiexponential and the values presented in Table I are the average (1/e) lifetimes.

### ODMR transitions of N in micelles

Slow passage ODMR transitions of the lowest triplet state of N were observed in all anionic micellar solutions, in 20% aqueous glycerol, and in n-decane by monitoring the center of the N phosphorescence (0,0)-band observed in the respective media with 3 nm emission slit widths at 1.2 K. In each case two transitions, the  $|D|+|E|$  and the  $2|E|$ , were observed. The  $|D|$  and  $|E|$  values are presented in Table I. All transitions except  $2|E|$  in 20% aqueous glycerol appeared as an increase in the relative phosphorescence intensity. Values for the  $|E|$  parameter show little change between anionic micelles of differing alkyl chain length. The  $|D|$  values, however, show a linear decrease with an increase of chain length. The value of  $|D|$  is highest in a 20% glycerol medium and lowest in the non-polar n-decane.

Although the value of  $|D|$  observed in  $\text{NaC}_{12}\text{S}$  micelles does not change as a function of added NaCl up to a final concentration of 0.2 M  $\text{Na}^+$ , it decreases with the addition of

CsCl as shown in Fig. 3.

Table I also lists the results of slow passage measurements for the cationic micellar series  $C_nTABr$  ( $n = 10, 12, 14, 16$ ) and for  $C_{12}TACl$ . For  $C_{12}TABr$  and  $C_{12}TACl$  micelles only the  $|D|+|E|$  and the  $2|E|$  transitions appear strongly. In the other cationic micelles, on the other hand, all ODMR transitions including the normally unobserved  $|D|-|E|$  transition are seen. The signal-to-noise ratio of the  $|D|-|E|$  transition increases with a decrease in the chain length in the  $C_nTABr$  series for  $n \leq 14$ .

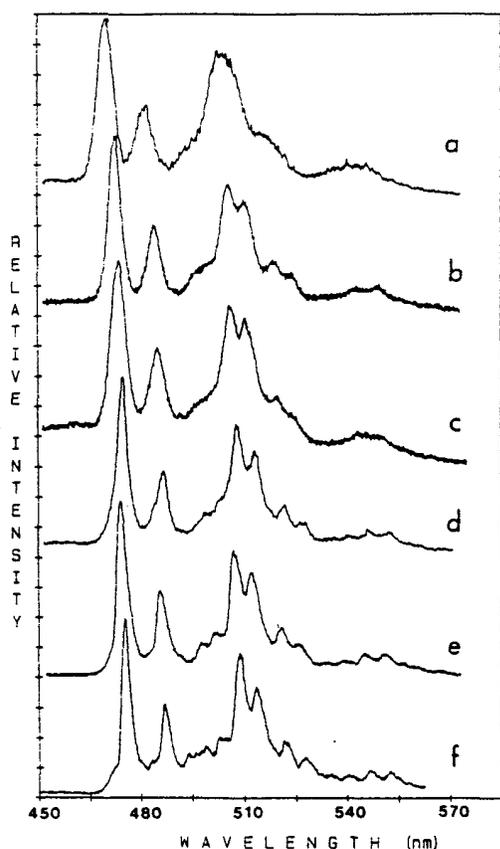


Figure 1. Phosphorescence spectra of N at 4.2 K with excitation at 300 nm with 16 nm bandpass and with emission slit width of 1 nm: (a) in 20% aqueous glycerol with N (0.001M); (b) in  $NaC_{12}S$  (0.34M) with N (0.003M); (c) in  $NaC_{12}S$  (0.086M) with N (0.0008M); (d) in  $NaC_{12}S$  (0.024M) with N (0.0002M); (e) in  $NaC_{12}S$  (0.086M) with N (0.001M) and added CsCl (0.2M); in pure n-decane with N (0.001M).

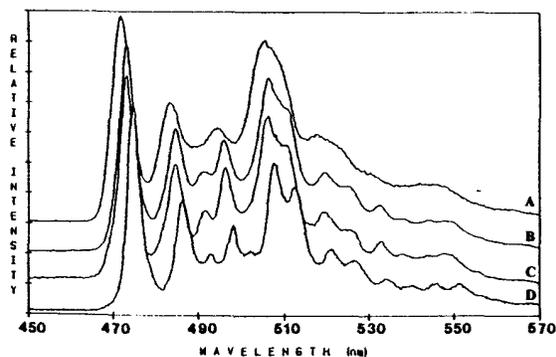


Figure 2. Phosphorescence spectra of N at 4.2 K with excitation at 300 nm using 16 nm bandpass and with emission slits of 1 nm; (A) in  $C_{12}TABr$  ( $6.5 \times 10^{-3}M$ ) with  $6.5 \times 10^{-3}M$ ; (B) in  $C_{12}TABr$  ( $1.6 \times 10^{-3}M$ ) with  $1.6 \times 10^{-3}M$ ; (C) in  $C_{12}TABr$  ( $3.5 \times 10^{-3}M$ ) with N ( $3.5 \times 10^{-3}M$ ); (D) in  $C_{12}TABr$  ( $4 \times 10^{-3}M$ ) with N ( $4 \times 10^{-3}M$ ).

## Discussion

### Effect of anionic micellar environment on probe phosphorescence

The blue shift of the phosphorescence (0,0)-band of N and the accompanying loss of resolution in the vibrational structure in going from the non-polar solvent n-decane to a polar 20% aqueous glycerol solution may be attributed to the lower degree of stabilization of the N triplet state by a rigid solvation geometry organized to stabilize the ground state. The blue shift is seen to increase with an increase in the solvent polarity, as expected. The linear red shift of the (0,0)-band (Fig. 4) and the appearance of a more resolved phosphorescence emission which accompanies an increase in the chain length of the surfactant (Fig. 1) indicates a progressively less polar environment surrounding N as the chain length of the anionic micelle is increased. This red shift and the increased structure of the N phosphorescence in  $NaC_{12}S$  micelles observed with the addition of CsCl also indicate that N experiences a less polar environment in  $NaC_{12}S$  micelles in the presence of  $Cs^+$  counterions. Thus, the association of  $Cs^+$  ions with the  $NaC_{12}S$  micelles could act to decrease the extent of hydration of the micelle.

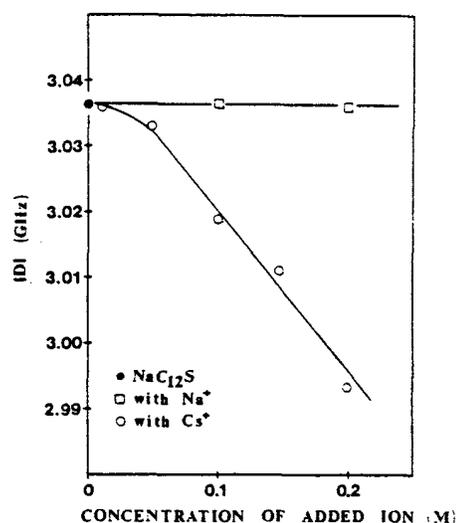


Figure 3. Plot of the triplet state ZFS parameter  $|D|$  for N in  $NaC_{12}S$  micelles containing varying amounts of added CsCl and NaCl. The concentration of surfactant is 0.086M and N is 0.001M.

### Probe phosphorescence in cationic micelles

The (0,0)-band energies of the N triplet state in the cationic  $C_nTABr$  micelles are plotted against chain length in Fig. 4. In Fig. 5 the width of the N phosphorescence (0,0)-band in different micelles is plotted against the chain length. The gradual decrease in width accompanying an increase in chain lengths demonstrates that N experiences a progressively more homogeneous environment as surfactant length in the micelles is increased.

The spectral resolution and the (0,0)-phosphorescence band energy are essentially the same for N-solubilized into  $C_{12}TABr$  and  $C_{12}TACl$  micelles. This indicates that the microenvironment of N in cationic micelles having the same head group and chain length is independent of a change in the counterion from  $Br^-$  to  $Cl^-$ . This insensitivity to counterion has been observed for pyrene solubilized in  $C_{12}TABr$ ,  $C_{12}TACl$  and  $C_{12}TAOH$  micelles [8].

Comparison of Figs. 4 and 5 demonstrates that for a given alkyl chain length, cationic and anionic micelles exhibit a difference in the polarity and in the homogeneity of the microenvironment of the micelle solubilized N probe. The greater polarity and more inhomogeneous environment experienced by N in the cationic  $C_nTABr$  micelle compared with those in the anionic  $NaC_nS$  micelle having the same alkyl chain length may be explained as follows:

(a) The effective chain length of a  $NaC_nS$  surfactant molecule is greater than n since the ester oxygen which is involved in binding the alkyl chain to the sulfate group is

Table I. Parameters of the lowest triplet state of N in different micelles and media

Micelle system <sup>a</sup>	$\lambda(0,0)$ (nm) <sup>b</sup>	$\tau_{avg}$ (sec) <sup>c</sup>	D  (GHz) <sup>d</sup>	E  (GHz) <sup>d</sup>	Transition polarity <sup>e</sup>		
					D + E	D - E	2 E
NaC <sub>10</sub> S	472.6	2.36	3.040	0.471	+	no	+
NaC <sub>11</sub> S	473.6	2.35	3.034	0.469	+	no	+
NaC <sub>12</sub> S	474.7	2.34	3.027	0.468	+	no	+
C <sub>10</sub> TABr	472.0	1.21	3.033	0.464	-	-	+
C <sub>11</sub> TABr	473.0	1.44	3.036	0.464	-	-	+
C <sub>12</sub> TABr	473.2	1.56	3.034	0.468	-	-	+
C <sub>11</sub> TABr	474.6	1.97	3.009	0.466	+	-vw	-
C <sub>12</sub> TACL	472.8	2.35	3.032	0.463	+	-vw	+
20% glycerol	470.0	2.40	3.054	0.469	+	no	-
n-decane	475.3	2.40	2.980	0.461	+	no	-

<sup>a</sup>Aqueous solutions except for n-decane. <sup>b</sup>Measured at 4.2 K with  $\pm 0.1$  nm accuracy. <sup>c</sup>The 1/e lifetime measured at 4.2 K with  $\pm 5\%$  accuracy. <sup>d</sup>Obtained at 1.2 K in zero field with  $\pm 2$  MHz accuracy except for C<sub>12</sub>TACL and C<sub>11</sub>TABr (n=10,12,14), where the accuracy is  $\pm 5$  MHz. <sup>e</sup>A "+" sign indicates an increase in phosphorescence intensity, a "-" indicates a decrease, "no" indicates that the transitions are not observed, and "vw" indicates that the transitions are very weak.

not particularly hydrophilic [12]. Head group repulsion is also more prominent in the cationic micelles due to steric factors. Thus NaC<sub>n</sub>S micelles may have more compact and less water permeated structures than the corresponding C<sub>n</sub>TABr micelles.

(b) The existence of a weak interaction between neutral arenes and the quaternary ammonium head groups of cationic micelles of type C<sub>n</sub>TAX (X = Cl, Br, OH) has been suggested [8,9]. This interaction is presumably due to the attraction of the pi-electron cloud of the arene and the positively charged head groups [8], and draws N closer to the surface than in the case of a NaC<sub>n</sub>S micelle where the negatively charged sulfate groups will repel the pi-electron cloud of the solubilized probe. This weak interaction should be more prominent for surfactants of shorter chain length which have correspondingly smaller micellar dimensions. This trend is clearly demonstrated by the ODMR results discussed in a later section.

#### Effect of counterions on the triplet lifetime

Comparison of lifetime data for N in different micelles clearly indicates the perturbation of the N triplet state by the heavy-atom Br<sup>-</sup> counterions in the cationic C<sub>n</sub>TABr micelles. The external heavy-atom effect of Br<sup>-</sup> counterion on some arenes including anthracene, its derivatives and fluorene in C<sub>10</sub>TABr micelles have been observed at room temperature by Wolff [13], as a decrease in the fluorescence quantum yield and an increase in the triplet quantum yield while changing the surfactant from C<sub>11</sub>TACL to C<sub>11</sub>TABr.

The multiexponential decays which we observe for C<sub>n</sub>TABr micelles are explained by the fact that N experiences a variable distribution of counterions from micelle to micelle after freezing. The monotonic linear decrease in the average lifetime of N observed as n decreases confirms that N is completely solubilized within the micelles. It further suggests that N does not occupy a region very close to the polar region of the micelle surface, nor does it reside in the interior core of the micelle. If either situation prevailed, the lifetime would be insensitive to the variation of chain length since the ratio of the probe to micelle concentration is kept invariant throughout the series of surfactants investigated. Our results show that the average distance between N and Br<sup>-</sup> decreases as the chain length decreases, resulting in an increasing heavy-atom perturbation in the shorter chain surfactants.

#### Effect of environment on ODMR transitions and the external heavy-atom effect.

The observation of the normally unobserved |D|-|E| transition of N in all C<sub>n</sub>TABr micelles combined with the fact that its intensity increases with a decrease in n definitely can be associated with an external heavy-atom perturbation of the N triplet state by Br<sup>-</sup> counterions, since the probe to micelle concentration ratio is maintained constant throughout the series.

The |D|+|E| transitions observed for N in C<sub>n</sub>TABr micelles of n  $\leq$  14 appear with a decrease in the relative phosphorescence intensity (negative polarity), in contrast with the positive polarity observed for this signal in the

other systems. The polarity of the 2|E| signal is found to be positive for all micelles studied. The |D|-|E| transition in all cationic micelles appears with negative polarity, although it is very weak in C<sub>10</sub>TABr and C<sub>12</sub>TACL.

For the N triplet state it is known that the sublevel radiative quantum yields are in the order  $Q_x \gg Q_y > Q_z$  [7], where x, y and z are the long, short, and normal axes, respectively. Positive polarity of |D|+|E| and 2|E| signals and the absence of a |D|-|E| signal imply that  $N_x^0 < N_z^0 \approx N_y^0$ , where N<sup>0</sup> is a steady state population. Reversal of polarity of only the |D|+|E| signal as a result of the Br<sup>-</sup> heavy-atom effect implies that now  $N_x^0 < N_z^0 < N_y^0$ , assuming no change in the relative Q's. This set of assumptions enables us to predict negative polarity |D|-|E| signals for Br<sup>-</sup> perturbed N in agreement with observation. Since the lifetime reductions are relatively minor in the C<sub>n</sub>TABr micelles, it is reasonable to assume that Q<sub>x</sub> remains the dominant radiative sublevel. The only possible remaining pattern of quantum yields is then  $Q_x > Q_z > Q_y$ . For this pattern, a negative |D|+|E| and positive 2|E| signal imply that  $N_z^0 < N_x^0 < N_y^0$ , as above, but now the |D|-|E| signal is predicted to be positive, contrary to that observed. This leads to the conclusion that the pattern of the N radiative quantum yields remains unaltered by the heavy atom effect in C<sub>n</sub>TABr micelles.

This interpretation is corroborated by the results of fast passage microwave transient experiments [11] performed on these systems. It is not possible to give a quantitative measure of the relative radiative or overall rate constant of the sublevels since the decays observed are multi-exponential as a result of sample heterogeneity. Although the SLR rates between the triplet sublevels of N are sensitive to host structure [10], they appear to be negligible compared with the  $k_i$  at 1.2 K in the cationic micelle series studied. From these measurements, we can ascribe the change in the pattern of the steady state populations of the N triplet in C<sub>n</sub>TABr (n < 14) to both a change of the populating rates and the total decay rates of the sublevels. The enhancement of S<sub>1</sub>  $\rightarrow$  T<sub>1</sub> ISC rates in arene probes by a heavy atom has been suggested by Wolff [13] to occur in C<sub>10</sub>TABr micelles.

#### Variation of triplet state ZFS parameters of N in micelles

The ZFS parameters, |D| and |E| should decrease in a more polarizable environment [14], the magnitude of the decrease depending on their absolute values. The value of |D| is the highest in a 20% aqueous glycerol medium and the lowest in the non-polar medium n-decane. |D| is intermediate between these extremes in both the anionic and cationic micelles. In the anionic micelles |D| decreases with increasing chain length, while in the cationic series it does not decrease with increasing n until n = 16.

A more pronounced decrease in |D| is observed when the Cs<sup>+</sup> concentration is increased in an anionic micelle of fixed

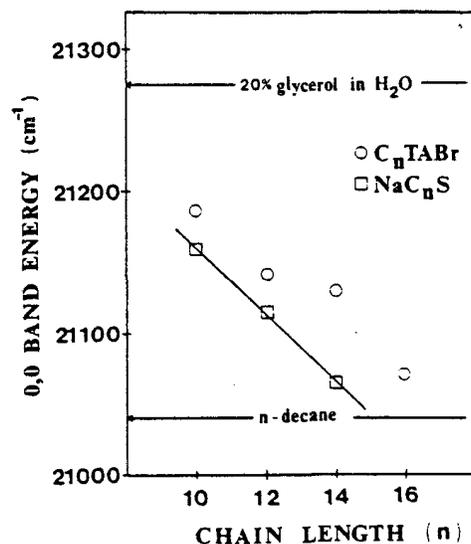


Figure 4. Plot of the (0,0)-phosphorescence band energy of N in cationic and anionic micelles studied at 4.2 K as a function of chain length. The (0,0)-band energy observed in 20% glycerol and n-decane are indicated by horizontal lines.

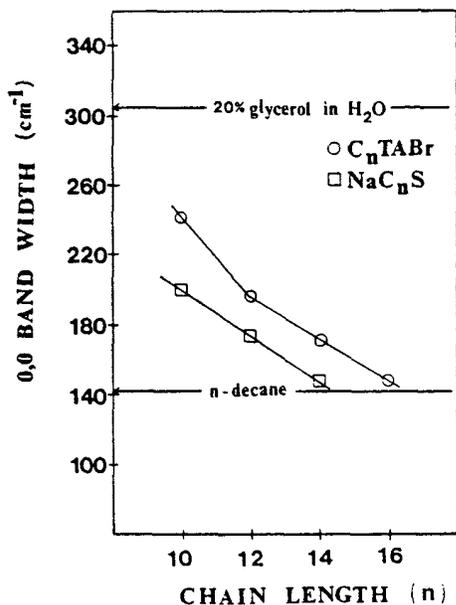


Figure 5. Plot of the (0,0)-phosphorescence band width (full width at half maximum) observed at 4.2 K for N in cationic and anionic micelles as a function of chain length. The (0,0)-band width observed in 20% glycerol and in n-decane are shown by horizontal lines for comparison.

chain length as shown in Fig. 3. We believe that this effect is due to an increase in polarizability of the N environment which results from the substitution of heavily hydrated  $Na^+$  ion by the less hydrated  $Cs^+$  in the outer regions of the micelle.

Whatever differences in polarizability exist at the N solubilization site as a function of chain length in  $C_nTABr$  micelles ( $n = 10, 12, 14$ ) are probably masked by the effects of specific interactions with the cationic head groups of the surfactant. A significant decrease in  $|D|$ , however, occurs in  $C_{14}TABr$ , indicating that N moves into a relatively polarizable environment less influenced by the cationic head groups.

#### Linewidth of ODMR transitions of N

Narrower ODMR linewidths are observed for N in all surfactants compared with those found in 20% aqueous glycerol solution, indicating that N experiences a more homogeneous environment in the micelles. In fact, the micellar environment is in some cases more homogeneous than that found in n-decane. The ODMR linewidths in micelles are greater than those observed for N in an n-pentane polycrystalline Spol'skii matrix, however, where N exhibits phosphorescence from a single site with narrow ODMR transitions frequencies of ca. 5 MHz width at 1.2 K [10]. It is possible that some heterogeneity may result from multiple occupancy of micelles by N in the Poisson distribution.

The widths of the ODMR transitions for  $NaC_nS$  micelles studied are found to be nearly independent of n. (Fig. 6). The widths of the  $|D|+|E|$  transitions in the case of  $C_nTABr$  micelles, however, increase with a decrease of n. Although the triplet state of N senses a somewhat different average environment in going from  $NaC_{14}S$  to  $NaC_{10}S$ , the inhomogeneous broadening originating from the spacial and orientational distribution of N within the micellar ensemble results in the same widths for the transitions in these surfactants. The linewidths observed in the anionic micelles are comparable to those observed for N in 3-methyl pentane [15]. The linewidth variation of the  $|D|+|E|$  transition definitely suggests that the  $C_nTABr$  cationic micelles have a more open structure than the corresponding  $NaC_nS$  micelles of the same alkyl chain length. The greater extent of solvent intrusion and the presence of a weak specific interaction between N and the charged head groups probably are the main contributors to the larger degree of inhomogeneous broadening.

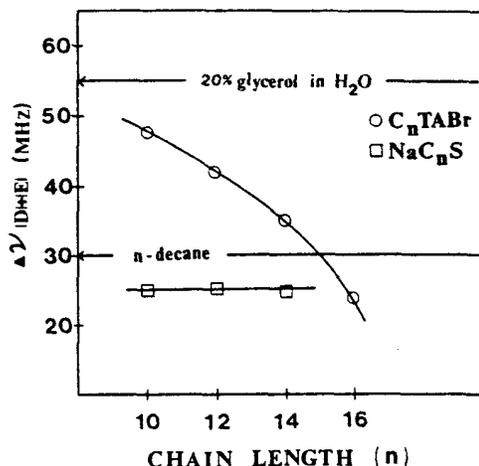


Figure 6. Plot of the  $|D|+|E|$  band width (full width at half maximum) observed at 1.2 K for N in cationic and anionic micelles as a function of chain length. Band widths obtained in 20% glycerol and in n-decane are indicated by horizontal lines.

#### Solubilization site of N and micellar structure

Although fluorescence lifetime measurements in anionic micelles [16] suggest that N is solubilized into an inner core of hydrophobic nature, UV absorption studies [1a] promote a relatively polar environment for N in  $NaC_{12}S$  micelles. The phosphorescence of N at room temperature in  $NaC_{12}S$  has not been observed, but triplet emission has been detected at room temperature from micelles composed of  $NaC_{12}S + TiC_{12}S$  and  $NaC_{12}S + AgC_{12}S$  surfactant mixtures [17,18]. In the presence of  $Ti^+$  or  $Ag^+$ , micellar bound N exhibits a drastically shortened triplet ( $T_1$ ) lifetime compared with that observed in organic glassy solvents which has been attributed to an external heavy-atom perturbation [19].

The monotonic variation of both the phosphorescence and ODMR frequencies with chain length obtained in this present work suggest that N is neither buried in the essentially hydrophobic core of the micelle nor adsorbed near the very polar surface region. This supports the idea that N is located preferentially in the palisade layer where it is sensitive to slight changes in the degree of hydrocarbon-water contact as a result of changing the surfactant chain length or when the extent of hydration is affected by the presence of  $Cs^+$  ion. As the chain length increases or the  $Cs^+$  concentration increases, N experiences a more compact and less hydrated environment surrounding its solubilization site. Similar conclusions have been found in the case of pyrene solubilized into cationic micelles of varying surfactant chain length investigated by fluorescence techniques [4].

Investigations of the triplet state of N in frozen  $NaC_nS$  micelles suggest that the Hartley model [20] which proposes a hydrocarbon-like interior with a definite double layer is suspect at short chain lengths, but provides a better description for surfactants with longer hydrocarbon chains as suggested by Evans et al. [21], and demonstrated experimentally by several others [1e,6b,22,23]. The present work employing a naphthalene probe solubilized into micelles supports this line of thinking. A comparison between cationic and anionic surfactants suggests a more open structure for the  $C_nTABr$  micelles, and indicates a higher degree of water and counterion penetration into micelles of shorter chain length. In cationic micelles this is accompanied by a minor heavy-atom perturbation of the N triplet state in the presence of  $Br^-$  counterion. In addition, results support the existence of a specific interaction between the arene probe and the quaternary ammonium headgroups of the shorter chain-length cationic surfactants.

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