ELECTRON SPIN RESONANCE STUDIES OF MICELLES

A thesis submitted in partial satisfaction of the requirements for the degree of Master of Science in Physics

by

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August, 1973
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ACKNOWLEDGEMENT

I am sincerely appreciative of the suggestion for this research and the many hours of patient help and guidance from Dr. Barney Bales without whom this project would not have been successful.

I am grateful to the fine Physics Department at California State University at Northridge for providing support and making this work possible.

It is also my desire to acknowledge the support and kind understanding from my very close friends throughout the year.
ABSTRACT

ELECTRON SPIN RESONANCE STUDIES OF MICELLES

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Micelle systems composed of water, n-butanol, and cetyltrimethylammonium bromide were studied using Electron Spin Resonance. The spin probe was di-tert-butyl nitroxide. A transition from normal to reversed micelles was identified as the concentration of the components varied, and is shown to be consistent with previous investigations. Moreover, owing to the higher resolution of ESR, two forms of reversed micelles are believed to exist in the low water concentration range.

Values of the hyperfine coupling constant, the g-value, and linewidth in n-butanol, in water, and in ethanol are reported.
I. INTRODUCTION

Electron Spin Resonance Spectroscopy, (ESR), is a tool to detect and/or study paramagnetic atoms and molecules either in the gas, solid, or liquid state. If the system to be studied is not naturally paramagnetic, it is still possible to use ESR by the addition of a paramagnetic material called a spin probe or spin label. The use of paramagnetic nitroxide probes in liquids has been evolving since 1965. This technique has proved to be particularly useful in biological systems where much progress has been made. The spin label is a synthetic paramagnetic organic free radical which can probe its physical environment, and possibly provide the experimenter with information about its relative location, orientation, and motion. Nitroxide radicals have proved to be the most useful of the spin probes in biological studies for the following two reasons; (1) their reactivity can be greatly controlled, all the way from being unreactive to being specifically binding to certain active sites, and (2) they are stable compounds. This work concerns micelle emulsions which can be considered as simple model membrane systems, since both micelles and membranes are heterogeneous liquid systems. A micelle emulsion is generally a three component system of oil, water, and amphiphilic...
molecules. Ordinarily oil and water do not "mix", but with the addition of the amphiphilic molecule, which has properties of both, it is possible to solubilize oil and water. The three components in solution are arranged predominately in spherical shapes, but cylindrical and lamellar structures are also possible. Some work has been done using spin probes to study micelle systems and is reported in the next chapter. There have not been, however, studies of an important property of the spherical micelle system called "micelle inversion" using ESR. Inverse or reversed micelles have been postulated to be spherical, but other forms are possible. The purpose of this work is to study micelles in a simple system and to explore the phenomenon of "micelle inversion" via ESR.
II. HISTORICAL RESUME

We review here, the small amount of work that has been carried out using ESR in micelle systems.

Waggoner and Griffith\(^4,5\) have measured the ESR of the spin labels 2,4-dinitrophenyl hydrazone of 2,2,6,6-tetramethyl-4-piperidone nitrogen oxide and 2,2,4,4-tetramethyl-1,2,3,4-tetrahydro-\(\gamma\)-carboline-3-oxyl in micellar systems. These authors considered three models of the geometric relationship between the nitroxide spin probes and the micelles, (see figure 7). We note that the probes that Waggoner and Griffith used did not have the same chemical structure as the type in our work. The first model considered envisioned the probe was absorbed rigidly onto the surface of a rigid micelle, thus the probe would rotate with the micelle. One may estimate theoretical values of the tumbling rates of the micelles using the Stokes relation\(^6\) together with an approximate diameter of the micelle, but the estimated rate does not agree with the experimental values for the rotation of the probe calculated from the ESR spectra. The method used to determine the probe rotational rate is discussed in section IV. Experimentally, the probe rotates eighteen times faster than the Stokes value estimate for the micelle rotation rate.

In the second model, the probe is visualized as being oriented radially in the micelle with the polar
group fixed near the oil-water surface, and the third model has the probe being absorbed into the hydrocarbon interior of the micelle. Experimental values of the nitrogen nucleus hyperfine coupling constant in the nitroxide group, (an indicator of the environment of the unpaired electron that is localized largely on the nitroxide group), and optical absorption spectra revealed that the environment of the probe was 80% H₂O and 20% oil. Thus the third model is clearly not in agreement with experiment. The second model is not applicable without some modification.

In further work, Waggoner and Griffith⁷, performed an experiment similar to the one described above. The only difference being in the nature of the probes, the new probes had long hydrocarbon chains similar to those of the amphiphilic molecule. The tumbling rates and coupling constant data were found to be similar to those in the nitroxides used previously. Since it would be expected that the new probes would be absorbed into the hydrocarbon interior of the micelle, none of the three proposed models of probe-micelle interaction seem to be valid.

Atherton and Strach⁸ have carried out experiments using the probe, DTBN, in a pure water environment and also in various concentrations of water and the amphiphilic molecule, sodium dodecyl sulfate, (SDS). DTBN is the
spin label used in this thesis, but the amphiphilic molecule is different. Atherton and Strach did not use the third component of oil as is done in this work. They observed two distinct spectra. The first is a typical spectrum of DTBN in water. The second spectrum is one showing a smaller hyperfine coupling than the first spectrum. The hyperfine coupling constant for DTBN is smaller in an oil environment than it is in an aqueous environment, thus the second spectrum was attributed to the label being in the micelle interior, which is the hydrocarbon core of the micelle. The tumbling rate found from the DTBN-micelle spectrum is slower than DTBN in pure water but still fast compared to the theoretical micelle tumbling rate.

The work of Atherton and Strach\(^8\) was carried out using the same probe that is discussed in this thesis but in a system that is quite different from the microemulsions considered here. We now turn to experimental work using other techniques that have been carried out on the same system that we have investigated.

Friberg et al. have very recently\(^9\) measured the catalysis of the hydrolysis of p-nitrophenyl laurate in the system: water, n-butanol, and cetyltrimethylammonium bromide, (CTAB). Light scattering and Nuclear Magnetic Resonance, (NMR), measurements were also made. The simple, but reliable, light scattering technique, (Tyndall
effect), was used to detect the aggregation of molecules into micelles. The results showed a sharp increase in scattered light intensity as the water content was increased starting at 40% $H_2O$, leveling at 60% $H_2O$. Decreasing intensity began at 70% and ended at 90% $H_2O$ with a slight decrease in slope. The NMR technique provides linewidth data on the $^{81}$Br atom. The spectral linewidth showed a sharp reduction in the 40% to 60% $H_2O$ range, followed by a leveling between 60% and 70% $H_2O$, and another sharp reduction between 70% and 80% $H_2O$. A less sharp decrease was observed up to 95% $H_2O$. The important observation from the catalyzed reaction rate data, is that the rate has one maximum at about 45% $H_2O$ and another, much larger one, at 90% $H_2O$. Micelle structures are known to be catalytic agents for certain reactions and it is assumed, then, that the enhanced rates of reaction are caused by reversed micelles at 45% and normal micelles at 90% $H_2O$.

In summary, the work of Friberg et al. determines that at certain percentages of water, n-butanol, and CTAB reversed and normal micelles occur. In addition, these authors discussed briefly the interesting phenomenon of "premicellar aggregates" but could not definitively identify these aggregates.

Other experiments using probes with two nitroxide
centers\textsuperscript{11}, i.e., biradicals, and paramagnetic ions\textsuperscript{12} such as Mn\textsuperscript{++} to study micellar systems have been carried out. These experiments are not prerequisites to this work and will not be discussed.
III. ESR IN LIQUIDS

The ESR experiment is primarily the inducing and detecting of electronic spin transitions in a paramagnetic sample. Substances which contain permanent magnetic moments are defined as paramagnetic. Examples are found among the "transition elements", such as Mn	extsuperscript{2+}, the "rare earths", such as Gd	extsuperscript{3+}, and organic chemicals such as nitroxides. If the unpaired electron(s), which is the source of paramagnetism, is in an external magnetic field, \( \mathbf{H} \), its magnetic moment, \( \mathbf{\mu} \), will become aligned either parallel or anti-parallel with the field. The orientational potential energy is given by \(-\mathbf{\mu} \cdot \mathbf{H}\). The magnetic moment is proportional to the angular momentum, which for the free electron is just the intrinsic spin \( \mathbf{S} \). The Hamiltonian can be written in terms of the electron spin, \( \mathbf{S} \), and the external field, \( \mathbf{H} \),

\[
\mathbf{H} = g \beta \mathbf{H} \cdot \mathbf{S}
\]

which becomes

\[
\mathbf{H} = g \beta H S_z
\]

if the applied field is in the z-direction. The constant, \( \beta \), is the electronic Bohr magneton. The electronic g-factor will be discussed shortly. For an electron with \( S = \frac{1}{2} \), the z-component of the spin, \( m_S \), may take two values:
Thus the energy difference between the two orientations of the spin is \( g\beta H \). In order to induce spin transitions the electron must absorb or emit energy, and this energy is in the form of an electromagnetic field applied perpendicular to the external \( H \) field. The resonance is governed by the resonance condition,

\[
h\nu = g\beta H
\]

For a field, \( H \), of approximately 3000 G, a frequency of about 9.5 GHz is required. To facilitate the experimental technique, the frequency is held constant while the external field is swept through the resonant energy.

There is a slight excess of spins in the \( m_s = -\frac{1}{2} \) state, and the ratio of these spins to the \( m_s = +\frac{1}{2} \) state can be calculated using the Boltzmann factor. This population difference gives rise to a net absorption of microwave energy by the spin system. The power absorbed can be detected and is displayed on an x-y recorder as the derivative of the absorption curve.

Fundamental to the understanding of the spectral lines produced by the ESR spectrometer is the spin Hamiltonian. A worker in this field can construct a Hamiltonian and analyze the data according to this theory or he can do the reverse; collect experimental data and build a spin Hamiltonian to fit the spectral lines. The
strategy used here is of the first kind.

Nitroxide radicals contain the magnetic nucleus $^{14}\text{N}$, (I=1). Accordingly, then, the terms which make up the spin Hamiltonian are as follows:

\[ \mathcal{H}_0 = g\beta \vec{H} \cdot \vec{S} - g_\text{N}\beta_\text{N} \vec{H} \cdot \vec{I} \]

\[ \mathcal{H}_1 = g g_\text{N}\beta_\text{N} \left\{ \frac{\vec{S} \cdot \vec{I}}{r^3} - \frac{3(\vec{S} \cdot \vec{F})(\vec{I} \cdot \vec{F})}{r^5} \right\} \]

\[ \mathcal{H}_2 = g g_\text{N}\beta_\text{N} \frac{8\pi}{3} \delta(r) \vec{S} \cdot \vec{I} \]

$\mathcal{H}_0$ is the sum of the Zeeman energies; the interaction of the external magnetic field with the magnetic dipole produced by the spinning electron and the nuclear spin respectively. The $\beta$'s, which are constant, are the electronic and nuclear Bohr magnetons. The g-factor is a proportionality constant between the magnetic moment and the angular momentum. For free electrons $g$ has the value 2.0023. For electrons in most organic molecules, $g$ has the approximate value 2.0023 because the angular momentum is quenched, i.e. $\langle \vec{I} \rangle = 0$. Thus, in these molecules a "spin only" angular momentum is approximately observed. The $g$-value may change slightly from 2.0023 depending on the environment of the unpaired electron and this change gives experimental insight to the physical situation.

The classical interaction energy, $E$, between two magnetic moments $\vec{\mu}_e$ and $\vec{\mu}_n$ is given by:
\[ E = \frac{\vec{\mu}_e \cdot \vec{\mu}_N}{r^3} - \frac{3(\vec{\mu}_e \cdot \vec{r})(\vec{\mu}_N \cdot \vec{r})}{r^5} \]

The quantum mechanical version of the above equation can be obtained by substituting \( \vec{\mu}_e = -g_\beta \vec{S} \) and \( \vec{\mu}_N = \vec{\gamma}_N \beta_N \vec{I} \) in equation 7 which yields the dipolar interaction Hamiltonian of equation 5. This equation describes the magnetic interaction between the spinning electron and the nucleus. The isotropic hyperfine coupling term, equation 6, first introduced by Fermi, represents the interaction energy of the nuclear moment with the magnetic field produced at the nucleus by the electron. If the molecule containing the unpaired electron is rotating very fast and isotropically, which is the case here, the anisotropic, (dipolar), interaction Hamiltonian, \( \vec{H}_i \), averages to zero. Therefore, the total Hamiltonian is

\[ \vec{H} = \vec{H}_o + \vec{H}_i \].

If we define the direction of the external magnetic field to be the z-direction, then we can write the final approximate spin Hamiltonian in the form:

\[ \vec{H} = g_\beta H S_z - g_N \beta_N H I_z + \alpha_N \vec{S} \cdot \vec{I} \]

where

\[ \alpha_N = g_\beta g_N \beta_N \frac{8\pi}{3} \xi(\vec{r}) \]

and "\( \alpha_N \)" is called the isotropic hyperfine coupling constant.
Further discussion of the isotropic hyperfine coupling constant is necessary at this time since it is the main quantity to be measured. The $\delta(\vec{r})$ in "$a_n$" is the Dirac delta function, which insures that there is only isotropic coupling when the electron is at the position of the nucleus. The electron wave function must be non-zero for interaction to occur, such that the probability of the electron at the nucleus is non-zero; i.e., $|\psi(0)|^2 \neq 0$. Therefore $\delta(\vec{r})$ can be replaced by $|\psi(0)|^2$. Knowing $a_n$, then, gives a direct measure of the electron probability density at a given nucleus. To put it another way, it is proportional to the amount of time the electron spends at the nucleus. The probability density can be altered by the environment of the molecule. Placing the radical in a solvent alters the molecular wave function of the unpaired spin due to the resultant electric fields. It is found that nitroxide wave functions are altered in such a way that the unpaired electron spends more time on the nitrogen nucleus in polar solvents than in non-polar solvents. Therefore, $a_n$ is greater in water than in a solvent of lower polarity such as an oil. Also, a shift in the $g$-value results when a nitroxide is observed in various solvents. A smaller value of $g$ is found for nitroxides in the polar solvents than in non-polar solvents. Thus it is possible to experimentally determine where the electron is via relative values of the hyperfine split-
ting constant and \( g \)-values. More discussion of the im-
portant consequences of this result is given later.

In the presence of a magnetic field, the spin
system consists of various energy levels depending on
the spin quantum numbers of the electron and the nucleus.
Analysis of these energies using quantum theory leads
to the possible spin transitions and hence to the under­
standing of the ESR spectra. Primarily, then, one should
find the forms of the stationary state spin wave functions
and their energies. The spin angular momentum value for
the electron is \( S = \frac{1}{2} \), (measured in units of \( \hbar \)), and for
the nucleus, where we are concerned only with the nitro­
gen nucleus, the spin is \( I = 1 \). Along any one direction,
say the \( z \)-direction, the allowed quantum numbers, \( m_s \) and
\( m_I \), take on the values: \( m_s = \frac{1}{2} \) and \(-\frac{1}{2}\), while \( m_I = 1, 0, \) and
\(-1\). These can combine to make six possible basic wave
functions: \( \phi_1, \phi_2, \ldots \phi_6 \), which have thus been chosen
to be eigenfunctions of \( \mathbf{S}^z \), with unperturbed energy val-
ues: \( \varepsilon_1, \varepsilon_2, \ldots \varepsilon_6 \). These wave functions can be writ-
ten as products of the various spin wave functions using
Dirac notation:

\[
\begin{align*}
\phi_1 &= |\uparrow_2, 1\rangle \\
\phi_2 &= |\uparrow_2, 0\rangle \\
\phi_3 &= |\uparrow_2, -1\rangle \\
\phi_4 &= |\downarrow_2, 1\rangle \\
\phi_5 &= |\downarrow_2, 0\rangle \\
\phi_6 &= |\downarrow_2, -1\rangle
\end{align*}
\]

The eigenvalue equations, using the spin operators that
make up the Hamiltonian, are the following:
\[ S_z |\frac{1}{2} \rangle = \frac{1}{2} |\frac{1}{2} \rangle \]
\[ S_z |\frac{-1}{2} \rangle = -\frac{1}{2} |\frac{-1}{2} \rangle \]

and

\[ I_z |1 \rangle = |1 \rangle \]
\[ I_z |0 \rangle = 0 \]
\[ I_z |-1 \rangle = |-1 \rangle \]

The effect of applying a steady magnetic field, represented by the Hamiltonian, \( \mathcal{H}_o \), is to separate the degenerate states of the above wave functions given in equations 10. The result of operating with \( \mathcal{H}_o \) on the basis functions, 10, gives the zero-order energy values. For example:

\[ \mathcal{H}_o |\frac{1}{2}, -1 \rangle = (g \beta H S_z - g_N \beta N H I_z) |\frac{1}{2}, -1 \rangle \]
\[ = (\frac{1}{2} g \beta H + g_N \beta N H) |\frac{1}{2}, -1 \rangle \]

Thus we have the six zero-order energy values and their corresponding spin orientations:

\[ \mathcal{E}_1 = \frac{1}{2} g \beta H - g_N \beta N H \quad |\frac{1}{2}, 1 \rangle \]
\[ \mathcal{E}_2 = \frac{1}{2} g \beta H \quad |\frac{1}{2}, 0 \rangle \]
\[ \varepsilon_3 = \frac{1}{2} g \beta H + g_N \beta_N H \quad 1_{\frac{1}{2}}, -1 \]

\[ \varepsilon_4 = -\frac{1}{2} g \beta H - g_N \beta_N H \quad 1_{\frac{1}{2}}, 1 \]

\[ \varepsilon_5 = -\frac{1}{2} g \beta H \quad 1_{\frac{1}{2}}, 0 \]

\[ \varepsilon_6 = -\frac{1}{2} g \beta H + g_N \beta_N H \quad 1_{\frac{1}{2}}, -1 \]

The effect of the isotropic interactions is to perturb the ground state and cause first and second order hyperfine separation of the energy levels. The energy values and wave functions are given by perturbation theory:

\[ E_n = \varepsilon_n + \langle n | \mathcal{H}_2 | n \rangle - \sum_{m \neq n} \frac{\langle m | \mathcal{H}_2 | n \rangle \langle n | \mathcal{H}_2 | m \rangle}{\varepsilon_m - \varepsilon_n} \quad 14 \]

\[ \psi_n = \phi_n - \sum_{m \neq n} \frac{\langle m | \mathcal{H}_2 | n \rangle \phi_m}{\varepsilon_m - \varepsilon_n} \quad 15 \]

\( \mathcal{H}_2 \) can truly be considered a perturbation since in a field of 3000 G, the hyperfine splitting for the nitroxide radical used here is about 17 G.

The first order correction to the energies, using \( \mathcal{H}_2 \), are found by calculating \( \langle n | \mathcal{H}_2 | n \rangle \), where \( \mathcal{H}_2 = a_N \mathbf{S} \cdot \mathbf{I} \) and can be written as

\[ \mathcal{H}_2 = a_N (S_x I_x + S_y I_y + S_z I_z) \quad 16 \]

It is now useful to define two operators:

\[ S^+ = S_x + i S_y \quad 17 \]
and
\[ S^- = S_x - iS_y \] \hfill 18

such that
\[ S^+ | \frac{1}{2} \rangle = | \frac{3}{2} \rangle \] \hfill 19

and
\[ S^- | \frac{1}{2} \rangle = | -\frac{1}{2} \rangle \] \hfill 20

These are raising and lowering operators that shift the wave functions of the $z$-component of the spin angular momentum either +1 or -1. It can be shown that
\[ S_x I_x + S_y I_y = \frac{1}{2} (S^+ I^- + S^- I^+) \] \hfill 21

then the perturbing Hamiltonian, equation 16, becomes:
\[ \mathcal{H}_z = a_n \left[ \frac{1}{2} (S^+ I^- + S^- I^+) + S_z I_z \right] \] \hfill 22

The first order perturbation energies, $\varepsilon'_n$, are now in the form:
\[ \varepsilon'_n = a_n \langle n | \frac{1}{2} (S^+ I^- + S^- I^+) + S_z I_z | n \rangle \] \hfill 23

The only surviving terms are those of $\langle n | S_x I_x | n \rangle$. For example:
\[ a_n \langle \frac{1}{2}^-1 | S_z I_z | \frac{3}{2}^-1 \rangle = a_n \langle \frac{1}{2}^-1 | \frac{1}{2}^-1 | \frac{3}{2}^-1 \rangle = -a_n/2 \] \hfill 24
Using this method then:

\[ \epsilon_1' = \frac{a_n}{\tilde{Z}} \]
\[ \epsilon_2' = 0 \]
\[ \epsilon_3' = -\frac{a_n}{\tilde{Z}} \]
\[ \epsilon_4' = -\frac{a_n}{\tilde{Z}} \]
\[ \epsilon_5' = 0 \]
\[ \epsilon_6' = \frac{a_n}{\tilde{Z}} \]

Applying the second order perturbation requires evaluating the following terms:

\[ \epsilon_n'' = -\sum_{m \neq n} \frac{\langle m | \mathcal{H}_2 | n \rangle \langle n | \mathcal{H}_2 | m \rangle}{\epsilon_m - \epsilon_n} \]

The terms involving \( S_z I_z \) do not contribute and therefore only the following need be calculated:

\[ \epsilon_n'' = -\sum_{m \neq n} \frac{\langle m | \frac{a_n}{\tilde{Z}} (S^+ I^- + S^- I^+) | n \rangle \langle n | \frac{a_n}{\tilde{Z}} (S^+ I^- + S^- I^+) | m \rangle}{\epsilon_m - \epsilon_n} \]

For example:

\[ \epsilon_2'' = -\frac{\langle \frac{1}{2}, 0 | \frac{a_n}{\tilde{Z}} (S^+ I^- + S^- I^+) | \frac{1}{2}, 0 \rangle \langle \frac{1}{2}, 0 | \frac{a_n}{\tilde{Z}} (S^+ I^- + S^- I^+) | -\frac{1}{2}, 0 \rangle}{\frac{1}{2} g \beta H - g_n \beta_n H - \frac{1}{2} g \beta H} \]

\[ = \frac{a_n^2}{2(\Delta_e + \Delta_n)} \]

where \( \Delta_e = g \beta H \) and \( \Delta_n = g_n \beta_n H \).

The final corrected energy values and their corresponding ground state eigenfunctions are:
These levels are graphically illustrated by an energy level diagram showing the relative positions of the energy states in figure 1. The allowed transitions are $\Delta m_s = \pm 1$ for the electronic states, and $\Delta m_I = 0$ for the nuclear states. The allowed energy transitions are then; $E_1 \leftrightarrow E_4$, $E_2 \leftrightarrow E_5$, and $E_3 \leftrightarrow E_6$, each having equal probability to occur, and hence one observes three equally intense spectral lines. The second order hyperfine energy term, $\frac{a_n^2}{2(\Delta_e + \Delta_n)}$, is very small compared to $a_n$ and can be neglected for the nitroxide radical in high H fields. Then, $a_n$ can be measured directly from the ESR spectra as in figure 2.
Figure 1. First and second order spin energy levels of the nitroxide radical, and the allowed ESR transitions.

Zero Electron Nuclear Hyperfine
field Zeeman Zeeman coupling

\[ \pm g_\beta H \]

\[ \pm g_\beta H \]

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\[ \pm g_\beta H \]
Figure 2. Typical spectrum of a rapidly tumbling nitroxide probe showing the hyperfine coupling constant, $a_N$, and the peak-to-peak linewidth, $\Delta H_{\text{pp}}$. 
IV. SPIN PROBES

The necessary connection between the microscopic emulsion system and the ESR spectra is the nitroxide spin label. These molecules consist basically of organic compounds with an unpaired electron centered around the nitroxide, (N-O), group. There are a wide variety of spin probes available and one can choose a particular structure depending on the experiment.\(^5\) The spin probe used in this study is di-tert-butyl nitroxide, (DTBN), which has the following structure:

![Figure 3. Di-tert-butyl nitroxide spin probe. The unpaired electron localized largely on the nitroxide group.](image)

The main advantages of the nitroxides are their sensitivity to the local environment and ability to measure very rapid molecular motion. If the environment of the electron has a relatively high dielectric constant the unpaired electron tends to spend more time around the N-O group, as opposed to an environment with a lower dielectric constant. Therefore, the hyperfine coupling constant would be greater in the polar water environment than in the less polar hydrocarbon, butanol.
The rate of tumbling of the nitroxide molecule can be determined from the spectra, the quantity calculated is called the correlation time, $\tau_c$. It is defined as the average time for a nitroxide radical undergoing Brownian motion to rotate through an arc of approximately one radian. Typical $\tau_c$ values for fast and slow tumbling rates, (which are inversely proportional to the correlation time), are $5 \times 10^{-11}$ sec. and $5 \times 10^{-8}$ sec., respectively. Spin probes tumble rapidly in homogeneous solutions such as water and pure butanol, but decrease with increasing viscosity or inhomogeneity of the solutions. Examples of spectra where the probe, DTBN, is tumbling rapidly in ethylene glycol at $25^\circ$C can be seen in fig. 4, and the broadening of the spectral lines due to increased viscosity from lowering the temperature. It is expected then that the tumbling rates would decrease in a micelle emulsion since the mobility of the spin probe would be inhibited. $\tau_c$ can be calculated using the following expression:

$$\tau_c = \left[ \frac{W_1}{W_0} + \frac{W_{-1}}{W_0} - 2 \right] \frac{4\pi \sqrt{3}}{b^2} W_0$$

The correlation time is dependent on the linewidths: $W_1$, $W_0$, and $W_{-1}$, where 1, 0, and -1 represent high, medium, and low field lines, respectively, and on $b$, a constant for DTBN. $\tau_c$ is proportional to the width of the medium.
Figure 4. Spectra of DTBN in ethylene glycol at a.) 25°, b.) -25°, c.) -80°, and d.) -150°. The increased width of spectral lines is indicative of slower rotation of the probe. The broadening is noted to vary from one hyperfine line to the next.
field line. The larger value of $W_0$ the slower is the rate of tumbling of DTBN. Line broadening can also be caused by interactions among nitroxides, but can be neglected if the concentration of the probe is less than $10^{-3}$M as is the case in these experiments.

It is also possible in some cases, to determine from the spectra the preferred axis of rotation of the spin probe\textsuperscript{15}. For DTBN the x-axis is defined as parallel to the N-O bond, z-axis is parallel to the p-orbital of the nitrogen, and the y-axis is perpendicular to the x and z axes. If $R_x > 1$, where $R_x = h_1 / h_0$, and $h_1$ and $h_0$ are the heights of the low and middle field lines respectively, then there is x-axis anisotropy. For example:

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.png}
\caption{Nitrooxide probe spectra indicating x-axis anisotropic rotation, i.e. $R_x = h_1 / h_0 > 1$.}
\end{figure}
V. MICELLES AND REVERSED MICELLES

Necessary to a discussion of micelles is the introduction of the amphiphilic molecule. This molecule is characterized by having two types of groups that differ greatly in their solubility properties. These are: 1) a hydrophobic, or water-loving, group which tends to be soluble in water or other polar compounds and insoluble in hydrocarbons or non-polar compounds, and 2) a lipophilic group which tends to solubilize with the oily hydrocarbon and be insoluble in water. Typical hydrophobic groups are: -OH, -CO₂Na, -N(CH₃)₃Br, and typical lipophilic groups are -CₙH₂₅⁺, where N>10. Thus the dual nature of amphiphiles permits the unusual quality of being able to dissolve in both water and hydrocarbon solutions. For example, it is possible to dissolve into solution via the amphiphilic molecules an otherwise non-miscible solution of water and hydrocarbons. The amphiphile used in this work is cetyltrimethylammonium bromide, or CTAB.

A solution of amphiphilic molecules in water and oil are not random at all concentrations but orientate themselves in certain prescribed geometries that are critically dependent on the concentrations of the substituents. A simple form of a micelle, and one which is studied in this thesis, consists of spherical aggregates of the amphiphilic molecule. The surface consists of the polar...
hydrophobic groups dissolved in the water and the fluid interior are the hydrocarbon chains dissolved in the oil molecules. The intermicellular fluid is water in these micelles which are termed normal micelles. It is possible to reverse the roles of the polar and non-polar groups by altering their concentrations. A reverse micelle system is one with the non-polar oils on the spherical surface facing outwards, and the polar groups dissolved with the water in the interior. The intermicellular fluid in this case is the oil.

The number of amphiphiles per micelle is somewhat variable depending on the type of oil and amphiphile in the emulsion and their concentrations. An approximate number is from 50 to 100 molecules for CTAB in n-butanol.

Other geometrical forms of micelles are also possible. These include cylindrical micelles which are rod shaped structures, and can be either normal or of the reversed type depending on the concentrations. Lamellar or flat layered structures also exist at the appropriate concentrations of the substituents.

A schematic representation of normal and reversed spherical micelles, and the molecules used in this work that comprise them, are in figure 6.
Figure 6. Components of micelle system used in this work, and cross sections of spherical normal and reversed micelles.
water, $\text{H}_2\text{O} = \bullet$

n-butanol, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH} = \sim$

cetyltrimethylammonium bromide,

\[
\begin{aligned}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{CH}_2\text{N}^-\text{Br}^+ &= \\
\text{CH}_3\text{CH}_3
\end{aligned}
\]

- normal micelle
- reversed micelle
Figure 7. The three hypothetical models of probe-micelle interaction as proposed by Waggoner et. al.. Model 1 shows probe attached rigidly to the micelle surface. Model 2 shows the probe in both environments. Model 3 has the probe in the micelle interior.
model 1

model 2

model 3
VI. EXPERIMENTAL PROCEDURES

A.) ESR Spectrometer

The ESR spectrometer used in this work consisted of five main systems; 1) source, 2) cavity, 3) magnet, 4) modulation, and 5) detection systems. Figure 8 shows a block diagram of the ESR spectrometer.

The source system contains the Klystron which produces the x-band microwaves and an automatic frequency control. The electromagnet, driven by a Varian Fieldial, is controlled by the Hall effect. The modulation coils are driven by a 100 kHz. oscillator with an amplitude that is small compared with the spectral linewidth. The signal is detected by a crystal diode and the component at the modulation frequency is amplified with a lock-in amplifier. The detection scheme results in a d.c. signal proportional to the derivative of the ESR absorption.

The automatic frequency control, (AFC), is achieved by modulating the reflector of the Klystron. This results in the frequency modulation of the microwave power at a frequency different from the magnetic field modulation. The AFC signal is detected by the same crystal used to detect the resonance signal. This AFC signal is amplified by a lock-in amplifier and an error voltage is applied to the reflector to correct the Klystron frequency. Since the resonant frequency of the cavity can change
Figure 8. Block diagram of x-band ESR spectrometer.
slightly due to temperature and moisture variations, this method insures that the microwave frequency is the same as the resonant cavity frequency.

B.) ESR Measurements

The paramagnetic samples to be measured are placed in one of two types of resonant cavities used for these experiments. One rectangular cavity is constructed for a $\text{TE}_{102}$ mode and the other for a $\text{TE}_{104}$ mode. These are called single and dual cavities, respectively. A resonant cavity is matched to the microwaves via the iris located at the opening to the cavity. This matching insures a high $H$ field at the sample location. A large quality factor, $Q$, is achieved by these resonant cavities. Figure 9 shows the location of the paramagnetic sample in a $\text{TE}_{102}$ cavity. Note that the $E$ field is small in the region of the sample.

The liquid samples are sealed in slender capillary tubes to keep the samples away from the electric field and avoid dielectric losses of microwave power. These losses lower the $Q$ of the cavity and result in a loss of sensitivity. The dual cavity technique of providing accurate $g$-values and $\alpha_n$ measurements is done by placing a standard in one maximum $H$ field position and the sample in the other position. There are two sets of modulation
Figure 9. A.) A rectangular TE$_{102}$ cavity showing:
1.) the iris used to couple microwave energy into the cavity, and 2.) the capillary holder and capillary tube used to contain the paramagnetic sample. B.) Magnetic field contours. Note high flux in the center of the cavity at the position of the sample.
coils employed with the dual cavity, one set for each maximum H field position. The external magnetic field is swept through resonance while the modulating coils of one sample are turned on. These are then turned off and the other coils are turned on, and again the external magnetic field is swept through resonance.

The standard in these experiments was DTBN in water where \( a_N = 17.1 \) G. and \( g = 2.0053 \). The concentration of DTBN in all samples was of low enough concentration to avoid exchange broadening of the spectral lines, and all samples were kept at room temperatures. \( a_N \) is measured as in figure 2. The deviation of the \( g \)-value from 2.0053 is computed using the following procedure. Consider the resonant condition as given in equation 3,

\[ h\nu = g\beta H \]

and the two spectra: 1) the standard and 2) the sample spectrum with a shift in the \( g \)-value,

\[ a. \]

\[ b. \]

Figure 10. a.) The standard spectrum and b.) the sample spectrum used in conjunction to determine the \( g \)-value of sample.
Solving for $g$ in equation 3 gives

$$g = \frac{h\nu}{\beta H}$$

The derivative of this equation, holding the frequency constant, gives the change in $g$, $\delta g$, in terms of the resonant magnetic field and the change in the magnetic field,

$$\delta g = -\frac{h\nu}{\beta} \frac{\delta H}{H^2}$$

C.) Sample Preparation

1.) Ethanol-water series

A series of ethanol and water solutions were prepared varying relative amounts of ethanol from 0 to 100% by volume. The non-degassed samples were sealed in capillary tubes after DTBN was added to a concentration of $7.8 \times 10^{-4}$M.

2.) Partitioning of DTBN in water and n-butanol

A two phase mixture of triple distilled water and n-butanol was prepared using 50 ml. of each liquid in a 125 ml. separatory funnel. 10 $\mu$l. of DTBN was added and, after 30 seconds of shaking, the contents were allowed to equilibrate for 5 minutes. Samples were obtained from the lower water fraction and the upper oil fraction and each sealed in capillary tubes.
3.) N-butanol(0 to 5%)-water series

A series of "solutions" were prepared containing water and concentrations of n-butanol from 0 to 5% by volume. DTBN was added to each sample to a concentration of $7.8 \times 10^{-4}$ M. The non-degassed samples were sealed in capillary tubes.

4.) Emulsion preparation

A series of water, n-butanol, and CTAB emulsions were prepared by S. Friberg such that all mixtures are in the emulsion region of the phase diagram, figure 11. DTBN was added to a concentration of $7.8 \times 10^{-4}$ M in each sample, and the emulsions were sealed in capillaries. The author acknowledges the kind gift of these samples from S. Friberg of the Swedish Institute for Surface Chemistry, Stockholm, Sweden.

Figure 11. Three component phase diagram. Relative amounts of components in the sample can be extrapolated from points in the emulsion region.
VII. RESULTS

A.) Ethanol-water series

DTBN is soluble in water and ethanol at the concentration used and gives the expected three line spectra at all concentrations of water. The hyperfine coupling constants for DTBN in ethanol-water solutions as a function of percent water is shown in figure 12. It is seen that $a_{N}$ increases nearly linearly from its value at pure ethanol to pure water. The value of $a_{N}$ in ethanol is $16.1 \pm 0.3$ G.

The linewidth, $\Delta H_{pp}$, for DTBN in the same series was also measured. The change in the linewidth, as seen in figure 13, from pure ethanol to pure water decreases uniformly from 1.2 G. to .3 G. Both the coupling constant data and linewidth data show no discontinuities over the entire range of concentrations.

All of the ESR spectra in this series showed nearly equally intense hyperfine lines. Thus, according to equation 30, these spectra are indicative of fast rotation of the probe in all mixtures of water in ethanol.

B.) Partitioning of DTBN in water and n-butanol

The linewidths and intensities of the $m_f = 0$ line of the spectrum of DTBN in n-butanol and DTBN in water were measured. The relative concentrations of the probe
Figure 12. Hyperfine coupling constant of DTBN in the ethanol-water series showing nearly linear increase in $a_n$ from 0 to 100% $H_2O$. The data are plotted as $\Delta a_n = a_n(H_2O) - a_n$. 
Figure 13. ESR linewidth of DTBN in the ethanol-water series as water concentration is varied from 0 to 100%.
dissolved in equal quantities of the two solvents were
determined by evaluating $V_{pp}\Delta H_{pp}^2$, where $V_{pp}$ is the peak-to-
peak intensity of the first derivative spectrum. This
quantity is proportional to the number of spins in the
sample, the constant of proportionality being the same if
the lineshape is the same.\(^{18}\)

The concentration ratio is 30 to 1, the probe be-
ing more soluble in the "oil" fraction. This result is
not surprising considering the nature of the solute; DTBN
is mostly hydrocarbon and should dissolve predominately
in the "oil-like" butanol fraction.

C. N-butanol(0 to 5%)-water series

The ESR results of all six samples gave the expect-
ed three line spectra. The hyperfine coupling constants
were computed using DTBN in pure water as a standard.
The values of $a_N$ for concentrations of n-butanol from
1 to 5% are slightly greater than the value of $a_N$ in pure
water. $g$-values were not measured since a single, $(TE_{102})$,
resonant cavity was used. Linewidth and line intensity
data do not indicate inhibited tumbling of the probe in
any of the six samples.

D. Emulsion series

The three line spectra observed in this series are
typical nitroxide spectra. The hyperfine coupling con-
stants, g-values, and first derivative linewidths, ($\Delta H_{pp}$), are given in table 1.

In figure 14, the hyperfine coupling constant vs. water concentration is seen to differ markedly from the linear increase of $a_N$ vs. water in the ethanol series, (see figure 12). $a_N$ increases from its value of 15.8 G. in n-butanol as water is added, but there are discontinuities in this increase up to the final value of $a_N$ in pure water of 17.1 G. The error bars are about the size of the circles.

The g-values vs. the concentration of water is recorded in figure 15. The results, similar to $a_N$ results, (figure 14), show that the g-value is also non-linear as a function of water concentration. The non-linearity of the g-value is seen to be most severe from about 30 to 60% $H_2O$ where the curve levels. It is noted that the slope of the graph from 10 to 30% $H_2O$ is less than the slope from 60 to 90% $H_2O$. The g-value of DTBN in pure water is 2.0053 and in n-butanol is 2.0056.

The linewidth of the $m_z = 0$ line is given in figure 16. The linewidth decreases somewhat smoothly from 1.0 G. to about 0.7 G. The sharpest decrease is from 20 to 30% $H_2O$ where the linewidth changes from 1.05 G. to 0.95 G.

Rotational correlation times for DTBN were found
by measuring the intensities of the three hyperfine components. The results were computed using equation 30 and are shown in figure 17. Interestingly, the probe rotates very rapidly in water and in butanol but slows somewhat at intermediate concentrations of these components, and especially at 90% H₂O.

By inspection of the spectra there is no indication of anisotropic tumbling of DTBN in any of the samples; i.e., the height of the $m_τ = 0$ line was always greater than the height of the $m_τ = -1$ line in individual spectra.
TABLE 1. ESR parameters of DTBN in n-butanol-water-CTAB emulsion series.

<table>
<thead>
<tr>
<th>% Water</th>
<th>$\Delta a_n$(gauss)$^a$</th>
<th>$\Delta g$(x10$^4$)$^b$</th>
<th>$\Delta H_p$(gauss)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>-2.33</td>
<td>2.9</td>
<td>1.05</td>
</tr>
<tr>
<td>19.8</td>
<td>-2.31</td>
<td>2.7</td>
<td>1.05</td>
</tr>
<tr>
<td>29.8</td>
<td>-2.05</td>
<td>2.6</td>
<td>.95</td>
</tr>
<tr>
<td>39.6</td>
<td>-2.02</td>
<td>2.3</td>
<td>.95</td>
</tr>
<tr>
<td>49.5</td>
<td>-1.89</td>
<td></td>
<td>.91</td>
</tr>
<tr>
<td>59.4</td>
<td>-1.85</td>
<td>2.25</td>
<td>.88</td>
</tr>
<tr>
<td>69.1</td>
<td>-1.79</td>
<td>2.1</td>
<td>.86</td>
</tr>
<tr>
<td>79.1</td>
<td>-1.58</td>
<td>1.85</td>
<td>.79</td>
</tr>
<tr>
<td>89.1</td>
<td>-1.12</td>
<td>1.3</td>
<td>.74</td>
</tr>
</tbody>
</table>

$^a$ accurate to ±.03 gauss

$^b$ accurate to ±.1x10$^{-4}$
Figure 14. Hyperfine coupling constant of DTBN in n-butanol-water-CTAB emulsion series showing abrupt changes in $a_n$ at approximately 25% and 45% H$_2$O, and a steep slope near 90% H$_2$O.
Figure 15. The $g$-value of DTBN in the n-butanol-water-CTAB emulsion series. The data are plotted $\Delta g = g(\text{H}_2\text{O}) - g$. Non-linear behavior of the $\Delta g$-value is similar to the non-linear behavior of $a_N$. 
Figure 16. ESR linewidth of DTBN in the n-butanol-water-CTAB emulsion series.
Figure 17. Rotational correlational times of DTBN in n-butanol-water-CTAB emulsion series. Note slower tumbling rate in 90% H₂O range.
VIII. DISCUSSION

The effect that the dielectric constant, $K$, of the solvent has on the hyperfine coupling constant and $g$-values of DTBN is given in table 2. $a_n$ is greatest in water, ($K \approx 80$), and lowest in n-butanol, ($K \approx 17$). It is concluded from this and other similar data\textsuperscript{17} that the hyperfine coupling constant is directly proportional to the dielectric constant. The $g$-value, as seen in figure 15, is inversely proportional to the dielectric constant.

Table 2. Variation of ESR parameters of DTBN with dielectric constant of various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$a_n$ (gauss)</th>
<th>$g$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>17.1</td>
<td>2.0053</td>
<td>80</td>
</tr>
<tr>
<td>ethanol</td>
<td>16.1</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>n-butanol</td>
<td>15.8</td>
<td>2.0056</td>
<td>17</td>
</tr>
</tbody>
</table>
Thus, the fact that the hyperfine coupling constant in the ethanol-water series shows an almost linear increase as the water content is increased from 0 to 100% is easily understood in terms of the variation in K. Data from F. Frank reveal that the dielectric constant of an ethanol-water solution increases linearly as the concentration ranges from 0 to 100% H$_2$O. Therefore, $a_n$ of DTBN in the ethanol-water series follows the macroscopic dielectric constant almost linearly.

In contrast with the results in the ethanol series, a very rapid decrease in $a_n$ from 100 to 80% H$_2$O is found in the n-butanol-water emulsion series. This indicates that there are regions in the emulsion of lower than average dielectric constant and that the probe seeks these regions. We conclude that these regions are the interior of normal micelles. The large partitioning ratio of 30 to 1 is responsible for the probe seeking the region of low dielectric constant. These results show that micelles are formed in the 80 to 100% H$_2$O range and this is identical to the region of micelle formation as demonstrated by light scattering, NMR, and catalytic data.

Assuming that normal micelles dominate the emulsion at approximately 90% H$_2$O it is likely that DTBN is interacting with the micelle in more than a simple hydrophobic manner. A probable probe-micelle surface interaction at 90% H$_2$O can be supported by the following
Experimental evidence: 1.) The hyperfine coupling constant and g-values show the probe to be influenced by both water and oil environments because these values are intermediate between the values for full water or full butanol, (table 1). This is so even though the probe "likes" to be in the butanol 30 times as much as water.

2.) The correlation time shows that motion is inhibited by a factor of 5 compared to other concentrations of water. This indicates, again, that a probable position for the probe to be near or interacting with the surface of the micelle which would present a barrier to rotation. It is apparently inhibited from reaching the "oil".

A likely location for the probe is near the surface of the micelle such that the polar N-O group is facing out towards the aqueous surroundings, and the hydrocarbons are immersed in the oily part of the micelle interface.

To test this model, ESR spectra were recorded with the 90% H₂O sample at elevated and lowered temperatures. At lower temperatures the rotational correlation time slows even more, as expected, and a and g-values become more water-like. At higher temperatures, (64°C), a three line spectrum of equally intense hyperfine lines are observed indicating rapid rotation of the probe. Also at higher temperatures an and the g-values become more butanol-like. These findings are in complete accord
with the model described. For example, at low temperatures the rotation of the probe near the interface is inhibited, thus the N-0 group spends more time near the polar surface, and we detect the "water-like" ESR parameters. At high temperatures the probe rotates freely in the oil environment. As expected, the probe would be in the oil environment, rather than the water environment, if the temperature were sufficient to allow it to depart from its minimum energy configuration near the surface.

Using this model of probe-micelle interaction it is possible to interpret the results of the level region around 60 and 70% H$_2$O in the a$_N$ graph, figure 14. As the amount of "oil" and CTAB increases and the water decreases, the size of the micelles or the number of micelles increases. In either case, the environment of the probe will remain essentially the same. It would be expected that a$_N$ and g-values would level to a constant value in that region, and that is exactly what is observed.

As noted, in the ethanol-water series, the a$_N$ curve is essentially a linear one, but there are departures from this smooth curve in the n-butanol series. There are two distinct breaks occurring at 45% H$_2$O and at 25% H$_2$O. We interpret the one at 45% to be due to a change in the geometry of the micelles. This "break" is coincident with the region in which an enhanced
catalysis reaction rate of p-nitrophenyl laurate occurs\(^9\). This enhancement has been associated with the formation of reversed micelles. The break in the \(a_n\) curve, which is certainly an indication that the environment of the probe changes over a small concentration range, provides strong evidence for the formation of a form of reversed micelles. There is also a break in the \(g\)-value curve in this region which has the same implications. It is noted that the transition from normal to reversed micelles observed by this method is more abrupt than the transition observed by the method of enhanced catalysis\(^9\). We should point out that reversed micelles have not been observed thus far in this system by light scattering or NMR.

The other break in the \(a_n\) curve is in the 20 to 30\% \(H_2O\) range. The resolution of the catalysis experiment was not sufficient to indicate the existence of other geometrical forms of reversed micelles in the series considered here. However, in a similar series a maximum in catalysis was observed at 20\% \(H_2O\) indicating that reversed micelles were formed at these low water concentrations. We postulate that the break in \(a_n\) indicate that a different geometrical form of reversed micelle is present at this concentration. This interpretation is possible because of the higher resolution on the concentration scale of the present method. Friberg
had difficulty in explaining the slow rise of the catalytic reaction rate at the low water concentration side of the reversed micelles. Those authors suggested that pre-micellar aggregation might be responsible, but our suggestion is somewhat different and fully explains the results. We suggest that the catalytic rate is increased near 25% H₂O due to the second form of reversed micelles and that the two catalysis reaction rate increases due to the two forms give the appearance of a single broad increase in reaction rate.

In summary, we have shown for the first time that ESR can be a successful tool to detect the existence of normal micelles and geometrical changes to inverse micelles. The results in this thesis also substantiate the existence of reversed micelles with high resolution and show strong evidence for another form of reversed micelles in the low water concentration range.

We are unable, with the present data, to ascertain the details of the geometry of the various micelles.

The encouraging results in the present study suggest that further study of emulsion systems of this kind would be fruitful. Two types of work immediately come to mind: 1.) A larger nitroxide probe and 2.) a charged probe such as Fremy's salt. A larger probe would have the advantage of being more sensitive to changes in the
tumbling rate. With DTBN we have found that the rate of tumbling is very rapid in all but one region of concentration. The use of a large probe structured such that it rotates in solution about a preferred axis is an interesting possibility. The advantage of using Fremy's salt is two fold: The charged probe would interact with the ionic micelle differently than DTBN. Secondly, Fremy's salt has a much higher dielectric constant, and would undoubtedly show a large partitioning ratio in favor of the water fraction. This latter quality of Fremy's salt makes it an ideal complement to the oil-seeking DTBN.
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