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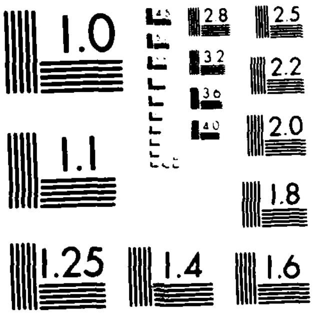

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**CHEMICAL SYSTEMS LABORATORY**

US Army Armament Research and Development Command
Aberdeen Proving Ground, Maryland 21010

TECHNICAL REPORT ARCSL-TR-83035

# DIFFUSION MEASUREMENTS IN MICROEMULSIONS

by

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June 1983

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Diffusion coefficient measurements in both aqueous micelles and microemulsions have been carried out using the techniques of polarography and quasielastic light scattering (QLS). The former method involves the determination of the diffusion coefficient of an electroactive oil soluble probe at a polarizable microelectrode. For high water content microemulsions, both methods yield the same diffusion coefficients which can be identified as the self diffusion coefficient. For cetyltrimethylammonium bromide (CTAB) micelles, both methods

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20. ABSTRACT (Contd)

yield the same result at the salt (NaBr) concentration at which the QLS measurements are independent of CTAB concentration. In more concentrated microemulsions, QLS data gave diffusion coefficients in agreement with polarography only for a sodium cetyl sulfate (SCS) system at 65-75 wt % water. For the SCS microemulsions at 60% water, and CTAB microemulsion at 60-75% water, the QLS data yielded rapid, nonexponential decays. However, consistent polarographic diffusion coefficients could still be obtained. By using probes of varying chain length (oil solubility), it has been demonstrated that these CTAB and SCS microemulsions containing butanol and pentanol cosurfactants respectively, are not cosolubilized systems but do contain distinct hydrophilic and hydrophobic regions.

# PREFACE

The work described in this report was authorized under Project 1L161102A71A. This work was started in September 1982 and completed in December 1983. The experimental data are recorded in CSL notebook 80-0055.

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# SUMMARY

For oil in water (O/W) microemulsions at high water contents, quasielastic light scattering (QLS) and polarography yield the same values for the translational diffusion coefficient. For more concentrated microemulsions, the interpretation of the QLS data is not straightforward; but, polarography can still yield values of the self diffusion coefficient. In the case of aqueous micelles, a similar situation is obtained. The cetyltrimethylammonium bromide (CTAB) and sodium cetyl sulfate (SCS) microemulsions, containing 1-butanol and 1-pentanol as cosurfactant, respectively, are not cosolubilized systems but do contain distinct hydrophilic and hydrophobic regions. These results, coupled with the simplicity of the polarographic probe method and its lack of dependence on any assumptions, show that it should be added to the arsenal of complimentary measurements which include classical diffusion measurements, QLS, Nuclear Magnetic Resonance (NMR) spin-echo measurements, and sedimentation.

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# DIFFUSION MEASUREMENTS IN MICROEMULSIONS

## 1. INTRODUCTION

There is a considerable amount of current research devoted to the study of the nature of microemulsions. Many of these systems appear to be thermodynamically stable single phases,[1-4] while some are demonstrably kinetically stable.[5-7] Some microemulsions are composed of three components, but the majority of the systems examined to date are composed of at least four components; oil, water, surfactant, and cosurfactant. Usually the cosurfactant is a medium chain length alcohol (e.g., $C_4$ - $C_6$). Some of these microemulsions contain droplets of oil in water (O/W) or water in oil (W/O), while the structure of the so-called surfactant or middle phase microemulsions is at present unresolved.[8-10] In addition, some systems contain clear, apparently single phase regions in their pseudo three component phase maps which virtually extend from the water (W) apex to the oil (O) apex,[11] particularly when a lower chain length alcohol such as butanol is employed as the cosurfactant. In these cases, there should be internal structural changes which occur as the clear region is traversed from the W to the O apex, as indicated for example by quasi-elastic light scattering (QLS) studies.[12] However, recent measurements of the diffusion coefficients of the various components of the microemulsion by a Fourier transform pulsed-gradient spin-echo method[13] have not indicated the presence of any sharp boundaries. The diffusion coefficients of oil and water continuously increase and decrease, respectively, as compositions are varied from the W to the O apex. It was suggested that one possible explanation is that these are cosolubilized systems,[10] i.e., molecular dispersions with no distinct hydrophilic and hydrophobic domains.

The properties of microemulsions by a variety of techniques including light scattering,[14] dielectric dispersion,[15] and electrochemistry have been investigated.[16-17] In particular, polarography has been employed to measure the diffusion coefficient of aqueous ions such as Cd(II) and ferricyanide in microemulsions stabilized by both ionic and nonionic surfactants.[18] These studies have demonstrated that the transport of aqueous species is accounted for by the obstruction (effective medium) effect, which indicates that some division into hydrophilic and hydrophobic domains must exist. The polarographic determination of the diffusion coefficient of oil soluble probes, in conjunction with QLS studies, on a variety of microemulsion systems is reported here.

## 2. EXPERIMENT

### 2.1 Polarographic Measurements.

As previously described, these measurements were performed at a dropping mercury electrode using a three electrode system.[16,18]

### 2.2 QLS Measurements.

A fixed angle (90°) laser light scattering photometer (Model LSA-1) from Langley-Ford Instruments was used. The LSA-1 was modified with a Spectra-Physics 15 mw 632.8 nm HeNe laser source, and contained a scattered light collection aperture which defines approximately one coherence area. The autocorrelation functions were computed with a Langley-Ford Model 1096 correlator. The analysis program employs the method of cumulants[19] to fit the correlation function to a single exponential curve directly in the correlator itself, without the use of a separate external computer. Calculations are then performed using the results of the cumulants analysis to yield the average translational diffusion coefficient and subsequently, from the Stokes-Einstein equation, the effective diameter of the particles.

The continuous phase was assumed to have the viscosity and refractive index of pure water unless otherwise indicated. The known dependence of these parameters with temperature was used.[20] To minimize dust incorporation, most samples were filtered through a 0.45 μm filter directly into the cuvet. The samples were then maintained at 25± 0.1 C, unless otherwise stated, by means of water circulation around the cuvet from a constant temperature bath.

## 2.3 Materials.

The materials used in the polarographic experiments have been described elsewhere.[16-18] Sodium dodecyl Sulfate (SDS) (Polysciences, electrophoresis grade) was used as received. Cetyltrimethylammonium bromide (CTAB) (Aldrich, reagent) was twice recrystallized from acetone. n-Octane, hexadecane, and dodecane (99%) were also obtained from Aldrich. Sodium bromide (Fisher, reagent) 1-butanol, and 1-pentanol (B&A, reagent) were used as received.

## 3. RESULTS AND DISCUSSION

## 3.1 Measurement of Diffusion Coefficients.

Some initial results employing an oil soluble electroactive probe, the 1-dodecyl-4-cyanopyridinium ion, were recently reported.[18] If particles composed of hydrophobic material are present in an aqueous continuous medium (e.g., micelles or "oil" droplets), then the diffusion coefficient ($D_p$) of the electroactive oil soluble probe (determined by means of polarography) should be the diffusion coefficient of the particle. In the absence of interactions between the particles, and assuming they are spheres, the hydrodynamic radius ($r_p$) can be determined from the Stokes Einstein equation (i), where

$$r_p = kT/6\pi\eta D_p \qquad \text{(i)}$$

η is the viscosity of the continuous medium, and k and T are Boltzman's constant and the absolute temperature respectively. If the spheres are polydisperse, the measured value of D will depend upon the size distribution as well as the distribution of probe among the particles. However, it might be expected that the probe distributes itself according to either the volume or surface area of the particle, and in either case the larger particles would be heavily weighted.

For the QLS measurements, monodisperse particles give rise to an autocorrelation function which decays exponentially with a (1/e) decay time $\tau = \Gamma^{-1}$. The diffusion coefficient ($D_z$) of the particle is given by $\Gamma K^{-2}$, where $K = (4\pi n/\lambda) \sin \theta/2$. Here λ, θ, and η are the laser wavelength, scattering angle, and refractive index of the continuous medium respectively. If the particles are spheres, a hydrodynamic radius $r_z$ can be calculated using equation (i). For monodisperse particles, providing that the presence of the probe does not effect the particle size, $D_z$ and $D_p$ should be equal. For polydisperse particles, $D_z$ is the z - average diffusion coefficient which is even more heavily weighted in favor of the larger particles than $D_p$. In general, if $\bar{D}$ is the number average value, then $\bar{D} \geq D_p \geq D_z$. The variance obtained from the QLS data analysis is a measure of the polydispersity. As a rule of thumb, variances less than 0.1 will be considered to be reasonably monodisperse.

If the phase volume ϕ (i.e., particle concentration) is high and/or the particles are interacting, then both $D_p$ and $D_z$ are not necessarily the "free particle" diffusion coefficient. Polarography might be expected to yield the self or trace diffusion coefficient, while QLS may yield a self diffusion coefficient, a collective diffusion coefficient, or non-exponential behavior to which both contribute.[21]

## 3.2 Comparison of $D_p$ and $D_z$.

In order to examine the validity of the polarographic probe method, values of $D_p$ (or $r_p$) have been compared with values of $D_z$ (or $r_z$) obtained by QLS on both high water-content microemulsions and micelles. Values of $D_z$ for octane/water (aqueous NaBr) microemulsions stabilized by CTAB and 1-butanol have been reported.[22] $D_p$ has been measured in this system and the results are presented in table 1. The agreement is excellent. The variance reported for the QLS measurements is $\leq 0.04$, indicating that the droplets are essentially monodisperse.

Table 1. Values of the Polarographic ($D_p$) and QLS ($D_z$) Diffusion Coefficients at 25°C in an Octane/CTAB/1-Butanol/Water Microemulsion[a]

| % NaBr[b] | $D_p$[c,d] | $D_z$[c,e] |
|---|---|---|
| 1.3 | 2.3 | 2.3 |
| 1.5 | 1.3 | 1.6 |
| 1.6 | 1.1 | 1.1 |
| 1.7 | 0.8 | 0.8 |

[a] composition given in reference 22.

[b] by weight.

[c] $cm^2/s \times 10^7$.

[d] using the probe 1-dodecyl-4-cyano pyridinium iodide at a concentration of 0.6 mM.

[e] estimated from figure 1, reference 22.

For CTAB micelles, QLS studies were reported as a function of temperature, CTAB, and NaBr concentration.[23] At NaBr concentration $< 0.08$ M, $D_z$ increased with increasing CTAB concentration. It was concluded however that this was principally due to intermicellar interactions rather than to a change in size. At NaBr concentrations $> 0.08$ M, $D_z$ actually decreased with increasing CTAB concentration. We have chosen a CTAB concentration (0.04 M) at which $D_z$ varies substantially with NaBr concentration, and have measured $D_p$ under the same conditons. The results are given in table 2.

The absolute agreement is not as good, but the same trend is certainly observed. The expected order (for a dilute polydispersion) of $D_p \geq D_z$ is observed for NaBr concentrations $> 0.08$ M, but the reverse is observed at [NaBr] $< 0.08$ M. Interestingly, $D_p = D_z$ within experimental error (± 10% on $D_p$) at [NaBr] = 0.08 M, the concentration at which $D_z$ is not a function of CTAB concentration. These results may also reflect the notion that $D_z$ is more a measure of the collective motion at these concentrations under the experimental QLS conditions employed,[23] while $D_p$ should more closely resemble a self diffusion coefficient . Table 3 presents some values of $D_p$ obtained at low CTAB and salt (KCl) concentration at 25°C. These concentrations of CTAB are only 2-7 times the critical micelle concentration (cmc) of CTAB ($\approx 0.7$ mM), and could also be influenced by the pyridinium probe (0.22 mM). However, these $D_p$ values agree very well with the value of $D_z \approx 8 \times 10^{-7}$ $cm^2/s$ for CTAB micelles near the cmc.[23,24]

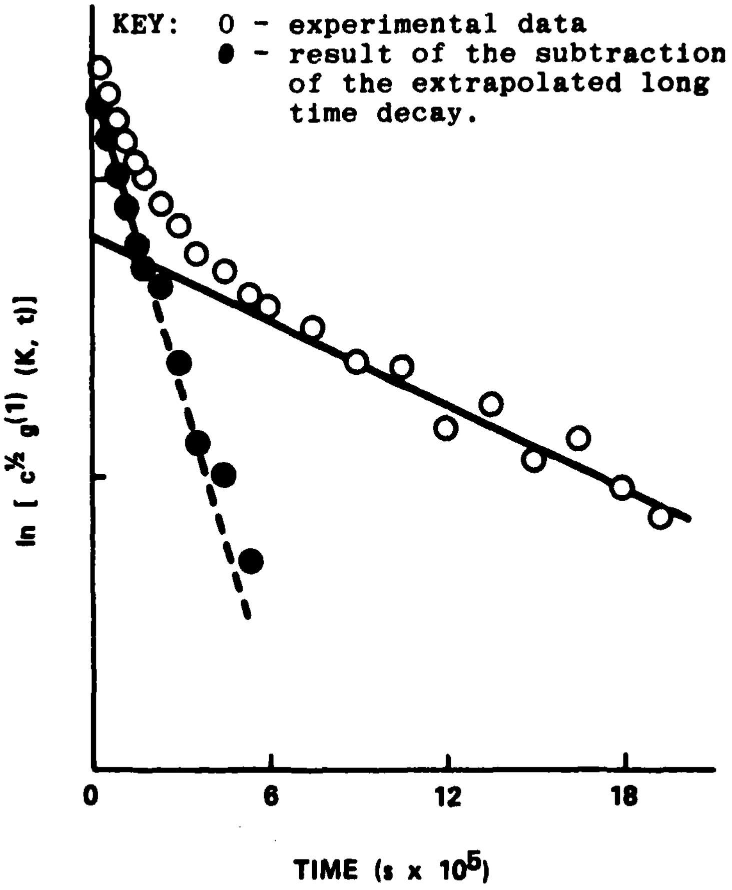

Figure 1. Auto Correlation Function for the 60% Water SCS Microemulsion *vide text*

Table 2. Values of the Polarography ($D_p$) and QLS ($D_z$) Diffusion Coefficients at 40°C in Aqueous CTAB (0.04 M) as a Function of NaBr Concentration.

| [NaBr]$^a$ | $D_p^{b,c}$ | $D_z^{b,d}$ | $r_p^e$ |
|---|---|---|---|
| 0.00 | 15.0 | - | 23 |
| 0.02 | 15.0 | 21.0 | 24 |
| 0.05 | 12.0 | 14.0 | 29 |
| 0.08 | 9.9 | 11.0 | 36 |
| 0.10 | 6.6 | 4.4 | 54 |
| 0.20 | 4.3 | 2.4 | 82 |

[a] moles $dm^{-3}$

[b] $cm^2/s \times 10^7$

[c] using 0.49 mM 1-dodecyl-4-cyano pyridinium iodide as the probe

[d] estimated from figure 2, reference 23

[e] calculated from equation (i) using the viscosity of water at 40°C (0.65 cp)

Table 3. Polarographic Diffusion Coefficients ($D_p$) for Aqueous CTAB Solutions at 25°C.

| [CTAB]$^a$ | [KCl]$^a$ | $D_p^b$ | $r_p^c$ |
|---|---|---|---|
| 1.51 | 0.12 | 7.7 | 32 |
|  | 0.29 | 7.7 | 32 |
|  | 0.60 | 8.2 | 30 |
| 3.52 | 0.29 | 9.7 | 26 |
| 4.53 | 0.37 | 9.3 | 27 |

[a] mM

[b] using 1-dodecyl-4-cyanopyridinium iodide (0.22 mM) $D_p$ in $cm^2/s \times 10^7$

[c] from equation (i), using the viscosity of water at 25°C (0.89 cp) $r_p$ in Å

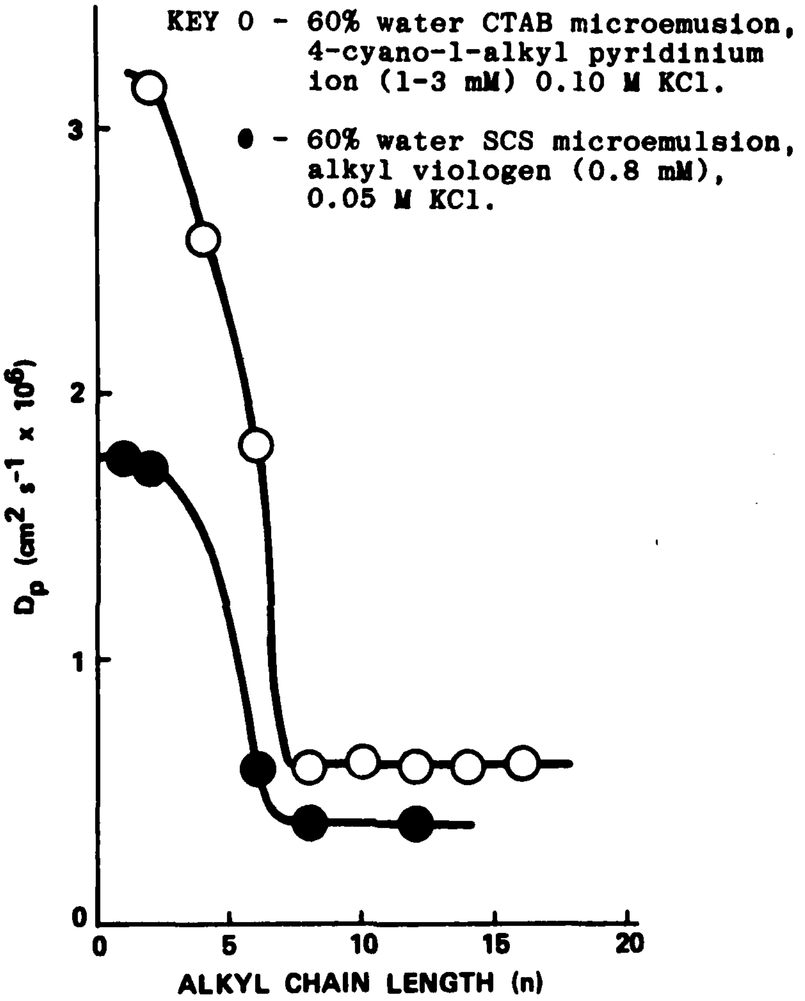

Figure 2. Polarographic Diffusion Coefficient ($D_p$) Versus Alkyl Chain Length at 25°C

We have also determined the value of $D_p$ for two-dodecane-in-water microemulsions stabilized by SDS and 1-pentanol. In these cases, droplet radii ($r_f$) were determined by fluorescence methods, one involving pyrene excimer formation[25] and the other the quenching of ruthenium (II) trisbypyridyl emission by 9-methylanthracene.[26] The former system is composed of 0.5 M SDS, 1.0 M 1-pentanol, and 9 vol % of dodecane (approximately 70% water by weight), and a radius of 40 Å was reported. Using the pyridinium probe, $D_p = 6.04 \times 10^{-7}$ cm$^2$/sat 25°C. Employing the viscosity of *pure water* in equation (1), $r_p = 41$ Å. This latter system is composed by weight of *ca.* 5.5% SDS, 5.1% dodecane, 10.3% 1-pentanol, and 79.1% water, with $r_f = 37$ Å. We obtain $D_p = 6.35 \times 10^{-7}$ cm$^2$/s, and again using the viscosity of water, $r_p = 37$ Å.

It is clear from these results that the polarographic determination of diffusion coefficients using an oil soluble probe yields usable values of $D_p$ which are comparable to those obtained by the other methods, particularly QLS. Naturally, the probe itself must be completely sorbed by the particle and not influence its size. In the case of micelles, caution must be exercised. However, in the case of microemulsions with their higher phase volumes, the probe apparently causes no significant perturbations at mM concentrations. It may also be noted that a knowledge of the refractive index of the continuous phase is needed in order to obtain $D_z$ from QLS, while no physical property of the microemulsion is needed to obtain $D_p$ at a dropping mercury electrode. Even if a rotating solid microelectrode is used (e.g., platinum or glassy carbon), only the **bulk** kinematic viscosity of the microemulsion is needed. This is easily measured, and involves no assumptions as to the actual composition of the continuous "phase." This can present some difficulty when performing QLS measurements on microemulsions with low water content.

## 3.3 Anionic and Cationic Microemulsions

A number of studies employing microemulsions stabilized by CTAB or SCS have been previously reported. Pseudo three component phase maps of a CTAB/1-butanol/hexadecane/water[1b] and a SCS/1-pentanol/mineral oil/water[18] microemulsion are available. The three "components" are the surfactant/alcohol mixture in a fixed ratio, termed the emulsifier (E), the oil (O) and water (W). We have carried out the QLS measurements at selected water dilutions along lines running from *ca.* 10% O, 90% E (CTAB) and 20% O, 80% E (SCS) by weight, to the W apex. These results are summarized in table 4. The QLS data consist of very rapid nonexponential decays for the CTAB microemulsion from 60-75 wt % water, and the SCS microemulsion at 60% water. Very different and considerably larger values of the diameter are obtained from polarography. One possibility is that the QLS data are representing a collective diffusion coefficient ($D_c$) or some combination of $D_c$ and the self diffusion coefficient ($D_s$). A second possibility is that these microemulsions are either cosolubilized (i.e., molecular dispersions) or contain only rapidly fluctuating small aggregates.[13] However, in the SCS microemulsion at 66% and 73% water, a double exponential decay was observed. After substraction of the baseline, the data were resolved graphically as shown in figure 1. If the nonexponential behavior is due to polydispersity, then the long term decay can be attributed to $D_s$.[21] This is consistent with the polarographic data with $D_p > D_z$ ($r_p < r_z$), discussed earlier. The same is true at 73% water. The short term decay then represents $D_c$ where $D_c >> D_s$ as expected. It may also be noted that the polarographic diameter of 117 Å at 60% water in the SCS microemulsion compares favorably with a value of *ca.* 100 A obtained from low angle X-ray scattering.[18]

Table 4. Summary of QLS and Polarographic Results on CTAB and SCS Microemulsions at 25°C *vide text*

| Microemulsion | wt % water | $d_z$ (A)$^a$ | $d_p$ (A)$^d$ |
|---|---|---|---|
| CTAB | 60 | $18^b$-26 | 68 |
| | 65 | $22^b$-34 | 73 |
| | 75 | $17^b$ | 125 |
| SCS | 60 | 51-$64^b$ | 117 |
| | 66 | $\left.\begin{matrix}21\\153\end{matrix}\right\}^{c}$ | $132^e$ |
| | 73 | $\left.\begin{matrix}17\\351\end{matrix}\right\}^{c}$ | $332^f$ |

a diameter, determined using the refractive index (1.33) and viscosity (0.89 cp) of pure water
b polydispersity index (variance) > 0.1
c obtained from a graphical analysis of the QLS data *vide text*
d from polarography, using equation (i) and the viscosity of water
e 65% water, 0.05 M KCl
f estimated from data at 75% $H_2O$, 0.05 M KCl and 80% water, 0.00 and 0.05 M KCl. Above 65% water, salt causes a decrease in $r_p$ in the SCS microemulsion.

Finally, some polarographic data are presented which bear on the possibility, raised above, that some of these microemulsion compositions represent colsolubilized systems. We have determined the value of $D_p$ for both 4-cyano-1-alkyl pyridinium ion and alkyl viologen as a function of the alkyl chain length (n). The long chain derivatives are insoluble in water, while the short chain derivatives are quite soluble.[27] In the former case, the probe should be completely solubilized in the "oily" aggregate, if such exists. In fact, both the $C_{12}$ pyridinium and viologen probes yield the same value of $D_p$ in the 60% water SCS microemulsion within experimental error. If no distinct hydrophilic and hydrophobic regions exist, then all chain lengths should give approximately the same value of $D_p$. This is clearly not the case, as shown in figure 2. For n = 1 or 2, the probe is apparently "free"; i.e., solubilized in the "aqueous" continuous phase. The value for 4-cyano-1-ethyl pyridinium ion in CTAB microemulsion is in reasonable agreement with that estimated from the value in water and the phase volume.[28]* It appears that this data is good evidence for the existence of distinct oil and water regions. The probes themselves do not micellize and their presence at the concentrations employed in the polarographic measurements has no effect on the QLS results. The values of $D_p$ are also unaffected by probe concentration.

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* The value of the diffusion coefficient of 1-ethyl-4-cyanopyridinium ion in water ($D_o$) is 9.1 x $10^{-6}$ cm$^2$/s. The observed value of the diffusion coefficient (D), if solubilized only in the aqueous phase, is given by $D = D_o(1-\phi')^{1.5}$, where $\phi'$ is the actual phase volume (including bound water) occupied by the "oil" drops. For the CTAB microemulsion at 60% water, $\phi' = 0.55 \pm 0.05$, and thus D - 2.7 ± 0.5 x 10-6 cm$^2$/s, is in good agreement with the polarographic value of 3.2 x $10^{-6}$ cm$^2$/s (see figure 2 in this report).

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