Investigation of Water-Containing Inverted Micelles by Fluorescence Polarization. Determination of Size and Internal Fluidity

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Water-containing inverted micelles of sodium di(2-ethylhexyl) sulfosuccinate (AOT) have been investigated by fluorescence polarization using fluorescent hydrophilic probes localized in the aqueous core of the micelles. Measurements of the stationary polarization in two apolar solvents of different viscosity but of the same chemical nature permit rapid determination of both micellar hydrodynamic volume and water pool fluidity as a function of water content up to $[H_2O]/[AOT] = 11$. The characteristics of AOT micelles appear to be unchanged in the *n*-alkane series from hexane to dodecane and slightly affected in various apolar solvents. Solvents of high polarizability such as benzene, toluene, and carbon tetrachloride penetrate into the amphiphile layer, presumably up to the water core boundary. No significant effect of sodium chloride was observed up to a concentration of 0.4 *M*. The inverse micelle size is independent of surfactant concentration below 0.3 *M*.

I. INTRODUCTION

Among the amphiphiles capable of forming inverted micelles, di(2-ethylhexyl) sodium sulfosuccinate (aerosol OT, AOT) has received particular attention in the last years. Besides its good wetting power, this surfactant has a marked ability to solubilize water in various nonpolar organic solvents, a model feature of great concern in a wide range of applications, whether industrial or biological (1–3). Solubilized water molecules are known to be encased by the amphiphile head groups thus forming the micelle aqueous core or water pool, whereas the hydrocarbon tails protrude into the organic solvent. At high $[AOT]/[H_2O]$ ratios, w, the inverse micelle picture is closely related to that of a water droplet bounded by a monomolecular amphiphile layer. At low w values, however, micellar aggregates do not behave as microemulsion particles (4). A variety of experimental studies were recently devoted to the interaction of water with the ionic moieties in the water pool, emphasizing the peculiar features of the clustered molecular states as compared to bulk solvent properties (5–8). Furthermore, the sensitive photon correlation technique was applied to measure the micelle size variations as a function of water content (4, 9, 10).

In the present investigation, the internal fluidity of the water pool and the micelle hydrodynamic volume are simultaneously

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determined by measuring the fluorescence depolarization of a solubilized hydrophilic probe. Singleterry and Weinberger (11) originally proposed the use of Perrin's relation to determine the hydrodynamic volume of calcium xenylstearate inverse micelles in benzene using rhodamine B as a fluorescent probe; they assumed that depolarization of the emitted fluorescence reflected only the rotational behavior of the micelle as a whole. Very recently the reversed micelles of AOT (12, 13) and dodecylammonium propionate (14) were investigated using time-dependent or stationary fluorescence polarization measurements, respectively, in order to evaluate the probe microenvironment fluidity. Over the past years such measurements were also performed to study aqueous micellar systems (15). In this work the measured fluorescence depolarization is analyzed in terms of both rotation of the micelle and motion of the probe within the water cluster. These combined contributions were previously either overlooked or incorrectly related. The method, outlined in our preliminary paper (16), is now extended to the study of salt, solvent, and concentration effects on the AOT inverse micelle size and water pool fluidity; the data obtained by using two different hydrophilic probes are analyzed and discussed in light of the possible structure of the micellar core.

II. EXPERIMENTAL

Materials

Fluorescent probes. Hydrolysis of 3,4,9,10-perylene tetracarboxylic dianhydride (Aldrich Co.) was performed in hot alkaline (NaOH) ethanol. The sodium salt obtained by precipitation with ethyl ether was dissolved in water, converted into the insoluble acid form by adding HCl down to pH 2, and filtered. 3,4,9,10-Perylene sodium tetracarboxylate (PTC) was finally precipitated with ethyl ether from a neutralized ethanolic solution of the acid form.

9,10-Anthracene diacetic acid was prepared by Rhône–Poulenc Company. Stock solutions of 9,10-anthracene sodium diacetate (ADA) were directly made in water by neutralization of the acid up to pH 8–9 with sodium hydroxide.

Surfactants. Sodium di(2-ethylhexyl) sodium sulfosuccinate (AOT) was obtained from Fluka A.G. and further purified by the procedure described in Ref. (17) using redistilled *n*-pentane (Merck, *pro analysi*) as the extracting solvent.

Solvents. *n*-Heptane (Phillips Petroleum Co., normal ASTM grade) and benzene (Carlo–Erba, fluorimetric grade) were distilled; this solvent and toluene (Merck, Uvasol grade) were dried over sodium. Carbon tetrachloride (Merck, Uvasol grade) and all other solvents (Fluka, Puriss grade) were used without further purification.

Methods

Instruments. Lifetime measurements and anisotropy decay experiments were performed on our single photon decay fluorimeter, which has been described previously (18, 19). The experimental decay curves were analyzed by the method of modulating functions, developed by one of the authors (18, 20), in order to perform the deconvolution and to determine the amplitudes and time constants of the exponential terms.

Stationary polarization experiments were done on a modified version (18) of the apparatus described in Ref. (21).

Preparation of samples. Weighted portions of the surfactant were heated overnight at 60°C under vacuum prior to the addition of solvent. Mild heating was helpful in some cases to ensure quicker solubilization of the surfactant. Solutions were made by injecting with a microsyringe initial known volumes of a concentrated aqueous solutions of the probe into 2 ml of 0.098 *M* (unless stated otherwise) AOT in organic solvent. Subsequent stepwise addition of tridistilled water directly into the fluorescence cuvette, together with the initial volumes, defines $w = [H_2O]/[AOT]$. Good

mixing was obtained by hand shaking of the cuvette, the use of an ultrasonic bath bringing no change in the polarization data. The optical density was kept under 0.2 at the excitation wavelength in order to avoid parasitic effects arising from energy transfer. Consequently less than 1 out of 100 micelles contains a probe molecule. Under these conditions, dividing the initial number of probe molecules by 2 or inverting probe and pure water injection order is immaterial. The temperature was kept at 25°C in all the experiments. No aging effects could be observed.

III. THEORETICAL CONSIDERATIONS

When the sample is excited by a short-duration pulse of vertically polarized light, it is possible to follow the decay of the emission anisotropy, as defined by

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}, \qquad [1]$$

where $I_{\parallel}$ and $I_{\perp}$ are the intensity components, respectively parallel and perpendicular to the electric vector of the incident wave. The quantity $I_{\parallel}(t) + 2I_{\perp}(t)$ represents the total intensity $I(t)$ of fluorescence. In most cases, the decay law is exponential: $I(t) = I_0 \exp(-t/\tau)$, where τ is the lifetime of the fluorophore.

The time dependence of $r(t)$ reflects the motions modifying the orientation of the transition moments between the time of adsorption ($t = 0$) and the instant t corresponding to the time of emission. In general, the emission anisotropy can be written in the form

$$r(t) = r_0 M_2(t) = r_0 \left\langle \frac{3\cos^2\theta(t) - 1}{2} \right\rangle, \qquad [2]$$

where $M_2(t)$ is the orientation autocorrelation function and $\theta(t)$ the angle through which the emission transition moment rotates between time zero and time t. r_0 is the limiting anisotropy which is observed in the absence of any rotation of the molecule.

The conventional fluorescence polarization technique, using constant illumination, gives a time-averaged value of $M_2(t)$, since the quantity actually measured is the mean anisotropy, defined by

$$\bar{r} = \frac{\int_0^{\infty} r(t)I(t)dt}{\int_0^{\infty} I(t)dt}. \qquad [3]$$

The pulse technique offers a major advantage over the conventional technique in the case of complex decay laws for $I(t)$ and $M_2(t)$, but it requires long experiments and sophisticated data processing in order to perform the deconvolution of the decay curves with respect to the flash profile and to determine the decay parameters. On the other hand, the stationary method can be applied only in simple cases, but measurements of the mean anisotropy can be done in a matter of minutes.

For molecules that can be approximated to a rigid sphere, $r(t)$ can be expressed as

$$r(t) = r_0 \exp(-6Dt),$$

where D is the rotational diffusion coefficient. This expression together with Eq. [3] and $I(t) = I_0 \exp(-t/\tau)$ leads to the well-known Perrin equation (22),

$$\frac{1}{\bar{r}} = \frac{1}{r_0}(1 + 6D\tau) = \frac{1}{r_0}\left(1 + \frac{3\tau}{\rho}\right), \qquad [4]$$

where the relaxation time ρ is related to the hydrodynamic volume V_h of the sphere (in milliliters per mole), the solvent viscosity η, the temperature T, by the Stokes–Einstein relation

$$\rho = \frac{1}{2D} = 3\frac{V_h\eta}{RT}. \qquad [5]$$

In the present problem of a spherical probe rotating within the water pool of an inverted micelle, two limiting cases can be considered for convenience:

(1) If the probe is rigidly bound to the micelle (which is actually observed at very low water contents), the emission anisotropy is given as

$$r(t) = r_0 \exp(-6D_m t), \quad [6]$$

where D_m is the rotational diffusion coefficient of the micelle which is assumed to be spherical.

(2) If the micelle is held in a hypothetical solvent of infinite viscosity, the probe experiences only internal motions; hence, for isotropic motions, we have

$$r(t) = r_0 \exp(-6D_i t), \quad [7]$$

where D_i is the internal rotational diffusion coefficient.

In fact, perylene tetracarboxylate, the probe we have chosen for the present work, undergoes isotropic motions in hydrogen-bonding solvents (23).

When both rotational processes take place, one may assume first that they are independent and therefore the overall orientation autocorrelation function is the product of the autocorrelation functions characterizing the two processes. This assumption leads to additivity of the rotational diffusion coefficients (12):

$$r(t) = r_0 \exp[-6(D_i + D_m)t]. \quad [8]$$

The mean anisotropy is then given by

$$\frac{1}{\bar{r}} = \frac{1}{r_0}[1 + 6(D_i + D_m)\tau]. \quad [9]$$

However, these expressions are not consistent with our data since they lead to erroneous variations in the micellar volume as a function of water content. Therefore we must consider a more realistic model which takes into consideration some coupling between the two rotational processes. The theoretical problem is complicated but G. Weber has shown (personal communication, to be published) by means of a simulation using the discontinuous approach (24) that the variations in $\bar{r}$ are satisfactorily represented by the expression

$$\frac{1}{\bar{r}} = \frac{1}{r_0}(1 + 6D_m\tau)(1 + 6D_i\tau). \quad [10]$$

Since $\bar{r}$ is given by

$$\bar{r} = \int_0^\infty r(t) \exp(-t/\tau)dt/\tau,$$

taking the inverse Carson–Laplace transform of Eq. [10] yields

$$r(t) = r_0 \frac{1}{D_i - D_m}[D_i \exp(-6D_i t) - D_m \exp(-6D_m t)]. \quad [11]$$

Equation [10], rewritten in the form

$$\frac{1}{\bar{r}} = \frac{1}{r_0}\left(1 + \frac{RT}{V_h \eta}\tau\right)\left(1 + \frac{3\tau}{\rho_i}\right), \quad [12]$$

provides a very simple way to determine the micellar hydrodynamic volume V_h and the internal rotational relaxation time of the probe ρ_i by measuring $\bar{r}$ in two apolar solvents of different viscosities. Evidently it is required that V_h be the same in the two solvents, which therefore must be of the same chemical nature. Thus, the expression for V_h can be written as

$$V_h = \frac{\bar{r}_1/\eta_1 - \bar{r}_2/\eta_2}{\bar{r}_2 - \bar{r}_1} RT\tau. \quad [13]$$

It should be noted that the value of r_0 is not required for the determination of V_h. Finally, ρ_i will be determined from Eq. [12].

IV. RESULTS AND DISCUSSION

1. Fluorescence Decay Experiments

The lifetime of perylene tetracarboxylate solubilized in the water pool of AOT inverted micelles in heptane was measured for various values of $w = (H_2O)/(AOT)$. The value (4.5 nsec) was found to be independent of w and identical to that in pure water.

Figure 1 shows an anisotropy decay experiment performed with a solution in heptane at $w = 2.1$. Analysis of the curves of $I_\parallel(t) + 2I_\perp(t)$ and $I_\parallel(t) - I_\perp(t)$ reveals

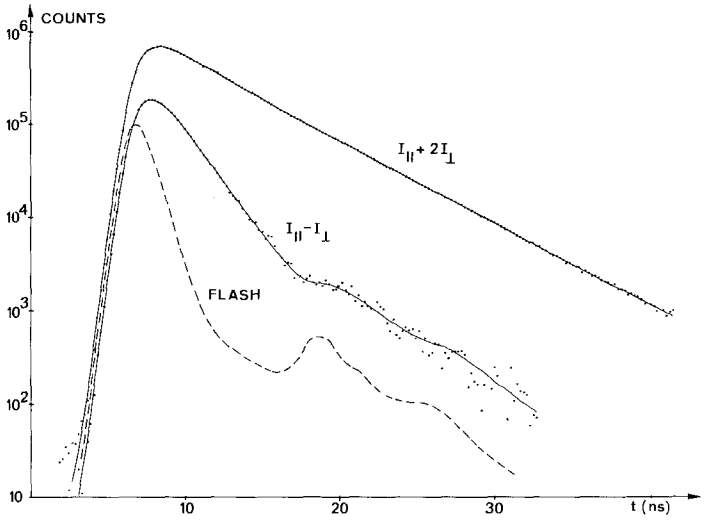

FIG. 1. Fluorescence anisotropy decay curves of PTC in AOT–heptane (w = 2.1): experimental points and reconvoluted curves (solid lines); time interval between two channels: 0.208 nsec.

very satisfactory curve fits with single exponential decays, the time constants being 4.5 (lifetime) and 1.8 nsec, respectively. In addition, this experiment yields $r_0 = 0.36$. According to Eq. [11], a single exponential decay should not be observed for $r(t)$ and for $I_{\parallel}(t) - I_{\perp}(t)$, but, at $w = 2.1$ the contribution of the internal rotation of the probe is very small and therefore the departure from a single exponential decay cannot be detected. From the observation of a single exponential decay, one can conclude that the micelles appear to be spherical.

At higher water contents, it becomes difficult to record $I_{\parallel}(t) - I_{\perp}(t)$ with sufficient accuracy to permit a detailed analysis of the shape of this curve. As a matter of fact, the width at half-maximum of the exciting light pulse is about 2 nsec and even at $w = 2.1$, the decay time constant of $I_{\parallel}(t) - I_{\perp}(t)$ is 1.8 nsec. Therefore at higher values of w, the relaxation will be much faster and departures from single exponential decays would be even more difficult to detect.

Considering, in addition, that recordings of the decay curves require a long time (several hours), the conventional method using constant illumination (i.e., the determination of the mean anisotropy) is more suitable to our problem since it permits rapid investigations under various conditions.

2. Determination of the Micellar Hydrodynamic Volume

We have chosen heptane and decane as solvents of the same chemical nature in which the micellar volume is expected to be unchanged. This assumption is supported by the fact that Peri (25) has observed the same micellar volumes, within the experimental errors, in isooctane, n-nonane, and n-dodecane solutions.

Figure 2 shows the variations of the mean anisotropy related to PTC as a function of $w = [H_2O]/[AOT]$ for heptane and decane solutions. At low water contents the contribution of the micellar rotational rate is predominant and an increase in $\bar{r}$ is observed. But, as w increases, the effect of the internal rotation of the probe becomes larger and $\bar{r}$ goes through a maximum before decreasing. At high water contents, the values of $\bar{r}$ finally approach those observed in pure water.

According to the theoretical treatment

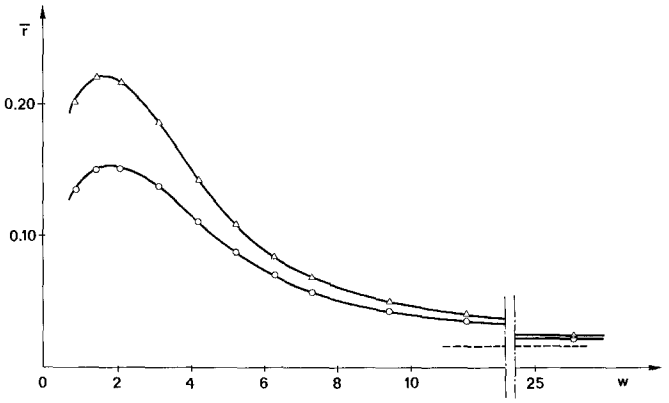

FIG. 2. Mean anisotropy of PTC measured in AOT–heptane (○) and AOT–decane (△) as a function of w. The dashed line indicates the mean anisotropy of the probe in pure water.

described above, Eq. [13] permits determination of the micellar hydrodynamic volume V_h whose variations are presented in Fig. 3. The accuracy of the data makes it possible to evaluate V_h up to $w \simeq 11$. It should be noted that the variations in V_h are almost linear.

As regards previous investigations, it is worthwhile comparing the values of the hydrodynamic radius R_h with those obtained by Zulauf and Eicke (4) in isooctane by photon correlation spectroscopy. The comparison is shown in Fig. 4 and reveals a reasonable agreement. In particular, extrapolation at $w = 0$ yields the same value, $R_h = 15 \pm 0.5$. This comparison is very important because it shows that the probe does not modify the size of the micelles significantly. In addition, our results seem to be compatible with those of Sein *et al.* (10) which concern the water pool radius.

On the other hand, Day and colleagues (9), also using photon correlation spectroscopy, have reported values of R_h in toluene which are significantly lower than ours. However, it is possible that solvent like toluene or benzene have specific effects (see Section IV.5.c).

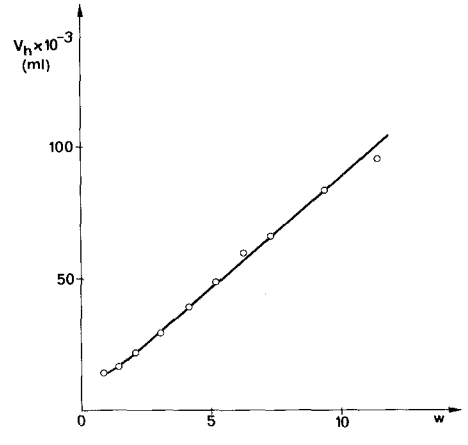

FIG. 3. Variation in micellar hydrodynamic volume as a function of w.

3. Evaluation of Water Cluster Fluidity

a. Investigation with 3,4,9,10-Perylene Sodium Tetracarboxylate (PTC)

Once V_h has been determined for a given value of w, the internal rotational relaxation time ρ_i of the probe can be calculated from Eq. [12]. Variations of ρ_i as a function of w are shown in Fig. 5. The width of ^{23}Na NMR absorption lines and the water proton NMR correlation times were found to follow a similar dependence (7). The sharp decrease in ρ_i at low water ratios is related to the increasing mobility of the probe embedded in a gradually more fluid framework of solvated sodium ions and

sulfonate end groups. The insert of Fig. 5, which represents the internal rotational rate of the probe, clearly indicates absence of rotation below $w \simeq 2$, whereas a linear variation of this rate is observed above $w = 5$. For enlarged water pools, ρ_i slowly decreases toward its value in pure water.

Bearing four carboxylate groups, PTC is repelled from the negatively charged sulfonate heads of the amphiphiles, thereby experiencing presumably genuine variations of the water pool fluidity. A straightforward evaluation of this parameter makes use of the Stokes–Einstein equation

$$\eta_i = \frac{kT}{4\pi a^3}\rho_i \qquad [14]$$

in which the probe of hydrodynamic radius a rotates in a bulk medium of viscosity η_i. The finite size of the water pool can be taken into account through the Couette viscosity formula for concentric rotating spheres as follows,

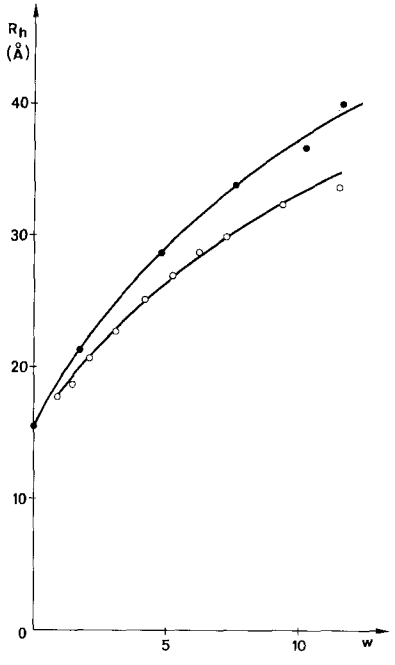

FIG. 4. Variation in micellar hydrodynamic radius as a function of w: (○) present work, (●) data of Zulauf and Eicke (Ref. 4).

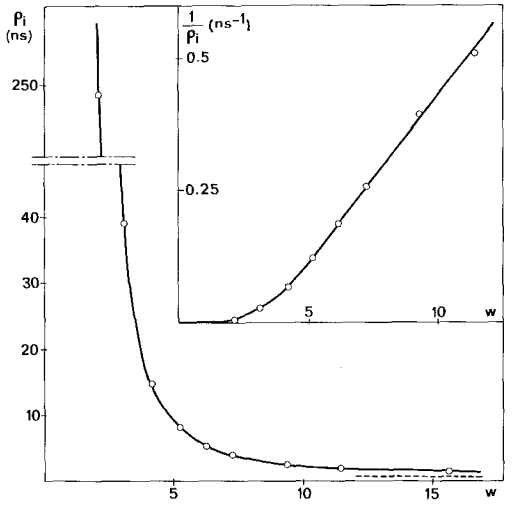

FIG. 5. Variation in internal rotational relaxation time of PTC. The dashed line indicates the value measured in pure water.

$$(\eta_i)_c = \frac{kT}{4\pi}\rho_i\left(\frac{1}{a^3} - \frac{1}{b^3}\right), \qquad [15]$$

where $(\eta_i)_c$ is the viscosity of the liquid located between the two spheres, the inner one, of radius a, rotating inside the other, fixed and of radius b. Introducing into Eq. [4] the measured mean anisotropy of PTC in water yields $a = 6$ Å. The radius b of the sphere is estimated by subtracting from the micellar hydrodynamic radius R_h the diameter of a water molecule[2] added to the length of the amphiphile.[3] This hypothesis tentatively emphasizes the Stern layer extension with regard to the classical picture of the double layer in direct micelles (28). However, the Couette correction underestimates actual boundary effects, whatever choice is made of the shear surface, because the location of the probe is not closely restricted to the water pool center. Variations in η_i and $(\eta_i)_c$ (estimated from Eqs. [14] and [15], respectively) as a function of w are collected in Table I together with V_h and R_h. It is worth noting that in

[2] 2.76 Å (26).

[3] Taken as 11 Å (27).

TABLE I

Micellar Parameters Obtained with PTC

w	V_h (ml)	R_h[a] (Å)	R_w[b] (Å)	ρ_1 (nsec)	η_i (cP)	$(\eta_i)_c$ (cP)
1.04	15,700	18.4		∞		
2.09	22,100	20.6	6.8	246	373	121
3.13	29,400	22.7	8.9	39.2	59.4	41.4
4.18	39,600	25.1	11.3	14.8	22.4	19
5.22	49,200	26.9	13.1	8.2_8	12.5	11.3
6.26	59,900	28.7	14.9	5.3_5	8.1	7.6
7.31	66,700	29.8	16.0	3.9_1	5.9	5.6
9.40	84,100	32.2	18.4	2.5_4	3.9	3.7
11.48	95,700	33.6	19.8	1.9_7	3.0	2.9

[a] $R_h = (3V_h/4\pi N)^{1/3}$; N: Avogadro's number.
[b] $R_w = b$ in Eq. [15]: see text for evaluation.

the aqueous core, the concentration of ionic moieties at $w = 11$ still corresponds to a high value of 5 M. However, as it will appear further on in the discussion of the salt effect (Section IV.4), electrostatic interactions in the water cluster cannot be compared to those prevailing in a 1–1 electrolyte solution of the same concentration. In this respect the high values obtained for the water pool microviscosities do not seem unrealistic if taken as average values of a presumably inhomogeneous medium. In a recent paper by Zinsli (13) describing the AOT water core, microviscosities much higher than ours were obtained from anisotropy decay measurements using 1-aminonaphthalene-4-sulfonic acid (1-N) as a probe. Besides the additivity hypothesis of both probe and micelle rotational diffusion coefficients, another source for this discrepancy arises from the less ionized character of 1-N as compared to PTC. In light of our results (subsequent Section b), 1-N could preferentially be located close to the water pool boundary.

b. Investigation with 9,10-Anthracene Sodium Diacetate (ADA)

An instructive comparison arises from probing with the smaller ADA molecule. In contrast with PTC behavior the fluorescence lifetimes of ADA measured in AOT–heptane solutions increase with the water content of the micelle from 8.5 (w = 0.5) to 10.5 nsec ($w = 7$) while a still higher value of 12.5 nsec is obtained in pure water. Decay curve fitting with a single exponential is satisfactory in all cases. A check made at $w = 7$ shows AOT–decane and AOT–heptane lifetime decay curves to be perfectly superimposable. The measurement of the limiting anisotropy yields $r_0 = 0.272$. Table II gives the micellar volumes V_h and hydrodynamic radii R_h obtained with ADA through Eq. [13]. Accuracy is not satisfactory beyond $w = 7$ because of the smaller r_0 value. Good agreement with the corresponding PTC data of Table I supports the validity of the determination procedure.

Internal relaxation times of ADA and PTC are compared in Fig. 6. The radius of the ADA molecule was found to be 3.2 Å. Despite its smaller size and a possibly more flexible carboxylate–anthracene nucleus linkage, ADA experiences decreasing rigidity in a more graduated way than does PTC. Remarkably, for $w > 3$, ADA relaxation times are seen to exceed those of the PTC probe, whose size is six times larger. When the probe size is taken into account, η_i values of ADA, collected in Table II, enhance the difference with PTC behavior (Table I). ADA thus appears to be located in closer vicinity to the water pool bound-

TABLE II

Micellar Parameters Obtained with ADA

w	V_h (ml)	R_h (Å)	ρ_1 (nsec)	η_i (cP)
0.52	15,700	18.4	95.2	951
1.04	17,900	19.2	71.2	711
1.57	20,600	20.1	57.3	572
2.09	23,700	21.1	47.1	471
2.61	28,100	22.4	37.4	374
3.13	31,400	23.2	32.2	322
4.18	41,500	25.4	21.9	219
5.22	51,700	27.4	16.3	163
6.26	59,200	28.6	13.5	135
7.31	69,800	30.3	11.0	110

aries than PTC. The observed variations in lifetimes which arise from the known sensitivity of the anthracene moiety to local structure and polarity also support this view.

As will be seen under Solvent Effects (Section IV.5.c), polarizable molecules appear to interact with the amphiphile polar groups. Recently, upshifts in pH-activity profiles of enzyme-catalyzed hydrolytic reactions were observed inside the AOT aqueous core (3). In a more specific study of this effect Menger and Yamada (29) gave several indications of lower apparent pH in the water pool as compared to bulk water. This effect which somehow increases at low water content could be related to local H_3^+O excess in the vicinity of the sulfonate amphiphile heads. A possible contribution to a partition mechanism of ADA between the water pool and its interfacial boundary could thus arise from a pK_a upshift of the acetate functional moieties. The alternate behavior of PTC may be due to its higher charge and to the direct perylene nucleus–carboxylate bonding which presumably depresses the total basic character of the four bound groups.

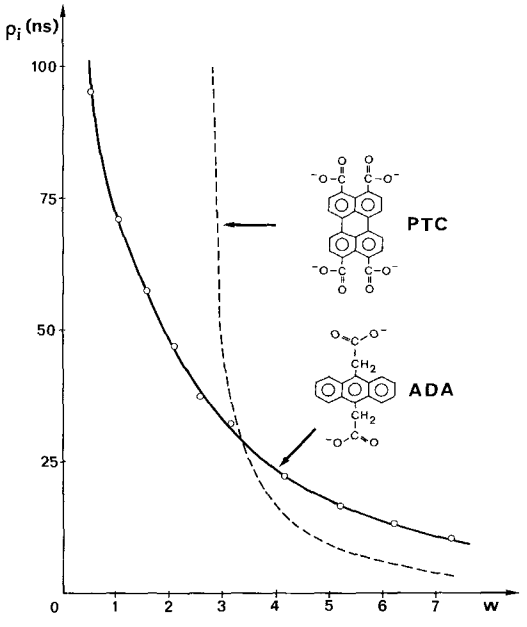

FIG. 6. Comparison between internal relaxation times of ADA and PTC (dashed line).

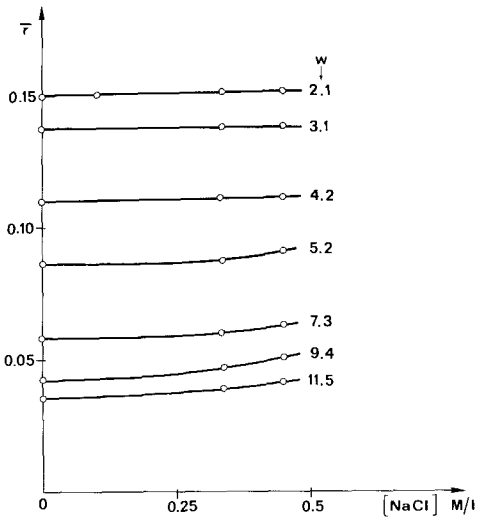

FIG. 7. Effect of concentration in NaCl on the mean anisotropy of PTC in AOT–heptane.

4. Salt Effect

Samples were prepared by adding determined volumes of NaCl (Merck Suprapur) aqueous solutions to AOT–heptane or AOT–decane solutions containing a known quantity of the PTC standard solution in water. Slight initial turbidities disappeared with time by further hand agitation of the fluorescence cuvette. This settling time, which increases at high NaCl concentration and w values, is an evidence of a salt-induced lowering of the system water solubilizing ability.

Variations in $\bar{r}$ as a function of w and NaCl concentration are given in Fig. 7 for solutions in heptane. The values of $\bar{r}$ are seen to increase weakly with salt concentration beyond $w \simeq 4$. Settling times of AOT–decane–NaCl solutions are comparatively longer and the $\bar{r}$ variations are irregular, albeit within 2% of those observed with the AOT–decane–H_2O solutions. Metastable states arising from the proximity of the phase separation line might account for this

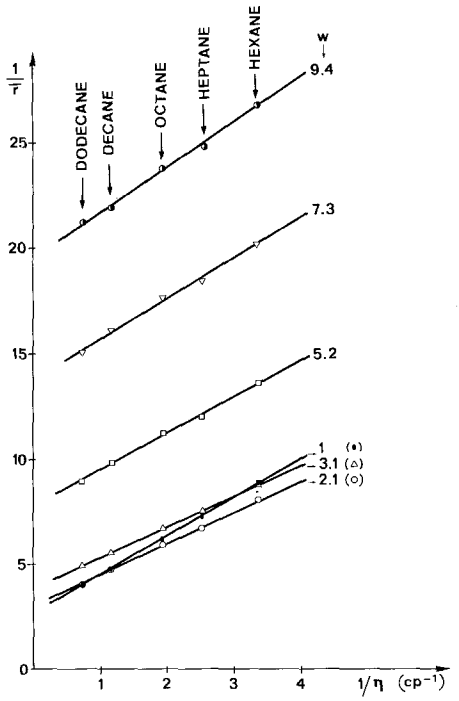

FIG. 8. Variation in reciprocal of the mean anisotropy of PTC vs $1/\eta$ in AOT–*n*-alkanes.

behavior. Thus it cannot be decided by use of Eq. [12] whether micellar volumes increase or decrease. Micelle size may therefore be taken as unchanged by the salt up to $w = 4.2$ and as slightly affected in the range $4.2 < w < 11$. The small magnitude of this perturbation is not surprising if the high local native concentration of Na^+ (emphasized in Section IV.3.a) is taken into account.

One can tentatively describe the water pool beyond $w \simeq 5$ (where variations in $1/\rho_i$ vs w become linear, inset of Fig. 5) in terms of double-layer theory and the osmotic pressure concept. With aqueous micelles, inorganic salts lower the electrical double-layer thickness and sometimes the micelle surface potential whereas osmotic pressure is also reduced in qualitative agreement with the observed increase in micelle size. Similar variations occurring inside very large water pools presumably reduce particle size in accordance with a decrease in the double-layer repulsion (33). The weak salt effect observed here brings into light the still poorly diffuse character of the electrical double layer at moderate water contents. High local concentrations and small polarizability of the hydrated sodium counterions, together with interface curvature, may be thought of as generating factors in this respect. Following this view, the rising trend in $\bar{r}$ values on Fig. 7 could conceivably reflect a mere increase of water pool microviscosity.

5. Solvent Effects

a. n-Alkanes

AOT solutions (0.098 *M*) in a series of *n*-alkanes were examined at various water contents. Inverse micelles were detected in all cases; the ability in solubilizing water decreased as the molecular weight of the solvent increased. Figure 8 shows variations in $1/\bar{r}$ vs $1/\eta$ from hexane to dodecane at various constant w ratios. Numerical values for the viscosities of solvents[4] are taken from Ref. (30). The choice of coordinates in Fig. 7 makes the check of Eq. [12] easier. The good linear fit supports the validity of this equation while extending the working range of Eq. [13]: the micellar hydrodynamic volume is therefore constant throughout this *n*-alkane series.

b. Miscellaneous Nonpolar Solvents

1. Solvents of low polarizability. Plots of $1/\bar{r}$ as a function of $1/\eta$ are presented in Fig. 9 for AOT in various nonpolar solvents, the solid lines recalling the linear variations observed for the previous *n*-alkanes. Solvent effects are seen to be small. Values of $1/\bar{r}$ for tetradecane solutions fall in the *n*-alkane line at $w = 3$ and lower ratios (unreported for sake of clarity), but phase separation occurs near $w = 5$. Pen-

[4] The viscosity of *trans*-4-decene was measured with viscomatic Fica equipment and found to be 0.846 cP at 25°C

tane solutions markedly deviate from the parent *n*-alkane solutions.[5] Figure 10 shows this deviation in terms of variations in $\bar{r}$ vs w, the actual pentane solution profile being compared to a hypothetical "well-behaved" pentane solution, for which the $\bar{r}$ values are extrapolated from the mean trend of the *n*-alkane series.

For very low water contents, at which internal rotation of PTC is totally restricted, the smaller $\bar{r}$ values of actual pentane solutions clearly indicate a lower hydrodynamic volume of the micelles as compared to the average micelle size in the other *n*-alkane solvents. At higher w values, however, the overall observed rotational rate is governed by the internal PTC rate

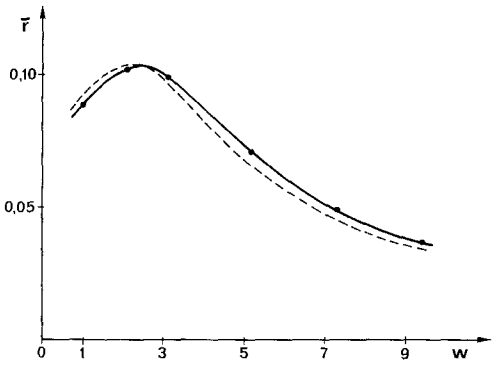

FIG. 10. Mean anisotropy of PTC measured in AOT–pentane vs w. The dashed line represents the extrapolated curve from the *n*-alkane series at the same viscosity as pentane.

which outweighs the effect of micelle rotation. Relative reduction in micelle size (i.e., water pool size) causes the PTC internal rotational rate to decrease and thus leads to a relative increase in $\bar{r}$ values, as observed beyond $w \simeq 3$.

Evaluation of such solvent-induced variations of micellar volume can be quantitatively estimated if it is assumed that the relationship prevailing in AOT–*n*-alkane solutions between PTC internal rotational rate $1/\rho_i$ and micellar volumes V_h is also obeyed in the considered AOT–solvent solution. Then, by using Eq. [12] in conjunction with the mean *n*-alkane values of V_h and $1/\rho_i$, an iterative procedure readily yields the unknown micellar volumes related to the observed $1/\bar{r}$ values.

The validity of the basic assumption, which was also involved in the preceding pentane argumentation, is ideal with respect to generating factors driving micelle size variations. The central water pool location of PTC and the small departure of the $1/\bar{r}$ interpreted values from the *n*-alkane lines incline us, however, to accept these calculated volumes as good approximations. The results are given in Table III for $w = 5.2$, with an accuracy of ±2%. Further inspection of Fig. 9 shows isooctane to be in line with *n*-alkanes whereas

[5] This effect is not due to differences in lifetime of PTC as checked by decay experiments.

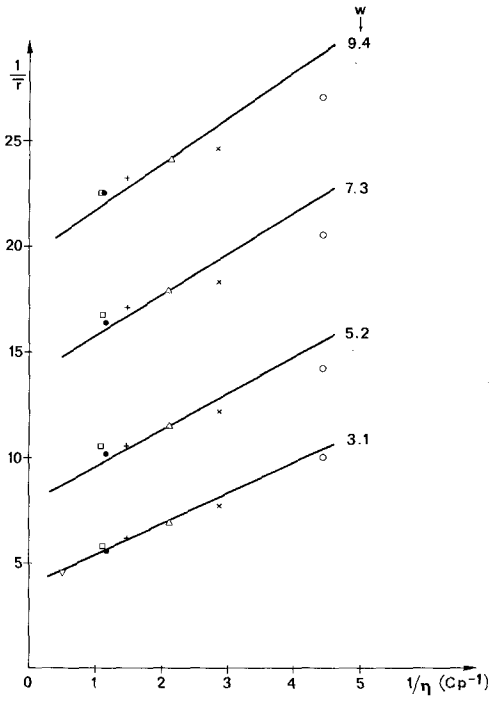

FIG. 9. Effect of the nature of the solvent. The solid lines represent the variations observed with PTC in *n*-alkanes (see Fig. 7). Pentane (○), tetradecane (▽), isooctane (△), cyclohexane (□), 1-chlorohexane (+), 2,2-dimethylbutane (×), *trans*-4-decene (●).

TABLE III

Size of AOT[a] Inverse Micelles in Miscellaneous Nonpolarizable Solvents[b]

Solvent	Percentage deviation
n-Alkanes	—
Pentane	−11
2,2-Dimethylbutane	−4
Isooctane	0
Cyclohexane	+9
trans-4-Decene	+4
1-Chlorohexane	+3

[a] [AOT] = 0.098 M, w = 5.2.
[b] Deviation from *n*-alkanes (V_h = 50,000 ml).

2,2-dimethylbutane[6] and pentane induce smaller micellar volumes. This trend could suggest a length correlation between the protruding part of the AOT molecule and the solvent; it might also be fortuitous.

2. Polarizable solvents. The three solvents studied were benzene, toluene, and carbon tetrachloride. Lifetime experiments performed on PTC in AOT–benzene and AOT–toluene solutions exhibit faster decay profiles than in the previous cases (4.5 nsec); in addition, the curves cannot be fitted with a single exponential. Thus only an averaged lifetime can be given (3.7 nsec for both cases). The lifetime decay profile of PTC in AOT–CCl_4 solutions measured at $w = 4$ was close to a single exponential, the time constant of which (3.9 nsec) being also smaller. These shorter lifetimes cannot be assessed unambiguously. A solvent-induced quenching process (as observed with perylene in bulk CCl_4) might affect emission of PTC molecules which would be dissolved in the organic phase. However, even in the extreme situation of water-saturated benzene, solubilization of PTC was checked to be very low and probably depressed in the presence of water-solubilizing micelles (31). Alternatively, quenching of PTC by solubilized solvent molecules inside the water pool is unlikely on the basis of a presumed salting-out effect. As a third possibility quenching might arise from encounters between PTC and solvent molecules localized at the water pool boundary. This picture can be related with the preferential solubilizing site of aromatic compounds as discussed in a recent review (32).

Measurements of $\bar{r}$ vs w were performed for AOT solutions in the three solvents under consideration. Using values of averaged lifetimes, and ignoring a possible deviation of the relation between $1/\rho_1$ and V_h, one obtains an increase in the micellar volume; these size variations, calculated at $w = 5.2$, reach 10% with benzene and toluene and 20% with carbon tetrachloride.

6. Effect of Concentration

AOT–heptane solutions were studied as a function of surfactant concentration c and water content w. A standard PTC aqueous solution was used for $c \leq 0.098\ M$ but in more concentrated AOT solutions the [PTC]/[AOT] ratios were lowered in order to keep the optical density below 0.2.

Figure 11 shows the plot of $\bar{r}$ vs log c at three values of w. Absence of variation in $\bar{r}$ up to $c = 0.3\ M$ is noteworthy at $w = 5.2$ and $w = 11.5$ whereas a significant increase in $\bar{r}$ appears at the same concentration at $w = 2.1$ (the accuracy being better at smaller w ratios). The AOT micellar volume is thus constant in a wide range of surfactant concentrations as previously demonstrated (4).

Beyond $c = 0.3\ M$, the trend in Fig. 11 at $w = 2$ is amplified, and values of $\bar{r}$ rise noticeably at low w, whereas at higher water contents they fall under the values of $\bar{r}$ obtained in heptane solutions. According to the argument given in Section IV.5.b for pentane profiles, such a variation implies an increase in micellar volume. However, as interactions between micelles are also

[6] A much larger size was reported (35) and recently denied (36) for AOT micelles in 2,2-dimethylbutane.

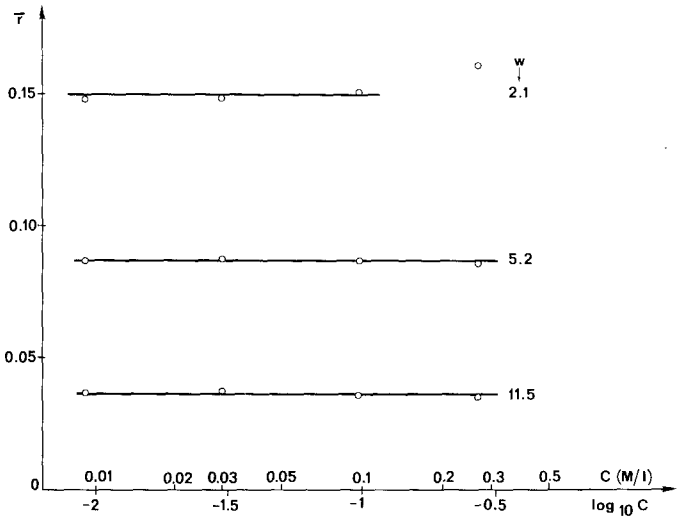

FIG. 11. Variation in mean anisotropy of PTC in AOT–heptane as a function of AOT concentration.

enhanced at smaller particle separation, this increase in size might be partly fallacious. Further investigation is required.

This effect of concentration above $c \simeq 0.3\ M$ is in agreement with the upper boundary limit recently ascribed to the AOT micelle by the hard-sphere approximation (10).

V. CONCLUSIONS

The fluorescence polarization technique provides a convenient and sensitive tool for determining the hydrodynamic volume and internal fluidity of an inverse micelle. However, the choice of the probe requires a careful examination: molecular structure, lifetime, and hydrophilic character of the compound are primarily concerned. Interactions with the species of the water pool boundary will control the location of the probe whereas this microenvironment in turn may drastically modify its photophysical features. Any sensitivity of the fluorescent molecule to order or polarity, which can be highly informative on other grounds, merely complicates such use of the polarization data. In amphiphile structures more ordered than AOT inverse micelles, the incidence of the local perturbation introduced by the probe cannot be overlooked. Such considerations must be kept in mind more specially in microviscosity determinations (34) as emphasized here by the comparison of PTC and ADA.

The method proposed in the present work is suitable to investigation of various problems. Thus, variations in size of inverse micelles induced by penetration of the amphiphile layer by aliphatic alcohols can be easily studied; such experiments are in progress in our laboratory.

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