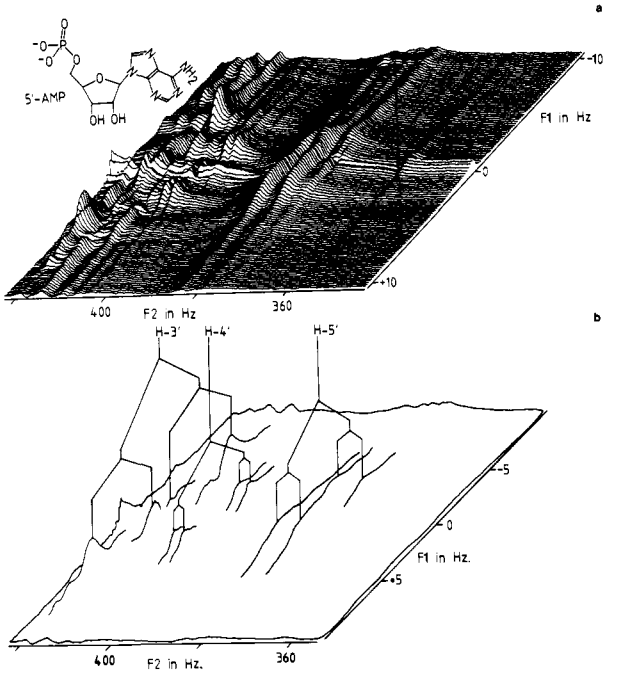

Figure 2. (a) The 2-D, homonuclear, *J*-resolved, ^{1}H NMR spectrum of the H-3′, H-4′, and H-5′,5″ protons in 5′-AMP at ambient temperature. (b) An outline sketch of the main peaks visible in Figure 2a, showing their origins.

Table I

coupling	value in Hz	coupling	value in Hz
$J(1',2')$	5.3	$J(4',P)$	1.9
$J(2',3')$	4.8	$J(5',5'')$	-12.0^a
$J(3',4')$	4.2	$J(5',P)$	5.3
$J(4',5')$	3.3	$J(5'',P)$	5.3
$J(4',5'')$	3.3		

[a] Reference 5.

splitting *between* pairs is due to homonuclear coupling to the 3′ proton. Each observed 4′ transition is, in fact, the strong, central part of a multiplet due to coupling to the two 5′ protons. Other parts of these multiplets were too weak to be observed. A similar coupling pattern is exhibited by the 5′ protons, except, in this case, the heteronuclear coupling is larger. The signals are also broader due to short T_2's. This makes the determination of the magnitude of the homonuclear coupling to 4′ inaccurate and obscures effects due to the possible nonequivalence of the 5′ protons.

Additional peaks appear in the spectrum along lines of constant F_2 corresponding to transitions in the conventional ^{1}H NMR spectrum. These extra signals are caused by the mixing of the transition at that particular F_2 with other connected transitions. This mixing can be due either to imperfections in the pulse or to strong coupling effects.[3,6] Any peak in the two-dimensional spectrum is associated with two connected transitions in the conventional NMR spectrum. The F_1 frequency of the peak is exactly one half the separation between these transitions in F_2.[3] Using this guide we have been able to assign nearly all the peaks in Figure 2.

Our analysis of the two-dimensional spectrum has enabled us to obtain both the homonuclear coupling constants and the couplings to ^{31}P. The coupling constants are given in Table I. These were then used in a seven-spin, spectral simulation, shown in Figure 1b. The correspondence with the observed spectrum is shown in Figure 1.

In nucleic acids the conformation of the phosphate backbone is extremely important in determining the overall conformation of the molecule.[5,7] Two-dimensional ^{1}H NMR not only allows us to probe these backbone conformations (via the ^{31}P-^{1}H coupling constants) but simultaneously allows the determination of all the homonuclear coupling information.[8]

Acknowledgment. We thank the National Science and Engineering Research Council of Canada for financial support.

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(4) 5′-AMP was lyophilized from D_2O and then dissolved in 100% D_2O which contained 0.01 M sodium phosphate buffer (pD 7.0) and 1.0 M sodium chloride. The solution concentration of 5′-AMP was 0.1 M. Spin-echo FID's were accumulated at 90 MHz on a Brucker WH 90 spectrometer equipped with a BNC-12 data system and a NIC-293 I/0 controller; 129 τ values were used at increments of 0.012 s. The data were transferred to and processed on a Nicolet 1180 computer system.
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An Investigation of the Fluidity of Alkyl Benzenesulfonate Aqueous Micelles by Fluorescence Spectroscopy

Sir:

The influence of supramolecular assemblies on chemical changes has lately become of increasing interest owing to the realization that many important biological processes occur at, or close to, such assemblies (membranes, peptides, nucleic acids) where effects such as charge density and amphipathic environment may be important.[1] Surfactant micelles have been extensively used to model the biological structures. This is justified by the fact that the same forces are responsible for holding biological and micellar aggregates together. Also the lipophilic boundary and hydrophilic regions of micelles find their counterparts in cellular structures. The popularity of the surfactant micelle as an experimental model arises from the ready availability of pure materials and the innate feeling that micelles offer a more tractable problem for quantitative investigation.

The use of fluorescent probes for studying the phenomena of micellization and solubilization has become widespread.[2] Thus, large aromatic hydrocarbons such as methylanthracene, pyrene, etc., have been employed as extrinsic probes to obtain information on rotational diffusion (through fluorescence depolarization)[3,4] and translational diffusion (through the dynamics of excimer formation).[5,6] However, the question must be raised as to whether a micelle which incorporates a relatively large guest residue is the same entity as the micelle without the probe.[7] Here we report some preliminary studies using a variety of alkyl benzenesulfonate isomers which are surfactants having an intrinsic fluorescent probe. These studies

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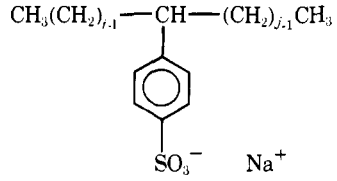
Chart I



$i + j = 11$; the $3C_{12}$ isomer has $i = 2$; $4C_{12}$ has $i = 3$ and so on

Table I

surfactant	P, %, ±0.20%	$(\bar{n}/\tau) \times 10^{-8}$ P s^{-1}	I_{350}/I_{290}
$3C_{12}$	10.50	14.85	0.319
$4C_{12}$	4.15	4.56	1.302
$5C_{12}$	3.50	3.76	1.382
$6C_{12}$	5.10	5.80	0.965

indicate that local viscous forces influence both rotational and translational motions of probes in a similar manner.

A modular spectrofluorimeter was employed throughout. This device, constructed at the Center for Fast Kinetics Research (CFKR), uses an Oriel 150-W xenon arc, Oriel excitation and emission monochromators, and two Hamamatsu multialkali photomultiplier tubes (R928) for detecting fluorescence from the sample and from a Rhodamine B quantum counter to correct for low-frequency fluctuations in the source output. For fluorescence depolarization measurements the emission monochromator was removed and the two photomultiplier tubes placed at opposite sides of the cuvette and at right angles to the excitation beam, which was linearly polarized with a Glan-Fouceault prism. Orthogonally oriented polarizing filters were positioned in the two fluorescence beams, one parallel and one perpendicular to the direction of polarization of the exciting light. Thus the intensities of emission, parallel ($I_\parallel$) and perpendicular ($I_\perp$), to the incident beam were recorded simultaneously by the two photomultiplier tubes which were read continuously by two digital voltmeters. These were interfaced to a Commodore PET microcomputer which was programmed to take 10 readings of each channel per second and compute the mean value and the degree of polarization (P) or the molecular anisotropy (r) according to

$$P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \qquad r = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp} \tag{1}$$

Prior to an experiment the detector gains were adjusted to be in balance with both polarizers set in the same direction. In this way depolarization measurements could be made with high precision without having to constantly reset polarizer angles during a run. The convenience of on-line data reduction allowed large numbers of readings to be made in a relatively short time. Temperature control was effected using quartz-jacketed cuvettes.

Isomeric dodecylbenzenesulfonates were used as surfactants in these experiments.[8] These materials were synthesized with the benzenesulfonate moiety at different positions along the alkyl chain according to Chart I.

In one set of experiments, solutions of the surfactants (2×10^{-3} mol L^{-1}) in water were prepared[9] and the degree of polarization (P) of the freshly prepared micellar systems was measured at 25.0 ± 0.2 °C. These data are collected in Table I along with the viscosity related parameter ($\bar{n}/\tau$) calculated from the equation[11]

$$r_0 = \frac{{}^1/_P - {}^1/_3}{{}^1/_{P_0} - {}^1/_3} = 1 + \frac{kT\tau}{\bar{n}V} \tag{2}$$

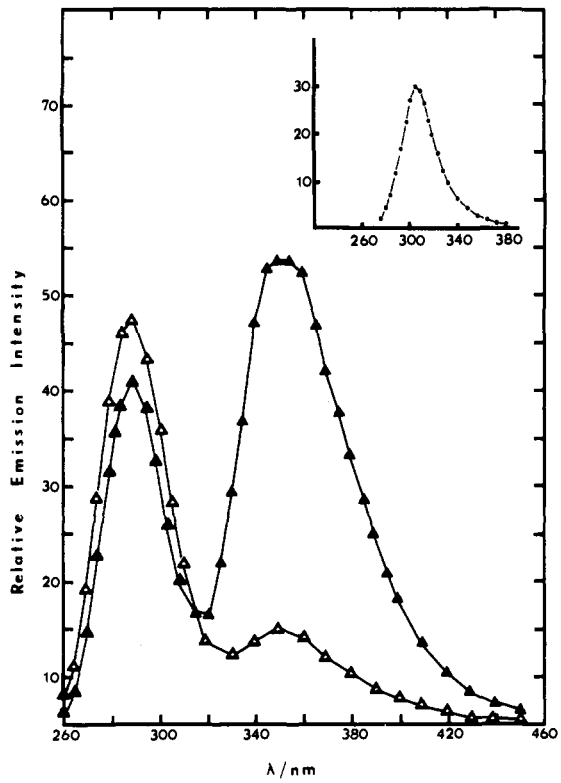


Figure 1. Emission spectra of sodium alkyl benzenesulfonates at 25.0 ± 0.2 °C: △, $3C_{12}$ (2×10^{-3} mol L^{-1}) in water; ▲, $4C_{12}$ (2×10^{-3} mol L^{-1}) in water; inset, $3C_{12}$ (2×10^{-3} mol L^{-1}) in dodecane.

where P_0 and r_0 are the limiting values of P and r when the emitting molecules maintain their orientation during excitation and emission, τ is the natural lifetime of the excited state, k is the Boltzmann constant, T is the absolute temperature, $\bar{n}$ is the local viscosity in the environment of the probe, and V is the effective volume of the fluorescent probe. r_0/r is defined as the degree of depolarization. The limiting polarization (P_0 expressed as percent), a function of exciting wavelength,[12,13] has been measured for the $3C_{12}$ system at 2×10^{-3} mol L^{-1} in glycerol at −40 °C and was found to be 33.07 at 337 nm. To evaluate $\bar{n}/\tau$ (Table I) we have assumed that the probe rotates about the bond joining the phenyl residue to the alkyl chain and have estimated the volume of the rotator (in eq 2) to be identical with the volume of an equivalent rotating sphere of radius 1.40 Å (carbon-carbon bond length in benzene).

In a second set of experiments, we measured the fluorescence spectra of the aqueous surfactant systems. Figure 1 depicts representative curves for the $3C_{12}$ and $4C_{12}$ systems at 2×10^{-3} mol L^{-1} in water at 25.0 ± 0.2 °C. Two bands are clearly seen at 290 and 350 nm with different relative intensities in the two solutions. Also shown is the fluorescence spectrum for the $3C_{12}$ system at 2×10^{-3} mol L^{-1} in normal dodecane. Only one band is seen at 305 nm. This, and the well-characterized monomer-excimer behavior of benzene derivatives in fluid media,[14] allows the conclusion that the band near 350 nm arises from excimers of the benzene sulfonate head groups. Ratios of the intensities at 290 and 350 nm (I_{350}/I_{290}) obtained for the four isomeric sulfactants are collected in Table I.

Figure 2 shows plots of both degree of polarization and I_{350}/I_{290} against isomer number. It is clear that the shapes are related in an inverse manner: when I_{350}/I_{290} is low (weak excimer fluorescence), P is high (high viscosity) and vice versa. Clearly these two different measurements are yielding the same information. The polarization data reports on the viscous resistance opposing molecular rotational diffusion. Excimer formation, a bimolecular process, depends on the translational

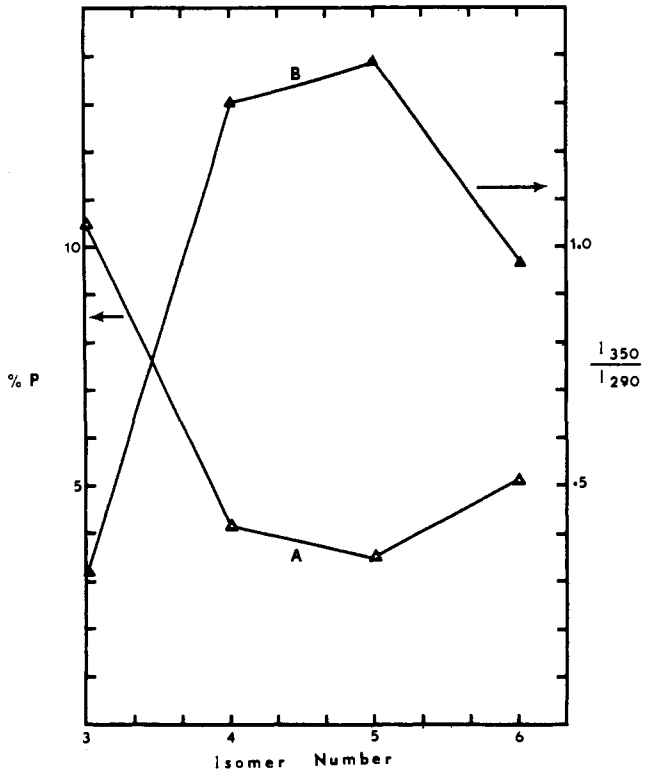


Figure 2. Plots of degree of polarization (left-hand ordinate) and I_{350}/I_{290} (right-hand ordinate) against isomer number for alkyl benzenesulfonate micelles in water at 25.0 ± 0.2 °C.

diffusion of molecules. Thus, the data in Figure 2 show that, in micelles composed of these surfactants, the environment around the benzene moiety resists both translational and rotational diffusion in a similar way. (Similar effects have been found[15] for a series of isomeric C_{16} alkyl benzenesulfonates.) This is the first instance that we know where translational and rotational measurements have been made on the same system.

Why the microviscosity in the vicinity of the fluorescent residue in micellar aggregates should vary in such a manner with isomer composition is not readily apparent. One possibility is that the configuration of the two alkyl chains about the benzene moiety is a determining factor. It is reasonable to expect that the *p*-sulfonate group in all cases lies at the periphery of the micelles at the water interface and that the micellar radius is governed by the length of the longer chain. Along the series $3C_{12}$–$6C_{12}$ the longer chain decreases from 9 to 6 carbon atoms and the short chain increases from 2 to 5 carbon atoms. Thus, as the micelles become smaller in radius, more room has to be found for the increasingly longer short chains. To accommodate this tendency toward crowding, it is possible that the head groups separate to greater distances. Thus, there exists two opposing effects, the interrelationship between which could conceivably result in the observed minimum in local viscosity. These possibilities are being tested using alkyl benzenesulfonate which have been synthesized with long chains of equal length and variable short chains.

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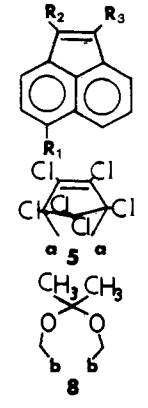
Dual Wavelength Fluorescence from Acenaphthylene and Derivatives in Fluid Media

Sir:

Fluorescence that occurs from upper excited states has been called anti-Kasha fluorescence (AKF) by Birks.[1] Azulene is a well-documented example of AKF,[2] and fluoranthene[3] and 1,12-benzoperylene[1] show similar characteristics. Fluorescence from the second excited singlet state of [18]annulenes was also reported.[4] Acenaphthylene (**1**) is a nonalternate hydrocarbon whose luminescence characteristics are largely unexplored because of extremely low quantum yields of fluorescence.[5] The major absorption bands of **1** recently were characterized by MCD studies.[6] Our interest[7] in the photochemistry of **1** led us to investigate the laser-induced emission from **1** and its derivatives. To our surprise, two well-separated emission maxima are observed,[8] one of which appears to be AKF.

The compounds under study are displayed in Chart I.[9] Dilute solutions (10^{-4}–10^{-5} M) of each compound in different solvents were subjected to laser excitation while being maintained in an oxygen-free atmosphere by continuous nitrogen sparging in the cuvette. Emission output was plotted by aver-

Chart I



	R_1	R_2	R_3
1	H	H	H
2	Ac	H	H
3	CN	H	H
4	H	D	D
5	H	a	a
6	H	CH_2OH	CH_2OH
7	H	CH_2OAc	CH_2OAc
8	H	b	b
9	H	CH_3	CH_2Cl
10	H	CH_2Br	CH_2Cl
11	H	Br	Br

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