Figure 2. Temperature dependence of I_d/I_m for probe Ia in (O) ethanol; (□) SDS; (■) CTAC; (●) CTAB; (△) EG. Activation energies for viscous flow (kilocalories/mole) are shown beside the curves.

were determined[2] which reflect, especially in viscous solvents, the activation energy for viscous flow of the medium.[1] These are also presented in Figure 2.

The microviscosities at 20 °C and the activation energies for viscous flow both increase in the order ETOH < SDS < EG < CTAC < CTAB. SDS is quite fluid with a viscosity between that of ethanol and ethylene glycol. CTAC and CTAB appear to be considerably more viscous but because of possible quenching of the excimer state by the chloride and bromide counterions[14,15] the estimated microviscosities must be considered upper limits.

Our results for SDS and CTAB micelles at 20 °C agree with those of Thomas[14] (SDS, 15–36 cP; no temperature given) and Weber[16] (CTAB, 19–30 cP; 27 °C) using fluorescence depolarization techniques, but conflict with those obtained by Smith[5] (SDS, 193 cP; CTAB, 151 cP, 23 °C) using the intermolecular excimer fluorescence of pyrene as a probe. Rodgers et al.[17] have explained the reported discrepancies by suggesting that the viscosity which characterizes translational motion is much higher than the viscosity which describes rotational diffusion. Since our probe system is independent of rotational diffusion and yields microviscosities which agree with or are lower than those obtained with fluorescence depolarization methods, it appears that the anisotropy of motion in micellar interiors is not so great as suggested by Rodgers.[17,18]

Because micellar microviscosities might be sensitive to the probe's position in the micelle, the fluorescence behavior of probe Ib in SDS and CTAC micelles at 20 °C was also investigated. This ionic probe should bind to the micellar interface and may experience an environment distinct from that felt by probe Ia. Probe Ib exhibited a 50% lower I_m/I_d ratio in both SDS and CTAC micelles than in water, suggesting a less viscous environment. Since the I_m/I_d ratio of aqueous Ib solutions increased at high concentrations of added electrolytes, the observed decrease of I_m/I_d in micellar solutions cannot be due to a simple salt effect. Models indicate, however, that in both the trans–trans and the trans–gauche forms, Ib must have one of the aromatic moieties extending into the Stern layer or beyond. Thus, we attribute the enhanced excimer yield of Ib to the fact that it adopts an almost eclipsed conformation even in the ground state so that both aromatic moieties could be directed towards the micellar interior. Probe Ia does not require this kind of packing.

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A Comparison of Intermolecular and Intramolecular Excimer Formation in Detergent Solutions. Temperature Effects and Microviscosity Measurements

Sir:

Photoluminescence involving excimers[1] in detergent solutions[2] has been employed to study both the photophysics of excimer formation[3] and the intrinsic properties of micellar aggregates.[4] The "microviscosity" experienced by a solute associated with a micelle has been measured by means of fluorescence depolarization[5] and by means of monomer–excimer dynamics.[6] A rather large variation exists between the derived value of microscopic viscosity obtained from the two luminescence methods. For example, for hexadecyltrimethylammonium bromide (HDTBr) micelles at 25 °C, values of ~20–30 cP and ~150 cP are obtained by the polarization[5] and excimer probes,[6] respectively. We report here a comparitive investigation of inter- and intramolecular excimer formation. From our studies and from data in the literature, we are able to derive values for the microviscosity of hexadecyltrimethylammonium bromide (HDTBr), chloride (HDTCl), and sodium dodecyl sulfate (SDS) micelles as a function of temperature.

Naphthalene (N), 1,5-dimethylnaphthalene (DMN), and 1,3-di-α-naphthylpropane (DNP) were employed as fluorescence probes (eq 1). In one series of experiments the N con-
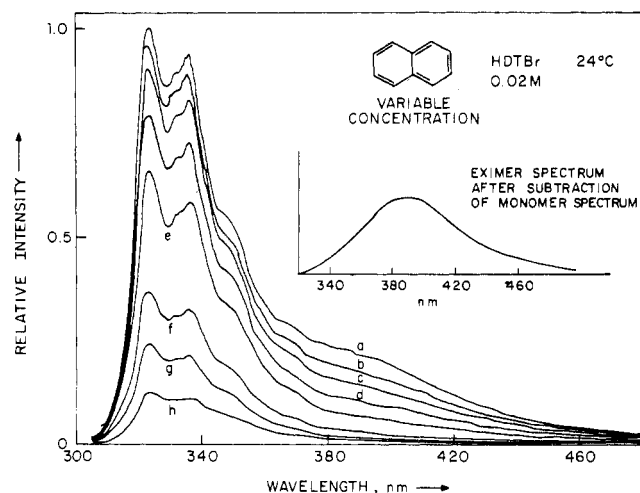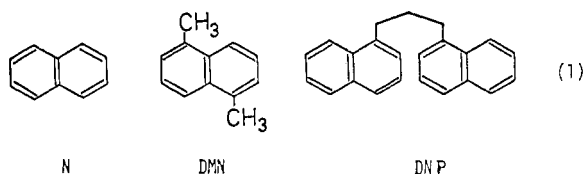
Figure 1. Dependence of luminescence spectra of aqueous HDTBr (0.02 M) solutions of N. The letters a–h indicate naphthalene concentration ($\times 10^3$ M), 4.4, 3.7, 2.9, 2.2, 1.5, 0.68, 0.43, and 0.21, respectively. Excitation at 310 nm.

$$(1)$$

N   DMN   DNP

centration was varied from $\sim 1 \times 10^{-5}$ to $\sim 5 \times 10^{-3}$ M (solubility limit) with detergent (HDTBr) concentration fixed at 0.020 M (cmc of HDTBr $\sim 1 \times 10^{-3}$ M).[7] For N concentrations $\gtrsim 7 \times 10^{-4}$ M the static emission intensity near 390 nm increases (Figure 1). The difference spectrum (insert, Figure 1) demonstrates the concentration-dependent appearance of a new broad band emission centered at 390 nm. At the wavelength expected for naphthalene emission *three* decay components are observed: (1) a long-lived component ($\tau \sim 40$ ns) assigned to the naphthalene in the aqueous phase,[9] (2) an intermediate-lived ($\tau \sim 20$ ns) and (3) short-lived ($\tau \sim 10$ ns) component assigned to naphthalene monomer–excimer dynamics in micelles. In confirmation of these assignments, *no* long-lived (water) emission is found for 1,5-dimethylnaphthalene, although both excimer and monomer emission (micelle) are observed. Increasing the detergent concentration (~ 0.001 to 0.20 M) at fixed N concentration results in a *decrease* in the emission intensity at 390 nm. At high concentrations of detergent only the long (N in H_2O) and intermediate (N in singly occupied micelles) components are observed. These results are consistent with Poisson distribution of N molecules in the HDTBr micelles. As the ratio of [N]/[HDTBr] decreases, the system shifts from one in which there is a high probability that two or more N molecules will occupy a single micelle (emission at 390 nm observed) to a low probability that more than one N will be found in a single micelle.

DMN and DNP differ from N with respect to their water solubility in that neither is significantly dissolved in the aqueous phase. Furthermore, emission decay shapes show that the long-lived monomer fluorescence analogous to that observed for N is absent. However, in both cases, excimer and monomer emission are readily observable. It should be noted that DNP differs from DMN in that the former may form excimers *intramolecularly*.

The temperature dependence of the excimer–monomer emission spectra for N and DNP in detergent solutions is displayed in Figure 2. The ratio I_{ex}/I_m *decreases* with increasing temperature for *intermolecular* excimer formation, but the ratio of I_{ex}/I_m *increases* for intramolecular excimers. The
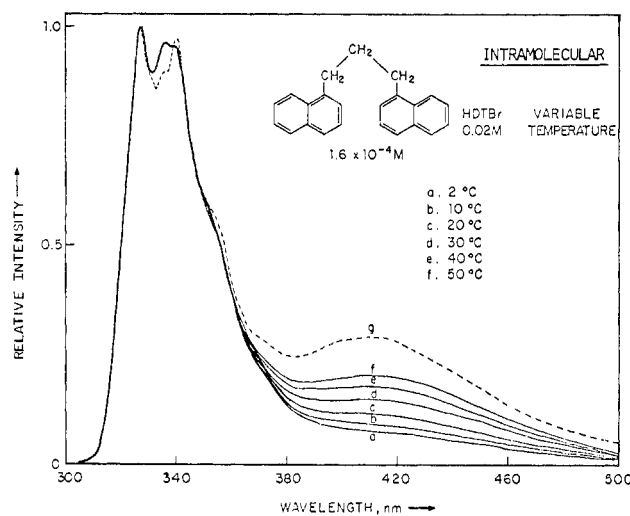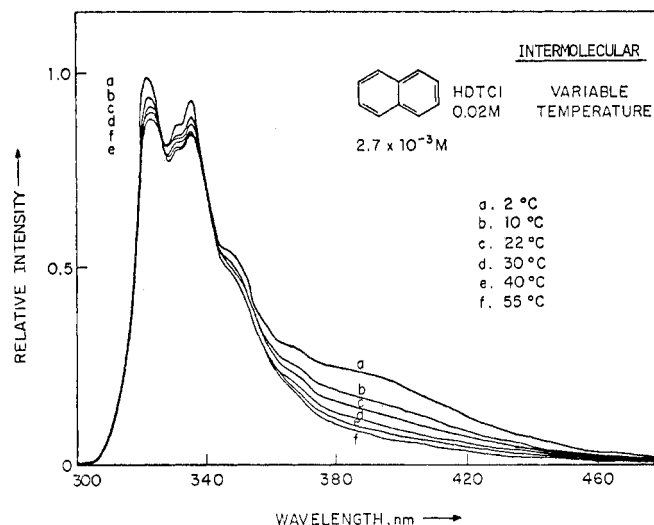
Figure 2. Top: Dependence of the luminescence spectrum of aqueous HDTCl solutions of N on temperature. Bottom: Dependence of the luminescence spectra of DNP on temperature in HDTBr (lettering a–f). The dashed spectrum is for DNP in hexane at 22 °C. Excitation at 300 nm.

results for intermolecular excimer formation are those expected for homogeneous solution.[10] In the case of intramolecular excimer formation the temperature effect is consistent with viscosity as the kinetically limiting feature for achievement of the proper geometry for excimer formation.[1,11] Since the microviscosity of micelles should decrease with increasing temperature, the rate of intramolecular excimer formation should increase with increasing temperature.

The microviscosity of various micelles can be derived from our experiments by employing an empirical scale. This work[11] uses DNP in ethanol–glycerol mixtures to correlate the observed relative intensity of excimer to monomer emission with macroscopic viscosity. The use of alcohol mixtures as comparison systems for macroscopic viscosity is justified by the fact that all tests of the environment of aromatic hydrocarbons in HDTBr, HDTCl, or SDS micelles are consistent with a polar environment of dielectric constant comparable with that of alcohols.[12] The results are given in Table I. For example, from our value of excimer to monomer emission I_{ex}/I_m in HDTBr and the literature scale relating I_{ex}/I_m to viscosity, we derive a value of ~ 39 cP for the microscopic viscosity of HDTBr micelles at 20 °C. This value is in good agreement with results based on fluorescence depolarization measurements (15–35 cP), but is not in agreement with results based on *intermolecular* excimer fluorescence.

Table I. Temperature Dependence of Microscopic Viscosities at 0.02 M Detergent

deter-gent	microscopic viscosities, cp					
	1 °C	10 °C	20 °C	30 °C	40 °C	50 °C
HDTBr	81	60	39 (30,[a] 151[b])	22	14	9
HDTCl	70	49	31	18	13	8
SDS	17	13	9 (16,[c] 193[b])	6	6	7

[a] Depolarization of fluorescence. (ref 5a at 27 °C). [b] Excimer dynamics (ref 6 at 24 °C). [c] Depolarization of fluorescence (ref 5c at 25 °C).

In the case of intermolecular excimer formation the probe molecules (naphthalene or pyrene[6]) may or may not distribute themselves among the available micelles in a manner that is accurately described by statistical methods.[4] Whatever the detailed nature of this distribution, a strict correlation between the measured values of I_{ex}/I_m for micellar systems and those for homogeneous solution is not expected. In other words, the statistical methods that are valid for homogeneous solution are unlikely to be appropriate for analyzing data and deriving microviscosity parameters for micellar systems. In the case of DNP, however, excimer formation is possible at low enough concentration to avoid interference from intermolecular excimer formation, and the unimolecular nature of excimer formation avoids the problem of explicitly including the distribution of probe molecules in deriving microviscosities from I_{ex}/I_m ratios. We thus feel that the use of excimer dynamics, per se, is a valid method for determining microviscosities,[13,14] but that the intermolecular method presents problems because of the difficulties of explicitly including a distribution of probe molecules in the derivation of micelle parameters from experimental parameters.

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Sensitivity Enhancement in Natural Abundance Proton-Coupled ^{15}N NMR Spectra Using the Selective Population Transfer Method

Sir:

The convenient observation of natural abundance ^{15}N nuclear magnetic resonance spectra promises to open to the areas of organic chemistry, bioorganic chemistry, and inorganic chemistry a structural tool comparable in significance with those afforded by two other spin $^{1}/_{2}$ nuclei, ^{1}H and ^{13}C. Furthermore, the spectra obtained will be of greater value if they yield spin-coupling information rather than merely chemical-shift data.[1,2]

Most of the spin-coupling values for ^{15}N currently available have been obtained from ^{15}N-enriched samples;[3,4] indeed, many coupling constants to hydrogen have been measured only from the ^{1}H spectra of enriched molecules.[2] Low abundance (0.365%), low sensitivity (6.54×10^{-2} relative to ^{13}C), long spin-lattice relaxation times (up to 250 s for nitrobenzene and 500 s for benzonitrile),[5-7] and the possible partial loss of nuclear Overhauser effect (NOE) because of relaxation mechanisms other than dipolar, a loss especially disasterous for a nucleus with negative magnetogyric ratio, combine to make the observation of natural abundance ^{15}N spectra tedious and time consuming.

We report here the direct observation of proton-coupled ^{15}N NMR spectra using the selective population transfer (SPT) π-pulse technique,[8] which is found to yield dramatic improvements in sensitivity, often as much as a ten- to onehundredfold increase in signal-to-noise ratio with corresponding time saving of between two and four orders of magnitude for repetitive pulse experiments. Indeed, proton-coupled natural abundance ^{15}N NMR spectra of high concentration samples
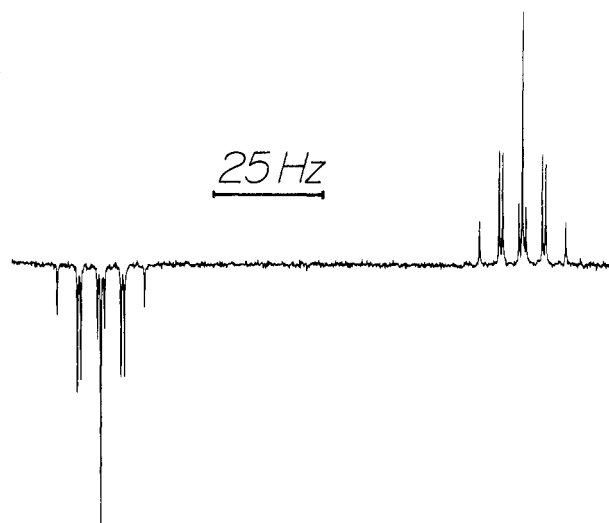

Figure 1. Natural abundance proton coupled ^{15}N SPT FT NMR spectrum of pyrrole, **1** (85% v/v in benzene-d_6; 512 transients. 8-s acquisition time, no line broadening). The ^{1}H π pulse ($\gamma_{H_2}/2\pi = 8.00$ Hz, $\tau = 0.06$ s) was applied at the center of the high-frequency multiplet (triplet of triplets, $^{3}J_{H(1)-H(2)} = 2.59$ and $^{4}J_{H(1)-H(3)} = 2.46$ Hz)[17] for the ^{15}N satellite in the $^{1}H(1)$ spectrum ($^{1}J_{15N-H(1)} = -96.40$, $^{2}J_{15N-H(2)} = -5.36$, and $^{3}J_{15N-H(3)} = -4.55$ Hz).