characteristic benzene bands of weak, medium, and high intensity are all clearly present. Vibrational structure in the longest wavelength band is not very pronounced and exhibits a slight shift toward shorter wavelength and lower intensity when compared with higher homologues. The IR spectrum of **3** ($CHCl_3$) shows bands at 2940, 2870, 1615, 1470, 1384, 1270, and 1100 cm^{-1}.

Unlike 6-radialene, tricyclobutabenzene appears to be a quite stable molecule. It can be remelted with decomposition, will survive VPC temperatures of 250 °C, and remains unchanged after room temperature storage for several days. We are continuing to investigate the chemistry of this intriguing molecule.

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(12) It was found that this yield could be increased to 3.6% (10.8 mg) when only 1 equiv of lead tetraacetate was employed. After chromatography, the material thus obtained appeared to be mostly **9** by NMR but could be smoothly converted to **3** by treatment with DDQ. The fate of the remaining organic material in this decarboxylation is a question which is now receiving our serious attention in an effort to further increase the yield of this reaction.

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Intramolecular Excimer-Forming Probes of Aqueous Micelles

Sir:

We describe here the use of intramolecular excimer-forming compounds of type I as microviscometric probes of the interior of aqueous micelles. Since the conformation of I required for excimer formation would be sparsely populated in the ground state, a conformational transition is required during the lifetime of the excited state.[1-3] For a given Ar and X, the rate constant for excimer formation (k_a) is inversely dependent on the viscosity of the medium.[1,2] At sufficiently low temperatures

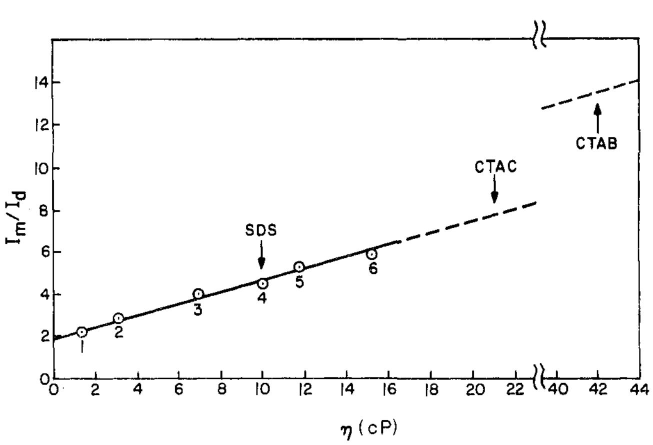
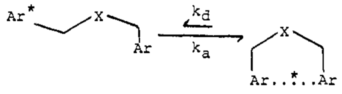


Figure 1. I_m/I_d vs. viscosity for probe Ia at 20 °C: (1) ethanol; (2) 1-butanol; (3) triethylcarbinol; (4) 19:10 (v/v) ethanol-glycerol; (5) tributyrin; (6) 40:60 (v/v) ethanol-glycerol. EG (viscosity of 19.9 cP) exhibited an I_m/I_d ratio of >15. Dotted line represents extrapolation of the experimentally determined plot. Arrows indicate I_m/I_d ratios of Ia solubilized in micellar solutions and their corresponding microviscosities in centipoises.



I

Ia: X=O; Ar=4-biphenyl
Ib: X=$NH_2^+Cl^-$; Ar=1-naphthyl

where the dissociation of the excimer (k_d) may be neglected, the ratio of the intensities of excimer and normal fluoresence (I_d/I_m) is characteristic of k_a.[1,4]

Since compounds of type I are solubilized in solutions of aqueous micelles, miceller microviscosities may be estimated from a comparison of the I_d/I_m ratios of the solubilized probes with appropriate references. This method has a distinct advantage over the *inter*molecular excimer fluorescence technique[5] because multiply occupied micelles are not required.

Ia[6] was chosen for our initial investigations because of its high quantum yield of emission and because the temperature at which k_d becomes significant is well above room temperature. Conditions were maintained so that >94% of the occupied micelles were singly occupied ([Ia] < 10^{-4} M; [surfactant] = 0.05-0.06 M).[7] Thus, the contribution from intermolecular excimer emission is negligible.

The micelles were labeled either by warming the aqueous micellar solutions containing the probe to 90 °C for 50 min and then cooling rapidly or by injecting an ethanol solution of the probe into the micellar solution (ETOH concentration <1%). Identical spectra resulted from the two labeling techniques. All solutions were prepared under nitrogen using deoxygenated solvents.

In Figure 1, I_m/I_d values for probe Ia dissolved in various solvents at 20 °C are plotted against viscosity. Except for ethylene glycol, a remarkably good correlation was obtained even though a wide spectrum of solvents and solvent mixtures were employed.[8] Using this plot as a reference, micellar microviscosities were estimated from the I_m/I_d ratios exhibited by the solubilized probe. These are shown on the plot for sodium dodecylsulfate (SDS), cetyltrimethylammonium chloride (CTAC), and cetyltrimethylammonium bromide (CTAB) micelles.[12] While previous workers[14] reported significant changes in the fluorescence depolarization of solubilized probes as the micelles aged, we observed little change in I_m/I_d with time.

Figure 2 shows the temperature dependent behavior of I_d/I_m for probe Ia in aquoues SDS, CTAC and CTAB micelles and in ethanol and ethylene glycol (EG) solvents. From the low temperature portion of the logarithmic plot, activation energies

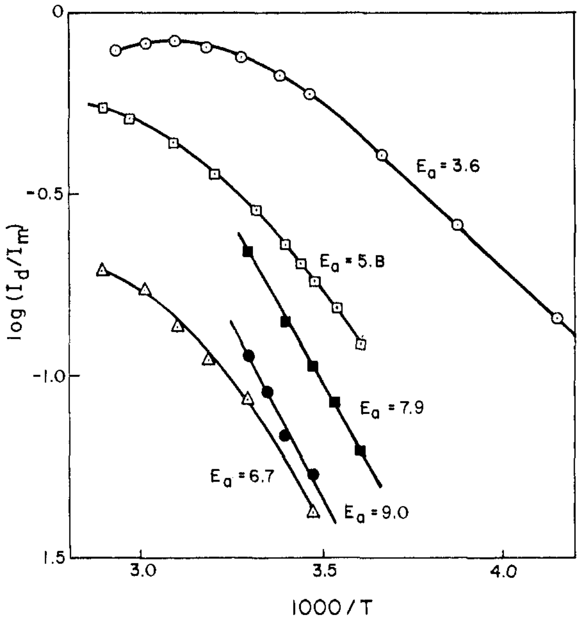


Figure 2. Temperature dependence of I_d/I_m for probe Ia in (○) ethanol; (□) SDS; (■) CTAC; (●) CTAB; (△) EG. Activation energies for viscous flow (kilocalories/mole) are shown beside the curves.

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-

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