

0.5 ms (neat dimethylformamide (DMF)) to 1.1 ms (DMF:C₂H₅OH, 3:2) were found. The difference in values reflects the influence of the solvent quality.

(iii) α,ω -Dianthrylpolystyrene was irradiated in dilute solution with 25 ns flashes of 347 nm light. From triplet-triplet (T-T) absorption measurements, rates of T-T annihilation, corresponding to rates k_{intra} of intramolecular end-to-end collisions, were obtained as functions of chain length N . In benzene at 22 °C $k_{\text{intra}} = \text{constant} \times N^{-1.0}$ with $N = 110$ to $N = 3000$. In cyclohexane at 34 °C $k_{\text{intra}} = \text{constant} \times N^{-1.5}$ for $N \leq 300$ and $k_{\text{intra}} = \text{constant} \times N^{1.0}$ for $N \geq 300$.

Fluorescence and energy transfer of dye-detergent systems in the premicellar region

HIROYASU SATO, MASAHIRO KAWASAKI and KAZUO KASATANI

Chemistry Department of Resources, Faculty of Engineering, Mie University, 1515 Kamihamacho, Tsu 514 (Japan)

The fluorescence lifetimes of dyes and also the energy transfer between dyes with closely located S₁ levels were studied in the presence of detergents. These dye-detergent systems can be considered as one of the model membrane systems of chloroplasts and show some peculiar features when the detergent has the opposite charge to that of the dye. A long dimer-like lifetime was observed in the acridine orange-sodium lauryl sulphate (AO-SLS) system in the pre-micellar region, *i.e.* for [SLS] a little less than the critical micelle concentration (CMC). The energy transfer efficiency between rhodamine 6G (Rh-6G) and pinacyanol (PC) in the presence of SLS showed a distinct peak in the pre-micellar region. These findings and the absorption and fluorescence spectra revealed that the dye molecules are associated with dye-rich induced micelles which reduce the average distance (AO-AO or Rh-6G-PC) between dye molecules in the premicellar region.

Twisted intramolecular charge transfer state formation and other properties of some triazinyl dyes

DAVID J. COWLEY

New University of Ulster, Coleraine BT52 1SA (Northern Ireland)

Fluorescence from the dipolar planar intramolecular charge transfer excited singlet state of the dye *N,N*-diethyl-4-(dichloro-1,3,5-triazinyl)aniline (TA) is strongly quenched by solvents of even moderate polarity (at room temperature

$\varphi_F = 0.81$ in C_6H_{12} and $\varphi_F = 0.03$ in tetrahydrofuran). A lowering of the acceptor character of the triazinyl ring decreases the susceptibility to such quenching. From variable-temperature studies the quenching process involves an increase in the dipole moment of the dye at a rate limited by the solvent dielectric relaxation. Flash photolysis and steady state studies of triplet state generation ($\varphi_T \cong 0.15$) and properties are reported for TA and related systems.

The data provide further evidence for the twisted intramolecular charge transfer model [1] and shed light on intersystem crossing in twisted charge transfer biradicaloid ($^+ \cdot D-A \cdot^-$) states.

1 Z.R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D.J. Cowley and W. Baumann, *Nouv. J. Chim.*, 3 (1979) 443.

Diffuse reflectance laser flash photolysis

FRANK WILKINSON

Department of Chemistry, University of Technology, Loughborough, Leics. LE11 3TU (Gt. Britain)

A laser flash photolysis system which has been developed to study transient absorption from highly scattering powdered samples after excitation by nanosecond dye-laser pulses is described. Transient spectra are reported from organic molecules adsorbed as monolayers on metal-oxide surfaces including activated catalysts and semiconductors as well as from powdered solids. Assignments of these spectra and numerical solutions to the differential equations for transient diffuse reflection from photoinduced inhomogeneous absorbing samples are discussed. The potential of this new technique [1] is illustrated with examples of flash photolysis studies at a variety of interfaces.

1 R. W. Kessler and F. Wilkinson, *J. Chem. Soc., Faraday Trans. I*, 77 (1981) 309.