

**Chlorobenzene.** The initial concentrations of **1**, and **2**, and tetracyclone were  $6.54 \times 10^{-4}$ ,  $6.5 \times 10^{-4}$ , and  $2.08 \times 10^{-3}$  M, respectively. The nitrogen-saturated solutions were thermolyzed at 87 °C for 18 h. The disappearance of tetracyclone and the appearances of **5** and **6** were monitored via absorption spectrometry at 510 and 520 nm. The average singlet oxygen yields from three independent runs are listed in Table I.

**Magnetic Field Effect on the Yield of Singlet Oxygen Generated by Anthracene Endoperoxides (1, 2, 3, and 4).** The magnetic field including 0.5 G was provided by an Alfa Model 4600 constant electromagnet. Typically, the initial concentrations of **1** and tetracyclone in 1,4-dioxane were  $2 \times 10^{-3}$  and  $4 \times 10^{-3}$  M, respectively. The solution was contained in a sealed glass tube with a 2-nm diameter. Sixteen of the sealed tubes were placed in a large tube, in which the temperature was controlled by circulating water. The position of the large tube was adjusted to have the sample tubes in the middle of the magnet. Eight of the sample tubes contained the solution of **1** and tetracyclone; the other eight samples which contained the solution of tetracyclone only were employed as control experiments. The control experiments were run to test the stability of tetracyclone and provide the initial optical density reading of tetracyclone at 405, 496, and 504 nm for the measurements of  $\Delta(\mathbf{5})$  and  $\Delta(\text{tetracyclone})$ . The typical conversions of **1** and tetracyclone were 45% and 8% at 90 °C for 5 h, respectively. Similar procedures were performed for thermolysis of **1** in benzene, chloroform, benzonitrile, dodecane, and toluene and for the measurements of singlet oxygen formed from **3** and **4** in dioxane. The initial concentrations of **3** and tetracyclone were  $1.78 \times 10^{-3}$  and  $4.01 \times 10^{-3}$  M, respectively. The initial concentration of **4** and tetracyclone were  $8 \times 10^{-4}$  M. The typical conversions of **3** and tetracyclone were 14% and 6% at 90 °C for 10 h, respectively. The typical conversion of **4** and tetracyclone were 50% and 5%, respectively. The data reported represent the average of eight (or sixteen) independent measurements in addition to eight (or sixteen) control experiments. The error refers to the standard deviation.

**Calibration of Mass Spectrometer with CO<sub>2</sub> and O<sub>2</sub>.** The isotopic composition of molecular oxygen was analyzed with a JEOL-JMS-07 mass spectrometer equipped with a voltage to frequency converter and multichannel analyzer. The analyses were calibrated with natural abundance CO<sub>2</sub> and O<sub>2</sub>. The measured ratio of CO<sub>2</sub> peaks 44, 45, and 46 is 100:1.12:0.427 which agrees well with the literature values<sup>21</sup> 100:1.19:0.408. The measured ratio of O<sub>2</sub> peaks 32, 33, and 34 is 100:0.06:0.36 which agrees well with the reported value<sup>21</sup> 100:0.072:0.408.

**Measurements of the Isotope Composition of Oxygen Molecules Generated from Endoperoxides.** The degassed solutions of **1** and **9** were thermolyzed 12 h at 90 and 40 °C, respectively. After thermolysis, the solution was frozen at 77 K and the product molecular oxygen was transferred directly by diffusion into the mass spectrometer in which the oxygen was analyzed. Typically, the initially concentrations of **1**, tetracyclone, **9**, and DMA were ca. 0.015 M. The conversions of **1** and **9** were over 90%. The data reported were an average of four or more independent samples, each sample being measured four times. The error limits in Tables III and IV refer to the standard deviation.

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(21) Beynon, J. H. "Mass Spectrometry and its Application to Organic Chemistry"; Elsevier: New York, 1960.

## Micellar Microviscosity of Ionic Surfactants under High Pressure<sup>†</sup>

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**Abstract:** The microviscosities of ionic micelles of sodium dodecylsulfate (SDS), hexadecyltrimethylammonium bromide (HDTBr), and hexadecyltrimethylammonium chloride (HDTCl) are estimated from the monomer-excimer ratio of 1,3- $\alpha$ -dinaphthylpropane (DNP) under high pressure (1 to 2610 bars). Excimer formation is inhibited with elevated pressure. The derived microviscosities ( $\eta$  of SDS, HDTBr, and HDTCl) are 12, 47, and 27 cP, respectively, at 25 °C, at atmospheric pressure. The  $\eta$  values increase with pressure from 27 cP (1 bar) to 101 cP (2610 bars) for HDTCl. Additions of sodium chloride, sodium sulfate, and ethanol to the surfactant solutions are found to generally decrease the  $\eta$  values. The intermolecular excimer formation of pyrene in surfactant solutions is retarded by application of high pressure. However, the excimer-monomer ratio of pyrene does not give values of micellar microviscosity that are consistent with those derived from the DNP method. The data on the pressure dependence of micellar microviscosity is consistent with the penetration of water into the interior of micelle cores.

Photophysical techniques afford very convenient and powerful methods for the investigation of the structures and properties of micellar solutions.<sup>1</sup> For example, the microviscosity experienced by the fluorophore associated with a micellar aggregate may be evaluated from the extent of excimer formation,<sup>2,3</sup> from the degree of fluorescence depolarization,<sup>4</sup> and from fluorescence fine spectra.<sup>5</sup> Among excimer methods, *intramolecular* excimer formation of bichromophores possesses the advantage that excimer emission is exclusively unimolecular and that statistical factors related to the probe distribution in the micelles may be ignored,<sup>2</sup> i.e., *intermolecular* excimer formation<sup>2b,3</sup> is a function of not only diffusional motion of the probes, but also the local probe concentration and probe distributions.

<sup>†</sup> This paper is dedicated to George S. Hammond in commemoration of his 60th birthday.

The macroscopic viscosity of liquid hydrocarbons is very sensitive to temperature and pressure,<sup>6</sup> whereas water viscosity is

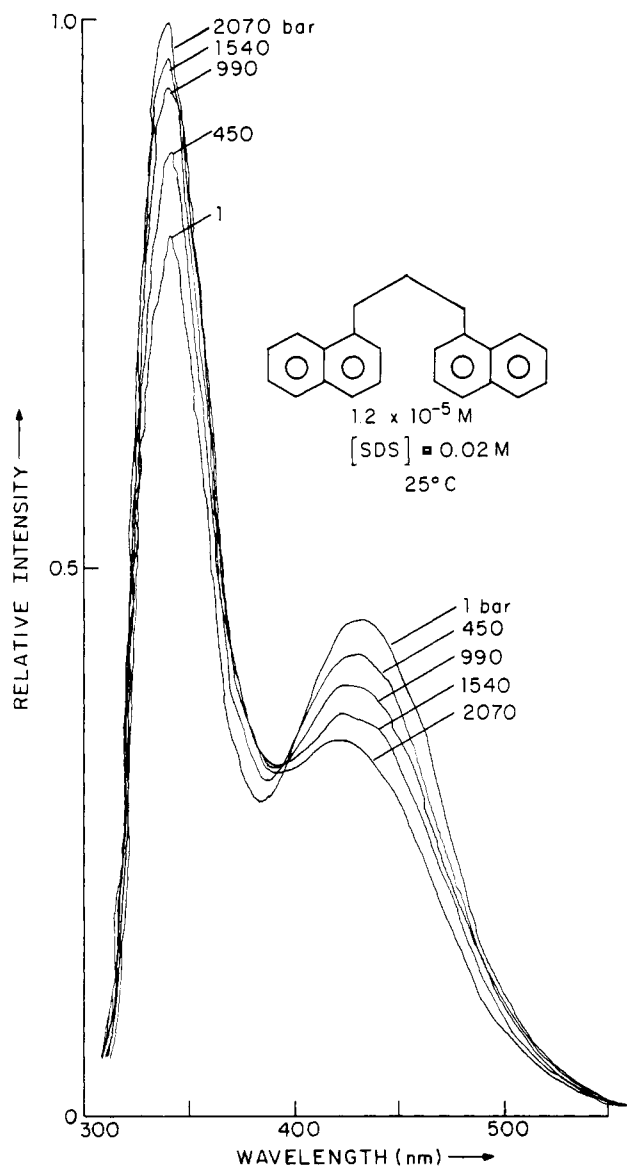
(1) (a) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press, New York, 1975. (b) Thomas, J. K. *Acc. Chem. Res.* **1977**, *10*, 133. (c) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675.

(2) (a) Zachariasse, K. A. *Chem. Phys. Lett.* **1978**, *57*, 429. (b) Turro, N. J.; Aikawa, M.; Yekta, A. *J. Am. Chem. Soc.* **1979**, *101*, 772. (c) Emert, J.; Behrens, C.; Goldenberg, M. *Ibid.* **1979**, *101*, 771.

(3) (a) Forster, T.; Selinger, B. K. *Z. Naturforsch.* **1964**, *19*, 38. (b) Hauser, M.; Klein, U. *Z. Phys. Chem.* **1972**, *78*, 32. (c) Pownall, H. J.; Smith, L. C. *J. Am. Chem. Soc.* **1973**, *95*, 3136.

(4) (a) Shinitzky, M.; Dianoux, A. C.; Gitler, C.; Weber, G. *Biochemistry* **1971**, *10*, 2106. (b) Gratzel, M.; Thomas, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 6885. (c) Kubota, Y.; Kodama, M.; Miura, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 100. (d) Rice, S. A.; Kenney-Wallace, G. A. *Chem. Phys.* **1980**, *47*, 161.

(5) (a) Kalyanasundran, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039. (b) Almgren, M.; Griesser, F.; Thomas, J. K. *Ibid.* **1980**, *102*, 3188.



**Figure 1.** Fluorescence spectra of the DNP + SDS + H<sub>2</sub>O system under high pressure at 25 °C: [DNP] =  $1.2 \times 10^{-5}$  M, [SDS] = 0.02 M.

rather insensitive to pressure.<sup>7</sup> Since the structure of micellar cores in the vicinity of typical probes is considered to be intermediate to that of a hydrocarbon and water in nature, a study of the micellar viscosity as a function of applied pressure may provide information that can impact significantly on our understanding of the structure and properties of micelle aggregates.

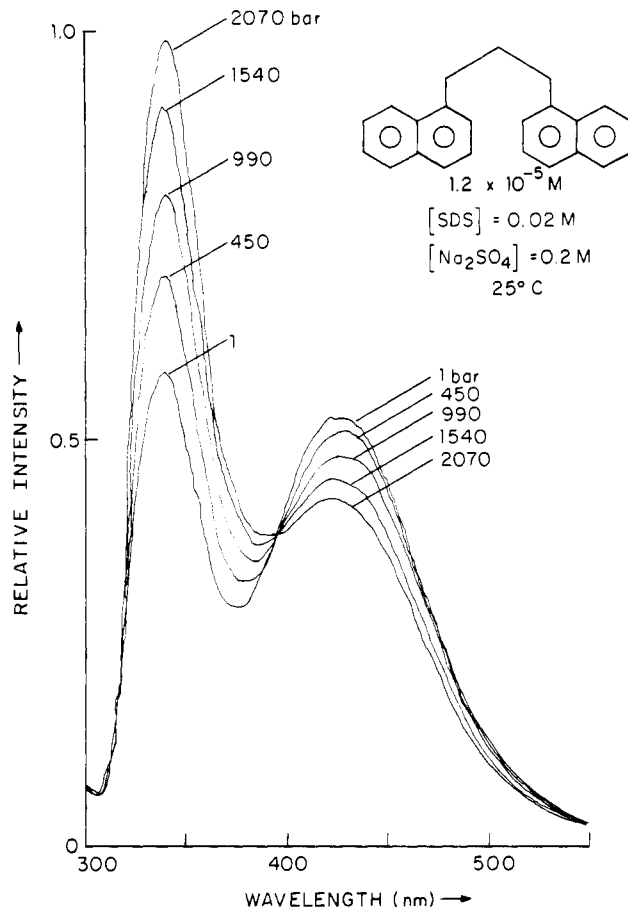
We report here the influence of pressure on the microviscosity of ionic surfactants, using 1,3-di- $\alpha$ -naphthylpropane (DNP) as an intramolecular excimer probe and pyrene as an intermolecular excimer probe.

### Experimental Section

**Materials.** Sodium dodecylsulfate (SDS), electrophoresis purity reagent of Bio-Rad Lab (Richmond, Calif.), was further purified by recrystallization from a mixture of ethanol and 1-butanol. Hexadecyltrimethylammonium bromide (HDTBr) and chloride (HDTCl) were available from previous studies.<sup>6</sup> Sodium chloride (Alfa, ultrapure grade) and sodium sulfate (Aldrich Chemical Co., gold label) were used as supplied. 1,3-Di- $\alpha$ -naphthylpropane (DNP) was prepared by Ms. Resel-Mattay according to the method described by Chandross and Dempster.<sup>7</sup> Pyrene (Aldrich) was recrystallized from an ethanol-water mixture.

(6) (a) Turro, N. J.; Liu, K.-C.; Chow, M.-F.; Lee, P. *Photochem. Photobiol.* **1978**, *27*, 523. (b) Turro, N. J.; Aikawa, M. *J. Am. Chem. Soc.* **1980**, *102*, 4866.

(7) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586.



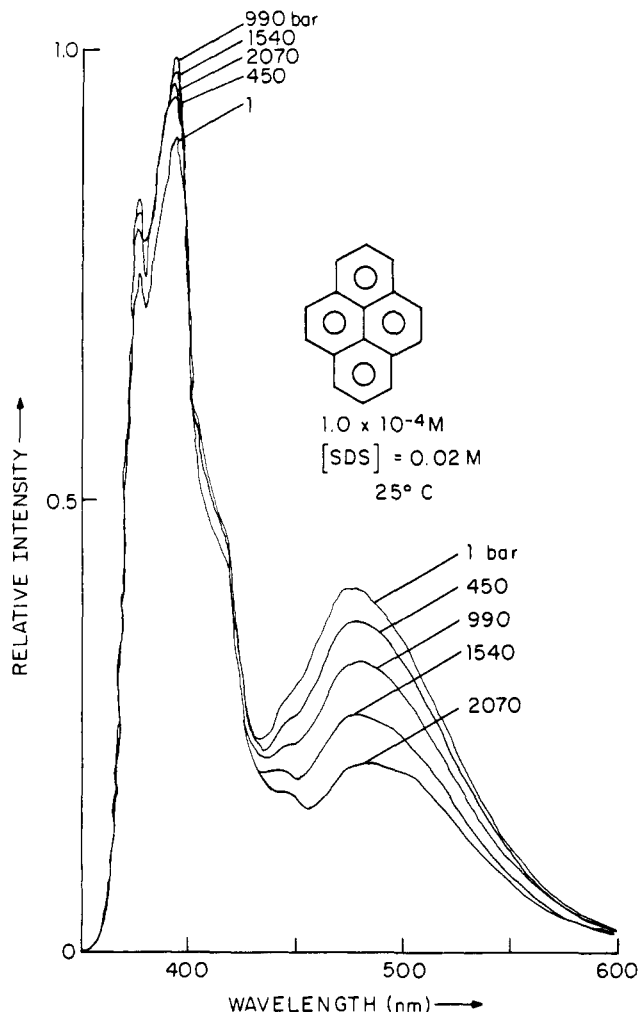
**Figure 2.** Fluorescence spectra of the DNP + SDS + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O system under high pressure at 25 °C: [DNP] =  $1.2 \times 10^{-5}$  M, [SDS] = 0.02 M, [Na<sub>2</sub>SO<sub>4</sub>] = 0.2 M.

**Measurements of Fluorescence Spectra under High Pressure.** All fluorescence spectra were taken on a SPEX Fluorolog Fluorimeter, using 290 nm excitation. A stainless steel cell (Union Giken Engineering, Hirakata, Japan) was employed for the high-pressure studies. The cell is a Drickamer type<sup>8</sup> and has three windows. The sample volume is about 3 mL, the path length is 10 mm, and quartz was used for excitation and emission windows. Silicon rubber, Teflon, and copper O-rings and back-up rings were used to prevent leakage of the sample solution from the vessel. The cell pressure (1–3000 bars) was generated through an intensifier by means of an oil hand pump (1–3000 bars). The intensifier factor was  $10 \pm 0.3$ . The pressure could be kept constant for up to 10 h except for the initial period of the setting (ca. 5 min). The pressure in the vessel was calibrated with a precision Burdon type pressure gauge (Heise, Model CM 23235). To check the reliability of the cell, the emission spectra of DNP and pyrene in aqueous SDS solutions were compared, using a conventional quartz cell and the high-pressure cell at atmospheric pressure. Good agreement between spectra observed by the two methods was obtained.

### Results

Figure 1 shows typical examples of the fluorescence spectra of DNP in aqueous SDS solution as a function of applied pressure. Monomer and excimer peaks appear at 340 and 430 nm, respectively. The intensity of excimer emission was decreased and the intensity of monomer emission was enhanced as the pressure increased. This tendency was more pronounced for the solutions containing a foreign salt such as sodium sulfate as is seen in Figure 2. Notice that at 1 bar the initial monomer to excimer ratio is much lower in the presence of added salt. The influence of pressure on the relative intensity of excimer and monomer emission of pyrene is qualitatively similar to that exhibited by DNP (Figure 3).

(8) (a) Taniguchi, Y.; Shimokawa, J.; Hisatome, H.; Tanamachi, S.; Suzuki, K. *Macromolecules* **1978**, *11*, 829. (b) Ise, N.; Maruno, T.; Okubo, T. *Proc. R. Soc. London, Ser. A* **1980**, *370*, 485.

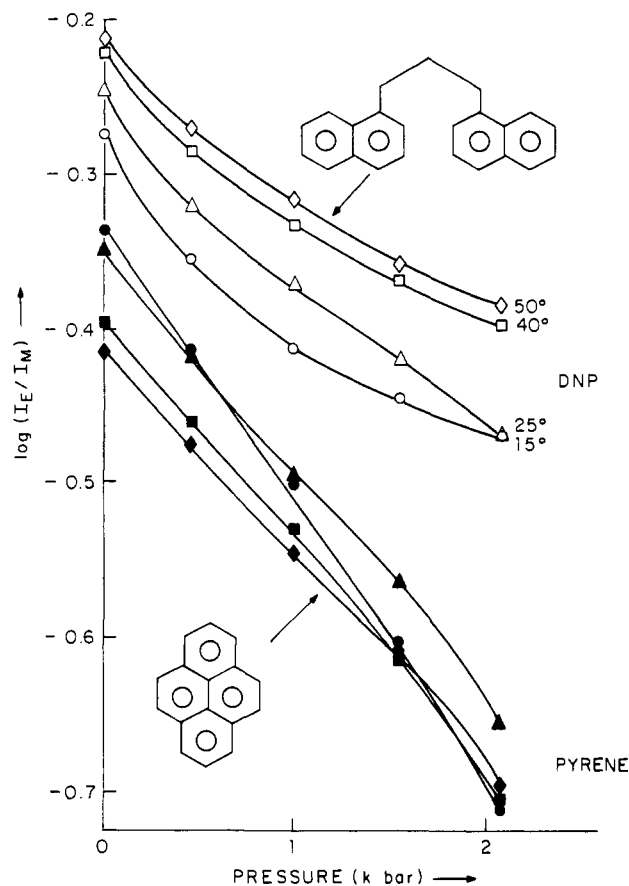


**Figure 3.** Fluorescence spectra of the pyrene + SDS + H<sub>2</sub>O system under high pressure at 25 °C: [pyrene] = 1 × 10<sup>-4</sup> M, [SDS] = 0.02 M.

The pressure dependence of the relative intensity of excimer-monomer emission ( $I_E/I_M$ ) for DNP and pyrene in SDS solution at various temperatures between 15 and 50 °C is displayed in Figure 4. At each temperature the ratio decreased strikingly with increasing pressure for both intra- (DNP) and inter- (pyrene) excimer formations. These observations can be explained qualitatively as the result of an increase in the microviscosity of the micelle cores induced by an increase in applied pressure. It was reported earlier that the  $I_E/I_M$  values of DNP increased with rising temperature, whereas those of pyrene decreased.<sup>2b</sup> The same general temperature dependence of  $I_E/I_M$  was observed even under high pressure.

Figures 4 and 5 demonstrate that excimer formation of DNP and pyrene shows a qualitatively similar pressure dependence even though excimer formation is intramolecular in one case and intermolecular in the other case.

From the ratio of  $I_E/I_M$  a value of the average microviscosity experienced by a probe can be evaluated by employing an empirical scale. In the present work, the correlation of the observed magnitudes  $I_E/I_M$  of DNP in ethanol-glycerol mixtures with macroscopic viscosity of these mixtures was used.<sup>9</sup> The results are listed in Table I and also shown graphically in Figure 6. Our values for micelle microviscosity at atmospheric pressure for SDS, HDTCl, and HDTBr are 11.5, 27, and 47 cP at 25 °C. These are in good agreement with the previous values<sup>2b,4a,c,10</sup> except for



**Figure 4.** Log ( $I_E/I_M$ ) vs. pressure plots at various temperatures for DNP and pyrene in SDS solution: [DNP] = 1.2 × 10<sup>-5</sup> M, [pyrene] = 1 × 10<sup>-4</sup> M; DNP, (○) 15 °C, (△) 25 °C (□) 40 °C (◇) 50 °C; pyrene, (●) 15 °C, (▲) 25 °C (■) 40 °C, (◆) 50 °C.

the value from the intermolecular excimer dynamics.<sup>3c</sup>

## Discussion

From the above results, the evaluated magnitude of the micellar microviscosity increases significantly for the ionic detergents studied with increasing pressure (Table I). If we compare the influence of pressure on the microviscosity of micelles, i.e., slopes in the microviscosity vs. pressure plots (Figure 6), with those of water<sup>11a</sup> and typical hydrocarbons<sup>11b,11c</sup> the magnitudes of the increase for micelles are initially similar to those of hydrocarbon liquids (1–500 bars). At high pressures (>500 bars) the micellar viscosity continues to increase at a pace that is roughly linear with pressure, whereas liquid hydrocarbons undergo a sharp nonlinear increase in viscosity as the pressure is increased above several hundred bar. Over the pressure range accessible to our equipment, the viscosity of water is constant. Our results may be interpreted in terms of a model for which the micellar core occupied by the probe contains some water molecules and is comparatively polar.<sup>12</sup>

The fusion activation energy,  $\Delta E$ , is derived from the temperature dependence of the microviscosity,  $\eta = Ae^{\Delta E/RT}$ . The values for SDS are 1.7, 2.7, 2.5, 2.4, and 3.4 kcal/mol<sup>-1</sup> at 1, 450, 990, 1540, and 2070 bars, respectively. The pressure coefficient of  $\Delta E$ , i.e.,  $\delta(\Delta E)/\delta P$ , therefore, is 0.57 kcal/mol<sup>-1</sup> bar<sup>-1</sup> for SDS.

(11) (a) Bett, K. E.; Cappi, J. B. *Nature (London)* **1965**, *207*, 620. (b) Lowitz, D. A.; Spencer, J. W.; Webb, W.; Schiessler, R. W. *J. Chem. Phys.* **1959**, *30*, 73. (c) Griest, E. M.; Webb, W.; Schiessler, R. W. *Ibid.* **1958**, *29*, 711.

(12) We should note here that the hydrocarbon core of micelle is not considered to be similar to a "droplet" of hydrocarbon, but a porous core penetrated with water molecules as strongly proposed by Menger and others. See ref 13 below.

(13) See, for example: (a) Muller, N.; Birkhahn, R. H. *J. Phys. Chem.* **1967**, *71*, 957. (b) Svens, B.; Rosenholm, B. *J. Colloid Interface Sci.* **1973**, *44*, 945. (c) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 1979. (d) Menger, F. M.; Bonicamp, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 2140.

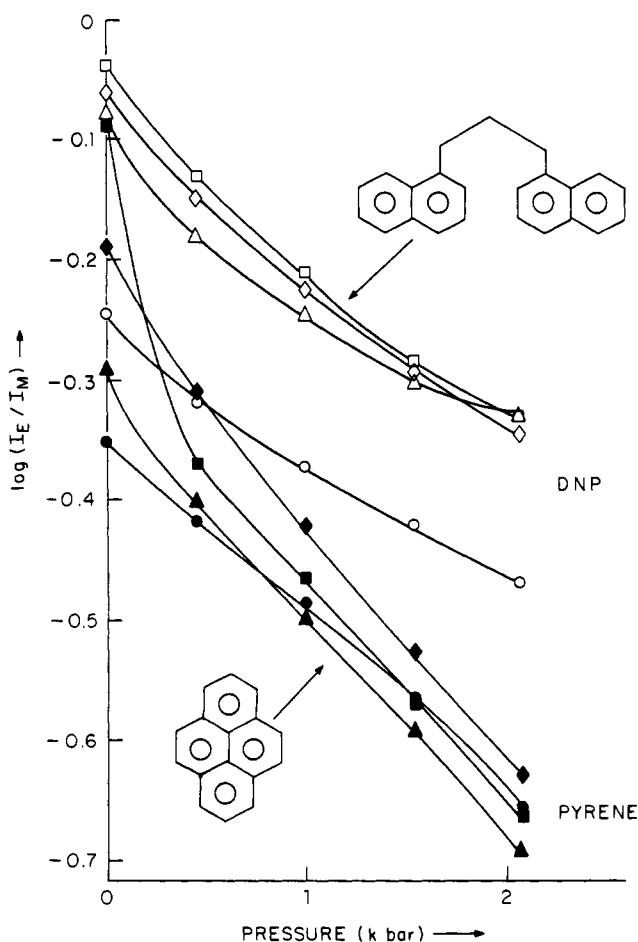
(9) Avouris, P.; Kordas, J.; El-Bayoumi, M. A. *Chem. Phys. Lett.* **1974**, *26*, 373.

(10) Turro, N. J.; Tanimoto, Y. *Photochem. Photobiol.*, in press.

Table I. Micellar Microviscosities of Ionic Surfactants<sup>a</sup>

surfactant	temp, °C	additives [M]	microviscosity, cP					
			1 bar	450	990	1540	2070	2610
HDTBr	25	none [0]	47	66	86	89 <sup>b</sup>		
HDTCl	25	none [0]	27	39	53	69	84	101
SDS	15	none [0]	14	22	29	35	50	
SDS	25	none [0]	11.5	18	25	31	39	
SDS	40	none [0]	10	14	19	24	29	
SDS	50	none [0]	10	13	17	23	27	
SDS	25	NaCl [0.1]	4.0	8.0	12	16	19	
SDS	25	NaCl [0.2]	3.1	5.8	10	14	19	
SDS	25	NaCl [0.4]	3.5	6.4	11	15	21	
SDS	25	Na <sub>2</sub> SO <sub>4</sub> [0.1]	3.3	6.9	12	17	24	
SDS	25	Na <sub>2</sub> SO <sub>4</sub> [0.2]	3.2	6.3	11	17	24	
SDS	25	Na <sub>2</sub> SO <sub>4</sub> [0.4]	4.7	7.9	13	20	33	
SDS	25	C <sub>2</sub> H <sub>5</sub> OH [0.1]	11	18	23	31	37	
SDS	25	C <sub>2</sub> H <sub>5</sub> OH [0.3]	11	16	23	30	36	
SDS	25	C <sub>2</sub> H <sub>5</sub> OH [1.0]	9.8	14	20	25	30	
SDS	25	C <sub>2</sub> H <sub>5</sub> OH [2.0]	7.6	12	16	22	27	

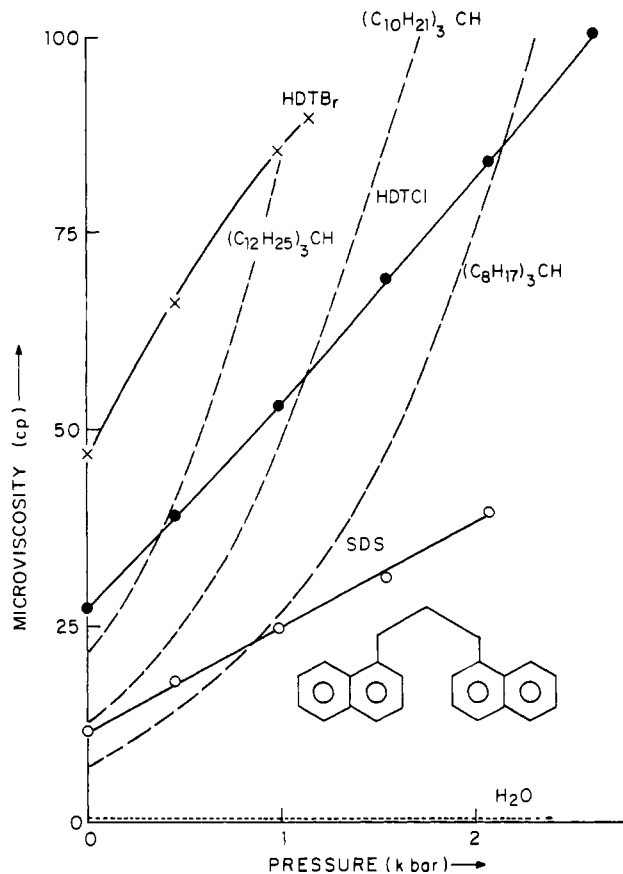
<sup>a</sup> [DNP] =  $3 \times 10^{-5}$  M (HDTBr, HDTCl),  $1.2 \times 10^{-5}$  M (SDS); [HDTBr] = [HDTCl] = [SDS] = 0.02 M. <sup>b</sup> At 1150 bars.



**Figure 5.** Log ( $I_E/I_M$ ) vs. pressure plots for DNP and pyrene in SDS solution at 25 °C: [DNP] =  $1.2 \times 10^{-5}$  M, [pyrene] =  $1 \times 10^{-4}$  M; DNP, [NaCl] = 0 (○), 0.1 (△), 0.2 (□), 0.4 M (◇); pyrene, [NaCl] = 0 (●), 0.1 (▲), 0.2 (■), 0.4 M (◆).

On the other hand, the pressure coefficients of water ( $n$ -C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH, ( $n$ -C<sub>10</sub>H<sub>21</sub>)<sub>3</sub>CH, and ( $n$ -C<sub>12</sub>H<sub>25</sub>)<sub>3</sub>CH are -0.15, 0.88, 0.86, and 0.68, respectively.<sup>11b,c</sup> The pressure coefficient of SDS is intermediate to that of water and hydrocarbon in magnitude. This result also is consistent with the partial penetration of water molecules into the hydrocarbon core.

Foreign salts such as NaCl and Na<sub>2</sub>SO<sub>4</sub> decreased the values of the evaluated microviscosity significantly (Table I). These results are consistent with a model in which salt ions cause disruption of the structure of the hydrocarbon core of the micelle,



**Figure 6.** Microviscosity of SDS (○), HDTCl (●), and HDTBr (×) as a function of pressure at 25 °C: [surfactant] = 0.02 M, [DNP] =  $1.2 \times 10^{-5}$  M; (---)  $\eta$  of (C<sub>12</sub>H<sub>25</sub>)<sub>3</sub>CH, (C<sub>10</sub>H<sub>21</sub>)<sub>3</sub>CH, and (C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>CH (from the top); (···)  $\eta$  of H<sub>2</sub>O.

for example, by causing a modification of the water structure near the core which in turn causes a break up of the core structure. Very recently, Miller evaluated the microviscosity of SDS in the presence of Na<sub>2</sub>SO<sub>4</sub> from the time-resolved pyrene excimer fluorescence.<sup>14</sup> The  $\eta$  values decreased by the addition of the salt in spite of a considerable increase in micelle size, which also is consistent with the partial penetration of water into the micellar core. However, Lianos and Zana suggested an opposite conclusion based on an analysis of the changes in fine structures of pyrene fluorescence in the presence of NaCl.<sup>15</sup> The basis for the dis-

(14) Miller, D. J. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 337.

(15) Lianos, P.; Zana, R. *J. Phys. Chem.* **1980**, *84*, 3339.

crepancy is not clear at present.

Ethanol addition also decreased the microviscosity. This result is explained as resulting from an increase in the micelle core's polarity and concomitant loosening of the core structure because of the interpenetration of ethanol molecules into the hydrocarbon core. A similar interpretation was put forth to explain the observed tendency for a decrease in the microviscosity with alcohol for SDS + 1-hexanol,<sup>14</sup> and for HDTBr + ethanol, 1-propanol, 1-butanol, or *tert*-butyl alcohol.<sup>16</sup>

The estimate of the microviscosity from the pyrene emissions is difficult because the pyrene forms an excimer in an intermolecular manner.<sup>17</sup> However, as is clear in Figures 4 and 5, the ratio  $I_E/I_M$  of pyrene appears to be a qualitative parameter of the microviscosity of the micelle core.

### Conclusion

From our measurements on microviscosities under high pressure, it is concluded that DNP molecules certainly experience an environment whose structure is somewhere between that of a hydrocarbon and water. These results are interpreted to be the results of partial *penetration* of water molecules into the hydrocarbon

core. The changes in the microviscosity with salt and alcohol additions may be explained as the result of *penetration* of the additives into the hydrocarbon core. Recently, Thomas et al.<sup>18,19</sup> estimated the polarity of hydrocarbon core from the fluorescence fine structure of pyrene. They found that the polarity of the environment of the probe was higher than that of pure hydrocarbon, from which the location of the probe was deduced to be near the micelle palisade layer between the core and the water phase. However, their results are also explainable by the water penetration mechanism.<sup>18</sup> We feel that the palisade positioning is conceivable if, say, one side of the pyrene molecule is stabilized by polar dispersion forces and the other side experiences hydrophobic stabilization. Decrease in the *polarity* in the presence of alcohols observed by Zana et al. can be also explained by the *penetration* mechanism of the additives into the micelle core instead of water exclusion and movement of the pyrene probe into the core.<sup>20</sup>

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(16) Turro, N. J.; Tanimoto, Y. *Photochem. Photobiol.* **1981**, *34*, 173.

(17) Miller has overcome this difficulty by an extrapolation technique. See ref 14 above.

(18) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.

(19) Thomas, J. K. *Chem. Revs.* **1980**, *80*, 283.

(20) Lianos, P.; Zana, R. *Chem. Phys. Lett.* **1980**, *76*, 62.

## Singlet Electronic Energy Transfer to Azoalkanes: Separation of Collisional and Long-Range Mechanisms by Steric and Solvent Viscosity Effects<sup>†</sup>

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**Abstract:** Absolute rate constants have been determined for quenching of the fluorescence of naphthalene and triphenylene by azo-*n*-butane (ANB) and azo-*tert*-butane (ATB) in five different hydrocarbon solvents of varying viscosity. The quenching process is attributed to singlet electronic energy transfer by the electron-exchange mechanism. Calculations indicate that energy transfer by the dipole-dipole (long-range) mechanism should be relatively inefficient. The observed rate constants show a linear dependence on reciprocal viscosity and are sensitive to steric effects, both indicative of a collisional mechanism for energy transfer. Rate constants for energy transfer from naphthalene to ANB are faster than those for ATB by a factor of 1.5–1.9. Rate constants for energy transfer from triphenylene exceed diffusion control in high viscosity solvents. It is suggested that a small component of the energy transfer may proceed by the dipole-dipole mechanism, and upper limits to these values are estimated.

Electronic energy transfer reactions have been demonstrated to follow at least three distinct mechanisms:<sup>4,5</sup> (1) "trivial" or radiative energy transfer, in which a photon is emitted by the donor and absorbed by the acceptor; (2) dipole-dipole energy transfer, in which the donor and acceptor transitions are coupled by relatively long-range Coulombic dipole-dipole interactions,<sup>6</sup> and (3) electron-exchange energy transfer, which requires electron-exchange interactions between the donor and acceptor molecular orbitals.<sup>7</sup> Triplet-triplet energy transfer can operate effectively only through the electron-exchange mechanism, while singlet-singlet energy transfer can operate through any of the three mechanisms. The electron-exchange mechanism requires close contact between the donor and acceptor, and steric effects on both triplet-triplet energy transfer<sup>8,9,10</sup> and singlet-singlet energy

transfer<sup>8,11-14</sup> have been demonstrated. In this paper we present rate constants for singlet energy transfer processes which dem-

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(4) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, Calif., 1978; pp 296-361.

(5) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: London, 1970; pp 518-624.

(6) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7-17.

(7) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836-50.

(8) Wamser, C. C.; Medary, R. T.; Kochevar, I. E.; Turro, N. J.; Chang, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 4864-9.

(9) Wallace, W. L.; Van Duyne, R. P.; Lewis, F. D. *J. Am. Chem. Soc.* **1976**, *98*, 5319-26.

(10) Scaliano, J. C.; Wubbels, G. G. *J. Am. Chem. Soc.* **1981**, *103*, 640-5.

(11) Loper, G. L.; Lee, E. K. C. *J. Chem. Phys.* **1975**, *63*, 3779-85.

(12) Loper, G. L.; Lee, E. K. C. *J. Chem. Phys.* **1975**, *63*, 264-71.

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