

# Influence of Binding Strength of Added Electrolytes on the Properties of Micelles and of Micellized Radical Pairs

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*p*-Methyldibenzyl ketone (1), pyrene (2), and 1,3-di- $\alpha$ -naphthylpropane (3) have been employed as probes of the effects of added electrolytes on the properties of micelles and of the effects of an applied magnetic field on the reactivity of micellized radical pairs. The effect of added electrolytes depends on the structure of the surfactant head group, the length of the hydrocarbon chain of surfactants, the added gegenions, and the temperature. The electrolytes added were found to exhibit both a "salt effect" on the physical properties of micelles, which is related to the strength of their binding to the micellar surface, and a "magnetic effect", which is related to the ability of a bound cation to relax the triplet state of a micellized radical pair and thereby modify the reactivity of the pair. In aqueous solutions of anionic surfactants,  $Gd^{3+}$  causes a large magnetic field dependent *internal* magnetic field effect in addition to a salt effect on micellar properties. The internal magnetic field effect is independent of the length of hydrocarbon chain, but is dependent on the surface density of bound  $Gd^{3+}$  ions. The salt effect on micellar properties decreases with the increase of the length of hydrocarbon chain of the surfactants and with the surface density of added ions. In aqueous solutions containing neutral TX-100 micelles or cationic micelles (cetyltrimethylammonium bromide, CTAB),  $Gd^{3+}$  shows only a small salt and a small internal magnetic field effect. Addition of lanthanide salts results in a dramatic increase in the aggregation number of sodium dodecyl sulfate (SDS) micelles, but has a negligible effect on the aggregation number of CTAB micelles. It is suggested that the degree of binding of ions to the surfactant is a decisive factor in determining the effect of electrolytes on the investigated properties of micelles.

## Introduction

Aqueous solutions containing micelles possess an outstanding ability to solubilize organic substrates. The properties of micelles sometimes respond markedly to relatively small concentrations of additives.<sup>1,2</sup> However, understanding the molecular basis of the effects of additives on micellar properties is sometimes very difficult, as many factors contribute to the observed effects of additives on micellar properties, e.g., the molecular structure of the surfactants, the charge (if any) on the surfactant head group, the ionic strength of the solution, the chemical nature of the additives and their concentrations, the pressure,<sup>3</sup> the temperature, and the pH value.<sup>4</sup> The measurement of photochemical and photophysical properties of probes solubilized in micelles allows the determination of *probe parameters* providing us with useful information concerning the *structure and dynamics of micellar aggregates*<sup>5,6</sup> and the influence of additives on *micellar properties*. For example, in an investigation of the effect of hydrocarbon and polar additives (alcohols, in particular), on the size of sodium dodecyl sulfate (SDS) micelles, it was found<sup>7</sup> that the surface charge density is

an important controlling factor in determining the micelle size. In another example, it was found<sup>8</sup> that the aggregation number of SDS micelles and the monomer-micelle exchange frequency are dependent on the ionic strength when NaCl is used as an additive.

Added alkali-metal salts produce a significant effect on the parameters of recombination ("cage") efficiency and exit rates of micellized benzyl radicals produced from the photolysis of dibenzyl ketone (DBK) and its simple derivatives.<sup>2</sup> The measured parameters parallel the strength of binding of the cations to SDS; i.e., the parameters increase in the order of  $Li^+ < Na^+ < K^+ < Cs^+$ . Theoretical calculations show<sup>9</sup> that the charge density of ionic surfactant micelles does not depend on the concentration of simple electrolytes, but the degree of micelle dissociation decreases as the concentration of the salts (NaCl, NaBr) increases. Recent investigations also showed that the size of mixed micelles of SDS and TX-100 are not a simple function of the concentration of NaCl.<sup>10</sup> Paramagnetic lanthanide ions have been reported to show a magnetic field dependent influence on the cage recombination of micellized radical pairs.<sup>11,12</sup> This effect was interpreted as an *internal* magnetic field effect which reverses the effect of the *external* applied field by causing relaxation of the  $T_+$  and  $T_-$  to  $T_0$  and  $S$  states. In understanding these results, questions arise as to how the paramagnetic lanthanide ions affect micellar properties

(1) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1985.

(2) Turro, N. J.; Zimmt, M. B.; Lei, X.-G.; Gould, I. R.; Nitsche, K. S.; Cha, Y. *J. Phys. Chem.* 1987, 91, 4544.

(3) La Mesa, C.; Ranieri, G. A.; Terenzi, M. *J. Surf. Sci. Technol.* 1990, 6, 152.

(4) Dai, Q.; Laskowski, J. S. *Langmuir* 1991, 7 (7), 1361.

(5) Turro, N. J.; Cox, G. S.; Paczkowski, M. A.; Boschke, F. L., Eds. *Photochemistry in Micelles*. In *Topics in Current Chemistry*; Springer-Verlag: New York, 1985.

(6) (a) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: Orlando, 1987. (b) Dederen, J. C.; Van der Auweraer, M.; De Schryver, F. C. *J. Phys. Chem.* 1981, 85, 1198.

(7) (a) Almgren, M.; Swarup, S. *J. Colloid Interface Sci.* 1983, 91, 256. (b) Almgren, M.; Swarup, S. *J. Phys. Chem.* 1982, 86, 4212.

(8) Yamaguchi, T.; Yamauchi, A.; Kimoto, E.; Kimizuka, H. *Bull. Chem. Soc. Jpn.* 1986, 59, 3029.

(9) Kurliand, D. E. *J. Colloid (Russ.)* 1985, XLVII, 705.

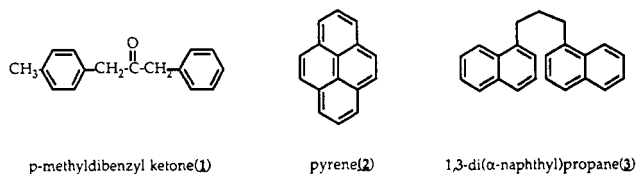
(10) Dubin, P. L.; Principi, J. M.; Smith, B. A.; Fallon, M. A. *J. Colloid Interface Sci.* 1989, 127, 558.

(11) (a) Sakaguchi, Y.; Hayashi, H. *Chem. Phys. Lett.* 1984, 106, 420.

(b) Hayashi, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* 1984, 57, 322. (c) Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem.* 1984, 88, 1437.

(12) Turro, N. J.; Lei, X.-G.; Gould, I. R.; Zimmt, M. B. *Chem. Phys. Lett.* 1985, 120, 397.

such as the aggregation number of surfactants, the extent of the contributions to salt effects and internal magnetic field effects, and the comparison of salt effects for uni- and bivalent ions. As part of a broad investigation of the effects of lanthanide ions on the properties of various micelles, we have employed photochemical reactions and fluorescent molecules as probes. Our purpose is to investigate the dependence of these effects on the strength of the binding of gegenions to the surfactants and on the size of surfactant micelles by examining the influence of additives on the parameters reported by photochemical probes 1–3.



### Experimental Section

**Chemicals.** *p*-Methyldibenzyl ketone (1) and 1,3-di- $\alpha$ -naphthylpropane (3) were prepared according to methods described in a previous paper.<sup>13</sup> Pyrene (2, Fluka) was recrystallized twice from ethanol–cyclohexane (1:1 v/v) or from 95% ethanol (for fluorescence decay measurements). Gadolinium chloride ( $\text{GdCl}_3$ , Aldrich), cetyltrimethylammonium bromide (CTAB, XiZhong Chemical Plant, Beijing), Triton X-100 (BDH, Great Britain), and sodium dodecyl sulfate (SDS, 12-carbon surfactant, Merck or Aldrich) were used as received. Sodium hexadecylsulfate (SHS, 16-carbon surfactant) and sodium octadecyl sulfate (SOS, 18-carbon surfactant) were prepared from their corresponding alcohols via chlorosulfonylation and neutralization.<sup>14</sup> Other chemicals were analytically pure and were used as received. Deionized water was used throughout.

**Photolysis of 1.** Stock solutions of 1 were prepared by ultrasonication and stirring an aqueous surfactant solution containing 1 for 2 h which was then allowed to stand overnight. Appropriate amounts of additives were added to the stock solution to bring the samples to the desired concentrations. Photolyses of the samples were carried out using a 500-W high-pressure mercury lamp in quartz vessels equipped with a thermostat. An argon-purged 1 mM micelle solution of 1 was irradiated in the presence and absence of a 2000-G magnetic field. After extraction with ether, the products (AA, AB, and BB, eq 1, vide infra) were determined quantitatively on a Hitachi GC-9A chromatograph using a SE-30 capillary column.<sup>13a</sup>

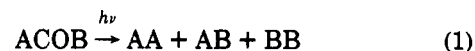
**Fluorescence Spectroscopy of 2 and 3.** Fluorescence spectra were recorded on a Hitachi M850 fluorescence spectrophotometer. The samples for the fluorescence measurement were prepared by adding 2 or 3 to the surfactant solution before ultrasonication. The excitation wavelength for molecule 2 was 335 nm and the  $I_3$  (383 nm) to  $I_1$  (373 nm) and  $I_e$  (488 nm) to  $I_m$  (373 nm) intensity ratios were measured by adjusting the excitation and emission slit widths to 5 and 2 nm, respectively. For 3, the excitation wavelength was 295 nm and the maxima of excimer and monomer emissions were monitored at 420 and 337 nm, respectively.

**Aggregation Number Measurements.** Aggregation numbers were measured by the pyrene excimer method, which involves the extraction of aggregation numbers from fluorescence decay measured by the single photon counting technique.<sup>15</sup> The time-resolved emission measurements were conducted at  $20.0 \pm 0.2$  °C, using a single photon counting unit equipped with an Edinburgh 199F nanosecond flash lamp, Ortec electronics, and a Tracor-Northern TN-1710 multichannel analyzer interfaced to an IBM PS/2 Model 70 computer. The aggregation numbers

were extracted from the fluorescence decay traces by application of a computer program generously provided by Professor F. C. De Schryver of the University of Leuven, Belgium.<sup>6b</sup> In the entire experimental concentration range employed in this study, the fluorescence spectra of pyrene in SDS micelles show strong excimer emission; e.g., at 0.4 mM pyrene concentration (lower than the lowest experimental concentration 0.42 mM) the  $I_e/I_m$  ratios are 0.32 and 0.63, respectively, in the absence and presence of 10 mM of  $\text{GdCl}_3$ .

### Results and Discussion

**The Probe Systems.** The well-studied<sup>16</sup> unsymmetrical ketone *p*-methyldibenzyl ketone (1, eq 1 where A =  $p\text{-MeC}_6\text{H}_4\text{CH}_2$ , and B =  $\text{C}_6\text{H}_5\text{CH}_2$ ) was used as a photochemical probe of micelles. Photolysis of 1 in homogeneous solutions gives (eq 1) nearly a quantitative yield of diphe-



nylethanes.<sup>17</sup> The paradigm mechanism for the formation of diphenylethanes from dibenzyl ketone serves as the model for the photolysis of 1 as follows:  $\alpha$ -cleavage of 1 occurs from its triplet state, yielding a primary triplet geminate arylacetyl, i.e., benzyl radical pair, which can regenerate the ketone after intersystem crossing followed by recombination, or can form a secondary geminate arylbenzyl radical pair through decarbonylation. The secondary geminate arylbenzyl radical pair can undergo cage recombination to form AB or diffuse out of the cage to form free radicals which then combine statistically to yield AA, AB, and BB. Irradiation of 1 in homogeneous non-viscous solvents (e.g., water, benzene) yields a statistical mixture of coupling products expected for a “zero” cage effect; i.e., AA:AB:BB = 1:2:1. It is only the reactions of the secondary radical pair leading to the products of eq 1 that concern us in this paper. Addition of surfactants to an aqueous solution of 1 causes an enhancement of the yield of AB.<sup>18</sup> This measured enhancement can be converted to a useful probe parameter, the “percent cage effect”, to monitor the properties of the micelle. The percent cage effect is defined in terms of the measured yields of the products given in eq 2.<sup>19</sup> In our studies, we have used percent cage effect to evaluate the micelle properties such as solubilizing ability and volume and their response to environmental effects.

$$\% \text{ CE} = \frac{\text{AB} - (\text{AA} + \text{BB})}{\text{AB} + (\text{AA} + \text{BB})} \times 100 \quad (2)$$

Pyrene (2) and 1,3-di- $\alpha$ -naphthylpropane (3) were employed as fluorescence probes. The  $I_3$  to  $I_1$  intensity ratio ( $I_3/I_1$ ) and the excimer to monomer intensity ratio ( $I_e/I_m$ ) of 2 are widely used as probe parameters for evaluating the polarity of the pyrene probe environments and the pyrene intermolecular collision probability, respectively.<sup>6</sup> The latter ratio depends both on pyrene concentration and on the microviscosity of the medium. The intramolecular excimer to monomer fluorescence intensity ratio of 3 is used as a parameter of environmental microviscosity.<sup>6</sup>

Gadolinium chloride was reported<sup>12</sup> to show the maximum internal magnetic field effect among the lanthanide chlorides owing to its seven unpaired electrons and thus

(16) Turro, N. J.; Graetzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 675.

(17) (a) Engel, P. S. *J. Am. Chem. Soc.* 1970, 92, 6047. (b) Robbins, W. K.; Eastman, R. H. *J. Am. Chem. Soc.* 1970, 92, 6076, 6077.

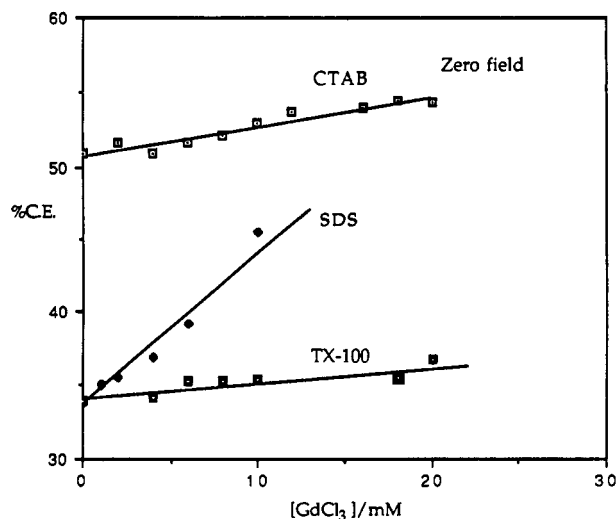
(18) Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* 1978, 100, 7431.

(19) Turro, N. J.; Weed, G.; Cheng, C. C. *J. Am. Chem. Soc.* 1983, 105, 6347.

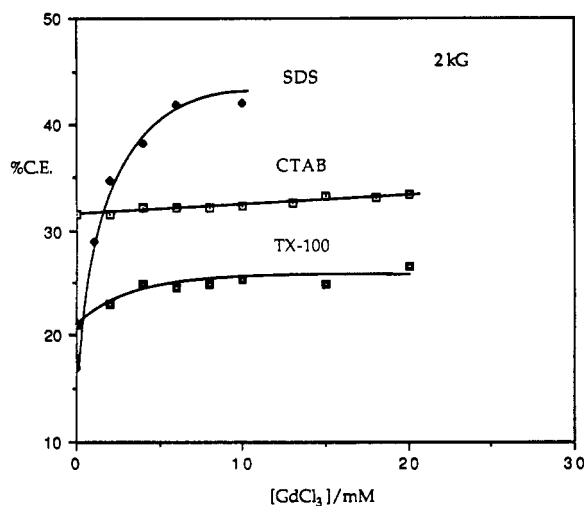
(13) (a) Lei, X.-G.; Tang, X.-D.; Liu, Y.-C.; Turro, N. J. *Langmuir* 1991, 7, 2872. (b) Lei, X.-G.; Liu, Y.-C. *Chin. J. Chem.* 1990, 3, 65.

(14) Jerchel, D.; Becker, H.; Varahamurti, M. K. *Z. Naturforsch.* 1956, 11b, 681; *Chem. Abstr.* 1957, 51, 12166f.

(15) (a) Lianos, P.; Zana, R. *J. Phys. Chem.* 1980, 84, 3339. (b) Lianos, P.; Lang, J. *J. Colloid Interface Sci.* 1983, 96, 222.



**Figure 1.** Percent cage effect in the photolysis of 1 in micelles in the earth's magnetic field as a function of  $[GdCl_3]$ .  $[SDS] = 70$  mM;  $[TX-100] = 70$  mM;  $[CTAB] = 25$  mM.



**Figure 2.** Percent cage effect in the photolysis of 1 in micelles at 2 kG as a function of  $[GdCl_3]$ .  $[SDS] = 70$  mM;  $[TX-100] = 70$  mM;  $[CTAB] = 25$  mM.

is used as a representative high-valence cation in investigating magnetic effects. These results are compared to those obtained with other lower valence metal cations such as  $Na^+$  and  $Mg^{2+}$ , and for  $La^{3+}$ , a nonmagnetic lanthanide. In all the experiments, unless noted, the surfactant concentration was above the cmc, the actual concentrations being listed in the figures or table.

**Cage Effect as a Function of Concentration of  $GdCl_3$ .** Figures 1 and 2 show the percent cage effect produced upon photolysis of 1 in SDS, CTAB, and TX-100 aqueous solutions as a function of concentration of added  $GdCl_3$  in the absence (Figure 1) or the presence (Figure 2) of an applied magnetic field of 2 kG. The percent cage effect measures the competition between the diffusive escape of hydrophobic radicals from the micelle and their geminate recombination in the micelle. The recombination process has been shown<sup>2</sup> to be more or less insensitive to micellar properties, whereas the diffusional escape process has been found to be quite sensitive to micellar properties such as hydrophobicity and volume. The cage effect thus reflects the strength of "solubility" of the probe radicals. From the data in the figures, the following observations stand out: (1) the sensitivity of the cage effect (slopes of the figures) to added  $Gd^{3+}$  is much greater for SDS micelles than for CTAB or TX-100 micelles, either

in the earth's field or in the presence of a 2000-G field; (2) in each type of micelle the effect of an increase in the magnetic field is to decrease the cage effect; (3) only for SDS does the system "recover" from the reduced cage effect when  $Gd^{3+}$  is added. More specifically, addition of 5 mM of  $GdCl_3$  to SDS causes a slight increase in the cage effect from ca. 34% to 38%, which is attributed to a small "salt" effect in the earth's field, but a significant increase from 17% to 38% attributed both to the salt effect and to the internal magnetic field effect is observed in the presence of a 2-kG field. In contrast, in the case of TX-100 and CTAB micelles addition of  $Gd^{3+}$  causes only a small increase in the percent cage effect. The ratios of the increments of percent cage effect per addition of unit  $GdCl_3$  to the percent cage effect in the absence of salt are about the same in the two cases. These results demonstrate that the internal magnetic field effect is much weaker for cationic and neutral micelles relative to anionic micelles.

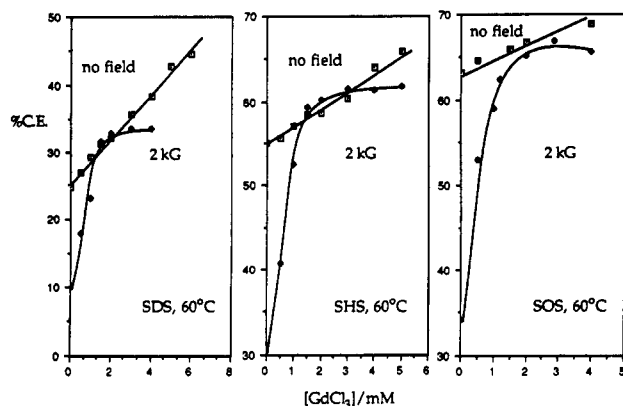
The above results may be correlated to the binding strength of  $Gd^{3+}$  to the micelles. Gadolinium ions associate strongly with SDS anions by electrostatic interactions, but there are only weak interactions of any type with the neutral TX-100 micelles, and the interaction is repulsive with CTAB cations. Thus, the binding strengths decrease in the order of  $SDS \gg TX > CTAB$ . Moreover, the strength of the binding of cations to SDS anions parallels the valence of the cations.<sup>20</sup> Because of its trivalent positive charge,  $Gd^{3+}$  has a much stronger binding than  $Na^+$  to anionic SDS micelles; as a result,  $Gd^{3+}$  shows a salt effect ca. 25 times as large as that of  $Na^+$  (compare this result with that in ref 2). Differences in binding can also be shown from the following observation: in a 70 mM aqueous solution of SDS, the quantities of salts which cause turbidity of the solution at room temperature are 10 mM for  $GdCl_3$  and 30 mM for  $MgCl_2$ , while no turbidity is observed when 3 M of  $NaCl$  is added. It has been reported that large monovalent cations, such as  $Rb^+$  and  $Cs^+$ , or multivalent cations, such as  $Cu^{2+}$  and  $Cr^{3+}$ , are much more strongly adsorbed on the SDS micelle surface than small monovalent cations  $H^+$  and  $Li^+$ .<sup>21</sup> These results suggest that only those cations which are strongly associated with the surface of the micelle can exert their maximum effect on the recombination of micellized radical pairs. These observations coincide with previous results<sup>2</sup> and those of the theoretical calculations.<sup>9</sup>

**Dependence of  $Gd^{3+}$  Effects on Anionic Micelle Size.** The effects of  $Gd^{3+}$  on the recombination of radical pairs in the absence or presence of an external magnetic field have also been investigated (Figure 3) in aqueous solutions containing anionic surfactants of different alkyl chain lengths, i.e., SDS ( $C_{12}$ ), sodium hexadecyl sulfate, SHS ( $C_{16}$ ), and sodium octadecyl sulfate, SOS ( $C_{18}$ ) (Figure 3). Formation of micelles for all these surfactants was measured at elevated temperatures (60 °C) because of Krafft point considerations.<sup>1</sup> The experiments were run at concentrations much higher than those for the reported<sup>22</sup> cmcs [ $1 \times 10^{-2}$  M (SDS, 60 °C),  $5.8 \times 10^{-4}$  M (SHS, 40 °C)]. Interestingly, from Figure 3 it can be seen that the cage effects observed at elevated temperatures are comparable to those obtained at room temperature. In the earth's magnetic field, the cage effect at zero concentration of  $GdCl_3$  increases with increasing the length of the hydrocarbon chain, as expected from simple considerations

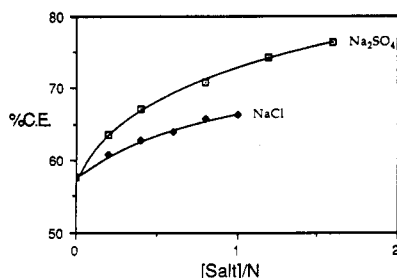
(20) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley-Interscience: New York, 1978.

(21) Hafiane, A.; Issid, I.; Lemordant, D. *J. Colloid Interface Sci.* 1991, 142 (1), 167.

(22) Critical Micelle Concentrations of Aqueous Surfactant Systems. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.)* 1971, 36227.



**Figure 3.** Percent cage effect in the photolysis of 1 in various sizes of micelles at 2 kG as a function of  $[\text{GdCl}_3]$  in the presence and absence of a magnetic field. The concentration of surfactants is 50 mM in all cases.



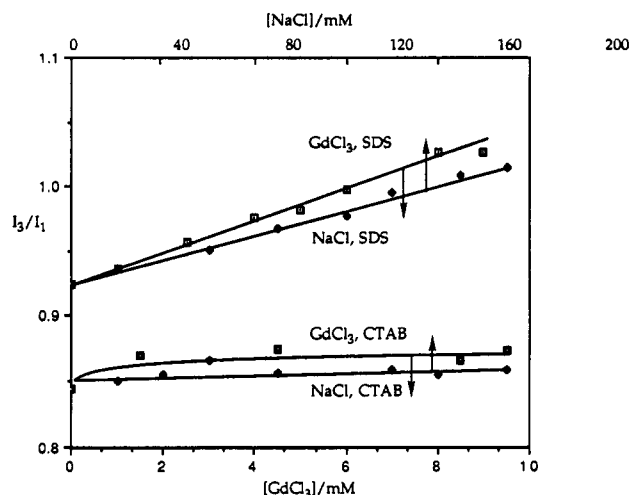
**Figure 4.** Percent cage effect in the photolysis of 1 in aqueous solutions of 25 mM CTAB as a function of added NaCl and  $\text{Na}_2\text{SO}_4$  (normal concentrations).

of micelle volume and hydrophobicity;<sup>2</sup> i.e., the micelle size increases with increasing length of alkyl chain of surfactant, and the larger micelles have larger cores and are therefore more hydrophobic.

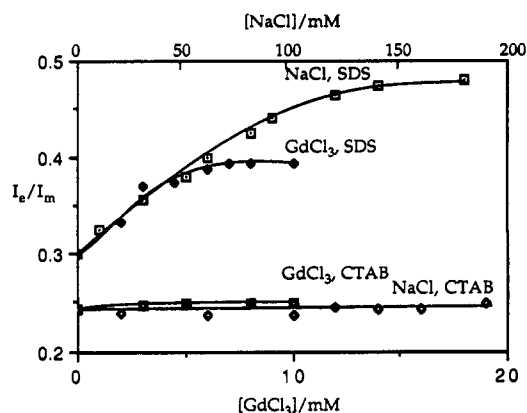
The magnitude of the slope of a plot of the cage effect versus  $[\text{Gd}^{3+}]$  at the earth's field is a measure of the contribution of the salt effect by  $\text{Gd}^{3+}$ , since the magnetic contribution is negligible under these conditions (Figure 3). A salt effect is observed in all three micelles when  $\text{GdCl}_3$  is added. Perhaps the most interesting result is that the salt effect of  $\text{Gd}^{3+}$  decreases with the increase in the length of the hydrocarbon chain; i.e., the slopes of percent cage effect vs  $[\text{GdCl}_3]$  plots are 3.6, 2.0, and 1.6  $\text{mM}^{-1}$ , respectively, for SDS, SHS, and SOS micelles. An interesting empirical observation is that if we multiply these values by the square number of carbons of the corresponding surfactant hydrocarbon chain (12, 16, and 18), a constant value of 520 is obtained. This correlation is expressed in eq 3, where % CE and %  $\text{CE}_0$  represent the percent cage effects in the presence and absence of  $\text{GdCl}_3$ , respectively, while  $C_n$  represents the number of carbons of the alkyl chain of the corresponding surfactants.

$$\% \text{ CE} = \% \text{ CE}_0 + 520[\text{GdCl}_3]/[C_n]^2 \quad (3)$$

Since the cmc decreases, but the aggregation number  $N$  increases with increasing the length of alkyl chain of the surfactants, the number of micelles in 50 mM of the three surfactants will be nearly the same. Thus, the above result qualitatively implies that the effect of  $\text{Gd}^{3+}$  on the percent cage effect is inversely proportional to the square of the radius of the micelle. In the presence of an external magnetic field, however, there is no observable difference between the effect of  $\text{Gd}^{3+}$  on the percent cage effect of radical pairs in micelles of different chain length (Figure 3). Thus, 1.5 mM of  $\text{GdCl}_3$  cancels the external magnetic



**Figure 5.** Fluorescence parameters  $I_3/I_1$  of pyrene as a function of the concentration of added electrolytes.  $[\text{SDS}] = 70 \text{ mM}$ ;  $[\text{CTAB}] = 25 \text{ mM}$ .



**Figure 6.** Fluorescence parameters  $I_e/I_m$  of 3 as a function of the concentration of added electrolytes.  $[\text{SDS}] = 70 \text{ mM}$ ;  $[\text{CTAB}] = 25 \text{ mM}$ . The absolute value of the monomer intensity decreases and the absolute value of the excimer intensity increases in the case of NaCl,  $\text{GdCl}_3$ , and SDS.

field effect completely for all the micelles investigated. However, the effect increases with the increase in the  $[\text{GdCl}_3]$  to  $[\text{surfactant}]$  ratio, indicating that the effect is proportional to the  $\text{Gd}^{3+}$  density on the surface of the micelles. It appears that  $\text{Gd}^{3+}$  screens the external magnetic field effect. The total effect of  $\text{Gd}^{3+}$  in the presence of an external magnetic field is not the sum of the salt effect and the internal magnetic field effect. In addition, the slope of the plots for experiments run in a 2-kG field is smaller than those at the earth's field; i.e., the salt effect is almost canceled as the concentration of  $\text{GdCl}_3$  is larger than 1.5 mM.

**Effects of NaCl and  $\text{Na}_2\text{SO}_4$  on CTAB Micelles.** For comparison with the effect of cations of different valences on anionic micelles, we have measured the dependence of the percent cage effect for CTAB micelles on the anions of different valences. Figure 4 shows some typical results. The trends are similar to those for NaCl and  $\text{MgCl}_2$  as additives to SDS<sup>2</sup> and TX-100<sup>13a</sup> micelles. However,  $\text{SO}_4^{2-}$  shows a somewhat larger effect than  $\text{Cl}^-$  on the basis of the normal concentration. In addition, the magnitude of the effect of NaCl and  $\text{Na}_2\text{SO}_4$  in CTAB are intermediate to those for NaCl and  $\text{MgCl}_2$  in TX-100 and in SDS. For example, for a 5% increase in the percent cage effect, the quantities (mM) of the salt required are 20 ( $\text{MgCl}_2$ ) and 80 (NaCl) for SDS micelles, 120 ( $\text{Na}_2\text{SO}_4$ ) and 370 (NaCl) for CTAB micelles, and 250 ( $\text{MgCl}_2$ ) and 570 (NaCl) for

Table I. Aggregation Number vs Additive Concentration

SDS		CTAB							
[NaCl], mM	<i>N</i>	[MgCl <sub>2</sub> ], mM	<i>N</i>	[GdCl <sub>3</sub> ], mM	<i>N</i> ( $\tau$ ) <sup>b</sup>	[LaCl <sub>3</sub> ], mM	<i>N</i> ( $\tau$ ) <sup>b</sup>	[GdCl <sub>3</sub> ], mM	<i>N</i> ( $\tau$ ) <sup>b</sup>
0.0	62, <sup>a</sup> 57	0.0	62, <sup>a</sup> 57	0.0	57 (182)	0	57 (182)	0.0	48 (168), 60 <sup>c</sup>
50	77 <sup>a</sup>	4	72 <sup>a</sup>	5	114 (177)	5	96 (182)		
100	88 <sup>a</sup>	8	80 <sup>a</sup>	7.5	124 (134)				
		20	91 <sup>a</sup>	10	171 (135)	10	136 (187)	10	51 (160)

<sup>a</sup> From ref 2. <sup>b</sup> Lifetime of pyrene. <sup>c</sup> From ref 4.

TX-100 micelles. If we take the [salt]/[surfactant] ratio into consideration, the effect of anions on CTAB will be close to those of cations on TX-100 micelles, indicating that the strength of binding of ions to the head group of surfactant is the controlling factor for the additive effect; i.e., the ammonium ion has a much smaller binding ability for anions than the sulfate anions of the SDS have for cations.<sup>22</sup>

**Additive Effects on the Fluorescence of Micellized Pyrene and 1,3-Di- $\alpha$ -naphthylpropane.** Figures 5 and 6 show the effect of (1) the  $I_3/I_1$  ratio of monomer fluorescence vibrational maximum of the 0-2 band ( $I_3$ ) to the maximum of the 0-0 band ( $I_1$ ) intensity and (2) intramolecular excimer to monomer intensity ratio ( $I_e/I_m$ ) of molecule 3 in SDS and CTAB aqueous solutions as a function of concentration of added NaCl and GdCl<sub>3</sub>.

From Figure 5, for SDS a linear correlation between the  $I_3/I_1$  ratio (polarity parameter) and the concentration of the additives is observed. Since the  $I_3/I_1$  ratio increases with decreasing environmental polarity,<sup>23</sup> this indicates that the interior micellar polarity decreases with increasing concentration of electrolytes. In the case of CTAB, however, the  $I_3/I_1$  ratio shows an initial increase and then remains constant as the concentration of the salts increases. The plots reveal that the effect of electrolytes on SDS, again, is much larger than on CTAB. In addition, the effect for Gd<sup>3+</sup> is 25 times as large as that for Na<sup>+</sup>.

As with the other parameters, both the intermolecular  $I_e/I_m$  ratio (viscosity parameter) of pyrene and the intramolecular  $I_e/I_m$  ratio of 3 show a much larger dependence on the concentration of electrolytes in SDS than in CTAB (Figure 6). These results confirm the conclusions of the other results; i.e., the strength of binding of the cations to the surfactant predominates the effects.

It is well known that the properties of micelles may be significantly altered by additives which serve to modify the micelle structure and/or the dynamics of the solubilized substrates.<sup>1,20</sup> The structural characteristics include the shape and the size (proportional to the aggregation number) of micelles, while the dynamics refer to the rates of intersystem crossing and escape of radical pairs from the micelles.<sup>24</sup> The latter is controlled by combination of factors such as micelle structure, interior micellar microviscosity, and hydrophobicity. A decrease in the interior micellar polarity will result in an increase in the hydrophobicity of the micelle. As a result, the exit rate of the radical pairs decreases and the cage effect increases. The influence of alkali-metal ions on the cage recombination has mainly been attributed to the increase in the aggregation number of SDS micelles,<sup>2,22</sup> although the salts may induce displacement of the probes from the micelle

surface.<sup>25</sup> The  $I_e/I_m$  ratios of 2 and 3 serve as a measure of microviscosity of the medium.<sup>4,26</sup> Upon addition of electrolytes, the decrease in the interior microviscosity will cause an increase in the exit rate of the radical pair, which will reduce the cage effect. In micelles, on the other hand, the intermolecular  $I_e/I_m$  ratio of 2 is also proportional to the aggregation number.<sup>27</sup> Since Gd<sup>3+</sup> produces (Figure 6) an effect on both the  $I_3/I_1$  ratio and  $I_e/I_m$  ratio of pyrene which is 25 times as large as that by Na<sup>+</sup>, and the effect of Gd<sup>3+</sup> on the  $I_e/I_m$  ratio of 3 is 10 times as large as that produced by Na<sup>+</sup>, it is concluded that Gd<sup>3+</sup> has a much larger effect than Na<sup>+</sup> on the aggregation number of anionic micelles.

**Additive Effect on the Aggregation Numbers of Micelles.** Aggregation numbers *N* of SDS and CTAB micelles in the absence and in the presence of some of the electrolytes were measured by the "pyrene excimer" method<sup>15</sup> and are listed in Table I. It is seen that the effect of trivalent cations on the *N* of SDS is much larger than that produced by univalent cations or bivalent Mg<sup>2+</sup>; e.g., the effect of Gd<sup>3+</sup> and La<sup>3+</sup> is 20 times as large as that by Na<sup>+</sup>. Addition of 5 mM of GaCl<sub>3</sub> or LaCl<sub>3</sub> causes increases in the *N* of SDS from ca. 60 to 114 and 96, respectively, while addition of 100 mM of NaCl results in an increase in *N* to only 90. However, as expected, Gd<sup>3+</sup> has a negligible effect on the *N* of CTAB since it does not bind to the cationic micelles.

The measured lifetime of pyrene in SDS upon addition of 10 mM of LaCl<sub>3</sub> is the same as that in pure SDS micelles and is close to those reported in the literature,<sup>28</sup> but decreases as GdCl<sub>3</sub> is added to the system. This quenching of pyrene fluorescence by Gd<sup>3+</sup> may cause a loss of accuracy of the values of *N* for SDS.

The surface charge density<sup>7</sup> is an important controlling factor for micelle size in the SDS-hydrocarbon and SDS-alcohol systems. An increase in the aggregation number will result in an increase in the dissociation of the surfactant until the number of ionic heads per surface area is about the same as in the original micelle. It is not clear how to reconcile this proposal with our results. The additive effects of the electrolytes parallel their ability to cause turbidness (increase in micelle size) and coincide with our previous results<sup>2</sup> and theoretical calculations;<sup>9</sup> i.e., added electrolytes cause a decrease and not an increase in the degree of dissociation of micelles.

## Conclusion

Scheme I shows a representation of the major conclusions of these investigations. The basic conclusion is the stronger binding, per gegenion added, the larger the micelle. The micelle may be made larger by simple structural change in the length of the surfactant or by adding simple electrolytes. The size of the micelle increases more rapidly,

(23) (a) Kalanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* 1977, 99, 2039. (b) Dong, D.; Winnik, M. A. *Photochem. Photobiol.* 1982, 35, 17.

(24) (a) Turro, N. J.; Zimmt, M. B.; Gould, I. R. *J. Am. Chem. Soc.* 1983, 105, 6347. (b) Gould, I. R.; Zimmt, M. B.; Turro, N. J.; Baretz, B. H.; Lehr, G. E. *J. Am. Chem. Soc.* 1985, 107, 1607.

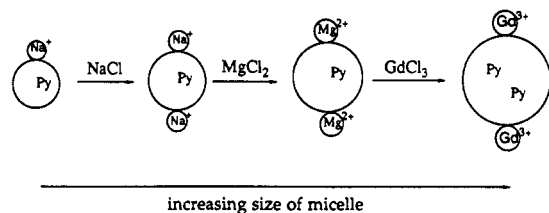
(25) Abuin, E. B.; Lissi, E.; Casal, H. L. *J. Photochem. Photobiol., A* 1991, 57, 343.

(26) Zachariasse, K. A. *Chem. Phys. Lett.* 1978, 57, 429.

(27) (a) Infelta, P. P.; Graetzel, M. *J. Chem. Phys.* 1979, 70, 179. (b) Atik, S. S.; Nam, M.; Singer, L. A. *Chem. Phys. Lett.* 1979, 67, 75.

(28) Lianos, P.; Zana, R. *J. Colloid Interface Sci.* 1981, 84, 100.

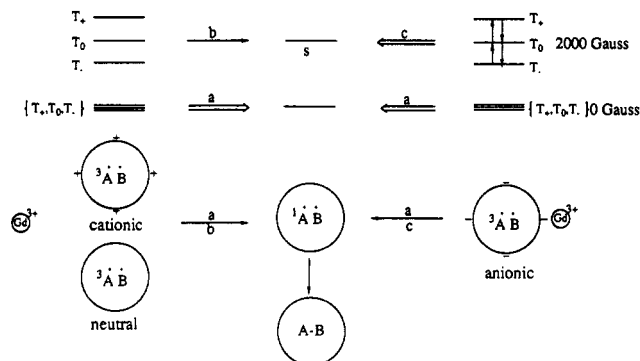
**Scheme I. Qualitative Description of the Effect of SDS Micelle Size as the Addition of an Equal Quantity of SDS and of Cations of Different Valence**



per gegenion, as the valence of the gegenion increases. In Scheme I this conclusion is shown in terms of the pyrene probe which reports polarity, viscosity, and size features of the micelles. From a given situation for SDS, the pyrene experiences a relatively polar environment and relatively low excimer formation. This results from the relatively small micelle size, which forces the pyrene to be sited near the micelle surface. Adding  $\text{Na}^+$  will cause the micelle size to increase somewhat, adding the same concentration of  $\text{Mg}^{2+}$  will cause a larger increase, and adding the same concentration of  $\text{Gd}^{3+}$  will cause the largest increase in micellar size. In Scheme I, the increasing micellar size is depicted as affecting the pyrene probe by moving its equilibrium site further into the hydrophobic core and by allowing more than one pyrene to occupy a micelle. If one replaces pyrene with a pair of benzyl radicals from 1, the increasing size of micelles causes an increase in the cage effect.

Scheme II depicts the interpretation of the results for the magnetic effects of  $\text{Gd}^{3+}$  on radical pair reactivity. In the earth's field or in an applied magnetic field of 2000 G for TX-100 and CTAB micelles, intersystem crossing is not influenced by the presence of  $\text{Gd}^{3+}$  ions, because they

**Scheme II. Proposed Mechanism for the Magnetic Field Effect Dependence on the Binding of  $\text{Gd}^{3+}$  to the Micelles**



do not bind strongly to the micelle surface. In the case of SDS, however, the strong binding does not influence the cage as strongly in the earth's field because intersystem crossing is too fast from the strongly mixed triplet to the singlet. When the intersystem crossing is slowed down by the presence of a magnetic field, the strongly bound  $\text{Gd}^{3+}$  ions can relax the triplet levels and assist intersystem crossing to the singlet.

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**Registry No.** 1, 35730-02-0; 2, 129-00-0; 3, 14564-86-4; TX-100, 9002-93-1; SDS, 151-21-3; CTAB, 57-09-0; NaCl, 7647-14-5;  $\text{Na}_2\text{SO}_4$ , 7757-82-6.