Critical Micelle Concentration. A Transition Point for Micellar Size Distribution

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A critical concentration is defined which separates two kinds of behavior of the size distribution of micellar aggregates of surfactant molecules. Below this concentration, the size distribution is a monotonic decreasing function of size; above this concentration, the size distribution is a function exhibiting two extrema and the contribution of larger aggregates becomes important. Quantitative results are obtained from the condition of thermodynamic equilibrium, decomposing the standard chemical potential per amphiphile of various aggregates into size-dependent and size-independent terms, and using for these terms the empirical expressions given by Tanford.

Introduction

Micellization has been treated either as a stepwise association phenomenon or as a phase transition process.[1,2] In the first approach the micellar aggregates and the single molecules of surfactant are assumed to be in association–dissociation equilibrium and the law of mass action is applied. The critical micelle concentration (cmc) is defined as the concentration above which any added surfactant molecules appear with high probability as micellar aggregates. In the latter approach, micellization is regarded as a phase separation starting at cmc which now represents the saturation concentration of the phase containing single molecules of surfactant. Although both approaches can explain some features of the micelle formation, the available experimental evidence seems to be in agreement with the first of these. In the region close to the cmc, the physico-chemical properties do indeed change rapidly, but continuously, and the concentration of the single surfactant molecules increases slowly. The addition of surfactant above the cmc not only leads to an increase in the number of aggregates but also gives rise to larger average sizes of the aggregates. It is therefore reasonable to assume that for all concentrations of surfactant there are micellar aggregates of various sizes. At low concentrations, however, the number and size of these aggregates is small. As the concentration increases, both the number and the average size of the aggregates increase. The particular kind of behavior occurring at cmc is caused by an essential change in the shape of the size distribution of the aggregates; above the cmc the participation of the larger sizes is more important.

The model suggested here is similar to that provided by the first approach. The nature of the transition taking place at cmc is, however, better identified. In the present paper it is shown that at low concentrations of surfactant the size distribution of the aggregates is a monotonic decreasing function of the size. As the concentration increases, the size distribution of the aggregates changes from a monotonic decreasing function to one which has two extrema, a minimum and a maximum.

From this description a well-defined critical concentration emerges as that total amphiphile concentration corresponding to a transition from the monotonic decreasing size distribution function to a size distribution function exhibiting two extrema. This critical concentration corresponds to a surfactant solution with no appreciable amount of aggregates, whereas the cmc, as defined in the earlier papers based upon the first approach, corresponds to systems with about 5–10% of amphiphiles in micellar form. Hence, the critical concentration defined here as the transition point separating the two different behaviors of the aggregate size distribution function constitutes a close lower bound on the observed value of the cmc.

In the present paper the equilibrium condition defined by the minimum of the total free energy determines the size distribution of aggregates for a given concentration of the single surfactant molecules. The standard chemical potential per amphiphile of aggregates is decomposed into size-independent and size-dependent parts for which the empirical expressions given by Tanford[3] are used. The value of the critical concentration is computed as the concentration for which the size distribution curve has an inflection point. More refined computations, based on statistical mechanics, following the methods of Poland and Sheraga[4] and of Hoeve and Benson,[5] will be published in another paper.

Thermodynamic Formulation

The standard chemical potential of a single molecule of the solvent is denoted by μ_S and that of a single molecule of amphiphile in the aqueous medium by μ_A. The number of molecules of the solvent and the monomeric amphiphile are denoted by N_S and N_A, respectively, and the number of aggregates containing g molecules each by N_g. The standard chemical potential of the micelle per amphiphile is separated into two components: one is independent of the size of the aggregate and the second is size dependent. The size-independent part of the standard chemical potential for a single amphiphile, μ_B, accounts for the liquidlike behavior of the micellar interior made up of hydrocarbon tails of amphiphiles. The size of the aggregate and the compactness of the packing of the amphiphiles affect the repulsive interactions between the head groups, as well as the magnitude of the hydrocarbon surface area exposed to the aqueous medium which does not take part in the hydrophobic bonding. The size-dependent part of the standard chemical potential accounts for these contributions and is denoted by μ_g for an aggregate of size g.

Assuming ideal behavior of the solution, the free energy of the system is given by

$$\Phi = N_S\mu_S + N_A\mu_A + \sum_{g=2}^{\infty} N_g(\mu_B g + \mu_g) +$$

$$kT\left[N_S\ln\frac{N_S}{F} + N_A\ln\frac{N_A}{F} + \sum_{g=2}^{\infty} N_g\ln\frac{N_g}{F}\right] \quad (1)$$

where

$$F = N_S + N_A + \sum_{g=2}^{\infty} N_g \quad (2)$$

k is the Boltzmann constant and T the absolute temperature. The total number of amphiphiles present as monomer and as aggregates is

$$N = N_A + \sum_{g=2}^{\infty} gN_g = \text{constant} \quad (3)$$

The equilibrium condition leads to the equation

$$-g\mu_A + g\mu_B + \mu_g + kT\left(-g\ln\frac{N_A}{F} + \ln\frac{N_g}{F}\right) = 0 \quad (4)$$

which can be rewritten as

$$\frac{N_g}{F} = \left(\frac{N_A}{F}\right)^g \exp\left(-\left[\frac{1}{kT}[(\mu_B - \mu_A)g + \mu_g]\right]\right) \quad (5)$$

Denoting by ξ the quantity

$$\xi = \left(\frac{N_A}{F}\right)\exp\left[-\left(\frac{\mu_B - \mu_A}{kT}\right)\right] \quad (6)$$

the size distribution function is expressed in the form

$$\frac{N_g}{F} = \xi^g \exp\left[-\left(\frac{\mu_g}{kT}\right)\right] \quad (7)$$

The decomposition of the standard chemical potentials per amphiphile of the aggregates permits the size distribution function to be written as a product of $\exp[-(\mu_g/kT)]$, which is a decreasing function of g, and another factor containing the size independent quantity ξ. If ξ is small, the size distribution is a monotonic decreasing function of g. If, however, ξ is sufficiently large compared to unity, the size distribution can have a maximum. Therefore, a critical value of ξ exists, separating the two kinds of behavior. To compute this critical value as well as the corresponding critical concentration of amphiphile, explicit expressions for the terms of the standard chemical potentials are needed.

Explicit Expressions for the Free Energy Terms

The size-independent free-energy change $\mu_B - \mu_A$ corresponds to the change in the standard free energy in transferring an amphiphile from the dilute aqueous phase to the hydrocarbon phase of the micellar core. The transfer of an amphiphile into a micelle differs from the transfer into a bulk hydrocarbon phase because of the orientation of the amphiphile within the micelle with the head groups in contact with the aqueous medium. This free-energy change has significantly different values for ionic and nonionic micelles and also depends on the specificity of the hydrophilic head groups.

For illustrative purposes, the expression given by Tanford[3b] is used for the size-independent part $\mu_B - \mu_A$ of the standard free-energy change.

In general, for an alkyl chain with n_c carbon atoms

$$\frac{\mu_B - \mu_A}{kT} = \frac{S + I(n_c - 1)}{RT} \quad (8)$$

where R has a value of 2 cal/mol K. The subtraction of

unity from n_c here accounts for the fact that the CH_2 group closest to the hydrophilic head group lies in its hydration sphere and, hence, does not contribute to the hydrophobic bonding energy. The term I depends upon the character of the head group. For nonionic head groups, it is virtually constant at a value of -700 cal/mol while for ionic head groups, it may be taken as having a value of approximately -420 cal/mol. The term S depends upon the specificity of the head group, particularly for nonionic micelles, but may be assumed to be of the order of -2000 cal/mol.

The size-dependent term μ_g/kT includes (a) the decrease in attractive hydrophobic bonding between hydrocarbon tails of amphiphiles, due to their partial exposure to the aqueous medium, and (b) the repulsive interaction between the hydrophilic head groups of the amphiphiles. This repulsive interaction is caused by steric repulsion between head groups in nonionic micelles and by electrical repulsion between the ionic head groups in ionic micelles.

The positive standard free-energy contribution due to contact between hydrocarbon tails of amphiphiles and the aqueous medium is given by Tanford[3b] as

$$\frac{\mu_g^I}{kT} = \frac{25(A - 21)g}{RT} \quad (9)$$

where A is the surface area in (ångstroms)^2 per amphiphile in an aggregate of size g. For a spherical aggregate of radius r_0

$$A = \frac{1}{g}4\pi r_0^2 \quad (10)$$

The radius r_0 of the aggregate, calculated from the volume v_0 of the amphiphile, is

$$r_0 = \left(\frac{3v_0}{4\pi}\right)^{1/3}g^{1/3} = \beta g^{1/3} \quad (11)$$

The volume of the hydrocarbon tail of an amphiphile is determined from[3b]

$$v_0 = 27.4 + 26.9n_c \text{ Å}^3 \quad (12)$$

The assumption of a spherical shape for the micelle is not a restrictive one and is used here for the sake of simplicity only. Any other shape of the aggregate or even changes in the shape of the aggregates with the growth in size can be incorporated in the formulation.

The second contribution to the size-dependent standard free-energy term arises from the repulsive head group interactions. The magnitude of this interaction depends on the separation between the head groups; the available area per head group is used as a measure of this separation. Tanford has shown[3b] that an expression of the form

$$\frac{\mu_g^{II}}{kT} = \frac{\alpha}{ART}g \quad (13)$$

can be used to represent this interaction, where α is a constant independent of g. The constant α has different values for ionic and nonionic micelles and depends, among other parameters, on the nature of the hydrophilic head group and the ionic strength. The size-dependent part of the free energy can now be written in the form

$$\frac{\mu_g}{kT} = \frac{25(A - 21)g}{RT} + \frac{\alpha g}{ART} \quad (14)$$

Expression for Critical Concentration

The value of the parameter ξ at which the size distribu-

tion function N_g/F has a point of inflection is denoted as ξ_{crit} and the corresponding value of the aggregation number is denoted as g_{crit}. The values of ξ_{crit} and g_{crit} are obtained from the solution of the system of equations

$$\frac{d}{dg}\left(\ln\frac{N_g}{F}\right) = \ln\xi - \frac{d}{dg}\left(\frac{\mu_g}{kT}\right) = 0 \quad \text{at } g = g_{crit} \quad (15a)$$

and

$$\frac{d^2}{dg^2}\left(\ln\frac{N_g}{F}\right) = -\frac{d^2}{dg^2}\left(\frac{\mu_g}{kT}\right) = 0 \quad \text{at } g = g_{crit} \quad (15b)$$

Substituting expression 14 for the size-dependent free-energy term μ_g and eq 10 and 11 for the surface area A per amphiphile in eq 15a and 15b yields for the inflection point

$$\left(\ln\xi + \frac{525}{RT}\right) - \left(\frac{25}{RT}\right)\left(\frac{2}{3}\right)4\pi\beta^2 g^{-1/3} -$$
$$\left(\frac{\alpha}{RT}\right)\left(\frac{4}{3}\right)\frac{1}{4\pi\beta^2}g^{1/3} = 0 \quad (16)$$

and

$$\left(\frac{25}{RT}\right)\left(\frac{2}{9}\right)4\pi\beta^2 g^{-4/3} - \left(\frac{\alpha}{RT}\right)\left(\frac{4}{9}\right)\frac{1}{4\pi\beta^2}g^{-2/3} = 0 \quad (17)$$

The aggregation number at the inflection point is obtained from eq 17 and is given by

$$g_{crit}^{1/3} = 4\pi\beta^2\left(\frac{25}{2\alpha}\right)^{1/2} \quad (18)$$

The value of ξ_{crit} at the inflection point, obtained from eq 18 and eq 16, is

$$\ln\xi_{crit} = \left(\left(\frac{800\alpha}{9}\right)^{1/2} - 525\right)/RT \quad (19)$$

The total amphiphile concentration at this value of $\xi = \xi_{crit}$ gives the critical concentration C_{crit}.

$$C_{crit} = \frac{N_A}{F}\bigg|_{\xi_{crit}} + \sum_{g=2}^{\infty} g\frac{N_g}{F}\bigg|_{\xi_{crit}} \quad (20)$$

Replacing the summation by an integral, eq 20 becomes

$$C_{crit} = \xi_{crit}\exp\left(\frac{\mu_B - \mu_A}{kT}\right) +$$
$$\int_2^{\infty} g\,\xi_{crit}{}^g\exp\left(-\frac{\mu_g}{kT}\right)dg \quad (21)$$

There is some analogy between the critical concentration as defined here and the critical temperature predicted by the van der Waals equation of state, since each of them separates two kinds of behavior of the size distribution function and pressure–volume relationship, respectively.

Phase Separation

There is a saturation value of the concentration of non-aggregated amphiphile at which phase separation occurs. The nonaggregated amphiphile and aggregates in solution are in this case in thermodynamic equilibrium with a bulk amphiphilar phase. The corresponding thermodynamic equilibrium condition introduces an upper limit, ξ_{max}, for ξ. The equilibrium condition leads to

$$\frac{N_A}{F} = \exp\left(\frac{\mu_B' - \mu_A}{kT}\right) = \xi_{max}\exp\left(\frac{\mu_B - \mu_A}{kT}\right) \quad (22)$$

and

$$\frac{N_g}{F} = \exp\left[\frac{g(\mu_B' - \mu_B)}{kT}\right]\exp\left(-\frac{\mu_g}{kT}\right) = \xi_{max}{}^g\exp\left(-\frac{\mu_g}{kT}\right) \quad (23)$$

where μ_B' is the chemical potential per molecule of the bulk amphiphilar phase. The value of ξ corresponding to this phase transition can be calculated from

$$\ln\xi_{max} = \frac{\mu_B' - \mu_B}{kT} = \left(\frac{\mu_B' - \mu_A}{kT}\right) - \left(\frac{\mu_B - \mu_A}{kT}\right) \quad (24)$$

The term $\mu_B' - \mu_A$ is the standard free-energy change for the transfer of an amphiphile molecule from the aqueous medium to the bulk amphiphilar phase. Since no information is available for this term at the present time, it is set equal to the standard free-energy change for transferring a hydrocarbon chain from an aqueous solution of monomer to a pure hydrocarbon phase.[3a] Consequently

$$\frac{\mu_B' - \mu_A}{kT} = \frac{(400 \text{ to } 2000) - 800n_c}{RT} \quad (25)$$

Results and Discussion

The size distribution of micellar aggregates N_g/F is plotted against the aggregation number, g, for an amphiphile with an octyl hydrocarbon tail and for $\alpha = 2 \times 10^4$ cal Å²/mol[3b] (Figure 1). Equation 19 leads to $\xi_{crit} = 3.88$. For $\xi < \xi_{crit}$, the size distribution is a monotonic decreasing function of g. At $\xi = \xi_{crit}$, the size distribution function has an inflection point. At $\xi > \xi_{crit}$, the size distribution function has two extrema. It can be seen that if ξ increases both the number and the average size of the micellar aggregates increase.

In deriving eq 16–19, the surface area A is taken as the surface area of the micellar core since it is based on the volume of the hydrophobic core. In reality the surface area should account for the surface roughness due to the presence of the head groups. The actual surface area can be calculated by increasing the radius of the micellar core by a value δ.[3b] A is calculated using eq 10 where r_0 is now given by

$$r_0 = \left(\frac{3v_0}{4\pi}\right)^{1/3}g^{1/3} + \delta = \beta g^{1/3} + \delta \quad (26)$$

The introduction of this correction makes the algebra leading to the equations for g_{crit} and ξ_{crit} more complex. For this case, the value of ξ_{crit} can be computed only by numerical methods. Figure 2 represents the size distribution function for $\delta = 3$ Å and $\alpha = 8 \times 10^4$ cal Å²/mol for an amphiphile with an octyl hydrocarbon tail.

The mole fractions of amphiphiles present both in non-aggregated form and as aggregates for various values of ξ are presented in Table I for the same parameters as in Figure 2. Table I shows that below $\xi_{crit} = 27.82$, the concentration of micellar aggregates remains extremely small. At $\xi = \xi_{crit}$, the concentration of micellar aggregates begins to increase even though their contribution to the total amphiphile concentration remains negligible. However as the value of ξ increases beyond ξ_{crit}, the number of aggregates increases significantly and their contribution to the total amphiphile concentration becomes important. The values of cmc normally reported should correspond to the total amphiphile concentration for values of ξ somewhat higher than ξ_{crit}.

The values of ξ_{crit} and the corresponding values of the

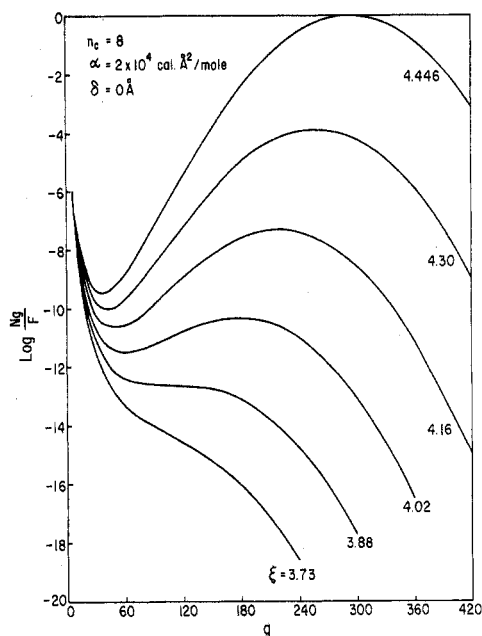**Figure 1.** Variation in the aggregate size distribution function with nonaggregated amphiphile concentration for $\delta = 0$ Å, $\alpha = 2 \times 10^4$ cal Å^2/mol, $n_c = 8$.
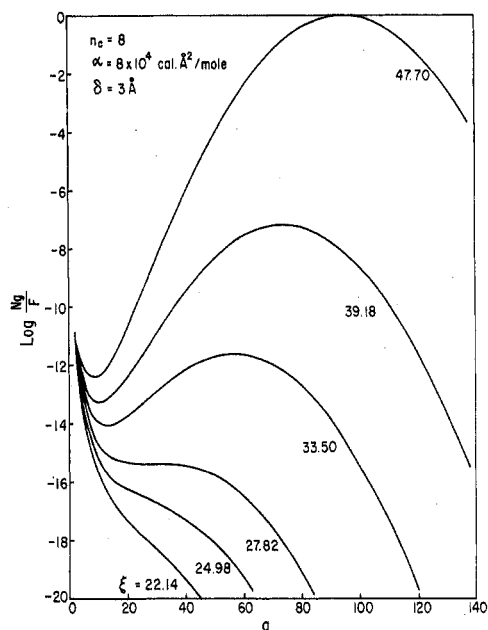

Figure 2. Variation in the aggregate size distribution function with nonaggregated amphiphile concentration for $\delta = 3$ Å, $\alpha = 8 \times 10^4$ cal Å^2/mol, $n_c = 8$.

critical concentration are computed for $\delta = 3$ Å, $\alpha = 8 \times 10^4$ cal Å^2/mol and for amphiphiles with various hydrocarbon chain lengths (Table II). Also shown in the table are the experimental cmc values[3a] of amphiphiles with hexoxyethylene glycol monoether head groups and various hydrocarbon chain lengths. It should be mentioned that the value of α used here is chosen for illustrative purposes and has not been computed on theoretical grounds for this amphiphile. It can be seen how closely the critical concentration C_{crit}, defined here predicts the cmc values normally reported.

For $\delta = 0$ the value of ξ_{crit} is solely determined by the repulsive interaction term α and remains a constant for am-

TABLE I: Variation of the Mole Fraction of the Aggregates as a Function of the Mole Fraction of the Nonaggregated Amphiphile[a]

ξ	N_A/F[b]	$\sum\limits_{g=2}^{\infty} g\,(N_g/F)^c$
22.14	2.09×10^{-4}	1.53×10^{-11}
24.98	2.34×10^{-4}	1.97×10^{-11}
27.82	2.61×10^{-4}	2.54×10^{-11}
33.50	3.14×10^{-4}	3.61×10^{-9}
39.18	3.67×10^{-4}	1.28×10^{-4}
44.86	4.21×10^{-4}	8.59[d]

^{a} $n_c = 8$, $\alpha = 8 \times 10^4$ cal Å^2/mol, $\delta = 3$ Å. ^{b} Mole fraction of nonaggregated amphiphile. ^{c} Mole fraction of the aggregates. ^{d} See the explanation in the text.

TABLE II: Variation of the Critical Concentration as a Function of Hydrocarbon Chain Length[a]

n_c	ξ_{crit}	Calcd C_{crit}[b]	Exptl cmc[b,c]
6	27	2.64×10^{-3}	2.76×10^{-3}
8	27.8	2.61×10^{-4}	2.59×10^{-4}
10	29.0	2.58×10^{-5}	2.44×10^{-5}
12	29.5	2.52×10^{-6}	2.30×10^{-6}
14	30	2.49×10^{-7}	2.16×10^{-7}
16	31	2.45×10^{-8}	2.04×10^{-8}

^{a} $\delta = 3$ Å, $\alpha = 8 \times 10^4$ cal Å^2/mol. ^{b} In mole fraction units. ^{c} Reference 3a.

phiphiles with different hydrocarbon chain lengths. When $\delta > 0$, the value of ξ_{crit} is determined not only by α but also by n_c and δ. However, the value of ξ_{crit} for $\delta = 0$ is a good first approximation even for $\delta > 0$.

Table I contains an aggregate molar fraction larger than unity because the corresponding value of ξ is larger than ξ_{max} which for this particular case is equal to 41. (The first constant in eq 25 was taken as 1750 cal/mol.) Of course, an upper bound of ξ_{max} can be obtained from the condition

$$N_A + \sum_2^{\infty} N_g + N_S = F$$

It has already been mentioned that the representation of aggregates as spheres is not essential to the definition of the critical concentration given here. Hoeve and Benson[5] suggest a spherical shape for micelles at low aggregation numbers and an oblate spherocylindrical shape at higher aggregation numbers. Tanford[3] suggests an ellipsoidal shape for the aggregates. It is possible to incorporate nonspherical shapes of aggregates as well as the variation in shapes accompanying growth in aggregate size in the present treatment. The quantitative results in terms of the size distribution function and critical concentrations will depend on these assumptions. However, the qualitative change in the pattern of the size distribution function from that of a monotonic decreasing function at low monomer concentration to one exhibiting extrema at higher monomer concentration is always present.

The explicit expressions used here for the various free-energy terms are of an empirical nature. Of course, it is possible to obtain expressions for the free energy on theoretical grounds following the approaches of Hoeve and Benson[5] or Poland and Scheraga[4] using the formalism of statistical thermodynamics.

Conclusions

A well-defined transition point in the aggregation process emerges as that separating two different types of behavior of the aggregate size distribution function. A critical concentration corresponding to this transition point is defined which is a close lower bound on the cmc values usually reported.

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Rate Constants of Triplet-State Ionic Photodissociation of Weak Charge-Transfer Complexes Formed between Pyromellitic Dianhydride (PMDA) and Naphthalenes

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The weak charge transfer (CT) complexes of PMDA with naphthalene and several of its derivatives have been excited in CT absorption bands by means of a laser flash technique in solution at room temperature. Transient absorption spectra due to the triplet–triplet transitions of the CT complexes initially appear, then followed by the absorption spectra of the radical anion of PMDA (PMDA$^-$) in the nanosecond region. By a first-order kinetic analysis, it has been indicated that the rise curves of the PMDA$^-$ absorption band give rise to approximately the same rate constants as those of the CT triplet decay. The rate constants of such triplet-state anion formations have been determined from the PMDA$^-$ rise curves. It has been found that the rate constant increases with the dielectric constant of solvent. In the photolysis of these CT complexes, it has also been suggested that PMDA$^-$ is produced via both the lowest excited singlet and triplet states of the CT complexes.

Introduction

Spectroscopic evidence of the ionic photodissociation of a ground-state charge transfer (CT) complex may be obtained by analyzing the rise curve of radical ions produced as a result of electron transfer. The first direct, spectroscopic evidence of ionic photodissociation in the excited triplet state was obtained with the PMDA–mesitylene CT complex at low temperature by Potashnik et al.,[1] who followed the decay curve of CT phosphorescence as well as the rise curve of the optical absorption of the radical anion. So far, several examples have been published on the triplet-state ionic photodissociation of CT complexes.[2–6]

In the present work, we considered it interesting to determine the rate constants of the CT-triplet ionic photodissociation using a nanosecond laser flash technique. It may also be interesting to study the effects of solvent and electron donor on the rate constant. The reason that PMDA has been used as an electron acceptor is that its CT complexes of naphthalenes can be excited in the CT bands by the second harmonic (347 nm) of the ruby laser and that the resulting radical anion of PMDA (PMDA$^-$) shows a strong absorption band at about 665 nm, which is well separated from the T–T absorption bands. Naphthalene and its derivatives (1-methyl-, 2-methyl-, 1-chloro-, 2,3-di-

methyl-, and 2-hydroxynaphthalene) have been used as electron donors, since their CT complexes with PMDA show considerably strong T–T absorption spectra.

Experimental Section

1,2-Dichloroethane (DCE) was repeatedly washed with dilute sulfuric acid (10%), alkaline aqueous solution (10%), and water, and finally purified by distillation after drying over CaCl$_2$. Tetrahydrofuran (THF), dimethoxyethane (DME), and butyronitrile were refluxed over CaH$_2$ and distilled. Acetonitrile was refluxed over phosphorus pentoxide and distilled. Naphthalene and 2-hydroxynaphthalene were recrystallized from ligroin, and 2-methyl- and 2,3-dimethylnaphthalene from petroleum ether. 1-Methyl- and 1-chloronaphthalene were purified by vacuum distillation and PMDA by vacuum sublimation.

Ordinary visible and ultraviolet absorption spectra were measured on a Cary 15 spectrophotometer and phosphorescence spectra on a Hitachi MPF-2A fluorescence spectrophotometer. Laser pulse excitation experiments were carried out with a giant pulse ruby-laser apparatus previously described by Takemura et al.,[7] the second harmonic (347 nm) of the ruby laser being generated by an ADP crystal. The laser pulse apparatus was combined with a 50-cm Nar-