

Photophysical Probe Studies of Polymer-Detergent Interactions

*Patricia M. Nassar, Lázaro C. Nogueira and João B.S. Bonilha**

Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, 14040-901 Ribeirão Preto - SP, Brazil

*Oscar Weissbluth Leiva and Frank H. Quina**

*Instituto de Química, Universidade de São Paulo, C.P. 26077,
05599-970 São Paulo - SP, Brazil*

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A interação de tensoativos com macromoléculas é de interesse básico e tecnológico. Um dos sistemas detergente-polímero mais estudado é dodecilsulfato de sódio (SDS)-poli(etilenoglicol) (PEG). Em solução aquosa, a interação entre PEG e SDS conduz à formação de agregados, semelhantes a micelas, sobre a cadeia polimérica do PEG. Comparado com micelas de SDS na ausência de PEG, os agregados SDS-PEG são de tamanho menor, apresentam um grau maior de dissociação dos contraíons e possuem uma estrutura mais "aberta". Neste trabalho, utilizaram-se técnicas fotofísicas para determinar os números de agregação dos agregados SDS-PEG sobre uma ampla faixa de [SDS], [PEG] e sal (NaCl) adicionado, para estudar encontros bimoleculares dentro dos agregados e para determinar solubilidades de alguns compostos orgânicos nos agregados. Os resultados enfatizam a natureza distinta dos agregados SDS-PEG quando comparados com as micelas de SDS formadas na ausência de PEG.

The interaction of surfactants with macromolecules is of both fundamental interest and technological importance. One of the most extensively studied detergent-polymer systems is sodium dodecyl sulphate (SDS)-poly(ethylene glycol) (PEG). In aqueous solution, the PEG-SDS interaction results in the formation of micelle-like aggregates or clusters of SDS attached to the PEG polymer chain. Compared to normal SDS micelles, these SDS-PEG clusters are smaller, are more highly dissociated, and have a somewhat more "open" structure. In the present work, photophysical probe techniques have been employed to determine aggregation numbers of SDS-PEG clusters over a wide range of [SDS], [PEG] and added common counterion salt (NaCl), to study bimolecular encounters within the aggregates and to determine solubilities of simple organic molecules in the SDS-PEG clusters. The results emphasize the distinct nature of the SDS-PEG aggregates as compared to normal SDS micelles formed in the absence of PEG.

Keywords: *polymer, detergent, photophysics, fluorescence, solubilization*

Introduction

The interaction of surfactants with macromolecules is of both fundamental interest and technological importance¹⁻³. Lipid-protein interactions, for example, play a vital role in living systems. Many commercial formulations contain both polymers and detergents as components and polymer-detergent contacts are commonplace in applications of surfactant-containing products.

One of the most extensively studied detergent-polymer interactions is that between the anionic detergent sodium dodecyl sulphate (SDS) and the non-ionic polymer poly(ethylene glycol) (PEG, also known as poly(ethylene oxide)) in aqueous solution. The SDS-PEG interaction has been studied using a wide range of techniques²⁻⁵, including surface tension, conductivity, viscosity, ultracentrifugation, solubilization, gel filtration, ion selective electrode measurements, equilibrium dialysis, nuclear magnetic

resonance, fast relaxation techniques, neutron scattering, fluorescence spectroscopy, electron spin resonance, catalysis or inhibition of chemical reactions and calorimetry. The SDS-PEG interaction is highly cooperative and occurs over a rather well defined range of detergent concentrations. The onset of the interaction, known as the critical aggregation concentration (CAC) of the detergent, is only slightly dependent on PEG concentration. The detergent concentration at which the polymer saturates with SDS increases in approximately linear fashion with [PEG]. The interaction is independent of PEG molecular weight (for MW > 4000), is somewhat enhanced by the addition of salt, and decreases with increasing temperature²⁻⁵. Specific counterion effects on the SDS-PEG interaction have also been reported⁶. Although other anionic surfactants also interact with PEG, cationic, non-ionic and zwitterionic detergents appear to have little or no affinity for binding to PEG³⁻⁵.

The PEG-SDS interaction results in the formation of micelle-like aggregates or clusters of SDS attached to the PEG polymer chain. Compared to normal SDS micelles, these SDS-PEG clusters are smaller, are more highly dissociated, and have a somewhat more "open" structure²⁻⁵. The PEG polymer chains appear to be located at the surface of the SDS clusters, but estimates of the fraction of the PEG segments bound to the micelles vary rather widely⁴⁻⁵. Although a number of theoretical models have been proposed to explain the onset of the interaction (CAC), the saturation and the aggregate size, none provides a completely satisfactory description of all of the aspects of the PEG-SDS interaction³⁻⁵.

In the present work, photophysical probe techniques have been employed to determine aggregation numbers of SDS-PEG clusters over a wide range of [SDS], [PEG] and added common counterion salt (NaCl), to study bimolecular encounters within the aggregates and to determine solubilities of simple organic molecules in the SDS-PEG clusters. The results emphasize the distinct nature of the SDS-PEG aggregates as compared to normal SDS micelles formed in the absence of PEG.

Materials and Methods

Materials

PEG of nominal molecular weight 10 000 (ATPEG-10000; Atlas-Ultra Divisão Química) was employed throughout. SDS (Merck, for biochemical use, or synthesised from *n*-dodecanol⁷) was purified by recrystallization from absolute ethanol. Purity was checked by surface tensiometric determination of the critical micelle concentration (CMC) in the usual manner. Tris(bipyridine) ruthenium(II) chloride ($\text{Ru}(\text{bpy})_3^{2+}$; Aldrich) and analytical reagent grade inorganic salts were used as received. Carbon tetrachloride (Merck), 1,3-dicyanobenzene (Aldrich) and 1,4-dicyanobenzene (Aldrich) were used as

received. Iodoethane (Aldrich) was filtered through grade I Alumina prior to use. Pyrene and 9-methylanthracene (Aldrich) were purified by sublimation. *N,N*-Dimethyldodecylamine, synthesised from *n*-dodecylamine (Aldrich) by the Leuckart reaction⁸, was purified by vacuum distillation (bp 125 - 130 °C/8 mm Hg; 99.9+% pure by capillary glpc). All solutions were prepared in distilled, freshly deionized water.

Methods

All measurements were performed at 30 °C. Apparent surface tensions were determined with a DuNoüy tensiometer equipped with a Pt ring. Emission measurements were performed with either a Perkin-Elmer LS-5B or a Hitachi F4500 fluorescence spectrometer on air-equilibrated solutions contained in Teflon-stoppered 1 cm path length fluorescence cuvettes (Hellma). Fluorescence lifetimes were determined by the single photon counting technique with an Edinburgh Analytical Instruments FL900 lifetime spectrometer. Excitation/emission wavelengths were 450/627 nm for $\text{Ru}(\text{bpy})_3^{2+}$ (7×10^{-5} M) and 337/374 nm for pyrene (2×10^{-6} M).

Aggregation numbers were determined by the method of Turro and Yekta⁹. Successive aliquots of a concentrated (0.02 M) stock solution of 9-methylanthracene in spectroquality acetonitrile were added to aqueous solutions containing the emissive probe $\text{Ru}(\text{bpy})_3^{2+}$, PEG (0, 0.2, 0.4 or 4% PEG wt/vol), NaCl (0 - 0.100 M) and SDS (0.005 - 0.080 M) and the emission intensity recorded following each addition. Aggregation numbers were obtained from the slopes of linear plots of $\ln(I^0/I)$ vs. [9-methylanthracene] as described⁹, where I^0 and I are the corresponding $\text{Ru}(\text{bpy})_3^{2+}$ emission intensities in the absence and presence of 9-methylanthracene. Pyrene fluorescence quenching experiments were performed in similar fashion. Successive aliquots of concentrated stock solution of *N,N*-dimethyldodecylamine in spectroquality methanol (Aldrich) were added to basic aqueous solutions (adjusted with NaOH to pH 11.6 to prevent protonation of the amine) containing pyrene, PEG (0.4 or 4% PEG wt/vol), SDS (0.005 - 0.030 M) and NaCl (0.050 M) and the fluorescence intensity registered after each addition. Quenching of pyrene fluorescence by carbon tetrachloride, iodoethane, 1,3-dicyanobenzene and 1,4-dicyanobenzene was performed in analogous fashion.

Results

Critical aggregation concentrations (CAC) for the onset of the interaction of SDS with PEG were determined by surface tension. The CAC values of 0.0042, 0.0026, 0.0020, 0.0016, 0.0013 and 0.0010 M in the presence of zero, 0.010, 0.020, 0.030, 0.050 and 0.100 M NaCl are insensitive to the PEG concentration (0.2 and 0.4% PEG) and in good agreement with literature data^{4,10}. As shown in

Fig. 1, a plot of $\log c_{ac}$ versus $\log (CAC + [NaCl])$ is linear and obeys the relationship:

$$\log CAC = -3.47 - 0.46 \log (CAC + [NaCl])$$

By analogy to normal micelles, the slope should be equal to $(1 - \alpha)$, providing an estimate of $\alpha = 0.54$ for the effective degree of counterion dissociation of the SDS-PEG aggregates at the c_{ac} . This value is in good agreement with conductimetric estimates of α of 0.65¹¹ and 0.56¹², above the CAC.

Average aggregation numbers (N) of the SDS clusters formed on the PEG polymer chain were determined by the method of Turro and Yekta⁹, which is based on the static quenching of the emission of the $Ru(bpy)_3^{2+}$ ion by aggregate-incorporated 9-methylanthracene. The aggregation numbers of SDS alone and of SDS clusters formed in the presence of 0.20 and 0.40% PEG are listed in Table 1; aggregation numbers determined in the presence of 4.0% PEG over a wide range of $[NaCl]$ and $[SDS]$ are collected in Table 2. The N values of SDS micelles and of SDS-PEG clusters at zero and 0.10 M added NaCl are in good agreement with scattered values reported in the literature^{6,11,13-15}.

As shown in Fig. 2, the fluorescence of pyrene solubilized in SDS-PEG clusters is quenched by added N,N -dimethyldodecylamine (DMDA), the efficiency being a function of both $[SDS]$ and $[PEG]$. The fluorescence quenching was analyzed on the basis of the assumption that neither pyrene nor DMDA exits the SDS-PEG cluster on the time scale of the quenching. The probability P_n of finding an excited pyrene in a cluster containing n quenchers is given by a Poisson distribution:

$$P_n = \frac{\langle n \rangle^n \exp(-\langle n \rangle)}{n!}$$

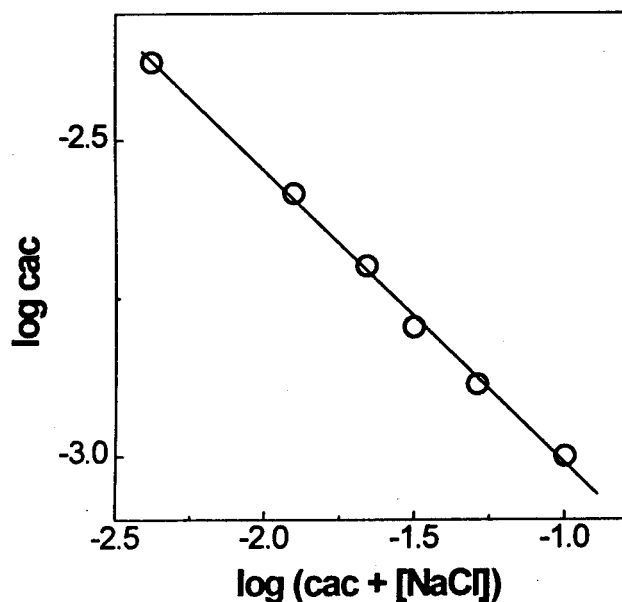


Figure 1. Correlation of $\log c_{ac}$ with $\log (c_{ac} + [NaCl])$ for the onset of the SDS-PEG interaction.

where $\langle n \rangle$ is the average number of quenchers per cluster:

$$\langle n \rangle = \frac{[Q_{tot}]}{[Cluster]} = \frac{[Q_{tot}]}{N} \frac{N}{[SDS_{ag}]}$$

and $[SDS_{ag}] = ([SDS_{tot}] - CAC)$ is the concentration of aggregated SDS (as polymer bound clusters or free micelles). The ratio of pyrene fluorescence intensities in a cluster with no quenchers (I^0) and a cluster with n quenchers (I_n) is taken to be directly proportional to the number of DMDA molecules solubilized in the cluster:

$$I^0/I_n = 1 + n k_q \tau^0$$

Table 1. Aggregation numbers of SDS in water and of SDS clusters in the presence of 0.2 and 0.4 wt% PEG 10 000 as a function of detergent and salt concentration.

[SDS] mM	Aggregation numbers (N)							
	% PEG							
	0			0.2			0.4	
	[NaCl] mM			[NaCl] mM				
	0	50	100	0	20	50	100	
5	-	-	42	43	-	-	38	43
10	38	33	46	49	28	37	42	45
15	-	40	50	53	31	40	44	50
20	55	45	56	58	34	43	48	53
25	-	42	55	62	36	44	46	51
30	59	43	57	64	39	46	49	56
35	-	44	58	63	41	48	50	53
40	64	47	62	66	40	49	52	55
45	-	50	60	69	37	51	53	58
50	64	55	62	69	38	52	52	59
60	68	-	-	-	42	58	54	60
70	68	-	-	-	-	-	-	-
80	71	-	-	-	-	-	-	-

Table 2. Aggregation numbers of SDS clusters in the presence of 4.0 wt% PEG 10 000 as a function of detergent and salt concentration.

[SDS] mM	[NaCl] mM							
	0	10	20	30	40	50	80	100
10	25	29	32	35	37	40	43	42
15	26	29	33	35	36	40	43	43
20	25	29	32	34	37	41	42	42
25	26	30	33	36	37	41	43	42
30	27	29	31	34	36	40	42	42
35	27	30	33	36	36	39	42	42
40	28	31	31	36	36	40	42	42

Table 3. Pseudophase incorporation coefficients (K_s) for solubilization of simple organic molecules in SDS-PEG clusters and SDS micelles in the presence of 0.100 M NaCl determined by the method of Encinas and Lissi¹⁷ using pyrene as the fluorescence probe. Estimated error in the K_s values is *ca.* 20%.

Solute	K_s (PEG-SDS), M^{-1}	K_s (SDS), M^{-1}
Iodoethane	20	10
Carbon tetrachloride	27	20
1,3-Dicyanobenzene	15	14
1,4-Dicyanobenzene	36	16

with the monomolar polymer concentration, [PEG], according to:

$$[SDS_{sat}] = 0.065 (\%PEG) + 0.008 = 0.29 [PEG] + 0.008$$

In the presence of 0.10 M NaCl, the saturation with SDS obeys the relationship:

$$[SDS_{sat}] = 0.15 (\%PEG) + 0.0015 = 0.66 [PEG] + 0.0015$$

Saturation of the polymer with SDS thus occurs at $[SDS_{ag}]/[PEG]$ ratios of about 0.30 - 0.35 (depending on %PEG) in the absence of salt and 0.66 in the presence of 0.100 M NaCl, where $[SDS_{ag}] = ([SDS_{tot}] - cac)$.

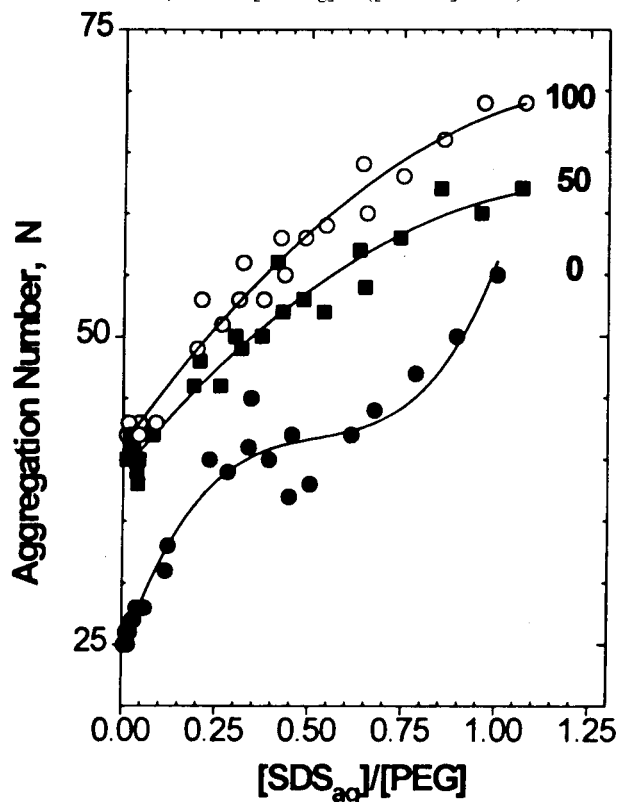


Figure 4. Correlation of the aggregation numbers of the SDS-PEG clusters with the ratio of concentrations of aggregated SDS and PEG. The aggregation numbers (Tables 1 and 2) were determined in the absence and presence of NaCl (50 mM or 100 mM, as indicated) by the method of Turro and Yekta⁹.

The average aggregation numbers of SDS in the presence of PEG are dependent on the $[SDS_{ag}]/[PEG]$ ratio (Fig. 4). In all cases, the value of N increases with [NaCl] and with increasing $[SDS_{ag}]/[PEG]$ ratio. In the absence of added salt, N levels off at $[SDS_{ag}]/[PEG]$ ratios of *ca.* 0.35, corresponding to saturation of the polymer with SDS. Above ratios of about 0.6, N increases again as free micelles form in the aqueous phase. Similarly, in the presence of 0.10 M NaCl, N shows signs of levelling off at $[SDS_{ag}]/[PEG]$ ratios above *ca.* 0.7, again corresponding to saturation. The small, rather uniform SDS clusters formed at high %PEG (Table 2) and the approximately linear increase of N with $[SDS_{ag}]/[PEG]$ prior to saturation support the model proposed by van Stam *et al.*¹³ These authors suggest that the initial interaction consists of the formation of relatively small clusters distributed along the polymer chain. Further addition of detergent leads simultaneously to growth of the existing clusters and formation of new clusters. The interaction terminates when the polymer saturates with clusters and the clusters have attained their maximal size.

Using the experimental aggregation numbers to calculate average occupation numbers ($\langle n \rangle$), the intracuster quenching of pyrene fluorescence by *N,N*-dimethyldodecyl amine can be satisfactorily fitted by a model that assumes a Poisson distribution of the quencher among the available SDS-PEG clusters. Consistent with data for quenching by molecular oxygen¹³ and for pyrene excimer formation¹¹, the k_q values for intracuster quenching in SDS micelles, suggesting a somewhat lower mobility of solutes in the SDS-PEG aggregates as compared to SDS micelles.

Witte and Engberts^{12,14} have reported that SDS-PEG aggregates solubilize 1-benzoyl-3-phenyl-1,2,4-triazole less efficiently than normal SDS micelles. The data of Table 3 compare the solubilization properties of SDS-PEG clusters to those of SDS micelles for four relatively simple organic molecules. Three of the four molecules examined solubilize better in the clusters than in the micelles, while the fourth shows similar solubility in both. More extensive studies with a wider variety of solutes are currently in progress in order to determine the factors that contribute to these observed differences in solubilization.

Conclusions

Taken as a whole, the present results emphasize the distinct nature of the SDS-PEG aggregates as compared to normal SDS micelles formed in the absence of PEG. The effect of added salt on the CAC is consistent with a much higher degree of counterion dissociation for the SDS-PEG aggregates. The aggregation numbers of the clusters, determined over a wide range of [SDS], [PEG] and added common counterion salt (NaCl), are smaller than those of SDS micelles and suggest that growth and formation of

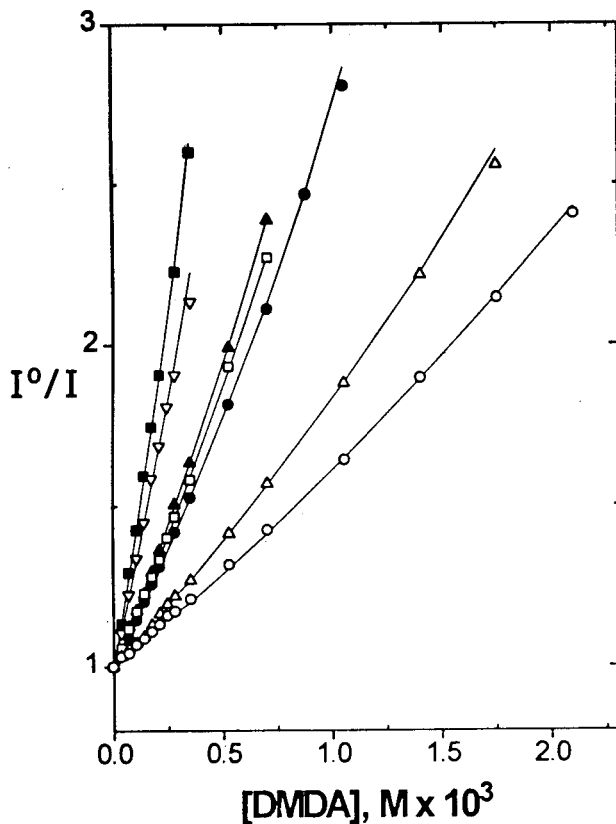


Figure 2. Stern-Volmer plots of the quenching of the fluorescence of pyrene by *N,N*-dimethyldodecylamine (DMDA) in SDS-PEG aggregates in pH 11.6 aqueous medium containing 0.050 M NaCl. Open symbols, 4% PEG, with, in descending order, 0.0050, 0.010, 0.020 and 0.030 M added SDS. Filled symbols, 0.4% PEG, with, in descending order 0.0050, 0.010 and 0.012 M added SDS.

where k_q is the pseudo-first order rate constant for intracuster quenching of excited pyrene by a single DMDA. In agreement with the report of van Stam *et al.*¹³, the fluorescence lifetime of pyrene ($\tau^0 = 190$ ns) in the SDS-PEG clusters in the absence of quencher is found to be slightly longer than that (170 ns) in micellar SDS under the same conditions. With these assumptions, the ratio of pyrene fluorescence intensities in the presence (I) and absence (I^0) of DMDA is given by¹⁶:

$$I^0/I = 1/[\sum\{P_n/(I^0/I_n)\}]$$

Using the experimental values of the cac and N (Tables 1 and 2) in the presence of 0.050 M NaCl, τ^0 and this equation, the experimental I^0/I values were fit (curves in Fig. 2) using k_q as the only adjustable parameter. For 0.4% PEG in 0.050 M NaCl, the best-fit values of k_q were 2.9 and $2.6 \times 10^6 \text{ s}^{-1}$ at total SDS concentrations of 0.0050 and 0.010–0.012 M; for 4% PEG in 0.050 M NaCl, the corresponding best-fit k_q values were 2.0, 2.6, 2.7 and $3.3 \times 10^6 \text{ s}^{-1}$ at 0.0050, 0.010, 0.020 and 0.030 M SDS.

Solute incorporation coefficients were determined by the fluorescence quenching method of Encinas and Lissi⁹.

This method assumes that, even when the quencher is only partially solubilized in the aggregate, the efficiency of quenching of the fluorescence of an aggregate-solubilized probe such as pyrene is entirely determined by the average number of bound quenchers per aggregate, $\langle n \rangle$. Thus, equal quenching efficiencies (identical I^0/I values) at different $[\text{SDS}_{\text{tot}}]$, $[\text{PEG}]$ and total quencher concentrations, $[\text{Q}_{\text{tot}}]$, correspond to identical $\langle n \rangle$ values. The quenching of the fluorescence of aggregate-solubilized pyrene by iodoethane (EtI), CCl_4 , 1,3-dicyanobenzene (1,3-DCB) and 1,4-dicyanobenzene (1,4-DCB) was studied in solutions containing 0.4% PEG and 0.10 M added NaCl. The values of $[\text{Q}_{\text{tot}}]_{\text{eqe}}$ required to attain a given fixed value of I^0/I at each $[\text{SDS}_{\text{tot}}]$ were determined from Stern-Volmer plots of I^0/I versus $[\text{Q}_{\text{tot}}]$. A graph of $[\text{Q}_{\text{tot}}]_{\text{eqe}}$ versus the concentration of detergent in the aggregate should be linear:

$$[\text{Q}_{\text{tot}}]_{\text{eqe}} = \langle n \rangle N / K_s + \langle n \rangle N [\text{SDS}_{\text{ag}}]$$

and the slope/intercept ratio should provide the value of the pseudophase partitioning coefficient, K_s , defined as¹⁸:

$$K_s = [\text{Q}_{\text{mic}}] / ([\text{Q}_{\text{aq}}][\text{SDS}_{\text{ag}}])$$

Representative plots for quenching of pyrene fluorescence by CCl_4 are shown in Fig. 3. Table 3 compares values of K_s for the four solutes in SDS-PEG aggregates and in SDS micelles in the absence of PEG.

Discussion

According to the phase diagrams of Cabane and Duplessix¹⁰, the detergent concentration at which PEG saturates with SDS in the absence of added electrolyte varies

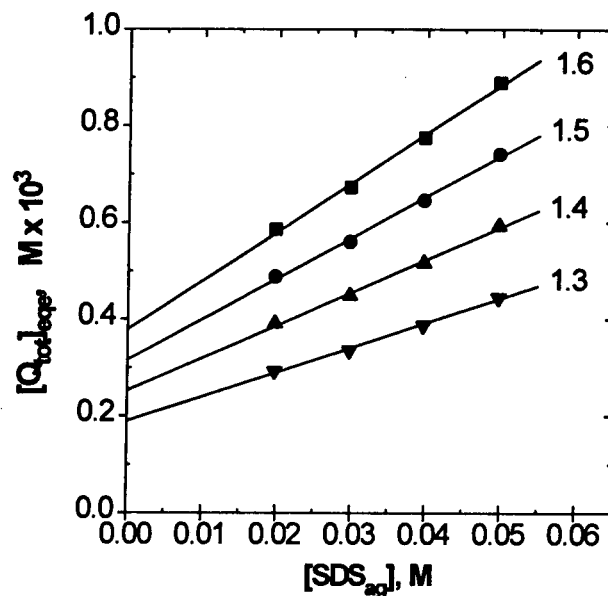


Figure 3. Determination of the pseudophase incorporation coefficient (K_s) for solubilization of CCl_4 in SDS-PEG aggregates (0.4% PEG and 0.100 M NaCl) from plots of $[\text{Q}_{\text{tot}}]_{\text{eqe}}$ versus $[\text{SDS}_{\text{ag}}]$ at four equal quenching efficiencies (I^0/I values indicated on each curve).

clusters occur simultaneously up to saturation of the polymer. Differences are also observed in the intracluster mobility and solubility of molecules in the SDS-PEG clusters.

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