

Fluorescence and Light-Scattering Studies of the Aggregation of Cationic Surfactants in Aqueous Solution: Effects of Headgroup Structure

Laura T. Okano, Frank H. Quina, and Omar A. El Seoud*

Instituto de Química, Universidade de São Paulo, C.P. 26077, 05513-970 São Paulo, S.P., Brazil

Received August 23, 1999. In Final Form: December 7, 1999

Aggregation of the following cationic surfactants has been studied in aqueous solution: cetyltrimethylammonium chloride, CMe₃ACl; cetyldimethylphenylammonium chloride, CMe₂PhACl; cetyldimethylbenzylammonium chloride, CMe₂BzACl; cetyldimethyl-2-phenylethylammonium chloride, CMe₂PhEtACl; and cetyldimethyl-3-phenylpropylammonium chloride, CMe₂PhPrACl. Critical micelle concentrations, cmc's, were obtained from surface tension and conductance measurements; data of the latter were also employed to determine the degree of the surfactant counterion dissociation, α . Static and quasi-elastic light-scattering measurements were employed to obtain micellar weight-average molecular weights, aggregation numbers, N_{agg} , micellar hydrodynamic radii, R_h , and interfacial area/surfactant headgroup. The latter area was also obtained from surface tension measurements. Finally, time-resolved fluorescence decay measurements with pyrene as probe were employed to obtain N_{agg} . The structure of micelles of CMe₂PhACl is different from that of the other phenyl-group-bearing surfactants because its aromatic ring cannot fold back on the micellar interface. Increasing the number of the methylene segments in the headgroup results in an increase in α and interfacial surface area/headgroup and a decrease in the cmc, N_{agg} , and R_h . There is good agreement between micellar properties obtained by the different techniques employed.

Introduction

Changes of the molecular structure of surfactants have important consequences for the physicochemical properties of their solutions, and hence on applications of the organized assemblies formed.^{1–3} For aqueous micelles, increasing the length of the surfactant hydrophobic tail results in a decrease of the degree of micelle counterion dissociation, α , and the critical micelle concentration, cmc, and an increase of the micellar aggregation number, N_{agg} , and the Kraft point (i.e., the temperature above which the solubility of the surfactant in water noticeably increases).^{1–3} For cationic surfactants, a change of the counterion from chloride ion to bromide ion decreases the charge density at the micelle interface and alters micellar effects on reaction rates and equilibria.^{1–4} Effects of variation of the structure of the surfactant headgroup on micellar properties have been much less studied, although this structural modification produces some interesting consequences. For example, rates of reactions that are sensitive to changes of solvent polarity (e.g., the spontaneous decarboxylation of the 6-nitrobenzoxazole-3-carboxylate ion) or to desolvation of the attacking nucleophile (e.g., elimination by the E2 pathway, S_N2 and nucleophilic aromatic substitution reactions) are enhanced by an increase of the hydrophobic character of the headgroup, e.g., upon going from trimethyl- to tri-*n*-butylammonium. The reason suggested is that large headgroups partially exclude water from the interface, resulting in a less polar reaction environment.^{5,6} This conclusion is supported by recent determinations of the

microscopic polarity of interfacial water of cationic surfactant micelles.⁷

The present study is a part of our interest in effects of the structure of the surfactant headgroup on the aggregation and catalytic properties of organized assemblies.^{8–10} We have studied micelles of the cationic surfactants shown in Chart 1 by four independent techniques, namely, surface tension, conductance, static and quasi-elastic light scattering, LS, and fluorescence.

We turned to cationic surfactants because the synthesis of homologous series with variable headgroup structure is much easier than that with anionic surfactants. Previously, extensive work has been carried out on cationic surfactants with the general structure RN⁺R'R''R''' X⁻, where X⁻ = halide ion, R = octyl to octadecyl, and R', R'', and R''' generally represent identical alkyl groups, e.g., trimethyl to tri-*n*-pentyl. Alternatively, a number of studies have employed R' and R'' = methyl and R''' = alkyl group (e.g., ethyl to *n*-octyl, or 2-hydroxyethyl), or R' = methyl and R'' and R''' = alkyl group (e.g., methyl to *n*-butyl, or 2-hydroxyethyl).^{1,2,8,11} Of the surfactants bearing a phenyl headgroup (see Chart 1), only CMe₂-

* Corresponding author. Fax: +55-11-818-3874. E-mail: elseoud@iq.usp.br.

(1) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley: New York, 1982.

(2) Attwood, D.; Florence, A. T. *Surfactant Systems: Their Chemistry, Pharmacy, and Biology*; Chapman and Hall: London, 1984.

(3) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213.

(4) El Seoud, O. A. *Adv. Colloid Interface Sci.* **1989**, *30*, 1.

(5) (a) Bacaloglu, R.; Bunton, C. A.; Cerichelli, G.; Ortega, F. *J. Phys. Chem.* **1989**, *93*, 1490. (b) Bacaloglu, R.; Bunton, C. A.; Ortega, F. *J. Phys. Chem.* **1989**, *93*, 1497. (c) Bonan, C.; Germani, R.; Ponti, P. P.; Savelli, G.; Cerichelli, G.; Bacaloglu, R.; Bunton, C. A. *J. Phys. Chem.* **1990**, *94*, 5331. (e) Cerichelli, G.; Mancini, G.; Luchetti, L.; Savelli, G.; Bunton, C. A. *J. Phys. Org. Chem.* **1991**, *4*, 71.

(6) Broxton, T. J.; Christie, J. R.; Theodoridis, D. *J. Phys. Org. Chem.* **1993**, *6*, 535.

(7) (a) Novaki, L. P.; El Seoud, O. A. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1957. (b) Novaki, L. P.; El Seoud, O. A. *Langmuir* **2000**, *16*, 35.

(8) (a) Okano, L. T.; El Seoud, O. A.; Halstead, T. *Colloid Polym. Sci.* **1997**, *275*, 138. (b) El Seoud, O. A.; Blásko, A.; Bunton, C. A. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 1214.

(9) Bazito, R. C.; El Seoud, O. A.; Barlow, G. K.; Halstead, T. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 1933.

(10) Possidonio, S.; Siviero, F.; El Seoud, O. A. *J. Phys. Org. Chem.* **1999**, *12*, 325.

(11) Zana, R. *Colloids Surf. A* **1997**, *123–124*, 27 and references therein.

Chart 1

- $C_{16}H_{33}N^+(CH_3)_3 Cl^-$, cetyltrimethylammonium chloride, CME_3ACl ;
 $C_{16}H_{33}N^+(CH_3)_2-C_6H_5 Cl^-$, cetyldimethylphenylammonium chloride, CME_2PhACl ;
 $C_{16}H_{33}N^+(CH_3)_2-CH_2-C_6H_5 Cl^-$, cetyldimethylbenzylammonium chloride, CME_2BzACl ;
 $C_{16}H_{33}N^+(CH_3)_2-CH_2-CH_2-C_6H_5 Cl^-$, cetyldimethyl-2-phenylethylammonium chloride, $CME_2PhEtACl$;
 $C_{16}H_{33}N^+(CH_3)_2-CH_2-CH_2-CH_2-C_6H_5 Cl^-$, cetyldimethyl-3-phenylpropylammonium chloride, $CME_2PhPrACl$.

BzACl has been studied in detail because it is a major component of "benzalkonium chloride", a product widely used as an antiseptic in pharmaceutical preparations.¹² Except for our previous NMR investigation of the aggregates of the cationic surfactants shown in Chart 1,⁸ and of Zana's and Lang's work on the formation of water-in-oil microemulsions by CME_2PhACl , CME_2BzACl , and $CME_2PhEtACl$,¹³ there appear to be no published data on the properties (e.g., α , N_{agg}) of aqueous micelles of CME_2PhACl , $CME_2PhEtACl$, and $CME_2PhPrACl$, respectively.

In the present study, cmc's and interfacial areas/headgroup were obtained from surface tension measurements, whereas α and cmc (in the absence of added electrolyte) were obtained from conductance measurements. Static and quasi-elastic LS measurements provided micellar weight-average molecular weights, M_w , and hydrodynamic radii, R_h , respectively, from which N_{agg} and area/headgroup were calculated. Values of N_{agg} independently obtained from fluorescence measurements with micelle-solubilized pyrene as probe were in good agreement with those obtained by static LS.

Experimental Section

Materials. The reagents, obtained from Aldrich and Merck, were purified as described elsewhere.¹⁴ The surfactants were available from a previous study.⁸ Before use, they were dried under reduced pressure over P_2O_5 to constant weight. All solutions were prepared in ultrapure water (Millipore Milli-Q).

Apparatus. Surface tensions of aqueous solutions were measured with a Lauda TE 1C digital De Nöuy tensiometer, equipped with a thermostated solution compartment. To prevent water evaporation, the latter was fitted with a glass cover. At 25 °C, measured cmc values for CME_3ACl and CME_2BzACl agreed with those reported elsewhere.¹⁵ Conductance measurements were carried out with a Fisher Accumet-50 pH meter, equipped with a Fisher conductivity cell (cell constant = 1.0 cm^{-1}) and interfaced to a microcomputer. Static and quasi-elastic LS measurements were performed with a Malvern 4700 MW system, equipped with a 60 mW He/Ne laser light source. Refractive index increments were obtained with a Wyatt Optilab 903 interferometric refractometer equipped with a He/Ne laser light source.

Steady-state emission measurements were performed at 35 °C with a Hitachi F4500 fluorescence spectrometer. Pyrene fluorescence decay curves were collected at 35 °C by the single-photon-counting technique, using an Edinburgh Analytical Instruments Model FL-900 Lifetime Spectrometer (H_2 flashlamp gas, 337 nm excitation; 390 nm emission).

Measurements and Calculations. *Surface Tensions.* Solutions were thermostated in the compartment for 15 min before

their surface tension was measured. Measurements were repeated until four successive readings gave a standard deviation of 0.12 $mN m^{-1}$. Cmc's were determined from plots of surface tension ($mN m^{-1}$) versus \log [surfactant]. The maximum area/surfactant headgroup at the micellar interface, A in Å^2 , was calculated from the following equations, as given elsewhere¹⁶

$$\Gamma_{R_4NCl} = \frac{1}{4.606RT} \left(\frac{d\pi}{d(\log[R_4NCl] + \log f_{\pm})} \right) \quad (1)$$

$$A = \frac{10^{20}}{N(\Gamma_{R_4NCl})} \quad (2)$$

where π is the surface pressure, Γ_{R_4NCl} is the maximum surface excess concentration, f_{\pm} is the mean activity coefficient of the surfactant, and N is Avogadro's number.

Conductance Measurements. Surfactant solutions were thermostated for 15 min before conductance was measured. Plots of specific conductance versus [surfactant] exhibited two straight lines intersecting at the cmc. Values of α were calculated from specific conductance results by the methods of Evans, eq 3,¹⁷ and Frahm, eq 4¹⁸

$$1000S_2 = \frac{(N_{agg} - \beta)^2}{N_{agg}^{3/4}} (1000S_1 - \lambda_{Cl^-}) + \alpha\lambda_{Cl^-} \quad (3)$$

$$\alpha = S_2/S_1 \quad (4)$$

where S_2 , S_1 , λ_{Cl^-} , and β refer to the slope of the linear portion above the cmc, the slope of the linear portion below the cmc, the equivalent conductance of Cl^- at infinite dilution, and the number of counterions attached to the micelle, respectively.

LS Measurements. N_{agg} was calculated from the aggregate molecular weight, M_w , and the molecular weight of the monomer. Static LS measurements were used to construct the Zimm plot, and M_w was obtained from the equation¹⁹

$$\frac{K[C_{R_4NCl}]}{R_\theta} = \frac{1}{M_w} + 2BC_{R_4NCl} \quad (5)$$

where C_{R_4NCl} is the surfactant concentration in g/cm^3 , K and R_θ are constants that depend on the wavelength of incident light, the intensities and angles of incident and scattered light, the refractive index of the solvent, the refractive index increment of the solution, and the distance from sample to the photomultiplier, respectively, and B is the second virial coefficient. Equation 6 was used to calculate A from R_h ¹⁹

$$A = \frac{4\pi R_h^2}{N_{agg}} \quad (6)$$

The latter was calculated from quasi-elastic LS measurements by the Stokes–Einstein expression (valid in the limit of infinite dilution), eq 7

$$R_h = \frac{kT}{6\pi\eta D_0} \quad (7)$$

where k , T , η , and D_0 refer to the Boltzmann constant, the absolute temperature, the shear viscosity of the solvent (cP), and the micellar translational diffusion coefficient, respectively. The latter coefficient is strongly dependent on intermicellar interac-

(12) Gump, W. In *Othmer Encyclopedia of Chemical Technology*; Wiley-Interscience: New York, 1979; Vol. 7, p 815.

(13) (a) Verrall, E. E.; Milioto, S.; Zana, R. *J. Phys. Chem.* **1988**, *92*, 3939. (b) Jada, A.; Lang, J.; Zana, R. *J. Phys. Chem.* **1990**, *94*, 381. (c) Jada, A.; Lang, J.; Zana, R.; Makhoulfi, R.; Hirsch, E.; Candau, S. *J. Phys. Chem.* **1990**, *94*, 387.

(14) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd. ed.; Pergamon Press: New York, 1988.

(16) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989.

(17) Evans, H. C. *J. Chem. Soc.* **1956**, 579.

(18) Frahm, J.; Diekmann, S.; Haase, A. *Ber. Bunsen-Ges. Phys. Chem.*

Table 1. Critical Micelle Concentrations, cmc's, and Degree of Micelle Dissociation, α , for the Surfactants Studied, at 25 °C^a

surfactant	10 ³ cmc, M, aqueous solution ^b	10 ⁴ cmc, M, electrolyte solution ^c	α , Frahm's method	α , Evan's method	α , literature ^d
CMe ₃ ACl	1.05	0.25	0.32	0.18	0.37, 0.38, 0.25, 0.26
CMe ₂ PhACl	1.26	0.20	0.37	0.20	
CMe ₂ BzACl	0.40	0.20	0.40	0.22	0.33
CMe ₂ PhEtACl	0.19	0.20	0.41	0.22	
CMe ₂ PhPrACl	0.10	0.06	0.42	0.24	

^a Literature cmc's, determined by conductance measurement, are 0.0013 and 0.0014 M for CMe₃ACl and 0.0004 and 0.0005 M for CMe₂BzACl.²³ ^b Determined by surface tension and/or conductance measurements. Results of both techniques were in good agreement. ^c At 35 °C, in the presence of 0.5, 0.08, 0.045, and 0.04 M NaCl for CMe₃ACl, CMe₂BzACl, CMe₂PhEtACl, and CMe₂PhPrACl, respectively, and 0.15 M LiCl for CMe₂PhACl. ^d Frahm's or Evan's method.^{5b,24}

tions,²⁰ which can be suppressed by addition of a strong electrolyte to the micellar solution. The appropriate [electrolyte] was taken to be the concentration at which D_0 became invariant with [surfactant]. NaCl was used for all surfactants except CMe₂-PhACl, which required the use of LiCl in order to avoid precipitation. Since solutions of CMe₂PhACl became turbid in the presence of 0.15 M LiCl at 25 °C, all LS and fluorescence measurements were carried out at 35 °C.

Fluorescence Measurements. The method is based on analyzing the fluorescence decay curves of a probe (pyrene) in the presence of variable concentrations of a micelle-bound suppressor, cetylpyridinium chloride. Aliquots of an aqueous suppressor stock solution, whose concentration was verified by UV-vis spectroscopy ($\epsilon = 4200 \text{ M}^{-1} \text{ cm}^{-1}$ at 260 nm),²¹ were added to 4.5×10^{-6} M solutions of pyrene in 0.040 M air-equilibrated cationic surfactant containing the same concentration of salt used in the quasi-elastic LS measurements.

Fluorescence decays in the absence of quencher were analyzed utilizing the standard single-exponential decay routines of the FL-900 operating software. The micelle-quenching module of Edinburgh Instruments Level 2 analysis software was employed to fit the corresponding decay curves in the presence of quencher. In all cases, the observed fits were consistent with the Infelta-Tachiya equation for a nonmobile quencher, given by²²

$$F(t) = F(0) \exp[-t/\tau^0 - \langle n \rangle \{1 - \exp(-k_q t)\}] \quad (8)$$

where $F(0)$ is the initial pyrene fluorescence intensity at time $t = 0$, τ^0 is the pyrene fluorescence lifetime in the absence of quencher, k_q is the rate constant for intramicellar quenching, and $\langle n \rangle$ is the average number of bound quenchers per micelle. N_{agg} values were calculated from the relationship

$$N_{\text{agg}} = \frac{\langle n \rangle C_{\text{surf}}}{[\text{CPyCl}]_{\text{tot}}} \quad (9)$$

where C_{surf} is the analytical concentration of micellized surfactant and $[\text{CPyCl}]_{\text{tot}}$ is the total concentration of added quencher.

Results

Electrolyte Type and Concentration Employed in LS Measurements. Intermicellar interactions consist of two opposing forces, repulsive and attractive.¹⁶ At low electrolyte (i.e., NaCl and/or LiCl) concentrations, the micellar interactions are predominantly repulsive and the micellar diffusion coefficient increases with [surfactant]. This electrostatic repulsion depends on the ionic strength of the medium, R_h , and the mean micellar charge Q

(20) (a) Evans, D. F.; Mukerjee, S.; Mitchell, D. J.; Ninham, B. W. *J. Colloid Interface Sci.* **1983**, *93*, 184. (b) Dorshow, R. B.; Bunton, C. A.; Nicoli, D. F. *J. Phys. Chem.* **1983**, *87*, 1409. Frenot, M. P.; Néry, H.; Canet, D. *J. Phys. Chem.* **1984**, *88*, 2884.

(21) Soldi, V.; Erismann, N. M.; Quina, F. H. *J. Am. Chem. Soc.* **1988**, *110*, 5137.

(22) (a) Gehlen, M. H.; De Schryver, F. C. *Chem. Rev.* **1993**, *93*, 199. (b) Barzykin, A. V.; Tachiya, M. *Heterogen. Chem. Rev.* **1996**, *3*, 105.

($=\alpha N_{\text{agg}}$). The slope of the D versus [surfactant] plot decreases as a function of increasing the initial electrolyte concentration because of the attractive term, whose strength is determined by the Hamaker coefficient and R_h . At a certain [electrolyte] there is a net balance between intermicellar attractions and repulsions, resulting in a slope of zero for the micellar diffusion coefficient vs [surfactant] plot.²⁰ The appropriate electrolyte concentrations at which D_0 becomes invariant with [surfactant] were found to be 0.5, 0.15, 0.08, 0.045, and 0.04 M for CMe₃ACl, CMe₂PhACl, CMe₂BzACl, CMe₂PhEtACl, and CMe₂-PhPrACl, respectively. The dependence of these "critical" salt concentrations on the surfactant headgroup is due to differences in α and the Hamaker constant.^{20b}

Critical Micelle Concentrations and Degrees of Micellar Counterion Dissociation. Table 1 collects the cmc and α values for the surfactants studied, at 25 °C, along with corresponding literature values, where available. This table also lists cmc's determined at the electrolyte concentrations employed in the LS measurements. As expected, addition of electrolytes decreases the cmc's and practically eliminates their dependence on headgroup structure (for CMe₂PhACl, CMe₂BzACl, and CMe₂PhEtACl) because of the compression of the Gouy-Chapman electrical double layer. The difference between α calculated by Evan's and Frahm's methods is due to the fact that the former takes into account the contribution of the micelle (as a macroion) to the measured conductivity.

LS and Fluorescence Measurements. Micellar aggregation numbers, calculated from static LS and fluorescence measurements, and hydrodynamic radii calculated from quasi-elastic LS measurements are shown in Table 2. This table also compares the areas/surfactant headgroup's calculated from LS and surface tension measurements. As shown in Tables 1 and 2, the values of the cmc, α , N_{agg} , and area/headgroup at the micellar interface agree with available literature values for CMe₃-ACl and CMe₂BzACl.

Discussion

Effects of Headgroup Structure on the Properties of Cationic Micelles. Interpretation of the consequences of increasing the surfactant headgroup size on the micellar

(23) (a) Paredes, S.; Tribout, M.; Sepúlveda, L. *J. Phys. Chem.* **1984**, *88*, 1871. (b) Fouda, A. A. S.; Madkour, L. H.; Evans, D. F. *Indian J. Chem.* **1986**, *25A*, 1102. (c) Weinert, C. H. S. W. S. *Afr. J. Chem.* **1978**, *31*, 81. (d) Treiner, C.; Makaysse, A. *Langmuir* **1992**, *8*, 794.

(24) (a) Sepúlveda, L.; Cortés, J. *J. Phys. Chem.* **1985**, *89*, 5322. (b) Fabre, H.; Kamenka N.; Khan, A.; Lindblom, G.; Lindman, B.; Tiddy, G. J. T. *J. Phys. Chem.* **1980**, *84*, 3428. (c) Treiner, C.; Makaysse, A. *Langmuir* **1992**, *8*, 794.

(25) (a) Reiss-Husson, F.; Luzzati, V. *J. Phys. Chem.* **1964**, *68*, 3504. (b) Roelants, E.; Gelade, E.; Van Der Auwerker, Croonen, Y.; De Schryver, F. C. *J. Colloid Interface Sci.* **1983**, *96*, 288.

Table 2. Micellar Aggregation Numbers, N_{agg} , Hydrodynamic Radii, R_h , and Areas/Headgroup, A , at 35 °C

surfactant	N_{agg} , LS ^a	N_{agg} , fluorescence ^b	R_h , Å ^c	A , Å ² , surface tension	A , Å ² , LS
CMe ₃ ACl ^d	118 ± 4	138 ± 6	24.2 ± 0.8	52 ± 5	62 ± 4
CMe ₂ PhACl	112 ± 3	110 ± 9	24.8 ± 0.5	56 ± 1	69 ± 3
CMe ₂ BzACl ^e	102 ± 4	90 ± 7	24.2 ± 0.4	62 ± 2	72 ± 2
CMe ₂ PhEtACl	94 ± 4	85 ± 6	23.4 ± 0.9	69 ± 1	73 ± 4
CMe ₂ PhPrACl	85 ± 6	82 ± 4	22.5 ± 0.2	71 ± 2	75 ± 1

^a In the presence of LiCl for CMe₂PhACl and NaCl for all other surfactants; see text for details. ^b In the presence of the same salt concentrations employed in the light-scattering measurements. ^c From quasi-elastic LS measurements. ^d For this surfactant, literature N_{agg} vary from 84^{25a} to 115,^{25b} R_h vary from 23.4^{25a} to 27 Å,²⁰ and area/headgroups vary from 80^{25b} to 84 Å².^{25a} ^e For this surfactant, literature area/headgroups vary from 74.5^{26a} to 85 Å².^{26b}

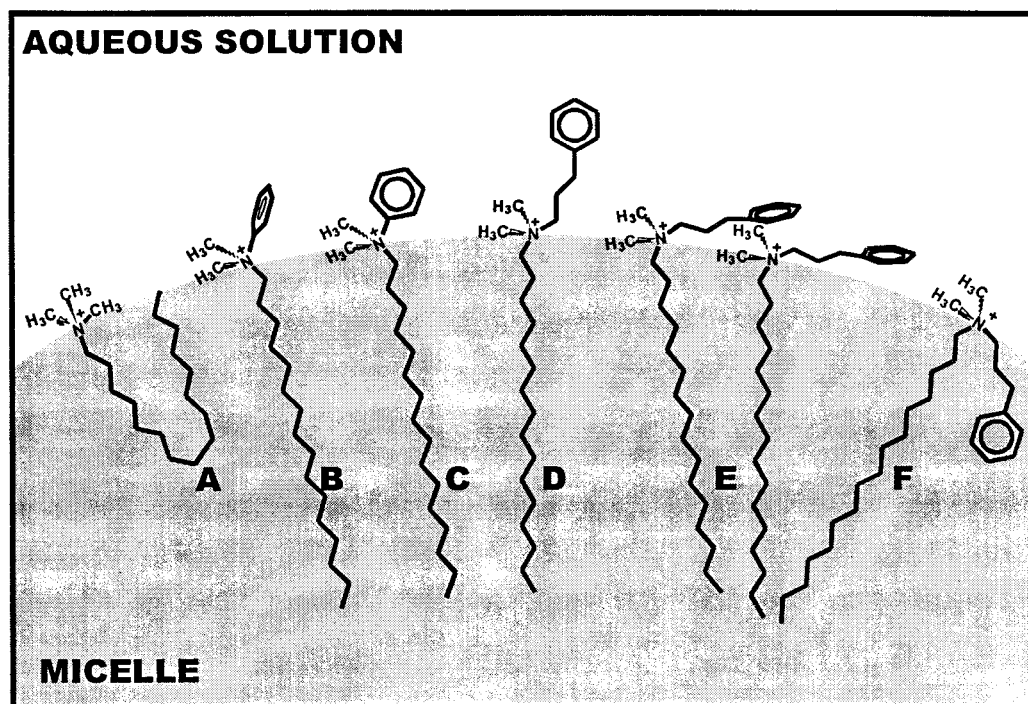


Figure 1. Schematic representation of limiting conformations of the phenyl group of CDPHACl and CDPHPrACl at the micellar interface. Structure A for CMe₂ACl indicates that all segments of the cetyl group come into some contact with water. B is energetically more favorable than C, whereas E is more favorable than F. See text for discussion.

properties is complex because the interfacial free energy of the micelle is affected by steric and electrostatic interactions between neighboring headgroups, by changes in the micellar surface charge density, and also by changes in the packing of the alkyl tails.²⁷ Additionally, long alkyl groups at the ammonium center may fold back onto the micellar surface, as well as into the micellar core, and thereby influence α and the intermicellar interactions. Therefore, the overall micellar structure depends on a balance of interactions of the headgroups with themselves and the counterions, and of the long alkyl tails in the micellar core.^{27–29} Thus, for example, several studies of the aggregation of cationic surfactants of the general structure RN⁺(R')₃Br⁻, where R = octyl to tetradecyl and R' = methyl to *n*-butyl, have shown that, for a given R, an increase in the length of R' results in a decrease in the cmc and N_{agg} and an increase in α .³⁰ Similar conclusions have been reported for a series of 1,20-bis(trialkylammonium) eicosane dibromide surfactants.³¹

We discuss our results with the aid of Figure 1, which presents a schematic representation of the limiting conformations of the surfactant monomers in the aqueous micelle. CMe₃ACl has been included because the other surfactants are derived from it by substitution of one of the methyl headgroups by a phenyl or a phenylalkyl group. Structure A was drawn to convey the notion that all segments of the cetyl chain come into some contact with water;^{12a,29} for simplicity, the cetyl chains of the other structures were drawn in the stretched, all-trans conformation. The figure also shows the limiting conformations of the two monomers in which the phenyl group is attached to the quaternary ammonium ion directly or via the *n*-propyl tether. On the basis of our previous ¹H NMR data, structure B represents the most probable conformation of the aromatic ring of CMe₂PhACl. This (average) position of the phenyl group with respect to the interface is similar to that suggested for the benzenesulfonate headgroup of micellized dodecylbenzenesulfonate.^{8,32} Three limiting conformations are depicted for CMe₂PhPrACl.

(27) (a) Chacachty, C.; Warr, G. G.; Jansson, M.; Puyong, L. *J. Phys. Chem.* **1991**, *95*, 3830. (b) Blackmore, E. S.; Tiddy, G. J. T. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1115. (c) Buckingham, S. A.; Garvey, C. J.; Warr, G. G. *J. Phys. Chem.* **1993**, *97*, 10236.

(28) Bacaloglu, R.; Blásko, A.; Bunton, C. A.; Cerichelli, G.; Shirazi,

(30) Jacobs, P. T.; Anacker, E. W. *J. Phys. Chem.* **1973**, *43*, 105. (b) Zana, R. *J. Colloid Interface Sci.* **1980**, *78*, 330. (c) Lianos, P.; Zana, R. *J. Colloid Interface Sci.* **1982**, *88*, 594. (d) Lianos, P.; Lang, J.; Zana, R. *J. Colloid Interface Sci.* **1983**, *91*, 726. (e) Malliaris, A.; Paleos, C. M. *J. Colloid Interface Sci.* **1984**, *101*, 354.

In D, the 3-phenylpropyl group stretches out into the aqueous pseudophase, perpendicular to the micelle interface. In E this group lies more or less parallel to the micellar surface, the driving force being the interaction between the aromatic ring and the quaternary ammonium ion.^{5b,29} In F this group folds back into the micellar interior, by analogy to the suggested structure of micellized dodecyltri-*n*-butylammonium bromide in water^{27b,c} and of dodecyltrimethyl-*n*-butyl- ammonium bromide in water-in-oil microemulsions.^{13a}

The change in Gibbs free energy of micellization ΔG_m° can be derived from²⁷

$$\Delta G_m^\circ = (2 - \alpha)RT \ln [\text{cmc}] \quad (10)$$

Calculated ΔG_m° are (in kJ/mol, using α obtained by Frahm's method, no added electrolyte) -28.6, -27.0, -30.8, -33.8, and -36.1 for CMe_3ACl , CMe_2PhACl , CMe_2BzACl , $\text{CMe}_2\text{PhEtACl}$, and $\text{CMe}_2\text{PhPrACl}$, respectively. For CMe_3ACl , ΔG_m° agrees with that reported elsewhere (-27.6 kJ/mol).^{23a} The fact that ΔG_m° (CMe_2PhACl) > ΔG_m° (CMe_3ACl) is opposite to the behavior observed upon incorporation of the phenyl group in 4-(alkylphenyl)-trimethylammonium halides; in the latter, the decrease in the cmc provoked by the phenyl group is equivalent to increasing the hydrophobic tail by ca. four methylene groups.³³ Regular packing of the (rigid) phenyl headgroup of CMe_2PhACl (Figure 1, conformer B) and its hydrophobic hydration probably results in a more hydrated, i.e., more polar, interface, and hence a smaller $|\Delta G_m^\circ|$. Indeed, the microscopic polarity of interfacial water, determined by the solvatochromic probe 1-methyl-8-oxyquinolinium betaine, decreases upon going from CMe_2PhACl to CMe_3ACl .³⁴ The contribution per interfacial CH_2 group decreases from 3.8 kJ/mol/ CH_2 upon going from CMe_2PhACl to CMe_2BzACl to 2.3 kJ/mol/ CH_2 upon going from $\text{CMe}_2\text{PhEtACl}$ to $\text{CMe}_2\text{PhPrACl}$. This may reflect the increased contact of the phenylalkyl group with water as the length of the "tether" is increased, e.g., as in conformer E, Figure 1.

There are several reasons for choosing conformer E as the most probable one for $\text{CMe}_2\text{PhPrACl}$. If D were preferred, the properties of the resultant micelle should not be very different from those of a CMe_3ACl micelle. Thus, with the 3-phenylpropyl group pointing away from the interface, its steric hindrance to the approach of the counterion would not be sizably different from that of a methyl group. One would expect, therefore, similar interfacial charge densities (hence similar α) and similar areas/headgroup and N_{agg} for both surfactants. Tables 1 and 2 show that this is not the case. It is also possible to calculate R_h for the surfactants employed, either from geometric considerations as outlined elsewhere^{30b,35} or by determination of the length of the surfactant monomer ($\text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_m\text{C}_6\text{H}_5\text{Cl}^-$) in the energy-minimized conformation (in the gas phase), e.g., by employing the PM3 Hamiltonian (implemented in the MOPAC93 R2 program package). The micellar radii, calculated for the extended conformation are 26.6, 28.2, 28.6, and 30.6 Å, for $m = 0, 1, 2,$ and $3,$ respectively. These radii are significantly larger than the corresponding experimental values, even when allowance is made for the fact that the optimum surfactant chain length in the micelle is less than its fully extended conformation.^{3,11} Energetic and geometric considerations imply that conformer F is unlikely. If the energy-minimization calculation (by the

PM3 method) is started with the phenylpropyl group bending inward, as shown in conformer F, then the lowest energy conformation obtained approximates that of E. On the other hand, if a constraint is imposed on the conformation of the phenylpropyl group, to maintain it as in conformation F, then the calculated surface area/headgroup is much larger than the one measured. Thus, conformers D and F are inconsistent with the micellar radii and areas/headgroup measured by quasi-elastic LS. The conclusion that they are unlikely is also in agreement with the results of our previous ^1H NMR study of the aggregation of this surfactant in D_2O .⁸ The gradual decrease in N_{agg} and R_h and the increase in the surface area/headgroup upon going from CMe_2PhACl to $\text{CMe}_2\text{PhPrACl}$ indicate that CMe_2BzACl and $\text{CMe}_2\text{PhEtACl}$ assume conformations similar to E, the interaction between the phenyl group and the quaternary ammonium ion increasing as a function of increasing m . This interaction screens the quaternary ammonium ion (α increases) and decreases the intermicellar attractive interactions. The last conclusion is in agreement with the observation that the [electrolyte] required to suppress the intermicellar interactions in the LS experiments decreases with increasing m .

Finally, there is good agreement between the aggregation numbers derived from static LS measurements and from fluorescence decay measurements. This is interesting in light of the fact that the first technique is noninvasive whereas the second one employs a relatively voluminous probe. This agreement indicates that pyrene is probably adsorbed in the interfacial region, as discussed elsewhere for this and other polycyclic aromatic compounds.^{5b,36}

Conclusions

Aggregation of a homologous series of cationic surfactants with the structure ($\text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_m\text{C}_6\text{H}_5\text{Cl}^-$), $m = 0, 1, 2,$ and $3,$ has been studied by several techniques: surface tension, conductance, static and quasi-elastic LS, and fluorescence. The properties of the anilinium type micelles, $m = 0,$ are different from those with $m \geq 1$ because the phenyl group cannot fold back onto the micellar surface. This latter conformation seems to be preferable for the other three phenyl-containing surfactants, its population increasing with m . An increase in the surfactant headgroup volume leads to a decrease in the cmc and N_{agg} and an increase in α and the interfacial area per surfactant headgroup. The good agreement between micellar weight-average molecular weights obtained from LS and fluorescence measurements indicates that pyrene is solubilized in the interfacial region.

Acknowledgment. We thank FAPESP for financial support and the CNPq and CENPES for a graduate fellowship to L.T.O. and for research productivity fellowships to F.H.Q. and O.A.E.S., and G. A. Marson for drawing Figure 1.

Supporting Information Available: Representative experimental data, showing determination of cmc for $\text{CMe}_2\text{PhEtACl}$ in water at 25 °C by surface tension; determination of cmc and α for CMe_2BzACl in water at 25 °C by conductance measurement; dependence of the diffusion coefficient of $\text{CMe}_2\text{PhPrACl}$ (measured by quasi-elastic light scattering) on $[\text{NaCl}]$; determination of the aggregate molecular weight, M_w , for $\text{CMe}_2\text{PhPrACl}$ by the Zimm plot (4 pages). Ordering and access information is given on any current masthead page.

LA9911382

(33) Wisniewski, M. *J. Colloid Interface Sci.* **1989**, *128*, 115.