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ORIGINAL CONTRIBUTION

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# A proton NMR study on aggregation of cationic surfactants in water: effects of the structure of the headgroup

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**Abstract** $^1$H NMR chemical shifts of solutions of the following cationic surfactants in $D_2O$ were determined as a function of their concentrations: cetyltrimethylammonium chloride, CTACl, a 1:1 molar mixture of CTACl and toluene, cetylpyridinium chloride, CPyCl, cetyldimethylphenylammonium chloride, CDPhACl, cetyldimethylbenzylammonium chloride, CDBzACl, cetyldimethyl-2-phenylethylammonium chloride, CDPhEtACl, and cetyldimethyl-3-phenylpropylammonium chloride, CDPhPrACl. Plots of observed chemical shifts versus [surfactant] are sigmoidal, and were fitted to a model based on the mass-action law. Satisfactory fitting was obtained for the discrete protons of all surfactants. From these fits, we calculated the equilibrium constant for micelle formation, $K$, the critical micelle concentration, CMC and the chemical shifts of the monomer, $\delta_{mon}$ and the micelle $\delta_{mic}$. $^1$H NMR-based CMC values are in excellent agreement with those which we determined by surface tension measurements of surfactant solutions in $H_2O$, allowing for the difference in structure between $D_2O$ and $H_2O$. Values of $K$ increase as a function of increasing the size of the hydrophilic group, but the free energy of transfer per $CH_2$ group of the phenylalkyl moiety from bulk water to the micellar interface is approximately constant, $1.9 \pm 0.1$ kJ mol$^{-1}$. Values of $(\delta_{mic}-\delta_{mon})$ for the surfactant groups at the interface, e.g., $CH_3$–$(CH_2)_{15}$–$N^+(CH_3)_2$ and within the micellar core, e.g., $\underline{CH_3}$–$(CH_2)_{15}$–$N^+$ were used to probe the (average) conformation of the phenyl group in the interfacial region. The picture that emerges is that the aromatic ring is perpendicular to the interface in CDPhACl and is more or less parallel to it in CDBzACl, CDPhEtACl, and CDPhPrACl.

**Key words** Cationic surfactants – aggregation – micelle formation – micellar structure – proton NMR – critical micelle concentration

## Introduction

Aqueous micelles affect rates of chemical reactions and the position of chemical equilibria that occur at the micelle-water interface [1–3]. An understanding of the nature of this interface, and the forces that come into play therein is, therefore, a prerequisite for a better understanding of micelle-mediated phenomena. In this regard, studies of cationic surfactants with headgroups of different

structures provide useful information. For example, an increase in the headgroup hydrophobicity of cetyltrialkylammonium halides (from trimethyl to tri-n-butyl) has marked effects on spontaneous decarboxylation [4] and $S_N2$ reactions [5–7]. Interfacial water is involved in, inter alia, solvation of reactants and transition states, solvation of surfactant headgroups and counterions, and in proton transfers. Interfacial water structure depends on the charge and hydrophobicity of the surfactant headgroup [8–11], this being the impetus for our interest in studying effects of headgroup structure on micellar properties.

In this paper we present a proton NMR study of the aggregation of the following cationic surfactants in $D_2O$:

$C_{16}H_{33}N^+(CH_3)_3Cl^-$,
cetyltrimethylammonium chloride, CTACl

cetylpyridinium chloride, CPyCl

$C_{16}H_{33}N^+(CH_3)_2{-}C_6H_5Cl^-$,
cetyldimethylphenylammonium chloride, CDPhACl,

$C_{16}H_{33}N^+(CH_3)_2{-}CH_2{-}C_6H_5Cl^-$,
cetyldimethylbenzylammonium chloride, CDBzACl,

$C_{16}H_{33}N^+(CH_3)_2{-}CH_2{-}CH_2{-}C_6H_5Cl^-$,
cetyldimethyl-2-phenylethylammonium chloride, CDPhEtACl,

$C_{16}H_{33}N^+(CH_3)_2{-}CH_2{-}CH_2{-}CH_2{-}C_6H_5Cl^-$,
cetyldimethyl-3-phenylpropylammonium chloride, CDPhPrACl.

Surfactant solutions at concentrations below and above the critical micelle concentrations (CMC) were prepared in $D_2O$ and the surfactant discrete protons were examined, where feasible, by $^1H$ NMR. Plots of chemical shifts versus [surfactant] are sigmoidal. Curve fitting of chemical shift data with a model based on the mass action law allowed us to calculate the following: equilibrium constant for the aggregate formation, $K$, and chemical shifts of the monomer, $\delta_{mon}$, and the micelle, $\delta_{mic}$. The last two parameters were found to be sensitive to the structure of the surfactant headgroup, and are used to probe the disposition in the interfacial region of the phenyl group relative to the surfactant quaternary ammonium ion.

## Experimental

Chemicals were obtained from Aldrich, Merck and Fluka and were purified by standard procedures [12].

### Surfactants

An aqueous solution (25%) of CTACl was evaporated to dryness, the resulting white solid was extracted with ethyl ether for 6 h. CPyCl was recrystallized in acetone.

CDPhACl was synthesised by the reaction of 21 $cm^3$ (0.18 mol) of N, N-dimethylaniline with 45.8 g (0.15 mol) of 1-bromohexadecane in refluxing absolute ethanol for 30 h. The solvent was evaporated and the residual solid was extracted with ethyl ether for 6 h, then recrystallized from acetone. M.p. 116–118 °C (literature m.p. 116–118 °C [13]). The bromide surfactant was converted into CDPhACl by ion exchange on Amberlyst A-26 macroporous anion exchange resin (Rohm and Haas). Complete bromide/chloride exchange was verified by the fluorescein test. M.p. 128–130 °C. Calculated for $C_{24}H_{44}ClN$, %: C: 75.45; H: 11.61; N: 3.67, analyzed, %, C: 75.53, H: 11.64, N: 3.54.

CDBzACl was synthesised by the reaction of equimolar amounts of purified benzyl chloride and N,N-dimethylhexadecylamine (Hoechst do Brasil, >99.5% purity) in acetone, under reflux, for 6 h. The solvent was removed, and the resulting solid was purified by extraction with ethyl ether for 6 h.

A sample of the chloride surfactant was transformed into (water insoluble, nonhygroscopic) perchlorate by the reaction with $NaClO_4$ aqueous solution. The perchlorate was filtered, washed with water and dried under reduced pressure. Calculated for $C_{25}H_{46}ClNO_4$, %: C: 65.26; H: 10.08; N: 3.04, analyzed, %, C: 65.30, H: 10.13, N: 3.26.

CDPhEtACl was synthesised by the reaction of 7.1 $cm^3$ (0.054 mol) of 1-chloro-2-phenylethane and 16.2 g (0.06 mol) of N,N-dimethylhexadecylamine in 25 $cm^3$ 1-butanol, under reflux for 20 h. The product was precipitated by the addition of ethyl ether, filtered, extracted with ethyl ether for 6 h, then recrystallized from acetone. M.p. 115–117 °C. Calculated for $C_{26}H_{48}NCl$, %: C: 76.14; H: 11.80; N: 3.42, analyzed, %: C: 76.23; H: 11.79; N: 3.48.

CDPhPrACl was synthesised by the reaction of 8 $cm^3$ (0.054 mol) of 1-chloro-3-phenylpropane and 17.5 g (0.065 mol) of N,N-dimethylhexadecylamine in 35 $cm^3$ 1-propanol, under reflux for 40 h. The work up was similar to that of CDPhEtCl. The surfactant showed two melting points at 59–60 °C and 132–134 °C, one of these is that of the hydrate (detected by I.R., KBr). It was analyzed in the perchlorate form (m.p. 65–67 °C), as given for CDBzACl. Calculated for $C_{27}H_{50}NClO_4$, %: C: 66.43; H: 10.32; N: 2.87. analyzed, %: C: 66.36; H: 10.23; N: 2.81.

### Apparatus

I.R. was carried out on Perkin–Elmer FT-1750 spectrometer. Microanalyses was carried out on a Perkin–Elmer

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CHN-2000 apparatus in the Microanalyses laboratory at the University of São Paulo. Surface tension measurements were carried out with a Lauda T-1C digital De Nöuy tensiometer, equipped with a thermostated solution compartment. In order to prevent evaporation, the latter was fitted with a glass cover. $^1$H NMR measurements were carried out with Bruker MSL-300, operating at 300 MHz for protons.

### Measurements

The Kraft temperature of CDPhACl is ca. 30 °C, so all measurements, surface tension and $^1$H NMR, were carried out at 35 °C.

*Surface tension*: Surfactant solutions were thermostated in the compartment for 15 min before carrying out the measurements. These were done automatically by the tensiometer, and were repeated until four successive measurements gave a standard deviation of 0.12 mN m$^{-1}$. Values of CMC were determined from plots of the surface tension (mN m$^{-1}$) as a function of log [surfactant].

*$^1$H NMR*: Surfactant solutions in $D_2O$ were made up, then transferred to Wilmad 528pp precision NMR tubes. These were left in the sample compartment for 15 min for thermal equilibration. Thermal stability of the spectrometer probe was ensured as given elsewhere [10, 11], and by the observation that successive measurements of the same sample were always within digital resolution limit, which was maintained at 0.18 Hz/data point. Chemical shifts were measured relative to $5.6 \times 10^{-4}$ mol dm$^{-3}$ internal dioxane, and then converted to the TMS scale. We found that the chemical shift of dioxane, relative to external 1,1,2,2-tetrachloroethane contained in a Wilmad WGS-5BL coaxial insert, is independent of [CTACl] in the concentration range $1 \times 10^{-4}$ mol dm$^{-3}$ to $1 \times 10^{-2}$ mol dm$^{-3}$.

## Results and discussion

The main thrust of the present study is to investigate effects of the variation of structure of the head group on properties of micelles formed by the cationic surfactants, CDPhACl, CDBzACl, CDPhEtACl, and CDPhPrACl. These can be considered as derived from CTACl by substituting a phenyl group, or a phenylalkyl group for one of the methyl headgroups. Therefore, we take CTACl as our reference surfactant, and compare the results accordingly. Two more systems were also investigated, namely, a 1 : 1 molar mixture of CTACl and toluene, and CPyCl. The association constant between components of the former system is relatively large, and there is indication that the distribution of aromatic solubilizates between the interfacial region and the micellar core is probably in favour of the former [14, 15]. The CTACl + toluene mixture is used as a model for the surfactants having the phenyl headgroup. It represents, however, a limiting case because the aromatic ring can assume all possible orientations with respect to the micellar interface. CPyCl represents the other extreme, i.e., a surfactant with a rigid headgroup, the heterocycle ring, whose movements with respect to the interface are severely restricted.

In order to investigate the average disposition of the phenyl group with respect to the interface, as a function of the length of the "tether" or "spacer" between the aromatic ring and the quaternary ammonium ion, we measured the dependence of the chemical shifts of the discrete surfactant protons on surfactant concentration above and, where possible below the surfactant CMC, which we determined by surface tension. As shown below, $^1$H NMR is a powerful technique, not only for probing (average) conformations of the headgroups at the interface, but also for the determination of some basic properties of the micelle, the CMC, and $K$.

### A model for the study of surfactant aggregation by NMR

Using the mass-action model for micelle formation [16], neglecting effects from the counterions, and assuming the formation of a micelle with an average aggregation number, $N$, we can write for the aggregation process:

$$N\,\mathrm{mon} \rightleftharpoons \mathrm{mic}$$

$$c_{\mathrm{mon}}/c^0 = (c_{\mathrm{mic}}/c^0)^{1/N} \cdot K^{(1-1/N)} \tag{1}$$

where $c_{\mathrm{mon}}$, $c_{\mathrm{mic}}$, and $c^0$ refer to the molarities of the monomer, the micelle, and the standard state concentration, $c^0 = 1$ mol dm$^{-3}$, respectively, $K^{(1-1/N)}$ is the association constant of the "all-or-nothing" process. The total surfactant concentration, $c_{\mathrm{tot}}$, is given by:

$$c_{\mathrm{tot}} = c_{\mathrm{mon}} + N \cdot c_{\mathrm{mic}} \,. \tag{2}$$

If the exchange of surfactant monomers between bulk solution and the micelle is fast on the NMR time scale (i.e., $k_{\mathrm{ex}} \gg |\delta_{\mathrm{mon}} - \delta_{\mathrm{mic}}|$, then the predicted average chemical shift is given by:

$$\delta_{\mathrm{av}} = (\delta_{\mathrm{mon}}\, c_{\mathrm{mon}}/c_{\mathrm{tot}}) + (\delta_{\mathrm{mic}}\, N\, c_{\mathrm{mic}}/c_{\mathrm{tot}}) \,. \tag{3}$$

The model, defined by Eqs. (1–3), fits the observed chemical shift data, $\delta_{\mathrm{obs}}$, reasonably well. The correlation between $K$ and $N$ is relatively strong, and a literature survey indicated that $90 < N < 120$ for CTACl, CDBzACl

and CPyCl [17], so that we took $N = 100$ for all surfactants. Best-fit values of the parameters, $\delta_{mon}$, $\delta_{mic}$ and $K$ were then determined by nonlinear regression. Although it is not possible to give the function $\delta_{av}(c_{tot})$ in analytical form, the function can easily be evaluated by a computer subroutine which evaluates $c_{mon}$, $c_{mic}$ and hence $\delta_{av}$ for any value of $c_{tot}$ by iteration. We used the "next-guess factor, $g$" described by Chaston [18]. In our case, $g$, is given by the expression:

$$g(i) = c_{tot}/[c_{mon}(i) + N\,c_{mic}(i)] \,. \quad (4)$$

For a given value of $c_{tot}$, the first next-guess value, $g(1)$, is calculated by taking $c_{mic}(1) = c_{tot}/N$ as the initial guess, and then using Eq. (1) to calculate $c_{mon}$ (1). The second, improved value of $c_{mic}$ (2), is obtained by using the expression (with $i = 1$):

$$c_{mic}(i + 1) = g(i)c_{mic}(i) \quad (5)$$

which is then used to calculate $g(2)$ , and so on. The concentrations converge on their equilibrium values as $g \rightarrow 1$. The number of iterations needed depended on values of $c_{tot}$, $K$ and the precision required. We found fewer than 100 iterations were adequate for our purpose, iteration being continued until either $|g - 1| \leq 0.001$ or $c_{mic}/c_{tot} \leq 0.001$. We used the Levenberg-Marquardt method of nonlinear regression (NLR) provided by the statistical data analysis package SPSS (SPSS Inc., 444 North Michigan Ave., Chicago, IL 60611) running on a microcomputer. The iterative subroutine for the function $\delta_{av}(c_{tot})$ was incorporated into the NLR model expression. Finally, it should be noticed that in terms of this model, the CMC is that when $c_{mic} = c_{mon}$, which from Eq. (1) gives:

$$CMC = c^0/K \,. \quad (6)$$

## Application of the model to cationic surfactant

Table 1 shows $K$, $\delta_{mon}$, $\delta_{mic}$ which was calculated from our $^1$H NMR data according to the above discussed aggregation model. The following is relevant:

1) CMC values calculated from $K$ by Eq. (6) are: 0.001, 0.0004, 0.0002, 0.0001 and 0.00005 mol dm$^{-3}$, for CTACl, CDPhACl, CDBzACl, CDPhEtACl and CDPhPrACl, respectively. The corresponding values which we obtained by surface tension measurements are: 0.001, 0.0008, 0.0003, 0.0001, and 0.00007 mol dm$^{-3}$, respectively. The agreement between the two sets of data is excellent, considering that the CMC of a surfactant in $D_2O$ solution is expected to be slightly lower than that in $H_2O$ because the former is a more structured liquid [19].

2) The standard free energy of micellization is calculated from $\Delta G^0 = -RT \ln K$. Taking CTACl as a reference surfactant, we obtain the following values for $\Delta\Delta G^0 = \Delta G^0$ CTACl $- \Delta G^0$ surfactant: 1.08, 2.52, 4.53, 6.39 and 8.27 kJ mol$^{-1}$, for CTACl + toluene (1 : 1 mixture), CDPhACl, CDBzACl, CDPhEtACl and CDPhPrACl, respectively. As expected, toluene enhances the aggregation of CTACl because of its interaction with the monomer below the CMC, as argued elsewhere [14, 15], and from the fact that the CMC of CTACl + toluene (1 : 1 mixture) is $5 \times 10^{-4}$ mol dm$^{-3}$, i.e., is lower than that in the absence of the solubilizate. Values of $\Delta\Delta G^0$ for the other surfactants indicate that the standard free energy of transfer of a $CH_2$ moiety in the phenylalkyl group, from bulk water to interfacial water, i.e., that at the micellar interface is $1.9 \pm 0.1$ kJ mol$^{-1}$. This value is lower than that calculated for the transfer of a $CH_2$ moiety in the surfactant hydrophobic tail from bulk water to the micellar interior, 3.2 kJ mol$^{-1}$ [20]. This is understandable in terms of the different environment of the $CH_2$ group at the two sites, being highly aqueous at the interface, and essentially anhydrous in the core of the micelle.

3) For each surfactant, we were able simultaneously to fit the chemical shift data ($\delta_{obs}$) for the five (in some cases, six) resolvable surfactant proton resonances, with a multiparameter model. One parameter, $K$, is characteristic of the surfactant, whereas each of the protons is characterised by two parameters, $\delta_{mon}$ and $\delta_{mic}$. The fits are shown in Figs. 1 and 2, in which we have plotted the reduced chemical shift ($\delta_{obs} - \delta_{mon}/\delta_{mic} - \delta_{mon}$) versus [surfactant]. The model may be regarded as being satisfactory, since in every case the correlation coefficient $R > 0.999$. Although data scatter is evident in some of the plots, the mean square residuals, in the best case, (CPyCl) 0.15 Hz$^2$, and in the worst cases, (CDPhEtACl and CDPhPrACl) ca. 8 Hz$^2$, can be accounted for by the uncertainties associated with the chemical shift data, especially in cases where the resonances are not sharp singlets and where the signal/noise ratio was less than was usual on account of the need to work with extremely dilute solutions, in the $10^{-6}$ to $10^{-3}$ mol dm$^{-3}$ range, in the case of surfactants with low values of CMC, vide supra, item 1).

4) Focusing on the individual chemical shifts of the *monomers*, we note that for the hydrophobic tail they are independent of the structure of the surfactant. For example, for $\underline{CH_3}$–$\overline{(CH_2)_{15}}$–$N^+$ the average $\delta_{mon}$ is $238.9 \pm 8.6$ Hz, and if the two extreme values are not considered (CDPhEtACl and CDPhPrACl), the shift narrows to $238.7 \pm 3.3$ Hz. The same applies to the $CH_3$–$\underline{(CH_2)_{14}}$–$CH_2$–$N^+$ whose average $\delta_{mon}$ value is $362.7 \pm 4.4$ Hz. Thus there is no detectable interaction between the phenyl headgroup and the long-chain alkyl group in the monomer.

5) One can probe the disposition of the phenyl headgroup with respect to the interface from the sign, and

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**Table 1** Equilibrium constant of aggregation, $K$, chemical shift of the monomer, $\delta_{mon}$, and difference between chemical shift of the micelle and the monomer, $\delta_{mic} - \delta_{mon}$, calculated from the data of Figs. 1 and 2 using Eqs. (1–3)[a]

| Surfactant/proton | K | $\delta_{mon}$/Hz | $\delta_{mic} - \delta_{mon}$/Hz |
|---|---|---|---|
| CTACl | 883.5 ± 57.1[b] | | |
| $\underline{CH_3}$-$(CH_2)_{15}$-$N^+$ | | 241.8 ± 0.4 | 11.9 ± 2.3 |
| $\underline{CH_3}$-$(CH_2)_{14}$-$CH_2$-$N^+$ | | 367.1 ± 0.4 | 8.6 ± 2.2 |
| $CH_3$-$\underline{(CH_2)_{14}}$-$CH_2$-$N^+$ | | 963.3 ± 0.4 | 10.4 ± 2.3 |
| $CH_3$-$(CH_2)_{15}$-$N^+\underline{(CH_3)_3}$ | | 912.4 ± 0.4 | 14.4 ± 2.5 |
| CTACl + Toluene (1 : 1) | 1344.8 ± 162.8 | | |
| $\underline{CH_3}$-$(CH_2)_{15}$-$N^+$ | | 241.9 ± 0.5 | 5.2 ± 1.5 |
| $\underline{CH_3}$-$(CH_2)_{14}$-$CH_2$-$N^+$ | | 366.9 ± 0.5 | 5.0 ± 1.5 |
| $CH_3$-$\underline{(CH_2)_{14}}$-$CH_2$-$N^+$ | | 962.3 ± 0.6 | 5.2 ± 1.6 |
| $CH_3$-$(CH_2)_{15}$-$N^+\underline{(CH_3)_3}$ | | 911.6 ± 0.6 | 8.0 ± 1.6 |
| CPyCl | 1241.5 ± 21.3 | | |
| $\underline{CH_3}$-$(CH_2)_{15}$-$N^+$ | | 239.3 ± 0.4 | −23.4 ± 1.2 |
| $\underline{CH_3}$-$(CH_2)_{14}$-$CH_2$-$N^+$ | | 362.0 ± 0.4 | −28.6 ± 1.2 |
| Ring o-H | | 2637.7 ± 0.4 | 36.2 ± 1.3 |
| Ring m-H | | 2412.2 ± 0.4 | 27.1 ± 1.2 |
| Ring p-H | | 2548.8 ± 0.4 | 26.2 ± 1.2 |
| CDPhACl | 2261.7 ± 152.8 | | |
| $\underline{CH_3}$-$(CH_2)_{15}$-$N^+$ | | 235.4 ± 1.3 | −39.5 ± 2.9 |
| $\underline{CH_3}$-$(CH_2)_{14}$-$CH_2$-$N^+$ | | 358.3 ± 1.5 | −48.7 ± 3.0 |
| $CH_3$-$\underline{(CH_2)_{15}}$-$N^+\underline{(CH_3)_2}$ | | 1061.0 ± 1.5 | 29.1 ± 2.9 |
| Ring o-H | | 2308.8 ± 1.7 | 25.0 ± 3.2 |
| CDBzACl | 5176.0 ± 593.0 | | |
| $\underline{CH_3}$-$(CH_2)_{15}$-$N^+$ | | 240.9 ± 1.2 | 8.7 ± 2.7 |
| $\underline{CH_3}$-$(CH_2)_{14}$-$CH_2$-$N^+$ | | 366.4 ± 1.1 | 4.2 ± 2.9 |
| $CH_3$-$\underline{(CH_2)_{15}}$-$N^+\underline{(CH_3)_2}$ | | 888.3 ± 2.1 | 2.0 ± 4.2 |
| $C_6H_5$-$\underline{CH_2}$-$N^+$ | | 1326.2 ± 1.3 | −8.5 ± 2.8 |
| Ring o-H | | 2247.3 ± 1.7 | −23.2 ± 2.5 |
| CDPhEtACl | 10643.2 ± 1008.1 | | |
| $\underline{CH_3}$-$(CH_2)_{15}$-$N^+$ | | 247.4 ± 3.3 | 5.4 ± 8.6 |
| $\underline{CH_3}$-$(CH_2)_{14}$-$CH_2$-$N^+$ | | 367.2 ± 2.5 | 7.9 ± 6.0 |
| $CH_3$-$\underline{(CH_2)_{14}}$-$CH_2$-$N^+$ | | 1034.2 ± 2.6 | −24.9 ± 6.0 |
| $CH_3$-$(CH_2)_{15}$-$N^+\underline{(CH_3)_2}$ | | 916.8 ± 2.8 | −9.3 ± 6.6 |
| $C_6H_5$-$CH_2$-$\underline{CH_2}$-$N^+$ | | 1018.5 ± 4.0 | −87.9 ± 7.0 |
| CDPhPrACl | 23583.3 ± 7154.7 | | |
| $\underline{CH_3}$-$(CH_2)_{15}$-$N^+$ | | 230.3 ± 11.4 | 39.3 ± 14.7 |
| $\underline{CH_3}$-$(CH_2)_{14}$-$CH_2$-$N^+$ | | 359.0 ± 5.9 | 29.9 ± 8.4 |
| $CH_3$-$\underline{(CH_2)_{14}}$-$CH_2$-$N^+$ | | 965.1 ± 6.9 | −62.6 ± 9.2 |
| $CH_3$-$(CH_2)_{15}$-$N^+\underline{(CH_3)_2}$ | | 886.2 ± 5.9 | −17.0 ± 8.4 |

[a] determined from measurements at 35 °C, at 300 MHz.
[b] The uncertainties given are for the 95% confidence interval.

magnitude of $\delta_{mic} - \delta_{mon}$. At the outset, the effect of aggregation on chemical shift can be attributed to a combination of "medium effect", resulting from the substitution of a sizeable part of the hydrocarbon/water contact in the monomer by hydrocarbon/hydrocarbon contact in the aggregate, and "conformation effect" resulting from a change in conformation of the alkyl chain. Both effects lead to a downfield shift of the $^1$H NMR peaks of the discrete groups of the aggregated surfactant [16, 21]. In other words, in the absence of any other specific

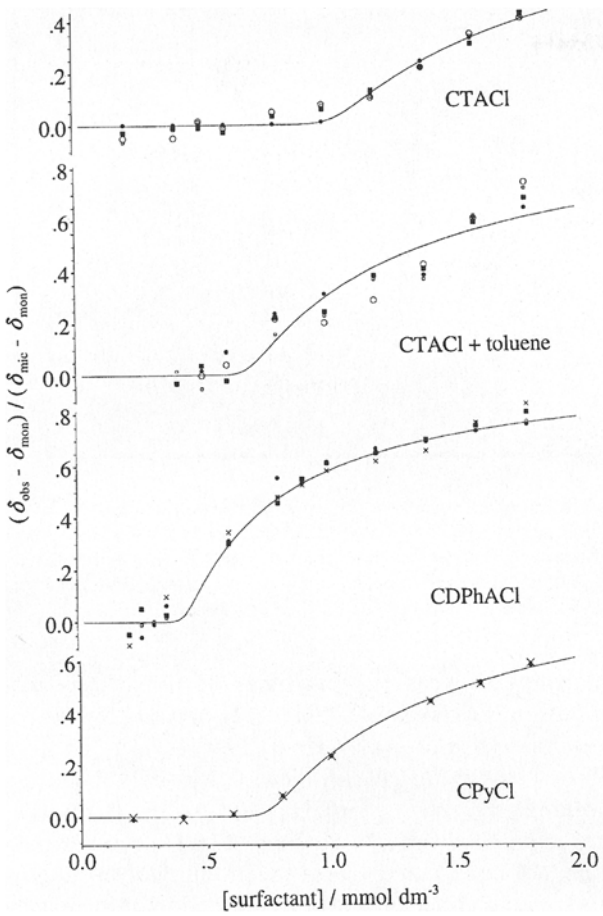


**Fig. 1** Variation of reduced chemical shifts for the discrete protons, $(\delta_{obs} - \delta_{mon})/(\delta_{mic} - \delta_{mon})$, with surfactant concentration, [surfactant] for CTACl, CTACl + toluene (1 : 1), and CPyCl. The points are for: $\underline{CH_3}$–$CH_2)_{15}$–$N^+$(○), $CH_3$–$\underline{(CH_2)_{14}}$–$CH_2$–$N^+$ (●), $CH_3$–$(CH_2)_{14}$–$\underline{CH_2}$–$N^+$ (□), $CH_3$–$(CH_2)_{15}$–$N^+$ $\underline{CH_3)_3}$ (■), o-, m-, and p-hydrogen of the heterocycle ringe (×). For CpyCl, many of the data points coincide

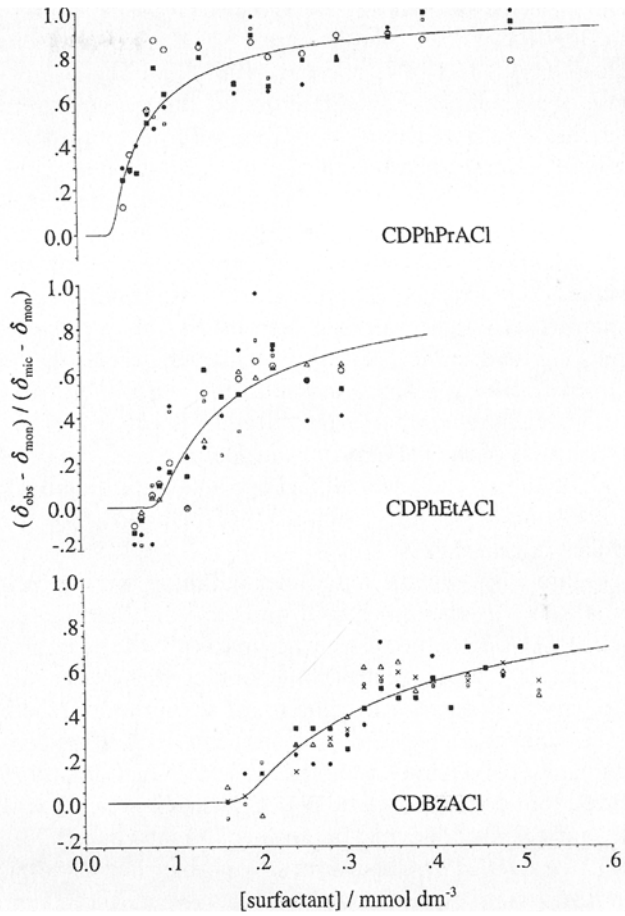


**Fig. 2** Variation of reduced chemical shifts for discrete protons, $(\delta_{obs} - \delta_{mon})/(\delta_{mic} - \delta_{mon})$, with surfactant concentration, [surfactant] for CDPhACl, CDBzACl, CDPhEtACl, and CDPhPrACl. The points are for $\underline{CH_3}$–$CH_2)_{15}$–$N^+$(○), $CH_3$–$\underline{(CH_2)_{14}}$–$CH_2$–$N^+$ (●), $CH_3$–$(CH_2)_{14}$–$\underline{CH_2}$–$N^+$ (□), $CH_3$–$(CH_2)_{15}$–$N^+$ $\underline{CH_3)_2}$ (■), $C_6H_5$–$\underline{CH_2}$–$N^+$ (△), $C_6H_5$–$CH_2$-$\underline{CH_2}$–$N^+$ (△), o-hydrogen of the aromatic $\underline{\text{ring}}$ (×)

interaction that affects the observed chemical shift, one expects a positive value of $\delta_{mic} - \delta_{mon}$, as can be seen for *all* discrete protons of CTACl, Table 1. An aromatic ring affects the chemical shift because of diamagnetic anisotropy (the so-called "ring current effect"); this leads to shielding (i.e., an upfield shift), or deshielding (downfield shift) depending on the (average) disposition of the phenyl ring with respect to the surfactant segment in question. The sum of these interactions gives the observed overall value of $\delta_{mic} - \delta_{mon}$, and sheds light on the orientation of the phenyl ring with respect to the interface. This agrees with the results of CTACl + toluene whose $\delta_{mic} - \delta_{mon}$ values are ca. half of the corresponding CTACl ones, undoubtedly because of the presence of the aromatic solubilizate. As given above, this mixture represents a limiting case because the aromatic ring can assume all possible orientations with respect to the micellar interface, and the overall (average) effect on the chemical shift appears to be deshielding.

It is instructive to divide the other surfactants into two classes, class I is that in which the freedom of motion of the aromatic or heterocycle ring is severely restricted, CPyCl and CDPhACl. In class II, CDBzACl, CDPhEtACl, and CDPhPrACl, the motion of phenyl group is less restricted, and probably its amplitude increases as a function of increasing the length of the molecular tether between the ring and the quaternary ammonium ion. Similarly, we separately discuss values of $\delta_{mic} - \delta_{mon}$ for the surfactant groups at the interface, $CH_3$–$(CH_2)_{14}$–$\underline{CH_2}$–$N^+$ and

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$CH_3$–$(CH_2)_{15}$–$N^+$ $(CH_3)_3$ or $CH_3$–$(CH_2)_{15}$–$N^+(CH_3)_2$, and those in the core of the micelle $CH_3$–$(CH_2)_{14}$–$CH_2$–$N^+$ and $CH_3$–$(CH_2)_{14}$–$CH_2$–$N^+$, because the additional shielding/deshielding contribution from the aromatic ring is most likely to depend on the location of the segment in the micelle, i.e., interface or core.

As shown in Table 1, for class I surfactants, values of $\delta_{mic} - \delta_{mon}$ are negative for groups in the micellar core, and positive for the ones at the interface; whereas the inverse is true for class II surfactants! These results can be explained by considering the orientations of the phenyl group at the interface, and the consequent effect on the value of $\delta_{mic} - \delta_{mon}$. The dynamic nature of the micelle has to be borne in mind, that is, the micellar "interface" fluctuates because of the movement of monomers, and the cetyl chain, including the terminal $CH_3$ group, by folding back on itself has a certain probability of being part of the micellar interface [22].

Figure 3 is a schematic representation of limiting conformations of the phenyl group in CDPhACl and CDPhPrACl. Structure A was drawn to convey the notion that the cetyl group comes into contact with water, for simplicity all other structures were drawn in the stretched, all-trans conformation. Calculations using the Mopac program package (version 6.0), and recent $^1$H NMR data [11] showed that conformer A or B of CDPhACl are energetically more favourable than conformer C. Likewise, conformer E of CDPhPrACl is more favourable than D [10]. It is clear from A, and from our $\delta_{mic} - \delta_{mon}$ data, that segments of the cetyl group that sample the interface are likely to be located (on the average) parallel to the $\pi$ electron cloud of the aromatic ring. From the conclusion of point (4), regarding the negligible interaction between the phenyl group and the long-chain alkyl group in the monomer, and the fact that this chain is shielded by the aromatic ring in the micelle, one expects that $\delta_{mic} - \delta_{mon}$ for class I surfactants $< \delta_{mic} - \delta_{mon}$ for CTACl, in agreement with results of Table 1. For the $CH_3$–$(CH_2)_{15}$–$N^+(CH_3)_2$, group of CDPhACl, $\delta_{mic} - \delta_{mon}$ is positive, but larger than that of CTACl, probably because of some deshielding by the aromatic ring.

The phenyl group in CDPhPrACl lies parallel to the interface, and its effect on the chemical shift of $CH_3$–$(CH_2)_{14}$–$CH_2$–$N^+$ and $CH_3$–$(CH_2)_{15}$–$N^+(CH_3)_2$, in the micelle will be (on the average) shielding, i.e., $\delta_{mic} - \delta_{mon}$ is negative, in agreement with the data of Table 1. Folding of the cetyl chain puts the segments of this group in the same plane as that of the aromatic hydrogens, i.e., the net effect, in the micelle will be deshielding, and $\delta_{mic} - \delta_{mon}$ is positive, Table 1.

Results of CDBzACl and CDPhEtACl are similar to that of CDPhPrACl, but the magnitudes of the effect of the phenyl group on $\delta_{mic} - \delta_{mon}$ depend on the number of

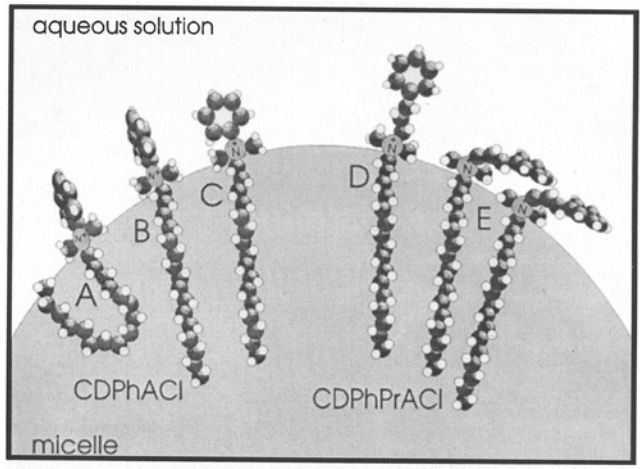


**Fig. 3** Schematic representation of limiting conformations of the phenyl group in CDPhACl and CDPhPrACl at the micellar interface. Structure A indicates that the cetyl group is in contact with water. A or B is energetically more favourable than C, and E is more favourable than D. See text for further discussion

$CH_2$ groups between the ring and the quaternary ammonium ion. For example, $CH_3$–$(CH_2)_{14}^{+}CH_2$–$N^+$ gradually increases from $-48.7$ Hz to 29.9 Hz in going from CDPhACl to CDPhPrACl. Likewise, for the same structural change, $\delta_{mic} - \delta_{mon}$ for $CH_3$–$(CH_2)_{15}$–$N^+(CH_3)_2$ decreases gradually from 29.1 Hz to $-17.0$ Hz. So, our data indicate, not unexpectedly, that the mobility of the phenyl group at the interface increases as a function of increasing the length of the molecular tether.

## Conclusions

$^1$H NMR is a powerful technique to study the aggregation of surfactants. Changes in the chemical shifts of discrete surfactant protons can be fitted to a mass-action low model, the results of the fit provide reliable estimates for the values of some important properties of the micelle, e.g., $K$, and CMC. Differences between the chemical shifts of the surfactant molecules in the monomeric and aggregated states give an insight into the structure of the different regions of the micelle, the core and the interface. The present work shows the importance of NMR in studying effects of systematic changes in the structure of the surfactant on its aggregation behaviour.

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