

Hydration of Alkylammonium Salt Micelles – Influence of Bromide and Chloride Counterions

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The micellization process of dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) was studied. Nuclear magnetic resonance method was used. The ^1H NMR and ^{13}C NMR spectra were taken at higher and lower concentrations than the critical micelle concentrations (CMC) of the compounds studied. Chemical shifts were analysed. The studies performed were prompted by earlier calorimetric measurements which showed that there were significant qualitative and quantitative differences in the micellization process of the compounds studied. Namely, DTAB micelle dissociation was found to be an endothermic process while that of DTAC was exothermic. The differences found must be the result of differentiated influence of bromide and chloride counterions on the micellization process, including the phenomenon of micelle hydration. The objective of the work was to check whether cationic surfactant counterions can influence the micelle hydration process. Indeed, DTAB and DTAC, as monomers, exhibit similar hydrophobic hydration, but DTAB micelles are more hydrated than DTAC ones.

It seems that the differences found in micellization of both salts studied may be attributed to different physicochemical properties of bromide and chloride ions, such as their mobilities and radii of their hydrated forms. Moreover, the effect of anions on the water structure must be taken into account. It is important whether the anions can be classified as water ordering kosmotropes, that hold the first hydration shell tightly, or water disordering chaotropes, that hold water molecules in that shell loosely.

Introduction

Bromide and chloride salts of the same amphiphile differ in their physicochemical properties in various experiments. For instance, the biological activity of some amphiphilic compounds was found to be dependent on the kind of the anionic partner of a cationic surfactant (Kleszczyńska *et al.*, 1998; Kleszczyńska and Sarapuk, 1998; Sarapuk *et al.*, 1998; 1999). They were also found to affect differently cationic surfactant adsorption to cationic-anionic monolayers (Góralczyk, 1993; 1994) and the rate of anion transport through liquid membranes (Christiansen *et al.*, 1979). Also substitution of the chloride counterion by bromide changes the critical micelle concentration of the compound (CMC), the enthalpy (ΔH_m), volume of the micelle (De Lisi *et al.*, 1988) and induces a structural change in the micelle. It was shown that the presence of a chloride ion leads to the formation of globular micelles while a bromide ion induces the formation of cylindrical micelles (Mikulski 1991; 1993).

The role of counterions in the micellization process is not quite clear. They may induce different hydration of micelles and this was the reason why we have undertaken hydration studies of the micellization. It must be underlined that both bromide and chloride belong to a group of ions that are referred to as chaotropic compounds affecting solute solubility. Such ions increase solubility by disordering the water structure (Collins and Washabough, 1985; Washabough and Collins, 1986; Collins, 1995; 1997; de-Paula and Schreier, 1996). Chaotropic properties of the bromide ion are significantly more pronounced than those of chloride.

To explain the significance of bromide and chloride ions in the micellization process we used NMR and calorimetric techniques. Some parameters describing behaviour of DTAB and DTAC in water (CMC and ΔH_m) were found earlier (De Lisi *et al.*, 1988; Różycka-Roszak *et al.*, 1988; Mosquera *et al.*, 1998). Calorimetric studies in the case of DTAC were repeated because the shape of the titration curves is more sensitive to any

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changes in its structure than the CMC and ΔH_m values (Różycka-Roszak *et al.*, 1988; Różycka-Roszak 1990).

Materials and Methods

Calorimetric measurements were done by means of the titration method with a home-made calorimeter at 298 K (Różycka-Roszak, 1990). The titrant containing an appropriate amount of the compounds studied was delivered to 20 ml of bidistilled water at a constant speed of $0.125 \text{ ml} \cdot \text{min}^{-1}$. The temperature was measured continuously as the volume of titrant increased. The experimental curves were corrected as described earlier and adiabatic curves of the dilution enthalpy ΔH were obtained (Różycka-Roszak *et al.*, 1988).

^1H NMR and ^{13}C NMR spectra were recorded by an Avance Bruker DRX 300 Spectrophotometer at 300.13 MHz. The compounds studied were dissolved in D_2O . The D_2O signal of the heavy water solvent was used as a chemical shift reference for ^1H -NMR. Reference capillaries with CDCl_3 were used in the case of ^{13}C NMR. Experiments were done at 298 K.

Dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) were purchased from Sigma Chem., St Louis, USA. They were dried under vacuum at least 24 h before use.

The carbon atoms in dodecyl chain were numbered as follows:

1 2 3 4

$[(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_9-\text{CH}_3]\text{X}$, with $\text{X} = \text{Br}^-$ or Cl^-

Results and Discussion

Examples of corrected adiabatic curves obtained by the calorimetric measurements are shown in Fig. 1 (titration to water). Significant differences were found in the behaviour of DTAC and DTAB compounds. Titration curves for both compounds are markedly different. The initial slope of the dilution curve corresponds to micelle dissociation (Kresheck and Hargraves, 1974; Różycka-Roszak *et al.*, 1988; Różycka-Roszak, 1990). For DTAC the process is exothermic while for DTAB it is endothermic. By a first approximation we can assume that the endothermic process of micelle dissociation implies that the energy breaking the hydrocarbon contact in the micelle interior

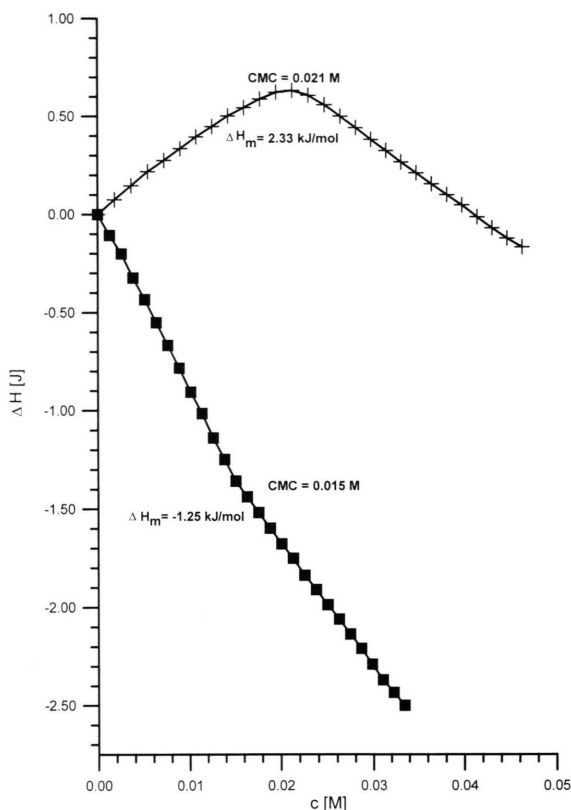


Fig. 1. Calorimetric titration curves of DTAC (+) and DTAB (■) to water. CMC, critical micelle concentration; ΔH_m , enthalpy of micellization; DTAC, dodecyltrimethylammonium chloride; DTAB, dodecyltrimethylammonium bromide.

is greater than the hydration heat released by the attachment of water molecules to the hydrocarbon chain. The opposite is true for the exothermic process. The enthalpies of micellization and the critical micelle concentrations calculated according to (Różycka-Roszak, 1990) were 2.33 kJ/mol and 0.021 M for DTAC and -1.25 kJ/mol and 0.015 M for DTAB, which is in good agreement with data obtained earlier (De Lisi *et al.*, 1988; Różycka-Roszak *et al.*, 1988).

^1H NMR spectra taken for a concentration range of 800 mM to 1 mM, i. e., above and below the CMC of DTAC and DTAB revealed that the nine methylene groups (no 3, see Materials and Methods) in the aliphatic chain give two overlapping signals. Protons of the first methylene group (no 1) give a multiplet. It was previously found

that DTAC micelles are hydrated to the depth of two $-\text{CH}_2-$ groups (Różycka-Roszak *et al.*, 1989). That is why the positions of chemical shifts of the first two methylene groups (nos 1 and 2) and methyl groups on nitrogen atom were analysed for both compounds as a function of concentration and shown in Fig. 2. The positions of particular groups of protons at concentrations below CMC are practically constant and the same for both compounds. These positions are downfield shifted at concentrations higher than CMC. The shifts are small but significant, and were observed more pronounced for DTAB. Such downfield shifts are typical for hydrogen bond protons (Slejko and Drago, 1973). In case of micelles the downfield shift suggests their hydration (Różycka-Roszak *et al.*, 1989). Since this shift is greater for DTAB micelles

than that for DTAC, the latter compound must be less hydrated.

^{13}C NMR spectra were recorded under the same experimental conditions. Spectra obtained at concentrations lower than CMC like those in proton NMR studies were concentration-independent. At concentrations above CMC the chemical shifts for 2- CH_2 and 3- CH_2 groups as well as for carbon atoms on the nitrogen atom were downfield-shifted in micelles (Fig. 3). The changes in chemical shifts were more pronounced for DTAB than DTAC micelles. The downfield shift is interpreted as a change from *cis* to *trans* conformation upon micellization (Söderman and Guering, 1986). Signals originating from the 1- CH_2 carbon for both types of micelles are, contrary to signals from all other carbons, upfield-shifted. The upfield shift is assumed to be the result of hydrogen bonding. The first methylene group hydrogen bonds are particu-

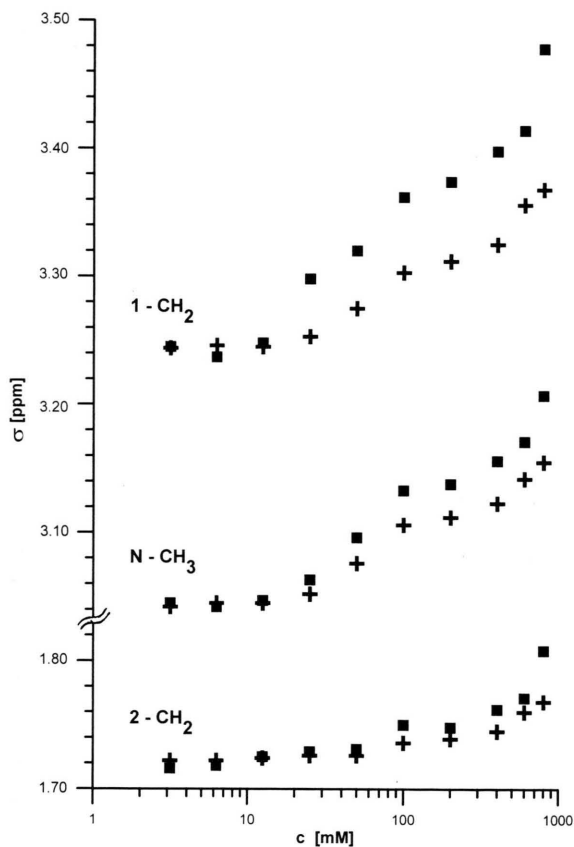


Fig. 2. Comparison of ^1H -NMR chemical shift σ in parts per million (ppm) of DTAB (■) and DTAC (+) solutions in D_2O as a function of concentration of DTAB and DTAC.

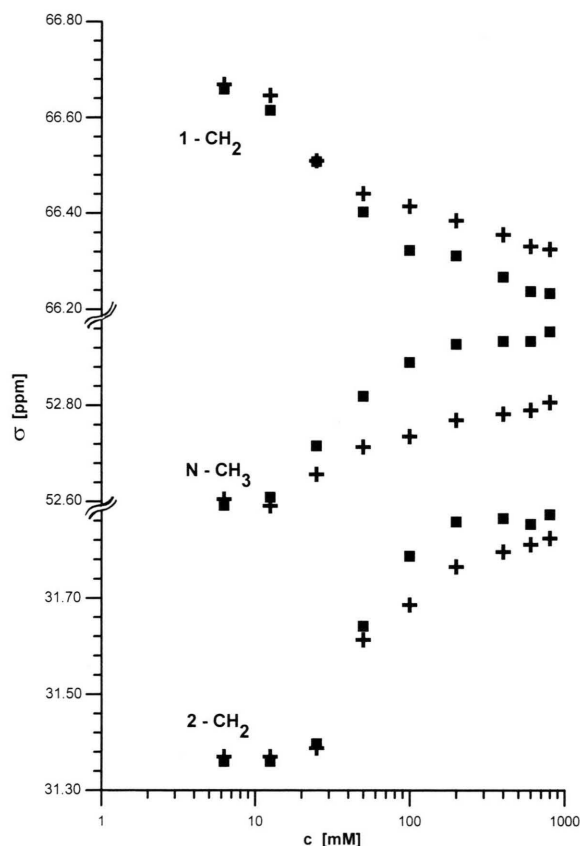


Fig. 3. Comparison of ^{13}C -NMR chemical shift σ in parts per million (ppm) of DTAB (■) and DTAC (+) solutions in D_2O as a function of their concentration.

lary strong because they involve $N^+ - C - H \cdots O$ interaction (Nina *et al.*, 1995). This interaction leads to delocalization of the positive charge over the $1-CH_2$ group. The upfield shift for DTAB micelles was more pronounced, indicating that DTAB micelles are more hydrated than DTAC ones. This conclusion agrees with that obtained by the 1H NMR results.

So, the experiments performed showed that both halides studied influence the micellization process in different degree. Better modifying properties exhibited bromide ion. This may be due to somewhat different physicochemical properties of counterions studied. For instance, both ions have different dimensions of hydrated or effective forms, charge densities and electrophoretic mobilities (Dołowy 1977). It results in their different capacity to disorder water molecules. Hence, chaotropes-induced micelle modification, especially the alteration of the electronic surface properties of a micelle becomes more evident with bromide coun-

terion and may lead to higher hydration of micelles. It must be noted that chaotropic properties of chloride are regarded as negligible (Collins 1995; 1997) or even slightly kosmotropic i. e., water molecules ordering (de-Paula and Schreier 1996). The higher degree of micelle hydration followed by stronger counterion binding decreases the head group repulsion between surfactant molecules in the micelle and decreases the interfacial area per molecule. This may explain the preference of the bromide counterion to induce rod-like structures. Calorimetric curves are most important evidence of different influence of halide anions studied on hydration of alkylammonium salt micelles. They clearly show a qualitative and quantitative dependence of this process on counterion used.

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