Micellization Process – Temperature Influence on the Counterion Effect

Bożenna Różycka-Roszak*, Romuald Żyłka and Janusz Sarapuk

Department of Physics and Biophysics, Agricultural University, Norwida 25,50–375 Wrocław, Poland. Fax: (+48)71–205–167. E-mail: BORO@ozi.ar.wroc.pl

* Author for correspondence and reprint requests

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The micellization process of dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) was studied at 313 K. Nuclear magnetic resonance and calorimetric methods were used. The calorimetric titration curves permitted determination of the critical micelle concentration (CMC) and enthalpy of the micellization process (ΔH_m) of the compounds studied. The results obtained were compared to those obtained at 298 K. It was found that calorimetric curves obtained at 313 K for both compounds were similar to each other in contrast to 298 K. Especially a great difference in the shape of curves was observed for DTAC.

NMR (^{1}H NMR and ^{13}C NMR) spectra were taken below and above the CMC values and chemical shifts (δ) analysed as a function of concentration of the compounds. Comparison of chemical shift-concentration plots with those obtained from measurements performed at lower temperature showed that chemical shifts are of very similar character in both cases for analyzed groups. However, there are some quantitative differences that indicate at smaller difference in hydration of DTAB and DTAC micelles at elevated temperature. This may be the reason of decrease of differences between micellization processes of DTAC and DTAB compounds. The smaller hydration may be, in turn, the result of diminishing differences in physicochemical properties of bromide and chloride ions with temperature.

Introduction

It is common knowledge that bromide and chloride salts of the same amphiphile differ in their physicochemical properties as shown in various experiments. Perhaps, the most spectacular example is the biological activity of some amphiphilic salts tested on biological objects and model membranes. Bromide salts were always found to exert stronger influence on those objects than chloride ones (Kleszczyńska *et al.*, 1998; Kleszczyńska and Sarapuk 1998; Sarapuk *et al.*, 1998; 1999). The influence of the electrolyte on surfactant activity was found to be greater when chloride ions were exchanged for bromide ones (Góralczyk 1993; 1994). Such substitution also changes parameters describing the micellization process, i. e., the critical micelle concentration of the compound (CMC), the enthalpy change for micellization (ΔH_m), the volume change for micellization (De Lisi *et al.*, 1988), and induces a structural change in the micelle (Mikulski 1991; 1993). However, the reason for these distinct differences in effects caused by both anions is still open.

We have already presented some data (Różycka-Roszak *et al.*, 2000) that confirm different quantitative and qualitative influence of dodecyltrimethylammonium bromide (DTAB) and chloride (DTAC) on the micellization process, and the present work is the continuation of those studies. The reason why we continued hydration studies of the micellization was to check whether the different influence of the anions studied on this process still exists at higher temperature.

Calorimetric measurements enabled us to determine the values for CMC and ΔH_m parameters for DTAB and DTAC in water and to compare them with previously obtained while NMR measurements which allowed the estimation of micelle hydration (Różycka-Roszak *et al.*, 1989; 2000).

Materials and Methods

Calorimetric measurements were done by means of the titration method with a home-made calorimeter at 313 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 (0.125 ml min^{-1}). The temperature was measured continuously. The experimental curves were corrected as described

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earlier and adiabatic curves of the dilution enthalpy (ΔH_m) were obtained (Różycka-Roszak *et al.*, 1988).

^1H NMR and ^{13}C NMR spectra were recorded by an Avance Bruker DRX 300 Superconducting Fourier Spectrophotometer at 300.13 MHz. The compounds studied were dissolved in D_2O. The residual water signal 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 313 K.

Dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) were purchased from Sigma Chem. Co., 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
$(CH_3)_3N^+$-CH_2-CH_2-$(CH_2)_9$-$CH_3)X$,with X = Br^- or Cl^-

Results and Discussion

Corrected adiabatic curves obtained by calorimetric measurements at 313 K are shown in Fig. 1 (titration to water). Shown are also, for comparative reasons, curves obtained previously at 298 K. The shape of titration curves at 313 K for both DTAC and DTAB compounds are similar in contrast to those obtained at 298 K. The initial slope of the dilution curve corresponding to micelle dissociation (Kresheck and Hargraves, 1974; Różycka-Roszak *et al.*, 1988; Różycka-Roszak, 1990) is negative for both DTAB and DTAC. The negative slope denotes that micelle dissociation is endothermic process. This implies that the energy breaking the hydrocarbon contact in the micelle interior is greater than the hydration heat released by the attachment of water molecules to the hydrocarbon chain. The enthalpies of micellization ΔH_m and the critical micelle concentrations CMC calculated as previously from the curves obtained are −1.65 kJ/mol and −4.82 kJ/mol for DTAC and DTAB, respectively. The value obtained for DTAB agrees with that obtained by other authors (−4.60 kJ/mol) (Espada *et al.*, 1970) while that for DTAC (−3.70 kJ/mol) differ (Różycka-Roszak and Fisicaro, 1992). Obtained values of ΔH_m for 298 K were about 4 kJ/mol higher than measured in this work (Różycka-Roszak *et al.*, 2000). The values of CMC obtained in this study were 0.021 mol/dm^3 and 0.016 mol/dm^3 for DTAC and DTAB, respectively. These values are in good agreement with obtained previously; 0.02 mol/dm^3 for DTAC (Różycka-Roszak and Fisicaro, 1992) and 0.016 mol/dm^3 for DTAB (Ingram and Jones, 1969).

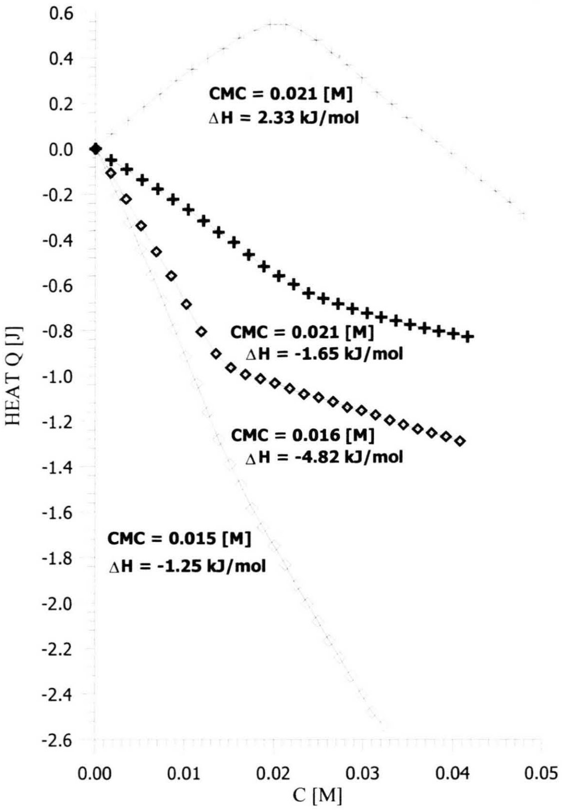

Fig. 1. Calorimetric titration curves of DTAC (+, **+**) and DTAB (◇, **◇**) to water at 298K and 313 K, respectively. CMC, critical micelle concentration;
ΔH_m, enthalpy of micellization;
DTAC, dodecyltrimethylammonium chloride;
DTAB, dodecyltrimethylammonium bromide.

Chemical shifts (δ) of ^1H NMR spectra for 1-CH_2, 2-CH_2 and $N(CH_3)_3$ groups (see Materials and Methods) were measured for the same concentration range as previously (Różycka-Roszak *et al.*, 2000), i. e., above and below the CMC of DTAC and DTAB. Mentioned groups were chosen for analysis because it was shown that DTAC micelles are hydrated to the depth of two -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 at the nitrogen atom were analysed for both compounds as a function of concentration. Fig. 3 contains the results of analysis of ^{13}C NMR for the same functional groups.

^{1}H NMR and ^{13}C NMR chemical shifts practically overlap for concentration of both compounds lower than their CMC (Figs 2 and 3) and remain constant. They start to change after the concentration of compounds cross CMC. Their changes were more pronounced for DTAB than DTAC micelles.

The ^{1}H NMR chemical shift is downfield above CMC and more pronounced for DTAB. The differences in δ below and above CMC for 1-CH_2, 2-CH_2 and $N(CH_3)_3$ groups are similar as those found by experiments performed at 298 K. A downfield shift (^{1}H NMR) is typical for hydrogen-bond protons (Slejko and Drago, 1973) and, as it was found, indicate the micelle hydration (Różycka-Roszak *et al.,* 1989). The greater shift the more hydrated the micelles are. In our case it means that DTAB micelles are more hydrated than DTAC micelles.

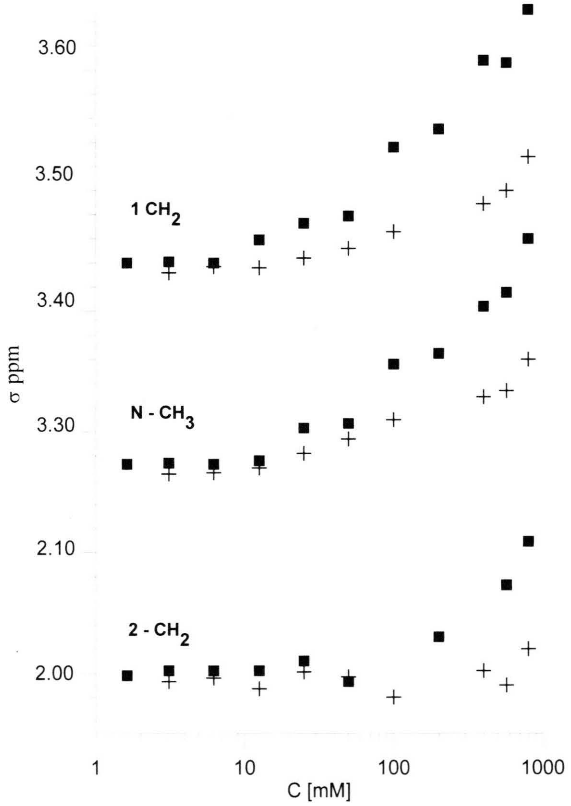

Fig. 2. Comparison of ^{1}H NMR chemical shift δ in parts per million (ppm) of DTAB (■) and DTAC (+) solution in D_2O as a function of concentration of DTAB and DTAC.

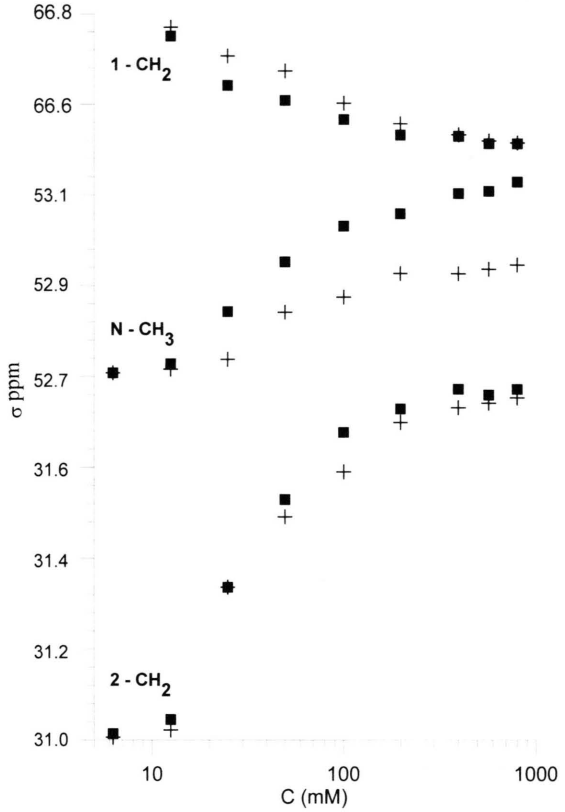

Fig. 3. Comparison of ^{13}C NMR chemical shift δ in parts per million (ppm) of DTAB (■) and DTAC (+) solution in D_2O as a function of their concentration.

^{13}C NMR shifts were also found to be downfield-shifted at concentrations above CMC for 2-CH_2 as well as for carbon atoms at the nitrogen atom while signals of the 1-CH_2 group are upfield-shifted. The upfield shift is assumed to be the result of hydrogen bonding (Różycka-Roszak *et al.*, 2000). Since upfield signals for both DTAC and DTAB micelles were almost the same this may indicate no differences in micelle hydration. Anyway, as mentioned above, ^{1}H NMR spectra showed differences in DTAC and DTAB hydration. This means that such differences in hydration may exist at 313 K but they are too small to be detected by ^{13}C NMR.

Summarizing, all performed experiments showed that both halides studied influence the micellization process to a different degree. Better modifying properties were exhibited by the bromide ion. The most important conclusion is that at elevated temperature qualitative differences between micellization processes of DTAB and DTAC compounds seem to decrease. This may be due to smaller differences in micelle hydration at higher temperature. All differences found may be due to somewhat variable physicochemical properties of the counterions studied. For instance, both ions have different dimensions of the hydrated or effective form and concurrent charge densities and electrophoretic mobilities (Dołowy, 1977). It may be the reason of their different capacity to disorder water molecules. This disordering potency is much stronger for the bromide ion but elevated temperature seems to compensate it as concluded from the experiments performed.

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