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 ($\Delta H_m$) 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 ($\delta$) 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.