Micellar properties of alkyldimethylphenylammonium bromides in water

Abstract  The synthesis and methods applied for the purification of dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromides are described. The results of surface tension measurements of aqueous solutions of these surfactants show that slight amounts of strongly surface-active nonionic impurities are persistent in the crystalline materials presumably due to their low thermal stability. The Critical micelle concentration (cmc) and the degree of ionization (β) of the micelles of the salts studied in aqueous solutions were determined at 25 °C from specific conductivity versus molality plots. The temperature dependence of the cmc and of β of the tetradecyl homologue was measured in the range 4–34 °C. A minimum cmc amounting to 1.20 mmol/kg was determined at about 14 °C. The values of β were found to grow linearly with temperature. From these results, the standard Gibbs energy, the enthalpy and the entropy of the process of micellization were obtained by application of the pseudo-phase-separation model. Enthalpy and entropy show a compensation effect in their contribution to the Gibbs energy. At low temperatures the process of micellization is driven mainly by the entropic term, whereas with increasing temperature the enthalpic term becomes predominant. At the temperature of the minimum cmc, the value of the enthalpy is far from being zero because of the important contribution of the (β/βT)R ln Xcmc term.

Key words  Alkyldimethylphenylammonium bromides – Conductivity – Critical micelle concentration – Degree of ionization – Temperature dependence
the micelles is oriented perpendicularly to the interface where its freedom of motion is severely restricted, similar to the case of the heterocyclic ring in alkylpyridinium halides. Furthermore, they determined the cmc value of the chlorides by surface tension measurements in H$_2$O.

In this paper we describe the synthesis and purification of dodecyl- (DBr), tetradecyl- (TBr) and hexadecyltrimethylammonium (CBr) bromides and present results of surface tension and conductivity studies of their aqueous solutions. The temperature dependence of the conductivity of TBr was studied in detail in the range 4–34 °C.

**Experimental**

**Surfactants**

The general procedure adopted was as follows. A mixture of 0.2 mol N,N-dimethylaniline and 0.16 mol of the appropriate alkyl bromide (Koch-Light) in 100 cm$^3$ of absolute ethanol was heated to boiling and, while hot, the flask was tightly stoppered and kept in a thermostat at 80 °C for 24 h (on some occasions the solution was turned to break the film that formed on the surface with time presumably due to partial oxidation of dimethylaniline). Ethyl alcohol was then distilled off in a vacuum rotatory evaporator. To enhance complete removal of the alcohol, the residue was dissolved in 50 cm$^3$ 2-butane and the solvent was distilled off again. The crude material was then dissolved in warm acetone and traces of the scarcely soluble dimethylanilinium hydrobromide were filtered off and discarded. Copious amounts of the surfactant were obtained upon cooling the filtrate. It was then recrystallized from acetone several times. TBr and CBr were additionally recrystallized from water. TBr crystallized in the form of a monohydrate as determined by the Carl Fischer method and had a melting point (m.p.) of 74–76 °C whereas CBr had a m.p. of 116–118 °C in accordance with previous reports [6, 7]. Electrospray mass spectrometry of DBr revealed some amounts of dimethylaniline and negligible amounts of the tetradeckyl and hexadecyl homologues. The well-defined crystals of DBr and TBr appeared to be impure judging by the opalescence which developed with time in the aqueous solutions at room temperature. CBr always yielded optically pure solutions presumably due to the efficient solubilization of the impurities in the micellar system. Prolonged extraction of TBr with ethyl ether in a Soxhlet apparatus did not improve the situation. DBr could not be purified in this manner because it appeared to swell in diethyl ether. We assumed that traces of dimethylaniline and of alkyl bromides and/or alcohols in the crystalline surfactants were responsible for the observed opalescence of the solutions. Substantial amounts of such impurities were removed in three ways.

1. By repeated contact of the aqueous solution of the cationic surfactant with $n$-heptane followed by boiling out the solubilized hydrocarbon.
2. By triturating the gelly material (formed by adding a small amount of water to the crystalline bromide) with $n$-heptane, followed by vacuum evaporation, drying over P$_2$O$_5$, and recrystallization from acetone.
3. By steam distillation (or heating to boiling) of the aqueous solution of the quaternary ammonium salts.

The last method appeared to be most simple and effective. CBr and TBr were recovered by cooling the aqueous solutions and were repeatedly recrystallized from acetone and water. DBr was recovered by removing water in a vacuum evaporator while keeping the temperature of the water bath below 50 °C. The residue was then dried over P$_2$O$_5$, recrystallized from acetone and finally dried under vacuum at room temperature. Electrospray mass spectrometry did not reveal the presence of dimethylaniline in the purified materials and their solutions were optically pure.

**Measurements**

Solutions of the surfactants were made by weighing. Surface tensions of the aqueous solutions were measured at 25 °C using a Kru¨ss model K12 digital tensiometer by the Wilhelmy plate method. Conductivities were measured using a Kyoto Electronics conductometer (model CM-117) and an Elmetron CX-732 conductometer. The cell constants were determined using KCl solutions [9]. The temperature was controlled using a thermostated bath with temperature variations of less than 0.1 °C. Two procedures for the measurement of the temperature and the concentration dependence of the conductivity were applied. In one series of experiments weighed amounts of concentrated solutions of the surfactants of known molalities were stirred continuously and the conductivities were measured at constant temperature while the solutions were successively diluted by adding pre-determined amounts of water from a Metrohm 665 Dosimat. In the second series (applied for TBr) solutions of known molalities were cooled in the bath and, while being continuously stirred, their conductivities were measured stepwise in the temperature range 4–34 °C. Appropriate corrections were made for the conductivity of pure water in the temperature range studied.

Electrospray mass spectrometry was performed on a Finnigan Mat 95S instrument by the Regional Laboratory of Physico-Chemical Analyses in Krakow.

**Results and discussion**

Samples of DBr purified in a standard way and additionally by applying the methods described earlier, yielded isotherms with a surface tension of about 38 mN/m in the micellar concentration range, a shallow minimum at a molality of about 5 mmol/kg and a hump (in the region of 42 mN/m) on the steep course of the isotherm in the premicellar concentration range. Surface tension measurements of aqueous solutions of a sample of TBr, purified in a standard way, i.e. by multiple recrystallizations from acetone and extraction with diethyl ether in a Soxhlet apparatus yielded at 25 °C an isotherm with a value of about 34 mN/m in the micellar range. Upon dilution a minimum in the surface tension occurred at a molality of about 1.3 mmol/kg. Additional purification, as described in the Experimental section, led to micellar solutions whose surface tension amounted to 38 mN/m. A minimum, however, could still be detected at about 1.3 mmol/kg. At lower concentrations, initially, the rate of increase of the surface tension was not as high as that found for surface tension in the region 42–50 mN/m. We ascribe this phenomenon to the existence of minute amounts of a strongly surface-active impurity (tetradeckyl bromide and/or alcohol) which had been solubilized in the micelles and which subsequently formed microdroplets of a second phase just below the cmc. Upon dilution, the