# DETERMINATION OF CRITICAL MICELLE CONCENTRATION OF 1-CARBETHOXYPENTADECYLTRIMETHYLAMMONIUM BROMIDE

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The critical micelle concentration of 1-carbethoxypentadecyltrimethylammonium bromide, $c_C = 7{\cdot}7 \,.\, 10^{-4}$ mol $l^{-1}$, was determined from surface tension measurements by using the method of the maximum bubble pressure. The $c_C$ value decreases markedly if a strong electrolyte (NaCl, $NaNO_3$) is added even in very low quantities; further increase of the electrolyte concentration — 0·1 to 1·0 mol $l^{-1}$ — does not bring about appreciable additional changes of $c_C$.

Various tensides, particularly cation-active ones, are finding ever-increasing application in spectrophotometric determinations of metals using metalochromic indicators and some other reagents. Their presence usually results in a lowering of the limit of determination of the element concerned, and in some instances enables the formation of a suitable colour system. The effect of the cation-active tensides on the metal cation-dye anion binary system is probably associated with the formation of tenside micelles, which can favourably affect the electronic structure of the binary complex through their high surface charge.

The values of the so-called critical micelle concentration $c_C$ of tensides, which are characteristic of the tenside micelle formation in a solution, have been published[1]; however, for 1-carbethoxypentadecyltrimethylammonium bromide (CPTB, Septonex), a tenside nowadays rather frequently used[2-6], the $c_C$ value has not been so far determined.

In this work, we determined for this substance the $c_C$ value as well as the dependence of the latter on the concentration of a strong electrolyte in the solution; we employed the frequently used technique[1] of measuring the surface tension $\gamma$ of differently concentrated solutions. The underlying concept is that with increasing concentration of the tenside ($c_T$) the surface tension drops rapidly until the $c_C$ value is reached, then it remains constant or decreases only slightly. The dependence $\gamma = f(\log c_T)$ can be regarded as linear over a wide span of the tenside concentrations except for the nearest neighbourhood of the point $c_T = c_C$, where the slope of this dependence alters. The $c_C$ value is then the coordinate (on the $c_T$ axis) of the point of intersection of the two linear segments in this functional dependence.

## EXPERIMENTAL

### Apparatus and Chemicals

The surface tension of the solutions was measured on an apparatus after Škramovský[7] with some technical adaptations[8]. A swing bolt was used for the clamping of the capillary, which allowed vertical, very subtle adjustment of the capillary such that the orifice was just in contact with the level of the solution to be measured. A constant temperature of the solution measured as well as of the manometric liquid, 20 ± 0·5°C, was maintained by using a thermostat U 10 (Medingen, GDR). As the air source served a Kipp apparatus filled with water; the air flow rate was controlled by means of a clamp with fine regulation. Kerosene was employed as the manometric liquid.

The $5 \cdot 10^{-2}$, $5 \cdot 10^{-3}$, and $5 \cdot 10^{-4}$M 1-carbethoxypentadecyltrimethylammonium bromide (CPTB) stock solutions were prepared by dissolving the substance Septonex (Slovakofarma, Hlohovec) in redistilled water; the purity of the substance complied with *Czechoslovak Pharmacopoeia*. The solutions of the desired concentrations were prepared in pairs for parallel measurements. The kerosene used as the manometric liquid was purified by shaking with concentrated sulfuric acid and 40% aqueous solution of sodium hydroxide, respectively, and dried by shaking with anhydrous sodium sulfate. NaCl and $NaNO_3$ used were reagent grade purity (Lachema, Brno).

### Measurement Procedure and Evaluation

The surface tension $\gamma$ was measured by employing the method of the maximum bubble pressure[9] modified by Škramovský[7]. Here the highest air pressure is determined in a bubble formed at the orifice of the capillary, which just touches the liquid examined. After rearrangement in the momentum balance, we obtain for such arrangement the relation

$$\gamma = r/2(hD - rd)\,,$$

where $r$ is the capillary radius, $d$ and $D$ are the densities of the liquid measured and of the manometric liquid, respectively, $h$ is the difference between the zero position of the manometric liquid meniscus $h_0$ and its maximum position $h'$.

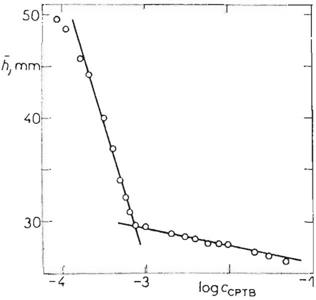

FIG. 1

Dependence of the Value $\bar{h}$ on the Concentration of 1-Carbethoxypentadecyltrimethylammonium Bromide

○ — Experimental points, ——— regression straight lines.

If the measurement parameters — the temperature of the solution measured and of the manometric liquid, the air flow rate, and the capillary radius — are kept constant, the surface tension is directly proportional to the $h$ value ($\gamma = \text{const.}\ h$). Since for the determination of the tenside $c_C$ value it is not necessary to know the surface tension absolutely — it is sufficient to establish its variation in dependence on the tenside concentration, the dependence $h = f(\log c_T)$ can directly serve for the evaluation. For the tenside concentration region of interest, a constant density of all the measured solutions was assumed within the series treated.

The dependence $h = f(\log c_T)$ was examined in the CPTB concentration region $8 \cdot 10^{-5}$ to $5 \cdot 10^{-2}$ mol $l^{-1}$ for twenty different $c_T$ values, and the results were statistically processed by applying the linear regresion method. Each measurement was duplicated using two different CPTB stock solutions. The air flow rate was maintained constant for all measurements (30 s between the detachment of two successive bubbles). The position of the meniscus $h'_i$ was read after the equilibrium established — the maximum pressure exhibited no ascending or descending tendency. The position was determined five times for every fifth bubble to obtain the average value of $h$. The dependence $\bar{h} = f(\log c_{CPTB})$ for a measurement series is plotted in Fig. 1.

In case that for a concentration the difference between the parallel $h$ values exceeded 1%, a third solution of this concentration prepared from a third stock solution was measured in addition. The $h'_i$ values thus obtained were added to the second series and the average $h$ was calculated for $n = 10$.

The $c_C$ value was obtained by calculating the point of intersection of the regression straight lines; graphical evaluation, *i.e.* reading of this point on the $\log c_{CPTB}$ axis, resulted in a considerable error. The numerical processing of the results was performed on a computer ICL 4/72 in the language FORTRAN.

## RESULTS

The coordinates of the point of intersection of the straight lines were calculated for each measurement series; the values $7{\cdot}74 \cdot 10^{-4}$ and $7{\cdot}77 \cdot 10^{-4}$ mol $l^{-1}$ were obtained for the two of them, respectively.

Furthermore, the effect of selected strong electrolytes on the $c_C$ value was investigated. A high effect of strong electrolytes on the micelle formation could be expected, and so it was of interest to examine those electrolytes that are frequently used in spectrophotometry for the adjusting of the ionic strength, *viz.* NaCl and $NaNO_3$. With these salts, the measurements were conducted in the same manner, except that twelve points were always read for the calculation of the point of intersection of the two linear branches of the $h = f(\log c_{CPTB})$ dependence. The following data were obtained for NaCl and $NaNO_3$ as the salts:

| $c_{salt}$, mol $l^{-1}$: | 0·02 | 0·05 | 0·1 | 0·5 | 1·0 |
|---|---|---|---|---|---|
| $c_C$ $10^{-4}$ mol $l^{-1}$ (NaCl): | 2·01 | 1·51 | 1·10 | 1·00 | 1·17 |
| ($NaNO_3$): | 1·23 | 1·12 | 1·16 | 1·25 | 1·40 |

Obviously, an addition of a strong electrolyte, even in a low concentration, brings about a decrease of the $c_C$ value. In the salt concentration range 0·1 to 1·0 mol $l^{-1}$ the $c_C$ value practically does not change in the case of NaCl and slightly increases in the case of $NaNO_3$. The results are in accordance with the published data for other cation-active tensides[1].

If the micelle formation has a decisive bearing on the ternary system metal–dye–tenside, then – as our results indicate – strong electrolytes must exert a marked effect on the colour system.

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