

# Conductivity Measurements as a Method for Studying Ionic Technical Grade Surfactants

The critical micellar concentrations (cmc) of cationic alkyltrimethylammonium bromides ( $C_{10}TAB-C_{16}TAB$ ) and of anionic alkyl sulfates (SDS, technical grade Sulfofon 12G and Sulfofon 1214G) were determined using specific conductivity and surface tension measurements. While the cationic surfactants were purified, the anionic surfactants were used as received. In the former case, surface tension and conductivity measurements lead to the same cmc values. In the latter case, measuring the specific conductivities (bulk property) proved to be superior compared to measuring the surface tensions (surface property) because the presence of highly surface active impurities creates a pronounced minimum in the surface tension isotherm, which makes it impossible to determine an accurate value for the cmc. On the other hand, these impurities do not influence the conductivities, i.e. that the conductivities can be used to determine cmc values of impure and technical grade ionic surfactants, respectively. Moreover, an evaluation of the specific conductivities allows for the determination of the degree of micelle ionization ( $\alpha$ ) of the ionic surfactant solutions and thus provides additional useful information.

**Key words:** Ionic technical grade surfactant, specific conductivity, surface tension, critical micelle concentration, degree of micelle ionization

**Leitfähigkeitsmessungen als Methode zur Untersuchung von technischen ionischen Tensiden.** Um die kritischen Mizellbildungskonzentrationen (cmc) kationischer Alkyltrimethylammoniumbromide ( $C_{10}TAB-C_{16}TAB$ ) sowie anionischer Alkylsulfate (SDS, technisches Sulfofon 12G und Sulfofon 1214G) zu bestimmen, wurden spezifische Leitfähigkeiten sowie Oberflächenspannungen gemessen. Die kationischen Tenside sind gereinigt worden, während die anionischen nicht weiter aufgearbeitet wurden. Es zeigte sich im Falle der  $C_nTAB$  Reihe, dass beide Messmethoden zum gleichen Ergebnis führen. Bei den anionischen Tensiden konnte mittels Oberflächenspannungen keine Aussage über die cmc gemacht werden, da das durch Verunreinigungen verursachte Minimum ein Auswerten der Kurven unmöglich macht. Hingegen lieferten Leitfähigkeitsmessungen die gewünschten cmc-Werte. Darüber hinaus kann aus den Leitfähigkeitsmessungen der Dissoziationsgrad der Mizellen bestimmt werden. Nicht nur wegen der aussagekräftigeren Ergebnisse, sondern auch wegen des geringen experimentellen Aufwands sind Leitfähigkeitsmessungen das optimale Werkzeug, um sowohl reine als auch technische ionische Tenside zu untersuchen.

**Stichwörter:** Technische ionische Tenside, spezifische Leitfähigkeit, Oberflächenspannung, kritische Mizellbildungskonzentration, Dissoziationsgrad von Mizellen

## 1 Introduction

It is well documented that the physico-chemical properties of surfactants vary dramatically at a specific concentration – the critical micelle concentration (cmc). The transition from pre-micellar to micellar solutions occurs over a narrow range of concentration. The cmc is an extremely useful quantity, as it captures the surface and interfacial activity of the surfactant molecules in solution. The ability of surfactants to reduce surface or interfacial tension is directly related to the cmc. A low cmc indicates that it is thermodynamically favorable for the surfactant to saturate the interface and to form micelles at low concentrations. The characteristic properties of surfactant solutions, such as detergency, wetting, emulsification, dispersion, and foaming, all depend on this tendency of surfactants to accumulate and reduce interfacial tension at the interfaces between the solution and the adjacent gaseous, liquid or solid phases [1].

Additives such as electrolyte, co-surfactants and long-chain alcohols have a marked effect on the cmc of a surfactant solution [2, 3]. The effect of organic additives on micellar properties is another important issue. A small amount of organic solvent is often added to the mobile phase to improve efficiency and separation of compounds. However, small amounts of organic materials may have a dramatic effect on the cmc in aqueous media and too high a concentration of the organic solvent may cause the micelle to disperse. The origins of the organic material are impurities or by-products from the synthesis of the surfactants. It is because of such components that similar commercial surfactants behave differently. Therefore knowledge of the effects of organic materials on the cmc of surfactants is beneficial from both a theoretical and practical point of view. Large amounts of small polar organic molecules such as ethanol or urea raise the cmc [4–6] and at sufficiently large concentrations sometimes inhibit micelle formation altogether [1, 7]. Small amounts of long-chain alcohols tend to lower cmc of both nonionic [8, 9] and ionic surfactants [10, 11]. Depression of the cmc appears to be greater for straight-chain compounds than for branched compounds and increases with the chain length to a maximum when the length of the hydrophobic group of the additive approximates that of the surfactant [1, 12]. A technical grade surfactant, which contains a blend of hydrophobic chain lengths along with additives such as electrolytes and polar organic molecules, may have a cmc value, which can vary significantly compared to that of its pure analogon. The cmc value is of significant interest as it represents the lowest surfactant concentration needed to get a maximum reduction of the surface tension. The general way to determine the cmc value is to plot a certain physico-chemical property versus the surfactant concentration and to determine the concentration at which this particular prop-